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The Disposal of Canada's Nuclear Fuel Waste: Engineered Barriers Alternatives

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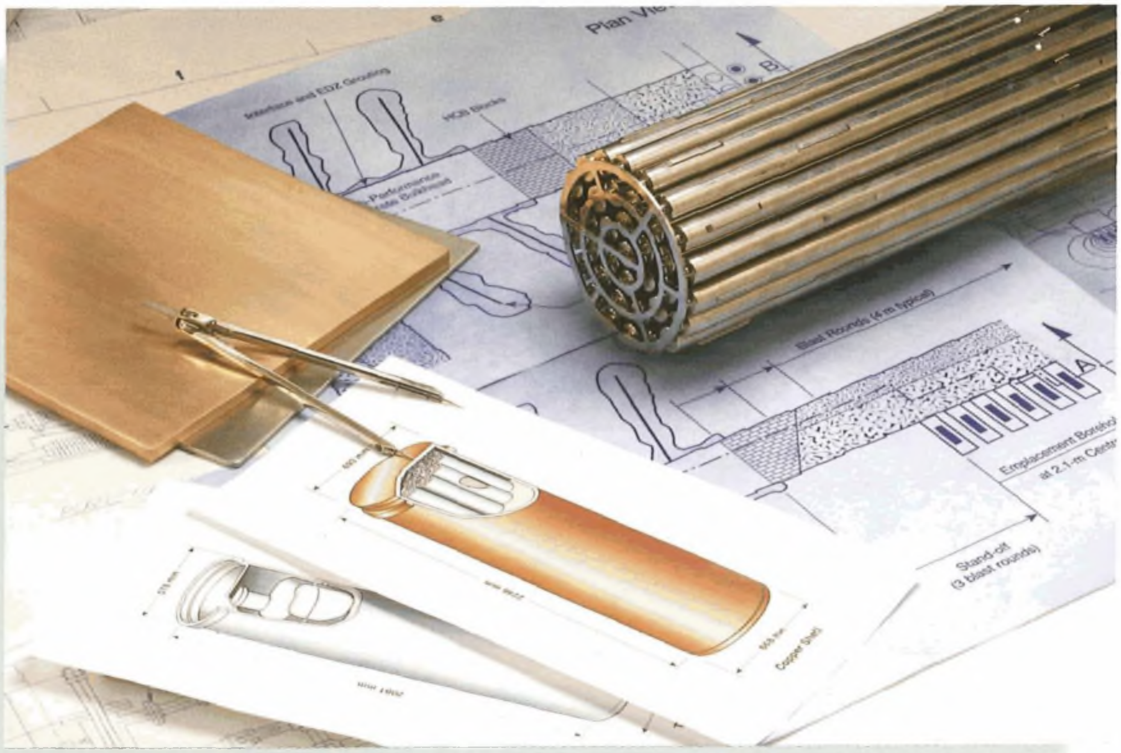

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AECL RESEARCH

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by

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The Canadian Nuclear Fuel Waste Management Program is funded jointly by AECL and Ontario Hydro under the auspices of the CANDU Owners Group.

Whiteshell Laboratories
Pinawa, Manitoba ROE 1LO
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LE STOCKAGE PERMANENT DES DÉCHETS DE COMBUSTIBLE NUCLÉAIRE DU CANADA : BARRIÈRES OUVRAGÉES POSSIBLES

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RÉSUMÉ

Le concept de stockage permanent des déchets de combustible nucléaire du Canada implique le stockage des déchets dans une installation souterraine excavée à une profondeur de 500 à 1000 m dans la roche plutonique du Bouclier canadien. Les déchets solides seraient isolés de la biosphère par un système de barrières multiples comprenant des barrières ouvragées, dont les conteneurs à longue durée de vie et les matériaux de scellement d'étanchéité à base d'argile naturelle et à base de ciment, et la barrière naturelle que constitue la formation géologique massive. La possibilité de réalisation technique de ce concept et son impact sur l'environnement et la santé des êtres humains sont documentés dans une Étude d'impact sur l'environnement (EIE) qui sera soumise à un examen en vertu du Processus fédéral d'évaluation et d'examen en matière d'environnement.

Ce rapport, qui est l'un d'une série de neuf documents de référence principaux, décrit les diverses conceptions et les divers matériaux possibles pour les barrières ouvragées que l'on a envisagées pendant l'élaboration du concept canadien de stockage permanent et résume les concepts de barrières ouvragées en cours d'évaluation dans d'autres pays. On présente la base de la sélection d'un système de barrières ouvragées de référence pour l'EIE. Ce système de référence comporte la mise en conteneurs de titane de grappes de combustible usé de réacteurs CANDU (Canada Deutérium Uranium) et ensuite la mise en place des conteneurs dans des trous forés dans le sol des chambres de stockage permanent. On se servirait de matériaux de scellement d'étanchéité à base d'argile pour remplir l'espace entre les conteneurs et la roche ainsi que les cavités excavées restantes.

À la section traitant des déchets conditionnées, on examine les propriétés des grappes de combustible usé et des déchets solidifiés de haute activité qui proviendraient du traitement des déchets de retraitement du combustible usé. On examine également des méthodes de solidification des déchets et la durabilité chimique des déchets solidifiés dans des conditions de stockage permanent.

On examine diverses conceptions possibles de conteneurs allant des conceptions préliminaires aux essais poussés de prototypes d'éléments. En outre, on résume les résultats des études de résistance de la structure, de soudage et d'examen. On examine en détail la corrosion du fer, de l'acier au carbone, des aciers inoxydables, des alliages à base de nickel, des alliages de titane et du cuivre quant à leur comportement possible en installation souterraine construite dans le Bouclier canadien.

On présente la stratégie de scellement d'étanchéité d'une installation souterraine ainsi que les matériaux à utiliser à cette fin. On examine les matériaux à base d'argile et à base de ciment et on explique la méthode de préparation de ces matériaux pour leur application particulière en examinant la méthode de sélection du retardateur, du remblai et du coulis de référence. On présente les conceptions de systèmes de scellement d'étanchéité des puits, galeries et trous de forage d'exploration et on décrit les méthodes d'application de ces systèmes de scellement d'étanchéité.

Les conceptions et matériaux présentés nous donnent la certitude qu'on peut réaliser en toute sûreté le stockage permanent de déchets de combustible nucléaire à l'aide d'un certain nombre de systèmes. Le choix définitif des conceptions et des matériaux se ferait sur la base d'études particulières à un site, d'études techniques d'installations souterraines et d'un retour d'information provenant de l'évaluation de systèmes de barrières.

Le Programme canadien de gestion des déchets de combustible nucléaire est financé en commun par EACL et Ontario Hydro sous les auspices du Groupe des propriétaires de réacteurs CANDU.

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ABSTRACT

The concept for disposal of Canada's nuclear fuel waste involves emplacing the waste in a vault excavated at a depth of 500 to 1000 m in plutonic rock of the Canadian Shield. The solid waste would be isolated from the biosphere by a multibarrier system consisting of engineered barriers, including long-lived containers and clay- and cement-based sealing materials, and the natural barrier provided by the massive geological formation. The technical feasibility of this concept and its impact on the environment and human health are being documented in an Environmental Impact Statement (EIS), which will be submitted for review under the federal Environmental Assessment and Review Process.

This report, one of nine EIS primary references, describes the various alternative designs and materials for engineered barriers that have been considered during the development of the Canadian disposal concept and summarizes engineered barrier concepts being evaluated in other countries. The basis for the selection of a reference engineered barrier system for the EIS is presented. This reference system involves placing used CANDU (Canada Deuterium Uranium) fuel bundles in titanium containers, which would then be emplaced in boreholes drilled in the floor of disposal rooms. Clay-based sealing materials would be used to fill both the space between the containers and the rock and the remaining excavations.

In the section on waste forms, the properties of both used-fuel bundles and solidified high-level wastes, which would be produced by treating wastes resulting from the reprocessing of used fuel, are discussed. Methods of solidifying the wastes and the chemical durability of the solidified waste under disposal conditions are reviewed.

Various alternative container designs are reviewed, ranging from preliminary conceptual designs to designs that have received extensive prototype testing. Results of structural performance, welding and inspection studies are also summarized. The corrosion of iron, carbon steel, stainless steels, nickel-based alloys, titanium alloys and copper is reviewed in detail, with reference to their potential performance in a disposal vault in the Canadian Shield.

The strategy for sealing a disposal vault and the materials for this application are presented. Both clay-based and cement-based materials are discussed, and the method of designing these materials for their particular application is illustrated through examination of the method of selecting reference buffer, backfill and grouting materials. Designs are presented for shaft, tunnel and exploration borehole seals, and methodologies for emplacing them are described.

The materials and designs presented give us confidence that disposal of nuclear fuel waste can be safely achieved using a number of approaches. Final selection of materials and design would be established on the basis of site-specific investigations, vault engineering studies, and feedback from system performance assessment.

The Canadian Nuclear Fuel Waste Management Program is funded jointly by AECL and Ontario Hydro under the auspices of the CANDU Owners Group

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PREFACE

In 1992, 15% of the electricity generated in Canada was produced using CANDU nuclear reactors. A by-product of the nuclear power is used CANDU fuel, which consists of ceramic uranium dioxide pellets and metal structural components. Used fuel is highly radioactive. The used fuel from Canada's power reactors is currently stored in water-filled pools or dry storage concrete containers. Humans and other living organisms are protected by isolating the used fuel from the natural environment and by surrounding it with shielding material. Current storage practices have an excellent safety record.

At present, used CANDU fuel is not reprocessed. It could, however, be reprocessed to extract useful material for recycling, and the highly radioactive material that remained could be incorporated into a solid. The term "nuclear fuel waste," as used by AECL, refers to either

- the used fuel, if it is not reprocessed, or
- a solid incorporating the highly radioactive waste from reprocessing.

Current storage practices, while safe, require continuing institutional controls such as security measures, monitoring, and maintenance. Thus storage is an effective interim measure for protection of human health and the natural environment but not a permanent solution. A permanent solution is disposal, a method "in which there is no intention of retrieval and which, ideally, uses techniques and designs that do not rely for their success on long-term institutional control beyond a reasonable period of time" (AECB 1987).

In 1978, the governments of Canada and Ontario established the Nuclear Fuel Waste Management Program "... to assure the safe and permanent disposal" of nuclear fuel waste. AECL was made responsible for research and development on "... disposal in a deep underground repository in intrusive igneous rock" (Joint Statement 1978). Ontario Hydro was made responsible for studies on interim storage and transportation of used fuel and has contributed to the research and development on disposal. Over the years a number of other organizations have also contributed to the Program, including Energy, Mines and Resources Canada; Environment Canada; universities; and companies in the private sector.

The disposal concept is to place the waste in long-lived containers; emplace the containers, enveloped by sealing materials, in a disposal vault excavated at a nominal depth of 500 to 1000 m in intrusive igneous (plutonic) rock of the Canadian Shield; and (eventually) seal all excavated openings and exploration boreholes to form a passively safe system. Thus there would be multiple barriers to protect humans and the natural environment from contaminants in the waste: the container, the very low-solubility waste form, the vault seals, and the geosphere. The disposal technology includes options for the design of the engineered components, including the disposal container, disposal vault, and vault seals, so that it is adaptable to a wide range of regulatory standards, physical conditions, and social requirements. Potentially suitable bodies of plutonic rock occur in a large number of locations across the Canadian Shield.

In developing and assessing this disposal concept, AECL has consulted broadly with members of Canadian society to help ensure that the concept and the way in which it would be implemented are technically sound and represent a generally acceptable disposal strategy. Many groups in Canada have had opportunities to comment on the disposal concept and on the waste management program. These include government departments and agencies, scientists, engineers, sociologists, ethicists, and other members of the public. The Technical Advisory Committee to AECL on the Nuclear Fuel Waste Management Program, whose members are nominated by Canadian scientific and engineering societies, has been a major source of technical advice.

In 1981, the governments of Canada and Ontario announced that "... no disposal site selection will be undertaken until after the concept has been accepted. This decision also means that the responsibility for disposal site selection and subsequent operation need not be allocated until after concept acceptance" (Joint Statement 1981).

The acceptability of the disposal concept is now being reviewed by a federal Environmental Assessment Panel, which is also responsible for examining a broad range of issues related to nuclear fuel waste management (Minister of the Environment, Canada 1989). After consulting the public, the Panel issued guidelines to identify the information that should be provided by AECL, the proponent of the disposal concept (Federal Environmental Assessment Review Panel 1992).

AECL is preparing an Environmental Impact Statement (EIS) to provide information requested by the Panel and to present AECL's case for the acceptability of the disposal concept. A Summary will be issued separately. This report is one of nine primary references that summarize major aspects of the disposal concept and supplement the information in the EIS. A guide to the contents of the EIS, the Summary, and the primary references follows this Preface.

In accordance with the 1981 Joint Statement of the governments of Canada and Ontario, no site for disposal of nuclear fuel waste is proposed at this time. Thus in developing and assessing the disposal concept, AECL could not design a facility for a proposed site and assess the environmental effects to determine the suitability of the design and the site, as would normally be done for an Environmental Impact Statement. Instead, AECL and Ontario Hydro have specified illustrative "reference" disposal systems and assessed those.

A "reference" disposal system illustrates what a disposal system, including the geosphere and biosphere, might be like. Although it is hypothetical, it is based on information derived from extensive laboratory and field research. Many of the assumptions made are conservative, that is, they would tend to overestimate adverse effects. The technology specified is either available or judged to be readily achievable. A reference disposal system includes one possible choice among the options for such things as the waste form, the disposal container, the vault layout, the vault seals, and the system for transporting nuclear fuel waste to a disposal facility.

The components and designs chosen are not presented as ones that are being recommended but rather as ones that illustrate a technically feasible way of implementing the disposal concept.

After the Panel has received the requested information, it will hold public hearings. It will also consider the findings of the Scientific Review Group, which it established to provide a scientific evaluation of the disposal concept. According to the Panel's terms of reference "As a result of this review the Panel will make recommendations to assist the governments of Canada and Ontario in reaching decisions on the acceptability of the disposal concept and on the steps that must be taken to ensure the safe long-term management of nuclear fuel wastes in Canada" (Minister of the Environment, Canada 1989).

Acceptance of the disposal concept at this time would not imply approval of any particular site or facility. If the disposal concept is accepted and implemented, a disposal site would be sought, a disposal facility would be designed specifically for the site that was proposed, and the potential environmental effects of the facility at the proposed site would be assessed. Approvals would be sought in incremental stages, so concept implementation would entail a series of decisions to proceed. Decision-making would be shared by a variety of participants, including the public. In all such decisions, however, safety would be the paramount consideration.

The EIS, Summary, and Primary References

Environmental Impact Statement on the Concept for Disposal of Canada's Nuclear Fuel Waste (AECL 1994a)

Summary of the Environmental Impact Statement on the Concept for Disposal of Canada's Nuclear Fuel Waste (AECL 1994b)

The Disposal of Canada's Nuclear Fuel Waste: Public Involvement and Social Aspects (Greber et al. 1994)

The Disposal of Canada's Nuclear Fuel Waste: Site Screening and Site Evaluation Technology (Davison et al. 1994a)

The Disposal of Canada's Nuclear Fuel Waste: Engineered Barriers Alternatives (Johnson et al., this volume)

The Disposal of Canada's Nuclear Fuel Waste: Engineering for a Disposal Facility (Simmons and Baumgartner 1994)

The Disposal of Canada's Nuclear Fuel Waste: Preclosure Assessment of a Conceptual System (Grondin et al. 1994)

The Disposal of Canada's Nuclear Fuel Waste: Postclosure Assessment of a Reference System (Goodwin et al. 1994)

The Disposal of Canada's Nuclear Fuel Waste: The Vault Model for Postclosure Assessment (Johnson et al. 1994)

The Disposal of Canada's Nuclear Fuel Waste: The Geosphere Model for Postclosure Assessment (Davison et al. 1994b)

The Disposal of Canada's Nuclear Fuel Waste: The Biosphere Model, BIOTRAC, for Postclosure Assessment (Davis et al. 1993)

GUIDE TO THE CONTENTS OF THE ENVIRONMENTAL IMPACT STATEMENT, THE SUMMARY, AND THE PRIMARY REFERENCES

ENVIRONMENTAL IMPACT STATEMENT AND SUMMARY

Environmental Impact Statement on the Concept for Disposal of Canada's Nuclear Fuel Waste (AECL 1994a)

- provides an overview of AECL's case for the acceptability of the disposal concept
- provides information about the following topics:
  - the characteristics of nuclear fuel waste
  - storage and the rationale for disposal
  - major issues in nuclear fuel waste management
  - the disposal concept and implementation activities
  - alternatives to the disposal concept
  - methods and results of the environmental assessments
  - principles and potential measures for managing environmental effects
  - AECL's overall evaluation of the disposal concept

Summary of the Environmental Impact Statement on the Concept for Disposal of Canada's Nuclear Fuel Waste (AECL 1994b)

- summarizes the contents of the Environmental Impact Statement

PRIMARY REFERENCES

The Disposal of Canada's Nuclear Fuel Waste: Public Involvement and Social Aspects (Greber et al. 1994)

- describes the activities undertaken to provide information to the public about the Nuclear Fuel Waste Management Program and to obtain public input into the development of the disposal concept
- presents the issues raised by the public and how the issues have been addressed during the development of the disposal concept or how they could be addressed during the implementation of the disposal concept
- discusses social aspects of public perspectives on risk, ethical issues associated with nuclear fuel waste management, and principles for the development of a publicly acceptable site selection process

The Disposal of Canada's Nuclear Fuel Waste: Site Screening and Site Evaluation Technology (Davison et al. 1994a)

- discusses geoscience, environmental, and engineering factors that would need to be considered during siting

- describes the methodology for characterization, that is, for obtaining the data about regions, areas, and sites that would be needed for facility design, monitoring, and environmental assessment

<u>The Disposal of Canada's Nuclear Fuel Waste: Engineered Barriers Alternatives (this volume)</u>

- describes the characteristics of nuclear fuel waste

- describes the materials that were evaluated for use in engineered barriers, such as containers and vault seals

- describes potential designs for containers and vault seals

- describes procedures and processes that could be used in the production of containers and the emplacement of vault-sealing materials

<u>The Disposal of Canada's Nuclear Fuel Waste: Engineering for a Disposal Facility (Simmons and Baumgartner 1994)</u>

- discusses alternative vault designs and general considerations for engineering a nuclear fuel waste disposal facility

- describes a disposal facility design that was used to assess the technical feasibility, costs, and potential effects of disposal (Different disposal facility designs are possible and might be favoured during concept implementation.)

- presents cost and labour estimates for implementing the design

<u>The Disposal of Canada's Nuclear Fuel Waste: Preclosure Assessment of a Conceptual System (Grondin et al. 1994)</u>

- describes a methodology for estimating effects on human health, the natural environment, and the socio-economic environment that could be associated with siting, constructing, operating (includes transporting used fuel), decommissioning, and closing a disposal facility

- describes an application of this assessment methodology to a reference disposal system (We use the term "reference" to designate the disposal systems, including the facility designs, specified for the assessment studies. Different disposal facility designs are possible and might be favoured during concept implementation.)

- discusses technical and social factors that would need to be considered during siting

- discusses possible measures and approaches for managing environmental effects

The Disposal of Canada's Nuclear Fuel Waste: Postclosure Assessment of a Reference System (Goodwin et al. 1994)

- describes a methodology for
  - estimating the long-term effects of a disposal facility on human health and the natural environment,
  - determining how sensitive the estimated effects are to variations in site characteristics, design parameters, and other factors, and
  - evaluating design constraints
- describes an application of this assessment methodology to a reference disposal system (We use the term "reference" to designate the disposal systems, including the facility designs, specified for the assessment studies. Different disposal facility designs are possible and might be favoured during concept implementation.)

The Disposal of Canada's Nuclear Fuel Waste: The Vault Model for Postclosure Assessment (Johnson et al. 1994)

- describes the assumptions, data, and model used in the postclosure assessment to analyze processes within and near the buried containers of waste
- discusses the reliability of the data and model

The Disposal of Canada's Nuclear Fuel Waste: The Geosphere Model for Postclosure Assessment (Davison et al. 1994b)

- describes the assumptions, data, and models used in the postclosure assessment to analyze processes within the rock in which a disposal vault is excavated
- discusses the reliability of the data and model

The Disposal of Canada's Nuclear Fuel Waste: The Biosphere Model, BIOTRAC, for Postclosure Assessment (Davis et al. 1993)

- describes the assumptions, data, and model used in the postclosure assessment to analyze processes in the near-surface and surface environment
- discusses the reliability of the data and model

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EXECUTIVE SUMMARY

ES.1 INTRODUCTION

The disposal concept for Canada's nuclear fuel waste involves permanent burial at depths of 500 to 1000 m in plutonic rock of the Canadian Shield. The waste, either used-fuel bundles or solidified fuel-reprocessing wastes, would be isolated in a mined excavation in long-lived containers surrounded by low-permeability sealing materials.

The development of the disposal concept has focused on meeting the following objectives:

- to develop and demonstrate the technology to site, design, operate and close a disposal facility in plutonic rock;
- to develop and demonstrate a methodology to evaluate the performance of a disposal system against safety standards; and
- to establish that technically suitable sites are likely to exist in Canada.

No disposal site has been selected; thus, the technical objectives were pursued by evaluating the safety of a hypothetical disposal facility, including an assumed geological setting.

This report describes the various materials and design alternatives that have been considered for engineered barriers during the development of the Canadian disposal concept, and discusses the principal factors that would affect the performance of these barriers under the conditions anticipated in the disposal vault. The basis for the selection of the design and materials for the reference engineered barriers system is outlined, and includes a discussion of alternative materials and designs and the approaches being developed in other countries. The reference disposal system includes

- a waste form consisting of intact CANDU[1] used-fuel bundles;
- a thin-walled (6.35 mm) Grade-2 titanium container, with internal support provided by a packed particulate consisting of glass beads;
- emplacement of containers in boreholes in the floor of disposal rooms in plutonic rock at a depth of 500 to 1000 m (the site characteristics are based on studies of the Whiteshell Research Area of Manitoba);

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[1] CANada Deuterium Uranium, registered trademark of AECL. CANDU reactors use natural (0.7% ^{235}U) uranium oxide fuel.

- a compacted clay-sand buffer material surrounding the containers in the boreholes;
- a compacted mixture of clay and crushed granite to backfill most of the other parts of the excavations; and
- buffer, backfill and cement-based materials to provide seals in shafts and other strategic locations in the vault.

The option of using geological media other than plutonic rock for disposal is outside the scope of this report; this is discussed in the Environmental Impact Statement (EIS) (AECL 1994a).

The report is divided into three sections:

1. Waste forms. In this section, the basic characteristics of used-fuel bundles and fuel-reprocessing waste forms are discussed.
2. Containers for nuclear fuel waste disposal. In this section, a variety of container options and the materials from which they could be constructed are presented. These studies have focused largely on titanium and copper. Various containment targets are discussed, including the rationale for selecting 500 a as the minimum container lifetime; however, the potential for longer-term containment is also reviewed.
3. Vault sealing. In this section, the strategy for sealing the vault and the different materials that have been considered are discussed. The principal focus is on clay- and cement-based materials.

Final selection of a waste form, container material and design, and sealing materials and methods will depend on technical considerations presented here, on actual conditions at the disposal site, and on future technical advances that occur prior to disposal implementation.

ES.2 WASTE FORMS

A used-fuel bundle discharged from a CANDU reactor consists of an assembly of Zircaloy-clad UO_2 fuel elements and weighs approximately 20 kg. Two options are available for the disposal of these fuel bundles. They could be emplaced in containers without any dismantling or processing and disposed of directly, an approach that would minimize the production of secondary wastes. Alternatively, the fuel bundles could be chemically reprocessed to recover uranium and/or plutonium for the fabrication of new reactor fuel. The resultant wastes would be solidified in the form of a glass or glass-ceramic and emplaced in disposal containers. No decision has been taken in Canada to reprocess used CANDU fuel, and fuel bundles are currently being stored in water-filled bays or concrete dry storage canisters at the reactor sites. Storage of used fuel is a well-established licensed technology and its safety has been demonstrated through decades of trouble-free experience. As of 1992 December 31, a total of about 900 000 fuel bundles (~17 000 Mg U) were stored at the various generating stations. The quantities that will have accumulated by the year 2035 have been estimated to range from 1.1 million to 10.1 million bundles, depending on the assumed future of nuclear power in Canada. The lowest projection assumes that all nuclear plants are shut down in 1995, whereas the highest value assumes 3% annual growth in nuclear generating capacity after 1995.

The properties of used-fuel bundles have been extensively studied and are well understood. The quantities of radionuclides in the fuel are a direct function of the burnup, which is the energy released in the reactor per unit mass of fuel. A reference burnup of 685 $GJ \cdot kg^{-1}$ U, based on historical average burnups, is assumed for the performance-assessment case study discussed in the EIS. At this burnup, approximately 1.3 wt.% of the fuel is made up of new nuclides (both radioactive and non-radioactive) produced by irradiation. Inventories of radionuclides in the fuel as a function of time after discharge from the reactor are calculated with extensively tested and validated reactor physics models.

During the first ten years after removal from the reactor, the activity of used fuel decreases by a factor of 1000, and within 500 a the activity will have decreased to less than 1/100 000 of the value at the time of removal. After 500 a the rate of decrease in activity will become slower, which was a major consideration in selecting a minimum design lifetime of 500 a for disposal containers. Similarly, the decay heat of used-fuel bundles decreases rapidly with time, declining by a factor of approximately 1000 during the first five years of pool storage.

No significant degradation of used fuel is expected to occur as a result of long-term storage or as a result of transportation to a disposal centre. Detailed examination of used-fuel bundles stored under both wet and dry conditions shows that degradation is extremely limited and would not affect fuel sheath or bundle integrity for at least 50 a. Similarly, studies of the effects of shock and vibration on used-fuel bundles indicate that fuel bundles are durable and that no fuel damage would be expected under normal transportation conditions.

Although only CANDU reactors fueled with natural uranium are now in use in Canada, it is possible that other reactor fuels could be used in the future. The use of slightly enriched fuel (~1.2 wt.%) in CANDU reactors would result in fuel bundles that would permit significantly higher burnup. As a result, the higher heat generation of the used fuel would have to be considered in the design of a disposal facility; e.g., higher burnups would require that the resultant heat generation be spread over a larger volume of rock in the vault to obtain the same temperature conditions.

A knowledge of the detailed structure and composition of used fuel is required to describe how it would behave after geological disposal. The pellets of used fuel are ceramic high-purity UO_2. After irradiation, the new radionuclides are largely uniformly distributed within the oxide lattice; thus, the dissolution of uranium oxide would be required for their release to occur. On average, approximately 2% of the inventory of some radionuclides, such as the noble gases Xe, Kr and Ar and the solids Cs and

I, are released from the UO_2 to void spaces within the fuel elements. A further 6% of these species, on average, are segregated to grain boundaries within the fuel.

Experimental studies of the dissolution of UO_2 and used fuel in groundwaters have shown that the fission products located in the void spaces in fuel elements are rapidly released upon contact with groundwater. The extent of release of fission products at grain boundaries during dissolution experiments is extremely limited. Dissolution of the UO_2 matrix containing the remainder of the fission products and the actinides is dependent on the redox condition of the groundwater, with oxidizing conditions accelerating the dissolution rate. Deep groundwaters in granite are oxygen-free, and dissolution of the used-fuel matrix would be extremely slow. Appropriate models for the dissolution of the UO_2 matrix have been developed, and they suggest that its behaviour would be similar to that of rich uraninite ores such as the ore body at Cigar Lake, which has experienced little dissolution since its formation 10^9 a ago. The dissolution model for used fuel has been described in detail by Johnson et al. (1994).

The technology for reprocessing UO_2 reactor fuels to remove fissile material for recycling in new reactor fuel is well established internationally, as are the processes for producing borosilicate glass waste forms for the vitrification of the liquid high-level wastes that arise from reprocessing. These processes have advanced to industrial-scale application. For example, France has been reprocessing fuels since about 1958 and has been producing containers of high-level-waste borosilicate glass since about 1969; the U.K. has been reprocessing fuels since about 1952 and is constructing new reprocessing and vitrification facilities at Sellafield.

The application of roto-spray and fluid-bed calciners for denitrating the liquid reprocessing wastes to produce a solid high-level waste has been demonstrated in the Canadian Nuclear Fuel Waste Management Program (CNFWMP). The continuous production of both borosilicate glasses and titanosilicate glass-ceramics containing simulated (non-radioactive) reprocessing wastes has been demonstrated using a continuously fed joule-heated ceramic melter, as has the batch crucible production of aluminosilicate glass blocks containing radioactive reprocessing wastes. Off-gas technology has been demonstrated for the abatement of NO_x gases from calcination and vitrification.

Borosilicate glasses are internationally accepted as a waste form for the immobilization of high-level reprocessing wastes, and there is a wide body of published data to support the understanding of the chemical and physical properties of these glasses as a function of their composition. The aqueous corrosion behaviour and mechanism of dissolution of borosilicate glasses continue to be the subject of international study; the factors most likely to affect the durability of the waste form under disposal conditions are well understood. Although physical property data exist for a wide variety of glass compositions, these properties would need to be determined in detail for any specific waste-form composition.

Our results on dissolution studies of borosilicate glass compositions have shown that their durabilities are comparable to borosilicate glasses developed internationally for the solidification of reprocessing waste. Our research has also indicated that glasses with a high silica content have the highest durabilities; however, these high-silica glasses would require higher fabrication temperatures and more complex fabrication technology than conventional borosilicate glasses. If these higher durabilities were required, further product and process development would be needed to optimize glass composition and fabrication processes.

Aluminosilicate glasses have been developed that also offer a greater corrosion resistance than most borosilicate glasses, again with the added complications of higher fabrication temperatures. An aluminosilicate glass was produced containing radioactive waste from used-fuel reprocessing experiments at the Chalk River Laboratories (CRL). The glass blocks produced were buried in a shallow sandy-soil aquifer at the CRL site. Radioactive releases from these blocks to the aquifer have been monitored for over 30 a; the results indicate that the glass is highly resistant to leaching. The results also suggest that this class of glasses forms an altered surface layer that strongly inhibits dissolution. This field-burial experiment is unique in the international waste management community.

High-durability sphene-based glass-ceramics have also been developed, with the additional benefit of incorporating virtually all of the actinide species and a majority of the long-lived fission products in a thermodynamically stable sphene ($CaTiSiO_5$) crystalline phase. The remainder of the waste ions have been shown to be incorporated in the highly durable aluminosilicate glass phase in this glass-ceramic. The glass-ceramic also offers the potential for using fabrication processes similar to conventional borosilicate glass production technology with only a moderate increase in fabrication temperature and technical complexity.

The corrosion behaviour of glasses and glass-ceramics has been examined in the presence of gamma-radiation fields comparable to those that would be present at the surface of a glass waste form after a period of 10 to 500 a. In all cases the corrosion rate observed was less than a factor of five greater than in the absence of a gamma field. In general, the effects of solid-state radiation damage and radiolysis of the groundwater are not expected to significantly increase the corrosion rate of the waste forms. Also, over the design containment period of 500 a, the gamma field would decrease by a factor of about 10^4, further reducing the effects of gamma radiation.

The development of models to describe borosilicate glass dissolution are internationally well advanced, and, in the CNFWMP, variations on these models have been developed to describe silicate glass dissolution in general. These models have been able to describe dissolution under both flowing and static dissolution conditions, as well as the dissolution of "simple" (three-component) borosilicate glasses and more complex glasses that develop alteration layers on their surface. The models could, in principle, be extended to describe the dissolution of aluminosilicate glasses; if combined with a thermodynamic model to describe the dissolution of crystalline phases, they could be extended to describe ceramic or glass-ceramic dissolution.

Other waste forms, such as Synroc (a synthetic assemblage of various minerals), ceramics, glass-ceramics, or cement-based products, have also been developed in international programs. The fabrication of most of these alternative waste forms has not been demonstrated on a fully radioactive industrial scale; they would require substantial process development work to bring them to the current operational status of borosilicate glasses. Synroc is one of the more advanced alternative waste forms and has been found to be more durable than conventional borosilicate glasses, particularly at temperatures above 100°C. Synroc is well characterized and inactive products have been successfully produced on a large scale. Testing of a fully active process would be required to evaluate the industrial application of this fabrication technology, and further tests would be required to assess the applicability of this waste form to any specific geochemical disposal environment.

Although not addressed in detail in the current phase of the CNFWMP, any future reprocessing program in Canada would have to develop waste forms for low- and intermediate-level wastes. The development of waste forms for these classes of waste is well advanced internationally and several countries, including Canada, have implemented programs for the disposal of low-level and reactor operations wastes in licensed facilities. Research on specific waste forms suitable for the immobilization of specific radionuclides, such as ^{3}H, ^{14}C, ^{85}Kr and ^{129}I, are ongoing in most national waste management programs; however, no candidate materials have been chosen as being most appropriate for these wastes. Several candidate materials have been defined and assessed in the CNFWMP for the immobilization of ^{14}C and ^{129}I under the anticipated geological conditions of a disposal vault in rock of the Canadian Shield.

A study of the volumes of solidified low-, intermediate- and high-level wastes likely to arise from reprocessing used CANDU fuel has shown that they would be very similar to the volume of used fuel entering the reprocessing facility. Moreover, the total inventory of fission products requiring disposal would be identical for the used fuel and for the waste form containing the wastes from the reprocessing of used fuel; thus, the disposal vault volume required for their disposal would be comparable, since the critical factor governing the size of the waste vault is the heat generated from fission-product decay. There would therefore be no major reduction in the volume of a disposal vault as a result of disposing of fuel-reprocessing wastes.

Our studies also indicate that the volumes of solidified waste arising from reprocessing CANDU fuel would be similar to those arising from reprocessing slightly enriched uranium (SEU) or light-water reactor (LWR) fuels, for the same fission-product loading and for the same electrical energy produced.

Other advanced technologies, such as actinide and fission-product waste separation (partitioning) from reprocessing wastes followed by nuclear transmutation, have been proposed to reduce the volume of specific long-lived radionuclides. Although these technologies are feasible in principle, they are at an early research and development stage and their technical and economic benefit and practical feasibility remain to be demonstrated. Moreover, these technologies would not eliminate the need for geological disposal, and may not significantly reduce the long-term hazard from that of disposing of used fuel or solidified high-level reprocessing wastes.

It is unlikely that any future decision to reprocess used CANDU fuel would be made exclusively on the basis of potential reductions in the volume of solidified high-level waste. In addition to economic considerations, any future decision to reprocess CANDU fuels would have to take into consideration the safety of the entire fuel cycle (reprocessing, vitrification and disposal).

ES.3 CONTAINERS FOR NUCLEAR FUEL WASTE DISPOSAL

The minimum target lifetime of the used-fuel disposal containers has been set at 500 a, the period during which the majority of the fission products would decay to stable isotopes. This design life would allow containers to be manufactured from either relatively inexpensive metals of a thickness that would provide sufficient corrosion allowance, or thinner, more expensive corrosion-resistant metals. Materials studies determined that, for the Canadian disposal concept, oxygen-free copper (a corrosion-allowance metal) and ASTM[2] Grade-2 titanium (corrosion-resistant) were the preferred choices for detailed study.

Within the reference disposal vault, the container would have to be structurally durable during the target lifetime, under external pressures up to 12.5 MPa at temperatures up to 100°C. This pressure would arise from the combination of up to 1000 m hydrostatic head, which would develop when the vault eventually resaturated with groundwater, and the swelling, due to water ingress, of the clay buffer that would surround each container. For the engineering study for a conceptual used-fuel disposal centre, locating containers within boreholes excavated in the floors of the disposal rooms was selected as the emplacement method. Structural durability could be achieved either by constructing the container with a sufficiently thick shell or by providing some means of internal support to a thinner-shell design. The geometrical arrangement of fuel bundles within the container would be maintained by installing the bundles inside tubes that would be welded together to form a "basket."

To investigate short-term structural integrity, full- and half-scale prototypes of four container designs have been tested under hydrostatic loading, and their deformation responses were monitored for comparison with analytical predictions. These prototype containers included a "stressed-shell" design, in which the corrosion-resistant shell was the only structural member resisting the load, and three "supported-shell" designs employing a thinner shell and internal support. All supported-shell prototypes were constructed of ASTM Grade-2 titanium. Internal support was provided by either (i) a compacted glass-bead particulate (packed-particulate

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[2] American Society for Testing and Materials

container); (ii) a fuel basket that both retains the bundles and provides support to the shell by the transference of the external load to it through compacted glass beads (structurally supported container); or (iii) a cast-in-place lead matrix (metal-matrix container).

All designs were found to possess acceptable short-term structural strength; however, development of the stressed-shell container was terminated when further studies showed that a very large shell thickness would be needed (≥70 mm for titanium) to prevent collapse of the container, during disposal, by creep-induced buckling.

Fabrication and inspection technology development has included studies of container closure welding, closure-weld inspection, compacted particulate materials, matrix casting, and reliability analysis (i.e., determination of the fraction of containers likely to have initial undetected defects).

From the container closure welding studies, it has been determined that the preferred closure techniques for titanium are resistance-heated diffusion (R/D) bonding or gas-tungsten-arc (GTA) welding; for copper, electron-beam welding is favoured. All techniques can be adapted for remote operation, such as in a shielded facility for container fabrication and loading at a used-fuel disposal centre.

In the closure-weld inspection studies, the feasibility of remote inspection by ultrasonic techniques was demonstrated using an industrial robot. At a used-fuel disposal centre, final inspection of the container-closure weld would be performed using both ultrasonic techniques and helium leak testing.

From an evaluation of twelve candidate materials, industrial glass beads (~1 mm in diameter) were selected as the preferred granular material for use in containers employing a compacted particulate as all or part of the internal support for the shell. The selection was based on compressive strength, material availability and ease of use. For metal-matrix containers, lead is the preferred casting material. Techniques to cast void-free matrices, on both an experimental and large-scale basis, have been developed.

Reliability analysis studies have determined that the proportion of containers that could be expected to be initially perforated or liable to early failure, as estimated from experience with present-day structures, appears to be between 1 in 1000 and 1 in 10 000.

To incorporate flexibility in our approach to container design, and to demonstrate that alternative concepts are possible for the disposal of nuclear fuel waste, a number of other container designs were investigated. Flexibility in approach is considered necessary to ensure that container design options could be developed to accommodate future changes in other parameters of the disposal system; for example, if specific characteristics of the disposal site changed, or if the potential economic advantages of integrated fuel storage, transportation and disposal options could be realized. The other container concepts investigated were as follows:

1. A dual-wall stressed-shell container. The specific design studied was the Ontario Hydro iron-based stressed-shell (IBSS) container. In this concept, a carbon-steel shell is provided with a corrosion-resistant overpack.

2. An integrated or multipurpose container suitable for storage, transportation and possibly disposal. This concept, called the dry storage container (DSC) concept, was developed by Ontario Hydro and has a concrete-based container capable of accommodating 384 used-fuel bundles. Future work will focus on the suitability of the concept for transportation and disposal.

3. Ceramics for long-life containers. To achieve very long container lifetimes (>100 000 a), the use of ceramic or vitreous materials, which can be produced with very high chemical stability, can be considered. While the non-metallic materials investigated have excellent corrosion resistance, we could not, without extensive further development, ensure that a container could be fabricated with high integrity. It was concluded that further work on the durability of ceramic materials for containers would be relevant only if it were linked with the full-scale fabrication of containers from such materials.

4. A container for fuel-reprocessing waste. The container designs investigated for disposal of used fuel could be readily adapted to accommodate fuel-reprocessing waste immobilized in a corrosion-resistant medium such as glass or glass-ceramic. To demonstrate this, a container design for the disposal of vitrified reprocessing waste was developed, based on the titanium-shell packed-particulate container design for used fuel.

To demonstrate engineering feasibility of the disposal concept, and the methodology to assess its long-term performance, it was necessary to develop a reference disposal facility design, including selection of the reference engineered barriers. This reference facility is described by Simmons and Baumgartner (1994). This reference facility design does not necessarily represent a final disposal concept selection; rather, it provides a common basis for the safety and engineering analysis that illustrates how a disposal facility design would be evaluated for implementation. Because the structural testing program conducted on the three candidate supported-shell container designs indicated no clear structural-performance advantage for one specific design, other factors were used to determine a reference container concept for the study. These included the ease of container fabrication, inspection, repair, handling, emplacement and retrieval; the chemical toxicity of the container construction materials; the degree of self-shielding provided by the design; its ability to provide an additional barrier; the temperature of the container after disposal; resource use; and cost. After consideration of these factors and the results of the short-term structural performance studies, the titanium-shell packed-particulate container was selected as the reference design.

Since container failure by mechanical overload can be avoided by prudent engineering design coupled with appropriate fabrication and inspection practice, it is expected that the container lifetime would eventually be limited by corrosion or other localized degradation processes. The specific corrosion/degradation process most likely to cause container failure would depend on the nature of the container material, its mode of construction, and the environment to which it was exposed.

A wide variety of different metals and alloys has been studied as potential container materials in the various national waste management programs. For purposes of comparison they can be divided into the following categories:

- corrosion-allowance materials, such as iron and carbon steels and copper and copper alloys; and
- corrosion-resistant materials, such as stainless steels, nickel-based alloys, and titanium and titanium alloys.

A problem in assessing the suitability of these materials for use in a Canadian disposal vault is that the available corrosion data may be specific to the particular disposal environment under study. The geological formations that have been considered for disposal can be grouped into three categories:

- crystalline rock (Canada, Sweden, Switzerland, U.K., U.S.A.);
- salt deposits (U.S.A., Germany); and
- sedimentary deposits, such as clay and seabed sediments (Belgium, U.K., U.S.A.).

The potential corrosiveness of each disposal environment is discussed and compared on the basis of the anticipated container surface temperature and the chloride concentration of the groundwaters.

Generally, a material's susceptibility to, and rate of, corrosion is expected to increase with an increase in temperature and chloride concentration (salinity). Of the crystalline rock environments, the plutonic rock of the Canadian Shield is potentially the most corrosive, with salinities comparable with or greater than those in sea sediments. The relatively benign nature of clay environments and the extreme aggressiveness of salt deposits are clearly apparent from the comparison discussed in this report.

The corrosion behaviour of various materials in these diverse disposal environments is compared in terms of the common controlling parameters. These parameters are the redox conditions within the vault, including the effects of irradiation; the surface temperature of the container; the concentration of aggressive species (particularly chloride) in the groundwater or vapour atmosphere; and the properties of the container material.

Iron and carbon steels are corrosion-allowance materials, and the required wall thickness for containers made from these metals is expected to be large. There exists a large database of published information on their corrosion under a wide variety of conditions. Their major disadvantage is that they are thermodynamically unstable in water. The two most significant modes of corrosion for iron and carbon steels are uniform corrosion and pitting, although microbial corrosion may also be significant if the supply of organic nutrients is not limited. Susceptibility to stress corrosion cracking (SCC) can generally be avoided by stress-relief heat treatments to reduce fabrication stresses.

A model has been developed in the U.K. to predict the corrosion allowance required for waste containers constructed from iron or carbon steel to survive for 1000 a in low-salinity crystalline rock environments. This model is for a combination of uniform corrosion and pitting and includes the effects of irradiation. By ignoring the possibility of protection against corrosion through the buildup of corrosion-product films, a conservative corrosion allowance of ~25 cm was predicted. This prediction should be contrasted with the corrosion allowance of 5 cm adopted for the reference container proposed in Switzerland. This latter value was based on the assumption that container corrosion would be uniform at a rate of 10 $\mu m \cdot a^{-1}$, which would remain constant over the lifetime of the container.

Of particular concern for iron or steel disposal containers are issues related to hydrogen gas phase formation in the disposal vault as a result of the reaction of iron with water. The effects of a buildup of hydrogen pressure in a vault and the potential for radionuclide transport under two-phase conditions require further study before iron or steel containers could be recommended for a Canadian disposal vault.

All of the major nuclear waste management programs have considered using copper or copper-based alloys as container materials. The major advantage of using copper is its thermodynamic stability when exposed to anoxic water. This makes it a particularly suitable candidate for granitic disposal environments in which anoxic conditions should be rapidly achieved once the waste vault is sealed. The corrosion modes anticipated for copper are uniform corrosion when oxidants are present, and pitting, although the latter process is very unlikely in the absence of substantial concentrations of species such as sulphide, which can induce passivity and thereby leave the metal susceptible to localized corrosion. Sulphide concentrations are expected to be negligible under Canadian disposal conditions. Microbially induced corrosion (MIC) is also a possibility, but Swedish calculations based on conservative assumptions regarding the activity of sulphate-reducing bacteria suggest a maximum of ~1 mm of MIC on copper containers. The maximum extent of MIC on a copper container in a Canadian vault is likely to be similar.

Assessments of the lifetimes of copper containers, based on uniform corrosion and pitting, have been carried out for both the Swedish and Canadian disposal concepts. Swedish groundwaters are more reducing than those in the Canadian Shield and contain more sulphide. Consequently, sulphide (or, more correctly, H^+ in the presence of sulphide) has been considered the major oxidant in Swedish assessments, whereas in Canada models have considered the presence of dissolved oxygen. Pitting is treated either by using a pitting factor (Sweden) or a statistical extreme-value analysis (Canada) of pit depth data available in the literature. Both assessments predict container lifetimes $>10^6$ a for thick-walled containers (6 to 10 cm in Sweden, 2.5 cm in Canada), providing anoxic conditions are achieved. Even if it is assumed that aerated conditions are maintained indefinitely, the lifetimes of copper containers under Canadian disposal conditions are predicted to range from 30 000 to $>10^6$ a.

Stainless steels have been considered as container materials in a number of environments, but remain as serious candidates only for the hot, dry and oxidizing conditions expected in the proposed tuff disposal facility (U.S.A.). In the highly saline environments anticipated in a Canadian vault, stainless steels are susceptible to localized corrosion processes, such as pitting, crevice corrosion and SCC. Since this susceptibility is higher for stainless steels than for the alternative corrosion-resistant materials (titanium alloys and nickel-based alloys), stainless steels are not considered viable materials for Canadian fuel waste containers.

Nickel can accommodate large additions of alloying elements without encountering phase instabilities, and a large number of alloys have been developed that take advantage of the passive nature of nickel and the properties of specific alloying elements. This prospect for designing materials with corrosion resistance to a wide range of severe environments has made nickel-based alloys popular candidates for waste containers, especially in the very aggressive saline environments associated with salt deposits (Germany).

For nickel-based alloys, uniform corrosion rates are generally negligible and processes such as pitting, crevice corrosion and possibly SCC are the likely degradation modes. At the relatively low temperatures anticipated in a Canadian waste vault, localized corrosion is not expected and these alloys remain potential candidates. However, irradiation has been shown to enhance localized corrosion at high dose rates, and, at present, it is not known whether a similar increased susceptibility would occur at the lower dose rates associated with Canadian waste containers. Without this information, these materials cannot currently be recommended for Canadian waste containers.

Titanium is generally the construction material of choice for applications involving exposure to warm saline environments. Titanium alloys exhibit negligible corrosion in seawater to temperatures in excess of 200°C; unalloyed titanium has been used for over 20 a in seawater applications such as power generation, desalination and oil refining. Other major advantages of these alloys are their apparent immunity to MIC, their very positive pitting potentials, and their lack of susceptibility to SCC. Failure of titanium waste containers would be either by crevice corrosion or hydrogen-induced cracking (HIC). These two processes are linked since the hydrogen required for HIC to occur is absorbed during crevice corrosion, making a thorough understanding of the latter process essential to any prediction of container lifetimes.

Within the context of nuclear fuel waste management programs, the crevice corrosion of three grades of titanium (ASTM Grades 2, 12 and 7) has been studied (Canada, U.S.A., Germany). Although it is difficult to claim total immunity to crevice corrosion for any of these grades, their crevice corrosion would be limited under waste vault conditions. Crevice propagation would be most extensive on the Grade-2 alloy and could proceed as long as oxidizing conditions endured within a vault. For the Grade-12 and Grade-7 materials, the extent of crevice propagation is severely limited by properties of the material, such as alloy content and phase composition, that result in a greater tendency for these materials to passivate. For these two materials, failure by crevice corrosion under Canadian waste vault conditions is very unlikely.

To date, a predictive model of container lifetimes has been developed only for the Grade-2 material using extremely conservative assumptions. Crevice corrosion is assumed to initiate rapidly and to propagate indefinitely because of the presence of sufficient oxygen to prevent repassivation of the crevices. Those containers that do not fail by crevice corrosion are assumed to fail by HIC once they cool sufficiently. According to this model >97% of containers in a Canadian waste vault would fail by crevice corrosion between 1200 a and ~6000 a. A small number, approximately 1 in 5000, would fail in the first 50 a as a result of undetected fabrication defects, and the remainder would fail by HIC. If this model was adapted to include the effects of repassivation when all the oxygen in the vault is consumed, or if an alloy more resistant to crevice corrosion was used, then much longer lifetimes (tens to hundreds of thousands of years) would be predicted.

In summary, the results of the container development program have shown that containers appropriate for not only meeting, but, if necessary, exceeding the minimum fuel-isolation objective of 500 a can be designed and manufactured. A variety of techniques are available to fabricate and inspect containers that would meet the required performance objectives. While future improvements in these technologies are virtually certain, and would likely be introduced for gains in quality control and/or manufacturing efficiency, they are not essential for fuel-waste container manufacture. For the engineering study of a conceptual used-fuel disposal centre, it has been possible to select a reference container design, taking into account the constraints of the study. Flexibility of design and choice of future container options has been demonstrated through the study of several alternatives, and further options can be studied.

Of the candidate container materials studied, both copper and titanium have been demonstrated to be capable of containing nuclear wastes under Canadian disposal conditions for >1000 a. Indeed, for copper, container lifetimes in excess of 10^6 a appear to be achievable. Lifetimes of tens of thousands of years appear feasible for titanium containers, but a more thorough assessment is required to demonstrate this. Of the alternative materials studied, nickel-based alloys may also be capable of providing the required containment, but their resistance to corrosion under irradiated conditions remains to be proven. Because of the problems associated with hydrogen production, irons and carbon steels cannot be recommended for disposal containers in crystalline rock in Canada, and stainless steels are no longer candidates in the Canadian program because of their susceptibility to localized corrosion in saline environments.

ES.4 VAULT SEALING

The disposal of nuclear fuel waste in crystalline rock would produce excavations that would require sealing to slow the movement of groundwater and delay the potential migration of radionuclides from the vault. The selection of materials for these seals and the seal designs will depend on the characteristics of the site, the design of the disposal vault and the design of the waste containers.

Three principal rock quality domains have been observed in Canadian Shield rock:

- fracture zones (faults), where intense fracturing occurs;
- moderately fractured rock, in which widely spaced discrete fractures exist; and
- sparsely fractured rock, which contains microcracks and very sparsely distributed fractures that are generally not interconnected.

Sparsely fractured rock, which has the lowest hydraulic conductivity, would be favoured for locating a vault.

The intersection of fracture zones during shaft and tunnel excavation and the degree of damage to the excavation boundary would be important considerations in the design of special shaft and tunnel seals and the application of grouts.

Several different vault designs have been considered both in Canada and in other countries, and the approach generally favoured is the room and pillar concept. This involves regularly spaced disposal rooms and connecting tunnels excavated on one or more levels. Two concepts for waste container emplacement, in-room and borehole, have been examined. The in-room concept involves emplacing containers within rooms at regular intervals, surrounded by sealing materials. In the borehole concept, containers surrounded by sealing materials would be emplaced within boreholes drilled in the floors of rooms. The borehole emplacement concept was selected as the basis for the study of a conceptual used-fuel disposal centre (Simmons and Baumgartner 1994). This study, while not the final selection of a design approach, permitted the examination of various engineering issues and provided a common focus for materials and design studies. Reference clay-based buffer material to surround the containers in the boreholes, and backfill material to fill the remaining excavations, were also developed.

The general objective of sealing is to minimize the hydraulic conductivity of the vault system as a whole by emplacing materials that would resist water flow. This would ensure that the slow process of diffusion would dominate the transport of radionuclides within the disposal vault. Specific seal applications include

- infilling vertical excavations such as shafts and exploration boreholes,
- infilling rooms, tunnels and horizontal exploration boreholes,
- creating special seals (buffer) around the waste containers,
- creating special seals where excavations intersected water-bearing fractures in the rock, and
- decreasing the hydraulic conductivity of the excavation-disturbed zone.

The most widely studied and preferred materials for sealing disposal vaults are clay- and cement-based materials. Clay minerals are characterized by small particle sizes and surface electrical charges as a result of imperfections in the lattice. Bentonite, a clay composed largely of the mineral montmorillonite, is a favoured sealing material because of its low hydraulic conductivity and an ability to absorb water and swell. Depending on the density, the hydraulic conductivity of bentonite may range from 10^{-10} to 10^{-13} $m \cdot s^{-1}$, and the swelling pressure may range from <1 to >10 MPa. The addition of aggregates, such as sand or crushed rock, can increase the thermal conductivity of the mixtures, increase the density to which the material can be compacted in situ, and decrease the shrinkage that occurs on drying, while maintaining low hydraulic conductivity. In contrast, to achieve low hydraulic conductivity and high swelling pressures, pure bentonite (i.e., without admixtures) must be precompacted as blocks at high density prior to emplacement. Bentonites can also be used for grouting fractured rock. Sufficient reserves of bentonite exist in Saskatchewan to supply the requirements for a large used-fuel disposal facility.

Cement-based materials can be tailored through the use of aggregates and additives to suit many applications where high strength and low hydraulic conductivities are required. One of the most important additives for high-performance concretes is silica fume, a material with a small particle size (<1 μm) that reacts with excess $Ca(OH)_2$ remaining after cement hydration. The $Ca(OH)_2$ is the weakest and most water-soluble constituent of the hardened material, and minimizing the quantity present improves the strength, decreases the porosity and reduces the amount of OH^- that may be released upon leaching by groundwater. Superplasticizers, which are organic additives used in small quantities (<2%), increase the fluidity and ease the emplacement of cement-based materials, which is particularly important for the injection and penetration of grouts into fractures. High-performance concretes and grouts that contain such additives can be virtually impermeable (hydraulic conductivity <10^{-15} $m \cdot s^{-1}$), and they demonstrate an ability to self-seal microfractures that may arise from shrinkage or thermal loads. Field experiments at Canada's Underground Research Laboratory (URL) have shown that fracture zones with a hydraulic conductivity of >10^{-8} $m \cdot s^{-1}$ can be effectively grouted with high-performance cement-based grouts.

Clay-based materials, in particular bentonites, are generally favoured for buffer materials that would surround waste containers and for backfill materials to fill rooms, tunnels and shafts. This preference arises because of their hydraulic and swelling properties and the near-neutral pH of pore water in bentonites, compared with the alkaline pH (~12) of pore water in concretes.

Reference buffer and backfill materials have been developed to provide a common basis for engineering studies and long-term performance assessment calculations. The reference buffer material consists of a 50:50 bentonite-sand mixture by dry mass compacted to an effective clay dry density of 1.21 $Mg \cdot m^{-3}$; it could be used in either the borehole or the in-room emplacement design. Compacted in situ, it has a hydraulic conductivity of 10^{-12} $m \cdot s^{-1}$ and a swelling pressure of ~2 MPa when fully saturated. As discussed by Johnson et al. (1994), this material has low diffusion coefficients for many radionuclides and is capable, upon resaturation, of resealing any shrinkage cracks that may result from drying after container emplacement. The reference backfill material, which would also be compacted in situ, is a 25:75 mixture by dry mass of glacial lake clay and crushed granite. To ensure that the upper regions of the rooms and tunnels are properly sealed, a pneumatically emplaced sand-bentonite mixture would be used; this technology has been demonstrated by the International Stripa Project (SKB 1993). The swelling properties of the backfill materials would ensure a full contact with the surrounding rock and an overall hydraulic conductivity of rooms and tunnels of $<10^{-10}$ $m \cdot s^{-1}$.

It is likely that composite seals of concrete and blocks of highly compacted bentonite would be used to seal entrances to rooms and any access tunnels that passed through hydraulically active zones. These seals would eliminate the possibility of groundwater flow in the backfill and at the rock-seal interface. The bentonite would likely penetrate some fractures in the excavation-damage zone and reduce hydraulic conductivity in this region. Similar composite seals would be used at various intervals to seal vertical shafts from the surface.

Small-diameter exploration boreholes drilled from the surface or from within the excavation would also need to be sealed. Methods for plugging both horizontal and vertical boreholes up to 100 m long with highly compacted bentonite have been demonstrated in the Stripa facility in Sweden. Cement-based plugs could also be used; this is the current practice for plugging oil and gas wells.

Field studies at the Stripa facility in Sweden and Canada's URL have examined a variety of sealing issues. At the Stripa facility, shaft sealing, backfill performance and buffer material behaviour at full scale have been studied. At the URL, grouting studies have been performed, and a full-scale buffer-container experiment is being performed using an electrical heater to simulate the decay heat of the waste.

Irrespective of the details of the vault design, it would be necessary to monitor components of the engineered barrier system after emplacement and throughout the operational lifetime of the vault to ensure performance requirements or criteria were being met. The purpose of this monitoring would be to confirm the performance of the engineered barriers over a period of several decades and to support the application for approval to decommission and close the disposal vault.

1. INTRODUCTION

The Nuclear Fuel Waste Management Program in Canada has focused on developing a concept for the geological disposal of nuclear fuel waste resulting from the operation of nuclear generating stations. The disposal concept proposes a method in which

- the waste form would be either used CANDU[1] fuel or solidified highly radioactive reprocessing waste;
- the waste form would be sealed in a container designed to last at least 500 a and possibly much longer;
- the containers of waste would be emplaced in rooms in a disposal vault or in boreholes drilled from the rooms;
- the vault would be nominally 500 to 1000 m deep in plutonic rock of the Canadian Shield;
- the waste containers would be separated from the rock by a buffer material;
- each room would be sealed with backfill and other vault seals; and
- all tunnels, shafts and exploration boreholes would ultimately be sealed such that the disposal facility would be passively safe; that is, long-term safety would not depend on institutional controls.

The disposal vault would be a network of horizontal tunnels and disposal rooms excavated deep in the rock, with vertical shafts extending from the surface to the tunnels. Rooms and tunnels might be excavated on more than one level. The vault would be designed to accommodate the rock structure and other subsurface conditions at the chosen site. The disposal container and vault seals would also be designed to accommodate the subsurface conditions at the chosen site. The disposal concept and its implementation constitute the proposed disposal strategy.

After the disposal facility was closed, humans and the natural environment would be protected from both radioactive and chemically toxic contaminants in the waste by multiple barriers: the container; the waste form; the buffer, backfill and other vault seals; and the geosphere.

The development of the concept has focused on meeting the following technical objectives regarding safety and feasibility:

- to develop and demonstrate the technology for the siting, design, construction, operation, decommissioning and closure of a disposal facility in plutonic rock;

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[1] <u>CAN</u>ada <u>D</u>euterium <u>U</u>ranium, trademark of AECL Research.

- to develop and demonstrate a methodology to evaluate the performance of a disposal system against established safety standards; and
- to establish that technically suitable disposal sites are likely to exist in Canada.

The disposal technology should not rely on long-term institutional controls as a necessary safety feature and should be currently available or readily achievable.

Because no disposal site has yet been selected and no disposal facility exists, the technical objectives can only be met by evaluating the safety of a hypothetical disposal facility, including the assumed geological setting, i.e., a reference disposal system. The major components and design features of this reference disposal system are outlined below:

- The waste form consists of 10-a-cooled, intact used-fuel bundles (Figure 1-1) with an average burnup of 685 $GJ \cdot kg^{-1}$ U. The used fuel is in the form of ceramic UO_2 pellets, which are encased in a Zircaloy-4 sheath.[2]
- The waste is in thin-walled ASTM (American Society for Testing and Materials) Grade-2 titanium containers with internal support provided by a packed particulate consisting of glass beads.
- The containers are placed in boreholes in the floors of disposal rooms excavated in plutonic rock at a depth of 500 to 1000 m, with a borehole spacing designed to give a maximum container surface temperature of 100°C. The geological and hydrogeological characteristics of the rock are based on studies of the Lac du Bonnet batholith in the Whiteshell Research Area of Manitoba (Davison et al. 1994b).
- A compacted buffer material consisting of 50 wt.% bentonite clay and 50 wt.% sand surrounds the containers in the boreholes.
- A compacted mixture of 75 wt.% crushed granite and 25 wt.% glacial lake clay is used to backfill most of the other parts of the excavations.
- A combination of buffer, backfill and cement-based materials provide seals in the shafts and other strategic locations in the vault.

The design of the reference disposal system, including both the surface and underground facilities, and the construction, operation, monitoring, decommissioning and cost are discussed by Simmons and Baumgartner (1994). They

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[2] Zircaloy-4 is an alloy of zirconium containing ~98 wt.% Zr, ~1.5 wt.% Sn and low concentrations of Fe and Cr (Wasywich 1993). The sheath material is subsequently referred to as either Zircaloy or Zr-4.

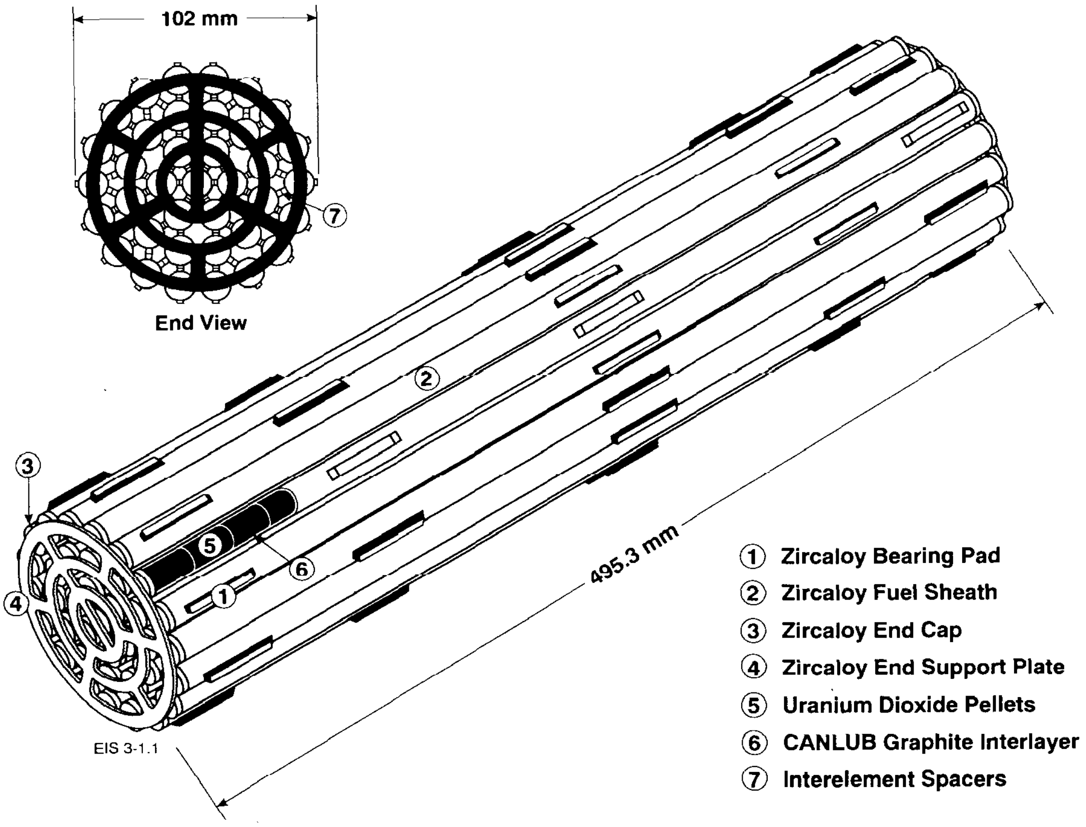

FIGURE 1-1: CANDU 37-Element Fuel Bundle

also discuss a number of vault design options for waste emplacement and vault layout, including in-room and borehole emplacement of containers, single- and multilevel vaults and long-borehole concepts.

The postclosure performance of the reference engineered barrier system has been evaluated with the vault model (Johnson et al. 1994). The vault model study presents conceptual and mathematical models for the postclosure performance of the disposal vault used in the reference disposal system, on the basis of the reference design and the properties of the engineered barriers and the surrounding rock.

Objectives of the Engineered Barriers Alternatives Report

The objective of this report is to describe the various materials and design options that have been considered and evaluated for engineered barriers during the development of the Canadian disposal concept. The principal factors that would affect the performance of these barriers under the conditions anticipated in a disposal vault are discussed. The basis for the selection of the design and materials for the reference engineered barriers system is outlined. In addition, alternative materials and designs are discussed, including approaches being developed in other countries. The option of using geological media for disposal other than plutonic rock of the Canadian Shield is outside the scope of this report and is discussed in the Environmental Impact Statement (EIS) (AECL 1994a).

The research programs on engineered barriers were originally laid out in a series of program documents that defined the scope and objectives of the various areas of research, including the following:

1. Fuel Isolation Research for the Canadian Nuclear Fuel Waste Management Program (Cameron 1982);
2. Advanced Containment Research for the Canadian Nuclear Fuel Waste Management Program (Onofrei et al. 1986a);
3. Fuel Characterization Research for the Canadian Nuclear Fuel Waste Management Program (Johnson and Crosthwaite 1984); and
4. Vault Sealing Research and Development for the Canadian Nuclear Fuel Waste Management Program (Lopez and Johnson 1986).

The approach has since evolved and has been further refined through consideration of regulatory requirements for nuclear waste disposal in Canada (AECB 1985, 1987). The following general principles summarize the basic approach adopted in developing and evaluating engineered barriers:

- The engineered barriers should be compatible with disposal at a depth of 500 to 1000 m in plutonic rock of the Canadian Shield.
- The designs and materials used for engineered barriers, and the operational activities necessary for their manufacture and emplacement, should be technically feasible with available technology or with reasonably achievable developments.
- The approach to designing engineered barriers should be flexible, so that a range of design options are available to accommodate potential constraints on vault design that might be imposed by the characteristics of an actual disposal site.
- The engineered barriers are integral components of the disposal system; consequently, their performance should be assessed in terms of the performance of the overall disposal system rather than by imposing quantitative performance targets for individual barriers.

With these principles in mind, the research and development program on engineered barriers has incorporated the following key components:

- small-scale laboratory experiments to understand the characteristics of materials of importance to engineered barrier design and performance;
- large-scale testing and demonstration to evaluate engineered barrier designs and materials at a scale and under conditions relevant to a disposal vault (the full- and half-scale structural

performance tests on containers discussed in Chapter 3, and the ongoing experimental program in the Underground Research Laboratory (URL) are important examples of this type of work);

- conceptual engineering studies of engineered barriers and the design of a hypothetical disposal facility to assess engineering feasibility and costs and to develop a reference system to demonstrate performance assessment methodologies (see Simmons and Baumgartner 1994);
- development of conceptual and mathematical models to describe the performance of the engineered barriers, e.g., container failure, the release of radionuclides from the used-fuel bundles and mass transport through the sealing materials into the surrounding rock (see Johnson et al. 1994); and
- studies of natural analogues to provide confirmation of our understanding of the long-term performance of engineered barrier materials in a disposal vault (see Cramer 1994).

In addition to these studies, in research areas where our own resources have been limited we have maintained close contact with waste management programs in other countries that are pursuing somewhat different approaches. In this report we present this information to illustrate the broad range of options that exist in the choice of engineered barriers. Of necessity, some of these approaches have received a much less detailed examination than has the reference system; thus, quantitative predictions of the performance of these alternative approaches are generally not available. In particular, it is noted that integrated models describing the performance of engineered barriers have been completed only for the design used in the postclosure assessment case study (see Johnson et al. 1994).

Scope

This document is divided into three sections. In the waste forms section (Chapter 2) the basic characteristics of used-fuel bundles and fuel-reprocessing waste forms are presented.

For the used-fuel disposal option, it would be possible either to stack an array of intact bundles within a container or to condition the fuel in some way prior to packaging. Early in the Canadian program (Cameron 1982) it was decided that the compact nature of used CANDU fuel bundles (see Figure 1-1) offered considerable flexibility with regard to the choice of container design options. Furthermore, any fuel conditioning or treatment process that involved dismantling the fuel bundles or breaching the fuel sheaths would result in the production of significant quantities of intermediate, low-level and, possibly, high-level radioactive wastes that would require processing and disposal. The approach to designing containment for used fuel and assessing its performance as a waste form has, therefore, focused solely on intact fuel bundles.

For fuel-reprocessing waste forms, we describe the technology for processing and solidifying the various waste streams that would be produced as a result of fuel reprocessing. Used CANDU fuel is not currently reprocessed, and no decision has been made on whether or not to do so in the future. The economics of reprocessing are currently unfavourable and are unlikely to become significantly more favourable in the next few decades. In discussing the solidification of fuel-reprocessing wastes, we rely heavily on information available from countries that have operational experience with this technology. It is emphasized that fuel reprocessing operations themselves are beyond the scope of this review; thus, the discussion in Chapter 2 is limited to aspects related to the production and performance of fuel-reprocessing waste forms. In addition, the prospects for developing models that describe radionuclide release from these waste forms after disposal are discussed.

In Chapter 3, we discuss containers for nuclear fuel wastes and present a variety of options. Our own studies have focused largely on titanium and copper containers. The prospects for providing containment with carbon steel and nickel-based alloys are also discussed in terms of fabrication and structural and long-term corrosion performance.

Various containment targets have been considered in the Canadian program, and a minimum container lifetime of 500 a was suggested (Cameron 1982). This choice is related to the relatively rapid decrease in radioactivity (also referred to as activity) of the waste (a factor of 100 000) in the first few hundred years. The provision of longer-term containment (10 000 to 100 000 a) results in relatively small further decreases in waste activity prior to potential release of radionuclides. As a result, the major focus in the Canadian research program has been on providing containment for a minimum of 500 a. The possibility of providing much longer-term containment using copper and titanium containers is also discussed.

In Chapter 4, on disposal vault sealing, we describe the sealing strategy and the different materials that have been considered. The principal focus is on clay-based and cement-based materials. The reader is referred to Simmons and Baumgartner (1994) for a discussion of alternative vault designs.

The final selection of waste form, container material and design, and sealing materials and methods will depend on technical considerations presented here, the characteristics of an actual disposal site and future technical advances that will occur prior to disposal implementation.

2. WASTE FORMS

2.1 INTRODUCTION

AECL has investigated two options for the packaging and disposal of used CANDU fuel: direct disposal of used-fuel bundles, and disposal of solidified high-level wastes that would arise if the used fuel were reprocessed at some time in the future. The purpose of reprocessing used fuel is to remove fissile materials (^{235}U, ^{239}Pu) that could be recycled in the fabrication of new power-reactor fuel. The two disposal options are shown schematically in Figure 2-1.

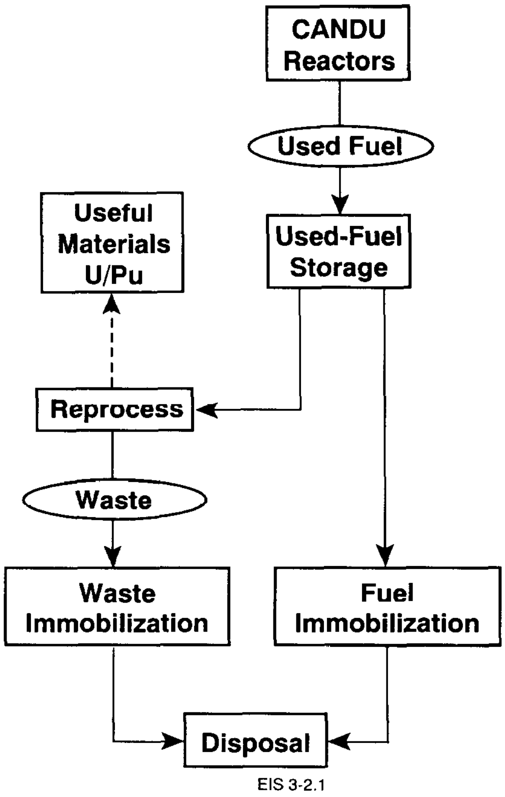

FIGURE 2-1: Options for the Storage and Disposal of Used CANDU Fuel

For the option of disposal of unreprocessed used fuel, the approach proposed in Canada involves disposal of intact fuel bundles. This approach is favoured both because CANDU fuel bundles are compact, providing flexibility in the selection of the size and shape of disposal containers, and because fuel-bundle disassembly or conditioning would produce additional wastes.

For the option of disposal of solidified high-level wastes from the reprocessing of used CANDU fuel, we have assumed that the Purex[3] process would be used. This is the technology currently used in reprocessing facilities in France and the United Kingdom. In this process, the dissolution of UO_2 fuel in nitric acid solution is followed by chemical separation procedures to remove the fissile materials. One of the waste streams generated in this separation is a highly radioactive (high-level) liquid waste solution containing the majority of the fission products. In addition, other low-activity (low- and intermediate-level) waste streams are produced. To convert these materials to a form suitable for permanent geological disposal, it is necessary to incorporate them into solids that can be conveniently packaged and will resist dissolution in groundwater.

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[3] Plutonium uranium reduction extraction.

Solidification (immobilization) of high-level liquid wastes is typically done using a process referred to as vitrification, in which the liquid wastes are evaporated to leave a solid residue that is mixed with glass-forming ingredients and melted at high temperatures. The molten mixture can then be poured into containers in which the glass solidifies. Borosilicate glass is the waste form used in commercial reprocessing facilities; it has been chosen because of its ease of fabrication and its high aqueous-corrosion resistance. A number of alternative glass, glass-ceramic and ceramic waste forms have been developed in various countries as candidate waste forms, although none has been used in full-scale waste solidification facilities. In Canada, borosilicate glasses, aluminosilicate glasses and titanosilicate glass-ceramics have been investigated as waste forms.

The intermediate- and low-level reprocessing wastes also require treatment or solidification before disposal. These wastes are the liquid chemical processing streams used in the Pu separation and purification steps; the fuel hulls (segments of Zircaloy fuel sheath) and other undissolved solids remaining after fuel dissolution; and the off-gases containing ^{85}Kr, ^{3}H, ^{129}I and ^{14}C released during the fuel dissolution stage and, subsequently, during the vitrification stage.

Different waste forms are required for the solidification of each of the waste streams arising from fuel reprocessing. The volumes of waste that would be produced from the reprocessing of used CANDU fuel have been estimated. In performing this analysis, we assumed that CANDU fuel would be reprocessed using the Purex process and that the wastes would be solidified in borosilicate glass. Waste solidification technologies currently in use in France and the U.K. were assumed to be used to process the medium- and low-level waste streams. On the basis of this approach, the total volume of solidified wastes was estimated to be similar to that of the initial volume of used fuel (see Appendix A, Table A-4 and Section 2.3.8) (Harvey, in preparation(a)).

The following sections briefly describe the characteristics of used fuel and discuss in more detail both the process technologies for solidification of high-level wastes and product development studies on waste forms. The technologies that have been developed for reprocessing used fuel, and the environmental impact and safety aspects of operating a reprocessing facility are beyond the scope of this review and are not discussed here. The factors that would control radionuclide release from used fuel in a disposal vault are described and the radionuclide release model is briefly summarized. The model is presented in detail by Johnson et al. (1994). Models suitable for incorporation into an overall performance assessment that describe the release of radionuclides from the various fuel-reprocessing waste forms in a disposal vault have not been developed to the same level, although conceptual models that have been developed are presented here.

2.2 USED FUEL

2.2.1 Description of CANDU Fuel

The CANDU reactor uses natural uranium oxide (UO_2) fuel, in the form of stacks of ceramic pellets contained within a Zircaloy sheath. The fuel elements are assembled into bundles as shown in Figure 1-1; a fuel bundle of this 37-element design contains approximately 21.5 kg of UO_2 and 2.3 kg of Zircaloy-4. Approximately 60% of the bundles in storage are of this design, used in the Bruce, Darlington and CANDU-600 reactors; most of the remainder are of the Pickering reactor 28-element design. The small dimensional and weight differences between the various bundle designs have no significant impact on disposal container design and dimensions, or on the radionuclide content of fuel bundles per unit mass of fuel. Details of the various bundle designs are given by Wasywich (1993).

2.2.2 Quantities of Used CANDU Fuel in Storage in Canada

In Canada, used fuel from power reactors is currently stored either in water-filled pools (wet storage) or in concrete storage canisters (dry storage). Table 2-1 lists the storage locations and, for each location, the licensee, storage method and amount of used fuel. Table 2-1 includes the used fuel from three prototype power reactors, Douglas Point, Gentilly 1, and NPD (Nuclear Power Demonstration Reactor, Rolphton, ON), that have been permanently shut down. Most of the used fuel from power reactors is currently stored at the sites where it was produced. About 900 000 bundles of used fuel from power reactors were in storage in Canada as of 1992 December 31.

Future used-fuel arisings will depend on a variety of socioeconomic and technical factors, as discussed in the EIS (AECL 1994a). Four scenarios have been considered in examining future fuel arisings, and the projections based on these are shown in Figure 2-2. The assumptions for the four scenarios and the resulting projections are as follows:

1. Canadian nuclear generating capacity existing or under construction as of 1985 is maintained; one additional CANDU 600 is built outside Ontario and begins operating in 1996; and the annual growth rate of nuclear-generated electricity in Ontario after 1995 is 3%. These assumptions formed the basis for a projection made in 1985 (Baumgartner et al. 1993). According to that projection, by the end of 2035, a total of about 10^7 bundles of used fuel would be produced in Canada.

2. Canadian nuclear generating capacity existing as of 1993 March 31 is maintained. By the end of 2073, a total of about 10^7 bundles of used fuel would be produced.

3. Canadian nuclear power reactors existing as of 1993 March 31 are operated for 40 a, but no new reactors are constructed. By the end of 2033, when the last reactor is shut down, a total of about 4.3×10^6 bundles of used fuel would be produced.

TABLE 2-1

STORAGE OF USED FUEL IN CANADA (1992 DECEMBER 31)

Location	Licensee	Storage Method	Number of Bundles in Storage	Reference for Data on Storage Methods and Quantities
Bruce	Ontario Hydro	wet	432 199	AECB 1993
Pickering	Ontario Hydro	wet dry	337 742 382	AECB 1993 AECB 1993
Darlington	Ontario Hydro	wet	6 533	AECB 1993
Point Lepreau	New Brunswick Power Corporation	wet dry	39 010 13 500	AECB 1993 AECB 1993
Gentilly 2	Hydro-Québec	wet	39 008	AECB 1993
Douglas Point	AECL	dry	22 256	AECB 1993
Gentilly 1	AECL	dry	3 213	AECB 1993
Chalk River Laboratories	AECL (fuel from NPD)	dry	4 853	Wasywich 1993
Whiteshell Laboratories	AECL (fuel from Douglas Point)	dry	360	Ohta 1978
Total			899 056	

4. Canadian nuclear power reactors existing as of 1993 March 31 are shut down as of 1995 January 1, by which time a total of about 1.1 x 10^6 bundles of used fuel would be produced.

For the postclosure assessment case study, the reference used-fuel production rate is the rate estimated in the first scenario involving additional reactors.

2.2.3 Burnup of Used CANDU Fuel

The quantities of radionuclides in used fuel increase with increasing burnup of the fuel, which is a measure of the energy released per unit mass of fuel as a result of irradiation in the reactor, expressed in the units $GJ\cdot kg^{-1}$ initial U.

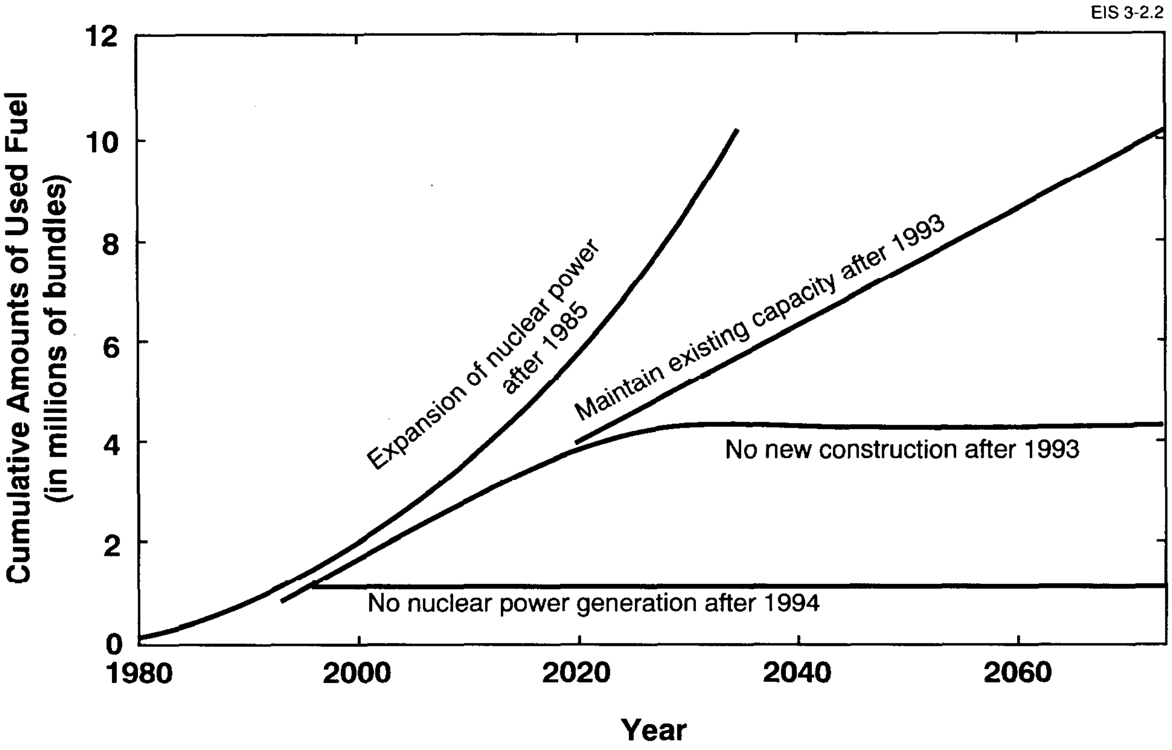

FIGURE 2-2: Four Projections of Cumulative Amounts of Used Fuel in Canada

The burnup of CANDU fuel bundles at discharge from the reactors varies considerably, depending on the in-core fuel management scheme. The discharge burnup distribution for fuel bundles from the Bruce A station in 1982 is shown in Figure 2-3 (Truant 1983). In order to calculate both the radionuclide content for purposes of disposal-facility design and performance assessment, and the decay heat of used-fuel bundles, it is necessary to determine an average fuel burnup. This can be estimated from reactor physics calculations. A reference used-fuel burnup of 685 $GJ \cdot kg^{-1}$ U was adopted for the EIS on the basis of predicted equilibrium burnups for Pickering, Bruce and Darlington nuclear generating stations (Mylvaganam 1992). Truant (1983) reported that the average discharge burnup of bundles at Pickering A and Bruce A is 704 and 708 $GJ \cdot kg^{-1}$ U respectively.

The difference between the reference burnup assumed for the EIS and the values reported by Truant is a result of changes in in-core fuel management practices to increase the fuel burnup. Recent data indicate that the average fuel-bundle burnup for Ontario Hydro reactors has increased to the 720-760 $GJ \cdot kg^{-1}$ U range. Should this increase in average discharge burnup be sustained, the average radionuclide inventories and decay heat of used-fuel bundles would be increased by 5 to 10% in comparison with the corresponding properties of the reference used fuel, although there would be a concomitant decrease in the rate of discharge of used fuel from the reactors.

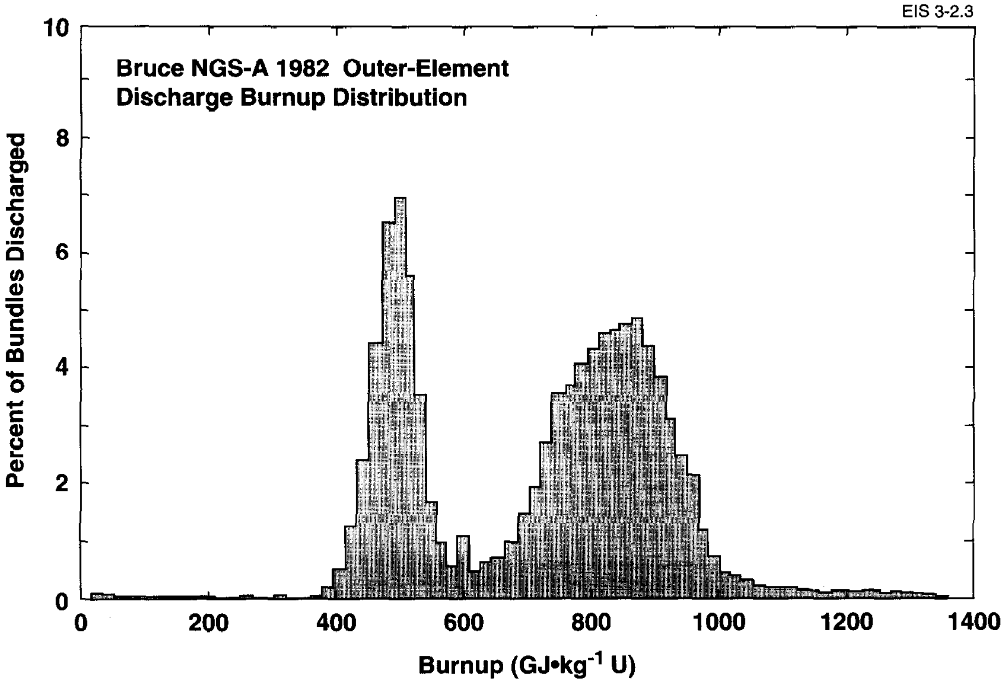

FIGURE 2-3: Bruce Discharge Burnup Distribution (Truant 1983)

2.2.4 The Radioactive Decay Properties of Used CANDU Fuel

Used CANDU fuel contains approximately 350 different nuclides, of which about 200 are radioactive; these include fission products, activation products, actinides and their decay products. For the reference fuel burnup of 685 $GJ \cdot kg^{-1}$ U, the new nuclides produced (both stable and radioactive) make up approximately 1.3% of the mass of used fuel. The composition of the reference fuel before and after irradiation is shown in Figure 2-4. In addition to radionuclides in the fuel itself, activation products are produced from impurities and alloying additives in the Zircaloy sheath as a result of the in-reactor capture of neutrons by stable nuclei. The concentrations of various nuclides in fuel bundles can be calculated using isotope generation/depletion codes, such as CANIGEN[4] or ORIGEN-S[5] (Smith et al. 1987, Tait et al. 1989). These codes use nuclear cross-section and decay-constant data, along with reactor physics models and data, to calculate the concentrations of nuclides in used-fuel bundles as a function of burnup. The agreement between the predictions of such codes is within ~±10% for the major heat-producing radionuclides. The radionuclide inventory values for CANDU fuel with a burnup of 685 $GJ \cdot kg^{-1}$ U

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[4] CANDU Isotope GENeration and Depletion.

[5] Oak Ridge Isotope GENeration and Depletion - Scale.

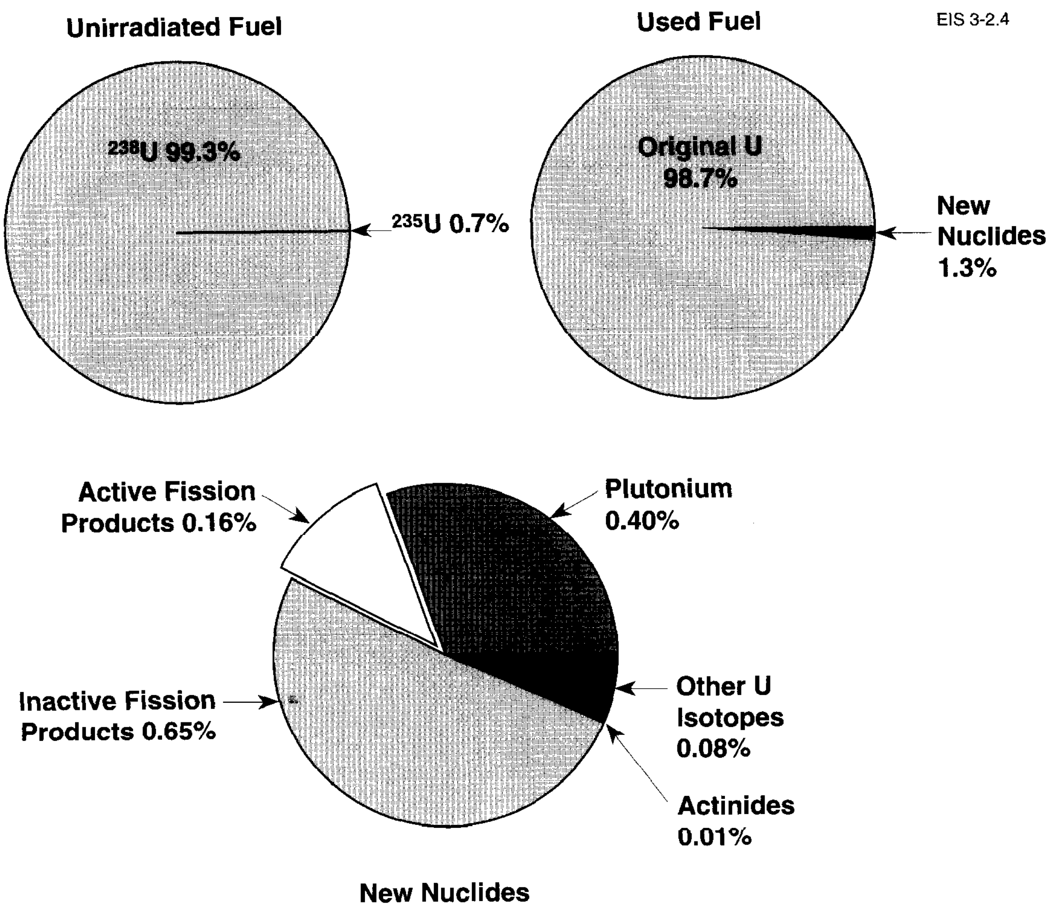


FIGURE 2-4: Composition of Fuel Before and After Burnup (685 GJ·kg^{-1} U, 10-a cooled)

have been calculated with ORIGEN-S and are reported by Tait et al. (1989); they list the concentrations, activity and heat output of the various radionuclides present in the used fuel. Table 2-2 lists some of the key radionuclides along with their half-lives and concentrations.

The codes that predict radionuclide inventories have been verified for both light-water reactor (LWR) fuel and CANDU fuel. For LWR fuel, radionuclide inventories predicted using ORIGEN2 have been compared with those measured using radiochemical techniques (Guenther et al. 1988). With minor exceptions, agreement is within 12%. Similar good agreement has been found by Tait et al. (in preparation) for used CANDU fuel.

TABLE 2-2

INVENTORIES OF KEY RADIONUCLIDES IN 10-a-COOLED USED CANDU FUEL AS CALCULATED WITH THE ORIGEN-S CODE FOR A FUEL BURNUP OF 685 GJ·kg^{-1} U (Tait et al. 1989)

Isotope	Inventory (g·kg^{-1} U)*	Activity (Bq·kg^{-1} U)*	Half-Life (a)
^{243}Am	2.63×10^{-3}	1.94×10^{7}	7 380
^{241}Am	8.72×10^{-2}	1.11×10^{10}	432
^{241}Pu	1.43×10^{-1}	5.37×10^{11}	14.7
^{240}Pu	1.03	8.70×10^{9}	6 537
^{239}Pu	2.76	6.36×10^{9}	24 000
^{239}Np	2.26×10^{-9}	1.94×10^{7}	2.35 (d)
^{237}Np	3.88×10^{-2}	1.01×10^{6}	2.14×10^{6}
^{238}U	985	1.22×10^{7}	4.40×10^{9}
^{235}U	2.02	1.61×10^{5}	7.00×10^{8}
^{234}U	4.31×10^{-2}	9.95×10^{6}	2.40×10^{5}
^{90}Sr	1.02×10^{-1}	5.14×10^{11}	29
^{93}Zr	1.68×10^{-1}	1.56×10^{7}	1.5×10^{6}
^{93m}Nb	5.82×10^{-7}	6.11×10^{6}	13.6
^{99}Tc	2.05×10^{-1}	1.28×10^{8}	2.13×10^{5}
^{126}Sn	4.94×10^{-3}	5.18×10^{6}	1×10^{5}
^{129}I	4.48×10^{-2}	2.93×10^{5}	1.6×10^{7}
^{135}Cs	2.37×10^{-2}	1.01×10^{6}	3.0×10^{6}
^{137}Cs	2.39×10^{-1}	7.66×10^{11}	30.17
^{14}C	2.58×10^{-4}	4.26×10^{7}	5 730
^{14}C**	3.82×10^{-4}	6.29×10^{7}	5 730
^{93}Zr**	1.51×10^{-1}	1.40×10^{7}	1.5×10^{6}
^{93m}Nb**	5.23×10^{-7}	5.48×10^{6}	13.6

* Units expressed as grams or becquerels per kilogram of initial uranium in the fuel

** Activation products of impurities in Zircaloy sheath (per kilogram Zircaloy)

The radioactive decay characteristics of used CANDU fuel and the Zircaloy sheath are shown in Figure 2-5. For comparison purposes, the calculated radioactive decay curve of concentrated natural uranium oxide (UO_2 and its associated daughter decay products) is also shown. During the first ten years after discharge from the reactor, the activity of used fuel decreases by a factor of 1000, and within approximately 500 a, the activity is less than 1/100 000 of the initial value, as a result of the decay of the great majority of fission products. The rate of decrease in activity becomes slower after approximately 500 a. This was a major consideration in selecting a minimum design lifetime of 500 a for disposal containers, as discussed in Section 3.1.

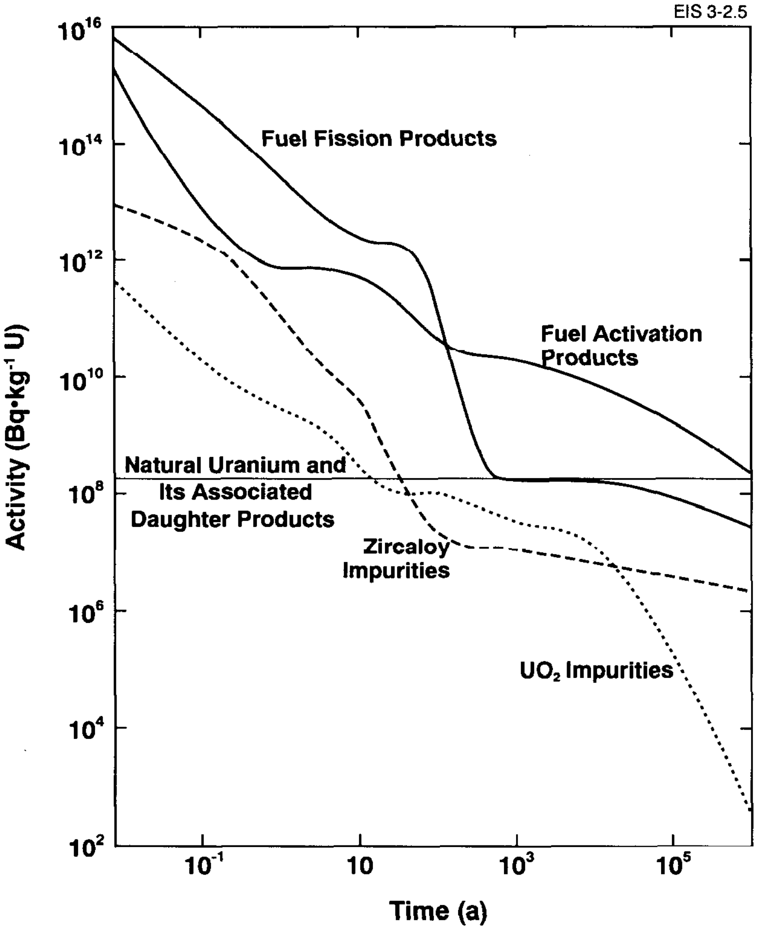


FIGURE 2-5: Radioactive Decay Characteristics of CANDU Fuel and Zircaloy Sheath (Burnup 685 GJ·kg^{-1} U). Activation products refers to actinides produced by neutron capture, whereas Zircaloy and UO_2 impurities refer to radionuclides produced by neutron capture on stable low concentration impurities present in the fuel and sheath prior to irradiation.

As a result of radioactive decay, used-fuel bundles emit penetrating gamma radiation and heat, both of which are major design considerations for the safe storage, transportation and disposal of used fuel. The radiation field produced by a used CANDU fuel bundle as a function of time is shown in Figure 2-6. Gamma-radiation emissions decrease by a factor of 10^4 between 1 and 500 a after discharge of the fuel from the reactor. Neutron emissions are low from CANDU fuel, and they decrease very gradually with time.

Immediately upon discharge from the reactor, the fuel bundles are placed in pool storage; the water provides both shielding and cooling. During the

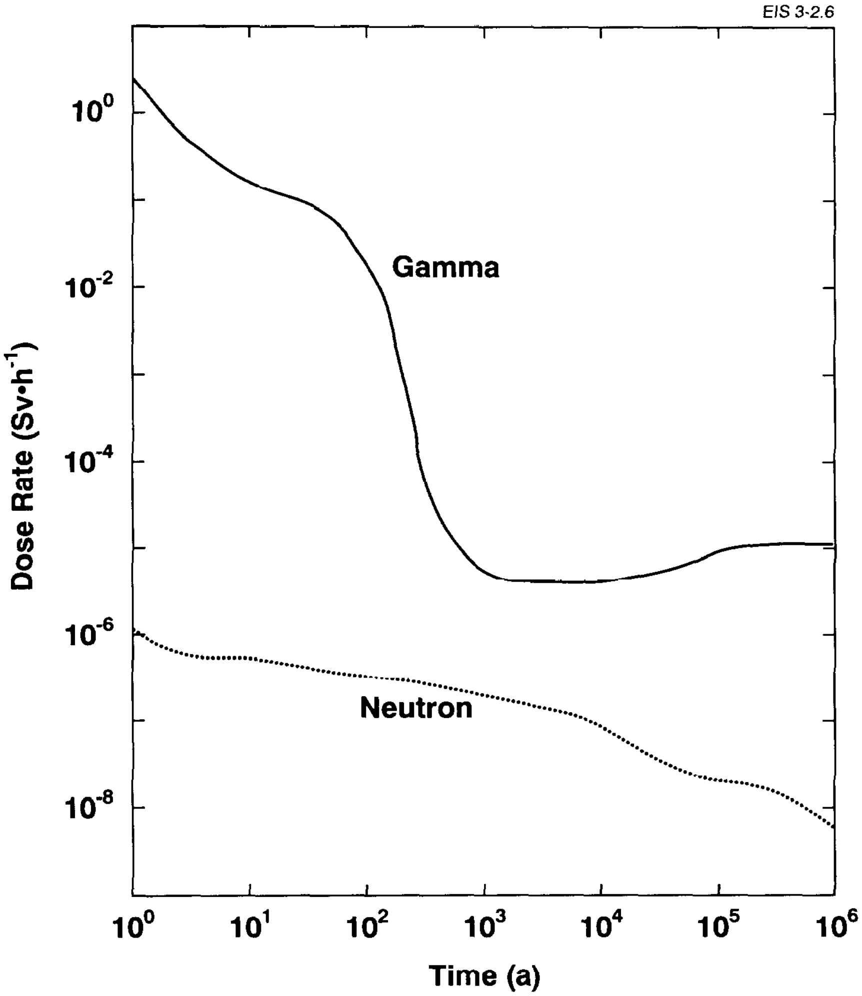


FIGURE 2-6: External Radiation Dose Rate from a 37-Element Used-Fuel Bundle (685 $GJ \cdot kg^{-1}$ U) at a Distance of 1 m (in air)

first five years of storage in the pool, the decay heat (i.e., the amount of heat generated per unit mass of fuel as a result of radioactive decay ($W \cdot kg^{-1}$ U) decreases by a factor of one thousand (Figure 2-7).

Because the heat output of used fuel changes with time, it was necessary to assume a reference age for used-fuel bundles when developing the reference disposal system design. The reference age was specified as 10 a. The actual average age of used-fuel bundles would be considerably greater than this by the time a disposal facility could be built and disposal begun.

The provision of appropriate radiation shielding during used-fuel transportation and during the operation of a disposal facility is discussed by Simmons and Baumgartner (1994). The impact of the radiation and heat emitted on the performance of engineered barriers in a disposal vault is discussed by Johnson et al. (1994).

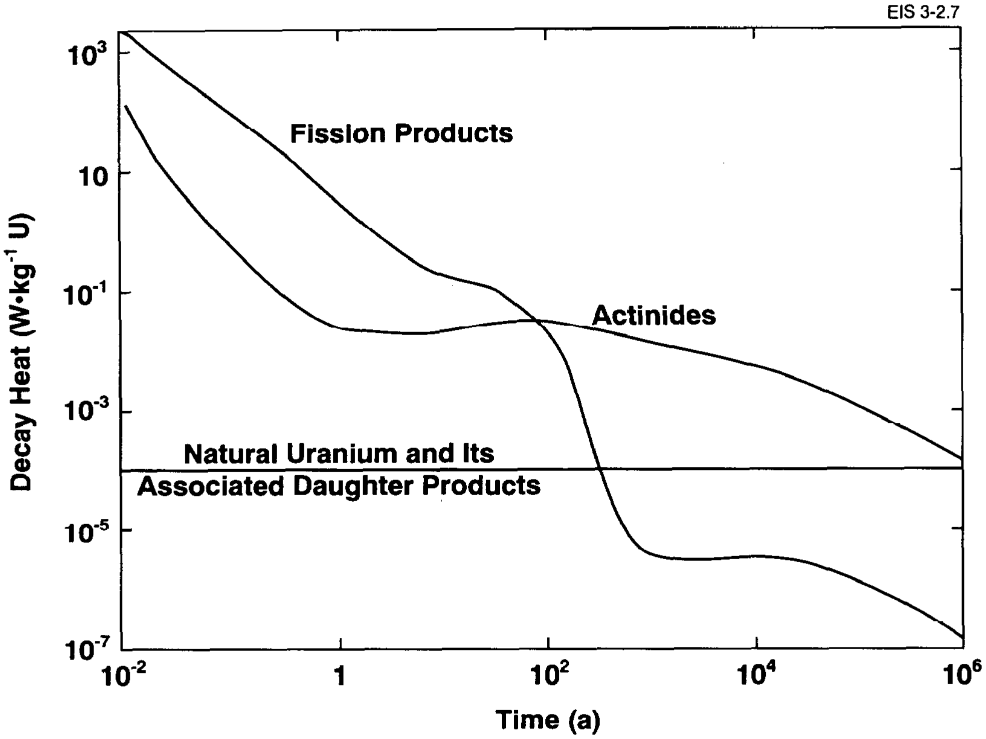


FIGURE 2-7: Decay Heat of a 37-Element Used-Fuel Bundle as a Function of Time (685 GJ·kg^{-1} U). The decay heat of natural UO_2 in equilibrium with its daughter products is shown for comparison.

2.2.5 The Condition of Fuel Bundles at Discharge from the Reactor

The primary coolant in CANDU reactors (heavy water) is routinely monitored during reactor operation to detect fuel-bundle failures, i.e., fuel elements that develop through-wall sheath defects during operation. As a result, fuel-bundle defect rates for each station are well documented. Prior to 1983, approximately 0.1% of CANDU fuel bundles in Ontario Hydro reactors developed defects (Truant 1983); more recently a figure of 0.06% has been reported (Hains et al. 1986). When a bundle defect occurs, only one fuel element per bundle is normally affected; thus, only about 0.003% of fuel elements would be defected for a 0.1% defect rate. For the reference fuel arisings of 10^7 bundles to the year 2035 (Section 2.2.2), approximately 10 000 bundles would be expected to be defected, assuming 0.1% of bundles have defects.

In the majority of cases, fuel defects involve a small penetration of the sheath; the fuel bundle as a whole maintains its integrity. Such bundles are typically handled at the generating stations in the same way as intact bundles; thus, no special considerations would be necessary for handling such fuel at the surface facilities where the fuel would be placed in disposal containers. Simmons and Baumgartner (1994) describe methods for handling more seriously damaged fuel bundles.

Surface deposits of corrosion products have been observed on used CANDU fuel bundles. These arise from corrosion of the primary heat transport system in the reactor and deposition of dissolved iron, cobalt, nickel and chromium species in the primary coolant water onto fuel sheath surfaces during reactor operation. Average quantities are typically less than 3 mg per fuel bundle. Neutron activation causes these deposits to become radioactive; the activity of these deposits has been measured and determined to be very small. For example, the activity of surface deposits of ^{60}Co on a 6.4-a-cooled Pickering fuel bundle was 4.6 x 10^4 Bq, whereas the total activity of the bundle (fuel plus sheath) was 7.3 x 10^{13} Bq (Wasywich 1993).

2.2.6 Changes in Fuel Properties During Storage, Transportation and Emplacement in Disposal Containers

Used-fuel bundles are stored either in water-filled bays or in air in concrete canisters at the generating stations. Wet storage of fuel is a well-established technology that has been in use worldwide for over 40 a. Several studies, including a recent study of CANDU fuel stored for up to 27 a in water, have concluded that undefected bundles experience insignificant degradation during wet storage (Wasywich 1992, Hunt et al. 1981). This is attributed to the exceptional corrosion resistance of Zircaloy in low-temperature high-purity water. In defected elements, some very limited oxidation of the fuel is observed, but the extent of alteration is far too small to affect fuel element or bundle integrity. On the basis of these studies, it has been concluded that used fuel can be safely stored in water pools for periods of at least 50 a (Wasywich 1992). Detailed destructive examinations of used fuel in water storage are performed every 10 a as part of a joint AECL Research/Ontario Hydro program; the most recent examination was carried out in 1990 (Wasywich 1992).

After five years of storage in water, the decay heat of used CANDU fuel has decreased significantly; it can then be stored in air in concrete canisters. This storage method, referred to as dry storage, has been adopted within the last 10 a in Canada and several other countries (Figure 2-8). Evidence indicates that the temperature of 10-a-cooled fuel will not exceed 125°C in such canisters (Wasywich and Frost 1988). Examinations of the condition of CANDU fuel bundles stored in air at 150°C are performed every one to two years in order to obtain data to predict possible changes to fuel-bundle integrity over very long storage times. Results from studies of defected and undefected CANDU fuel bundles in dry storage at 150°C have shown that the relatively small changes occurring in defected elements are unlikely to affect fuel element integrity (Wasywich and Frost 1988). No evidence of corrosion or other degradation of Zircaloy has been observed. It has been concluded (Frost et al. 1993) that used CANDU fuel in dry storage should retain its integrity for at least 100 a if the fuel elements are intact, and for at least 50 a if the fuel sheath has a through-wall defect.

A comprehensive review of used-fuel storage experience in Canada is presented by Frost (1994).

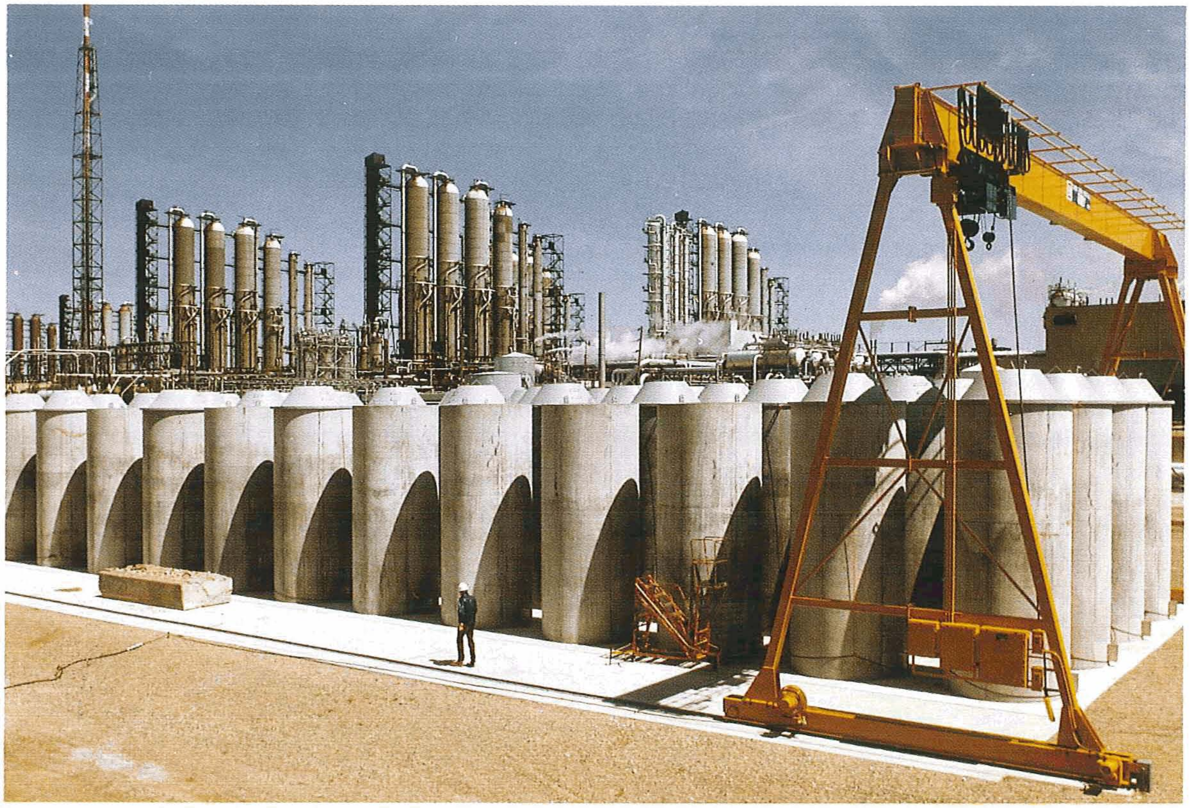


FIGURE 2-8: Dry Storage Canisters at the Douglas Point Reactor Site in Ontario

It is possible that remote handling operations and vibrations experienced by used-fuel bundles during transportation from the generating stations to a used-fuel disposal centre could affect fuel-bundle integrity. Such a loss of integrity, in particular by fracture of the end plate/end cap weld, would have an impact on subsequent fuel-bundle handling and emplacement in disposal containers. Extensive tests with used-fuel bundles, which involved simulation of accelerations experienced during fuel-bundle transport as well as exposure to higher accelerations for shorter periods of time, indicate that failures are highly unlikely during normal railcar or road transportation of the bundles (Forest 1980, Wasywich 1993).

The reference titanium container for disposal of used fuel would contain 72 fuel bundles in a vertical array of tubes; the void space in the container would be filled with glass beads. The container is discussed in detail in Chapter 3, and the procedure for emplacing fuel bundles into the reference container is described by Simmons and Baumgartner (1994). The glass-bead particulate would be vibratory compacted to ensure complete internal support of the container shell. During this procedure, movement of fuel bundles would be limited by the presence of the surrounding particulate; thus, this short-term (15 min) vibration is not expected to cause further fuel-bundle or element failures.

In the metal-matrix container design, an alternative to the reference container design, the residual volume in the container would be filled with cast metal (see Section 3.5.2.4). The most suitable metal is lead; maximum casting temperatures would be below 400°C and are not expected to affect the integrity of the fuel sheath (Wasywich 1993, Mathew et al. 1983).

2.2.7 Comparison of CANDU Fuel to Light-Water-Reactor Fuel

Several other countries besides Canada, for example, the United States, Sweden, the Federal Republic of Germany and Finland, are examining the concept of deep geological disposal of used fuel. Although in all cases the fuel is composed of uranium oxide pellets clad in Zircaloy, there are substantial differences in both fuel assembly design and fuel composition between the LWR fuel used in these countries and CANDU fuel. LWR fuel assemblies are typically 5-m-long arrays of fuel elements (see Figure 2-9a).

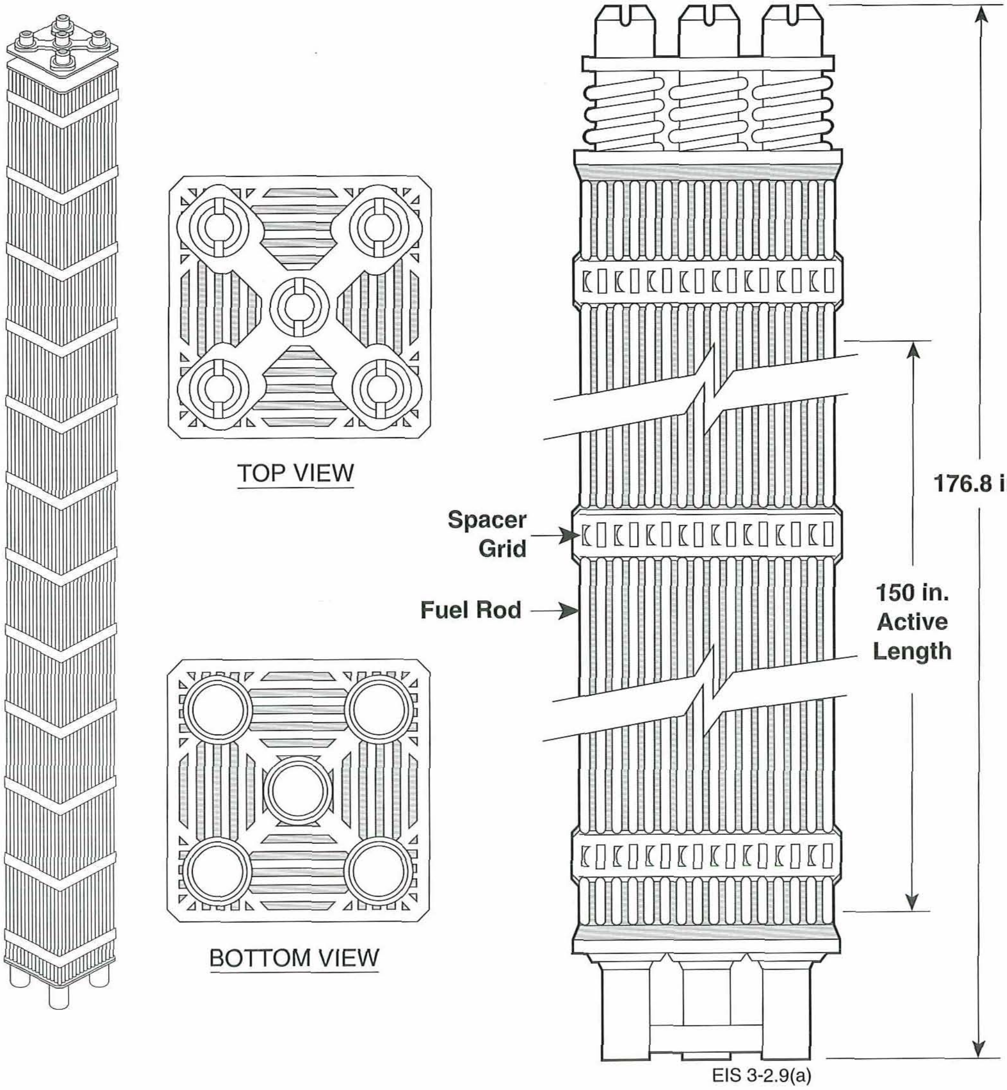


FIGURE 2-9(a): Typical LWR Fuel Assembly

The large fuel assembly size is the major reason for the significant difference in size between proposed containers for disposal of CANDU fuel (Chapter 3, Figure 3-11) and containers for LWR fuel (Figure 2-9b (Swedish container)).

The isotopic composition of LWR fuel both before and after irradiation also differs substantially from that of CANDU fuel. The uranium oxide in LWR fuel is enriched in ^{235}U to the 2.5 to 5 wt.% level (compared with the natural isotopic abundance of 0.7 wt.% in CANDU fuel). This permits irradiation of the fuel to a substantially higher burnup, typically

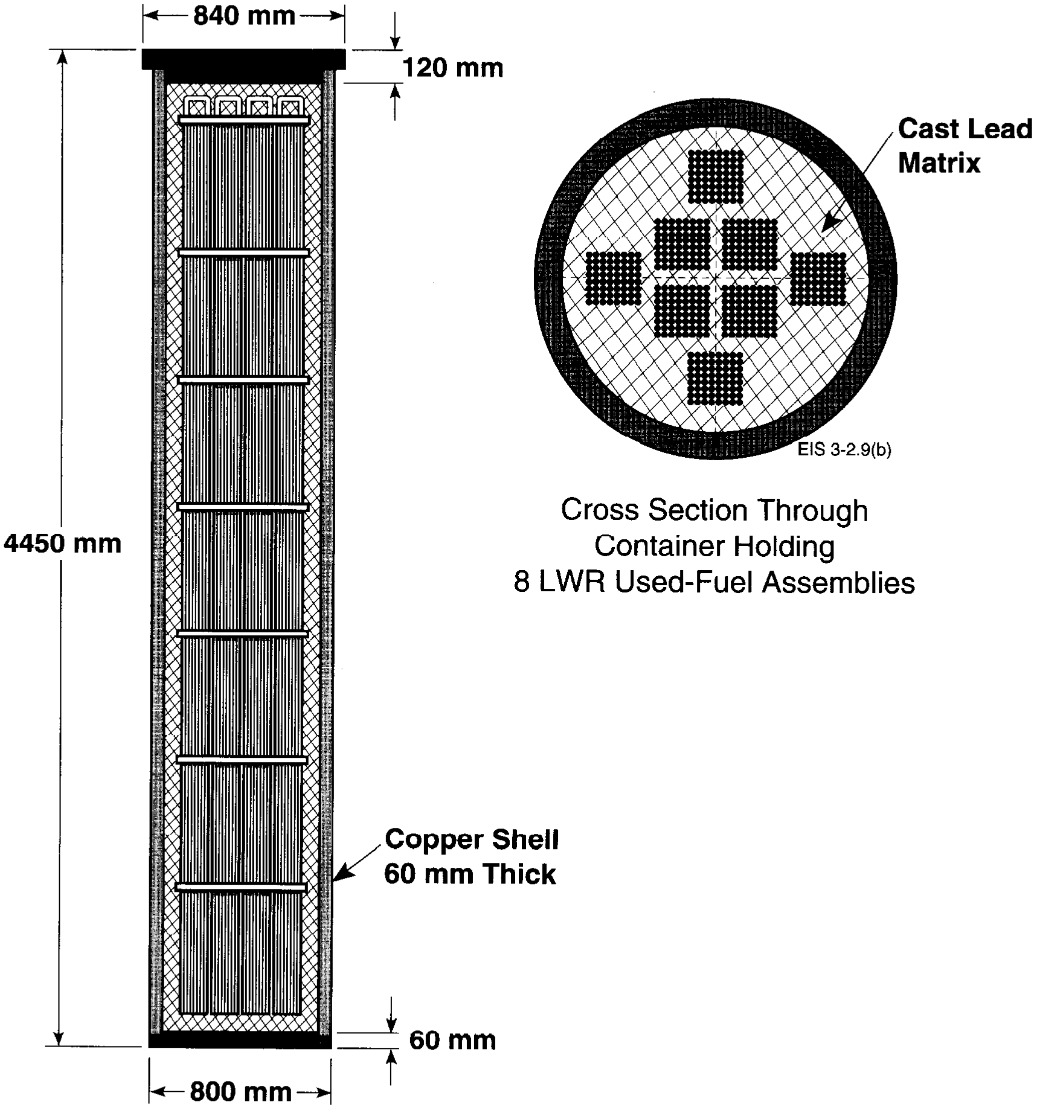


FIGURE 2-9(b): Swedish Container for LWR Fuel (described in SKB 91 report (SKB 1992a))

2500 $GJ \cdot kg^{-1}$ U (28 850 megawatt days per metric ton U). The total quantities of new radioactive isotopes produced are therefore 3 to 4 times higher than for CANDU fuel. The major impact of this difference is in the design of a disposal vault: to ensure that a given design maximum temperature in the disposal vault was not exceeded, it would be necessary to ensure that containers of LWR fuel were spaced farther apart.

The properties of both CANDU and LWR fuel have been discussed in detail by Johnson and Shoesmith (1988).

2.2.8 Impact of Other Fuel Cycles on Engineered Barriers Technology

It is possible that other types of used fuel would result from the adoption of different fuel cycles in Canada.

Although CANDU reactors operate with natural (0.7 wt.% ^{235}U) uranium oxide fuel, they are capable of operating with more advanced fuel cycles that use less uranium to produce the same amount of electricity. These are described briefly below.

For the slightly enriched uranium (SEU) fuel cycle, the fuel would be UO_2 with a slightly higher than natural percentage of ^{235}U (about 1.2 wt.%). The SEU would either be purchased abroad or an enrichment industry would be established in Canada. A once-through SEU cycle would decrease once-through fuel cycle costs by about 25-35% (Green et al. 1988, Lane et al. 1988).

For a mixed-oxide (MOX) fuel cycle, the fuel would be a mixture of UO_2 and PuO_2. The plutonium would be obtained by reprocessing used fuel, and the uranium would be either natural uranium or uranium recovered during reprocessing. Reprocessing could be purchased as a service or developed domestically. Upon removal from the reactor, the MOX fuel could be reprocessed to recover plutonium and perhaps also uranium. A MOX fuel cycle has the potential for uranium savings of 50-60% compared with the natural uranium once-through fuel cycle (Lane et al. 1988).

A tandem fuel cycle would entail the use of two types of reactors. The enriched UO_2 (2.5 to 5 wt.% ^{235}U) used in a light-water reactor could be reprocessed to recover the uranium and plutonium, which could then be used in a CANDU reactor. This cycle would use about 30% less uranium (derived from Green et al. 1988, Figure 2). An alternative would be to recover only the uranium. The recovered uranium (RU) would have about 1% ^{235}U (Moeck et al. 1989).

For the thorium fuel cycle, the fuel would be thorium, plutonium, and ^{233}U (a fissile uranium nuclide). Thorium does not have any fissile nuclides, but if plutonium is added to it, the fissioning of the plutonium produces neutrons that activate the thorium and result in the production of ^{233}U. The used thorium fuel would be reprocessed to recover the thorium and the ^{233}U. Plutonium would be obtained by reprocessing used natural-uranium fuel. Reprocessing could be purchased as a service or developed domestically. It is estimated that this cycle would use from 70 to 100% less uranium (Lane et al. 1988).

Although all advanced fuel cycles would conserve uranium, they would not necessarily result in the production of electricity at a lower cost. Only the SEU and RU cycles are potentially economical in Canada at present.

Because SEU fuel can be irradiated to much higher burnups than natural UO_2 (average values of 1820 $GJ \cdot kg^{-1}$ U for 1.2% enriched UO_2 vs. ~700 $GJ \cdot kg^{-1}$ U for natural UO_2), the quantity of used fuel produced per kilowatt of energy generated could be reduced by a factor of approximately three. Some savings in storage, transportation and disposal costs might result from adoption of an SEU fuel cycle (Lane et al. 1988), although a detailed analysis of SEU fuel disposal costs has not been performed. It is also important to note that, although the volume of used fuel could be reduced with SEU fuel, the total quantity of radionuclides produced would remain the same; i.e., the radionuclide concentrations in the fuel would be higher by a factor of approximately three. SEU fuel would have a higher heat output than CANDU fuel, meaning that containers would have to be spaced farther apart in the disposal vault to ensure that temperatures did not exceed the reference maximum of 100°C. As a result, the volume of rock required for disposal would not be significantly reduced.

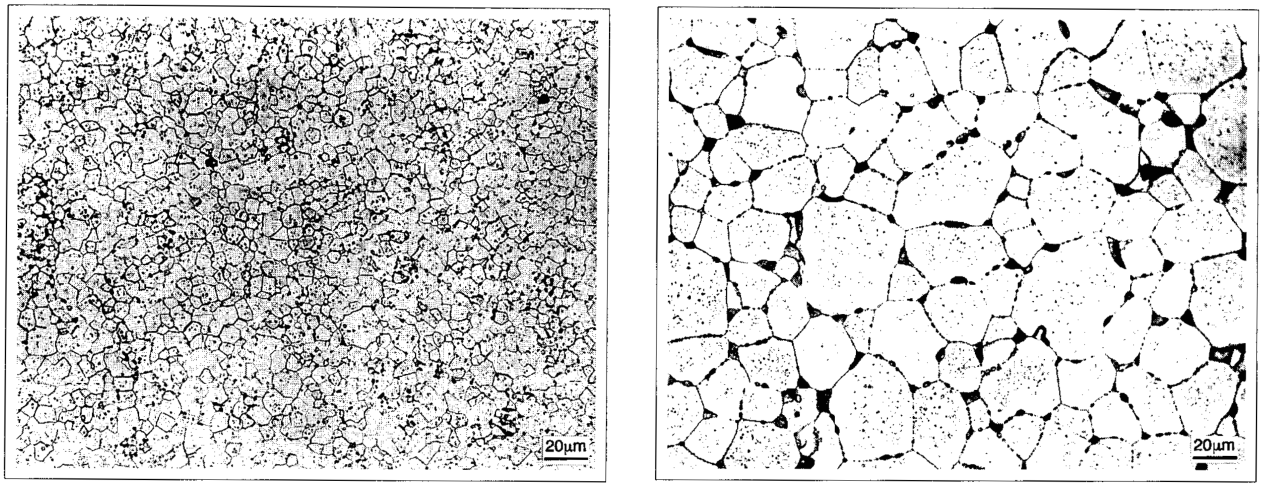
2.2.9 The Dissolution of Used Fuel

2.2.9.1 Composition and Structure of Used Fuel and Zircaloy Sheath

The uranium oxide fuel in CANDU fuel bundles is in the form of high-density (~97% of theoretical density), high-purity ceramic pellets with an oxygen-to-uranium ratio of 2.001. The pellets are polycrystalline with an average grain size of 10 μm. During in-reactor operation, the pellets crack and grain growth occurs, particularly at the centre of the fuel pellet, where operating temperatures may be as high as 1700°C. Typical microstructures of used fuel and unirradiated UO_2 are shown in Figure 2-10a.

After discharge from the reactor, used-fuel bundles contain approximately 1% by mass of new nuclides, including fission products, activation products and actinides other than uranium. The majority (>90%) of these species reside within the uranium oxide lattice very close to the location of their production (Johnson and Shoesmith 1988). The species produced can be grouped according to their chemical behaviour into the following categories:

1. Those that are gaseous or are somewhat volatile at fuel operating temperatures (i.e., 400-1700°C). These include Xe, Kr, Ar, Cs and I. Typically, because of relatively high diffusion coefficients in UO_2, approximately, on average, 2% of each of these species is released from the UO_2 pellets to the void space (fuel pellet cracks and the fuel-sheath gap) in a fuel element, and a further 6%, on average, segregates to grain boundaries within the UO_2 pellets. These average release values result from statistical averaging of release for the entire population of used-fuel bundles (Johnson et al. 1994).



(a) (b)

FIGURE 2-10(a): Microstructure of Used Fuel (a) Before and (b) After Irradiation

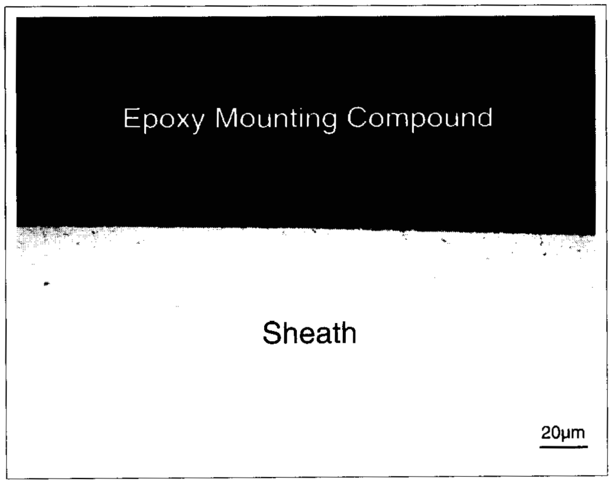


FIGURE 2-10(b): Cross Section of Irradiated Zircaloy Sheath

2. Those that are non-volatile but have a low solid solubility in UO_2, such as the metals Tc and Mo. Small quantities of these elements segregate as metallic phases at UO_2 grain boundaries, particularly in areas where UO_2 grain growth occurs. The majority of the atoms produced remains trapped within the UO_2 grains at interstitial sites because of their low diffusion coefficients in UO_2 at fuel operating temperatures.

3. Those that are soluble in UO_2. In this case, there is atomic substitution for U in the UO_2 lattice; this occurs for Pu, Am, Np and the lanthanide elements.

The release of a given radionuclide during dissolution in groundwater is governed by a combination of the degree to which it is segregated from UO_2 grains during in-reactor irradiation, the solubility of the radionuclide and the extent or rate of dissolution of the UO_2 grains. These processes are further discussed in Sections 2.2.9.2 through 2.2.9.4.

The Zircaloy-4 sheath consists of >98 wt.% Zr and ~1.5 wt.% Sn, with a number of other elements present as impurities. Irradiated sheath is a fine-grained material (grain size typically <10 μm) with neutron activation products, such as ^{14}C, ^{59}Ni and ^{63}Ni, present at lower than the 1 mg/kg Zr level. Because of the low temperature of the sheath during irradiation (<400°C), activation products cannot diffuse any significant distance from the site of their formation. They are therefore expected to be uniformly distributed throughout the sheath. In relation to chemical durability and activation product release as a result of corrosion, the principal changes to the sheath arising from irradiation are the formation of a thin zirconium oxide film on the outer surface and the formation of zirconium hydride precipitates within the metal (see Figure 2-10b). Analysis of the hydrogen precipitate shows that it results primarily from deuterium uptake from the heavy-water moderator. A significant fraction of the tritium produced in the fuel by fission and in the reactor moderator by activation is absorbed by the sheath, and presumably resides in the Zircaloy as hydride precipitates.

A model for the release of radionuclides from used fuel and Zircaloy sheath is described by Johnson et al. (1994). We present here some background information on the results of dissolution studies on CANDU fuel and UO_2, and a brief summary of the release model itself.

2.2.9.2 The Dissolution of UO_2

As discussed above, the majority of the fission product inventory and all of the actinide inventory of used fuel is contained within the UO_2 grains of used fuel. As a result, development of a predictive model for radionuclide release from used fuel requires an understanding of the dissolution of UO_2.

The mechanism of UO_2 dissolution as a function of redox chemistry and solution composition has been studied in detail (Shoesmith et al. 1986, Shoesmith and Sunder 1992). Upon contact with aerated solutions, the surface of UO_2 becomes progressively more oxidized, reaching a surface composition near $UO_{2.33}$. Dissolution becomes significant once this surface composition is reached, at a potential of -50 to -100 mV_{SCE} (Figure 2-11). Compositions less oxidized than $UO_{2.33}$, e.g., UO_{2+x} and U_4O_9, are formed by oxygen diffusion into UO_2, and naturally occurring uraninite ores are typically of this composition. At sufficiently low oxidation potentials, both UO_2 and U_4O_9 are thermodynamically stable, low-solubility solids. These observations are consistent with studies of uranium ore deposition (Langmuir 1978) and uranium oxide solubility (Parks and Pohl 1988). Redox potentials in a disposal vault in granitic rock are expected to be within the UO_2 or U_4O_9 stability fields, as a result of the presence of minerals containing ferrous iron, which would react with any oxidants present in the groundwater.

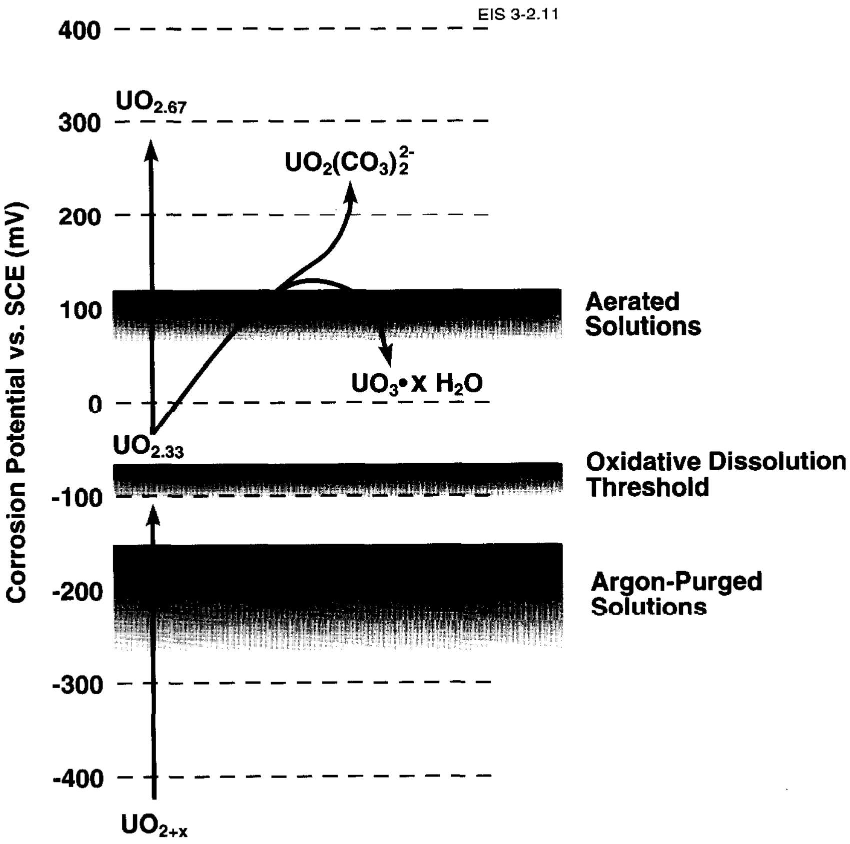


FIGURE 2-11: Schematic Illustration of Oxidation Dissolution Process in UO_2

Because oxidants would be produced by the alpha radiolysis of groundwater that might eventually contact the used fuel, extensive studies of the effects of O_2, H_2O_2 and radiolysis products on UO_2 oxidation and dissolution have been performed (Bailey et al. 1985; Sunder et al. 1987, 1990a). For the alpha fluxes and temperatures expected in a used-fuel disposal vault, Sunder et al. (1990b) have shown that oxidation proceeds no further than the U_4O_9 range.

2.2.9.3 Experimental Studies of Used-Fuel Dissolution

Studies of the dissolution of used fuel in groundwater have illustrated that there are several stages of dissolution (Johnson and Shoesmith 1988). In the first stage, typically a few days in duration, radionuclide release is dominated by the leaching of a fraction (typically several percent) of the inventory of fission products that may be volatile at in-reactor fuel irradiation temperatures. This fraction is often referred to as the fuel-sheath gap inventory. Rates of release gradually decrease with time over a period of months to years, depending on the fuel irradiation history and the experimental conditions. The dissolution rate of the UO_2 matrix eventually becomes constant, the final value being determined primarily by the solution composition, in particular the redox potential. Thus, the initial rates of release of radionuclides are governed by the fuel irradiation history, whereas long-term rates are controlled largely by matrix dissolution, which is redox-dependent.

The short-term leaching of fission products from CANDU fuel has been extensively studied (Stroes-Gascoyne and Sellinger 1986, Stroes-Gascoyne et al. 1987). The gap inventory of ^{137}Cs and ^{129}I has been measured for fuel bundles irradiated under a wide range of power conditions using leaching techniques. A comparison of gap inventories of ^{137}Cs and ^{129}I measured in leaching experiments with Xe gap inventories measured in fuel-element puncture tests is shown in Figure 2-12. The results are presented as the percentage of the total Cs and I inventory in the fuel that is released into solution. The approach for deriving average gap inventories for CANDU fuel has been described in detail by Johnson and Joling (1984) and Garisto et al. (1990). From this work, the average gap inventory for used CANDU fuel for each of the fission products ^{129}I and ^{137}Cs has been estimated to be 2.1% of the total amount present in the fuel. For some radionuclides, very little of the data needed to estimate short-term release were available. In the case of ^{14}C, for example, no measurements of gap inventory were available for CANDU fuel, and short-term releases were conservatively assumed to be within the range of 1 to 25% of the total inventory for the postclosure assessment case study (Johnson et al. 1994). Subsequently, measurements of ^{14}C release from used CANDU fuel have shown that actual short-term release values are much less than 0.1% (Stroes-Gascoyne et al. 1992).

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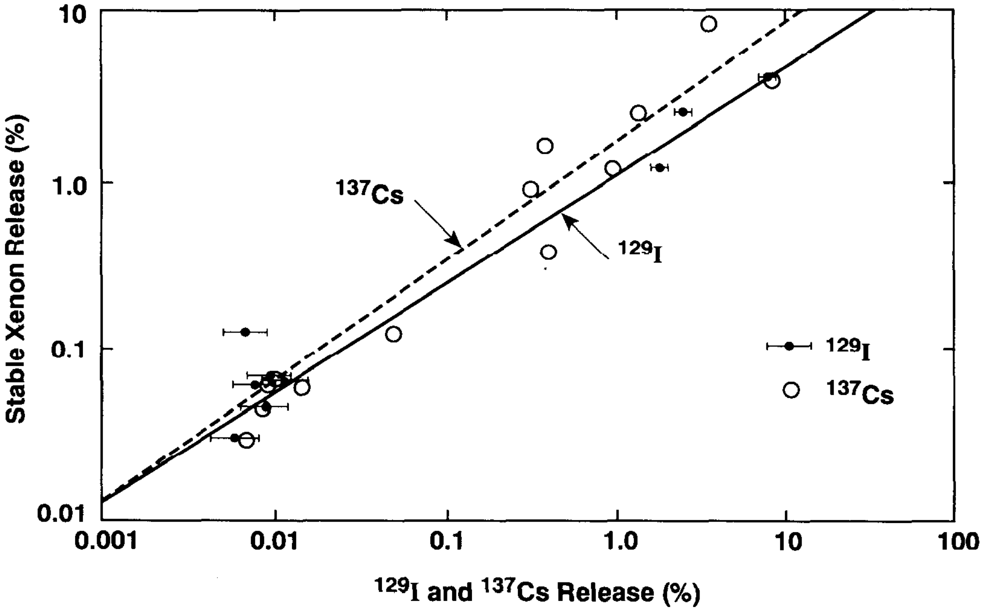

FIGURE 2-12: Comparison of Measured Gap Inventories of ^{137}Cs and ^{129}I with Xe Gap Inventory

Some fission products that are insoluble in UO_2 accumulate at grain boundaries in used fuel during reactor operation. The quantities present at grain boundaries have also been estimated (Garisto et al. 1990, Johnson et al. 1994). Recent studies suggest that, at least for ^{137}Cs, the estimated values are comparable to those measured using radiochemical techniques (Stroes-Gascoyne et al. 1993).

The degree to which the fission products at grain boundaries are released more rapidly than those present within the grains upon exposure to groundwater is uncertain. For the postclosure assessment case study, in the absence of such knowledge, it has been conservatively assumed that the inventory of fission products at grain boundaries is instantly released upon exposure to groundwater, along with the gap inventory. Recent studies (Stroes-Gascoyne et al. 1993) have shown, however, that the grain-boundary inventory is much more difficult to leach from the fuel than was previously assumed; extensive dissolution of the fuel may be required before it is released. As a result, the assumption that both gap and grain-boundary inventories are instantly released upon exposure to groundwater appears to be unduly conservative.

The rate of dissolution of the used-fuel matrix (grains) has been measured under both aerated and deaerated conditions. The results confirm that both the dissolution rate and uranium concentrations in solution decrease as the oxygen concentration in solution is decreased (Stroes-Gascoyne 1992, Forsyth and Werme 1992). The gamma-radiation field produced by used fuel can produce significant concentrations of oxidants in solution (Shoesmith and Sunder 1992), making it difficult to perform used-fuel dissolution experiments under conditions that would simulate the contact of groundwater with used fuel at the time of container failure, i.e., after at least 500 a, when the gamma-radiation field would be considerably lower (see Figure 2-6). The implications of this for modelling the dissolution of used fuel are discussed in Section 2.2.9.4.

2.2.9.4 A Model for the Dissolution of Used Fuel Under Disposal Conditions

A model that describes the rate of release of radionuclides from used fuel under disposal conditions has been developed. It is based on the following assumptions, some of which are conservative (i.e., they may result in overestimates of radionuclide release rates):

1. The Zircaloy sheath on all fuel elements is assumed to fail (i.e., be penetrated by groundwater) immediately upon failure of the containers.

2. Both gap and grain-boundary inventories of a number of radionuclides (e.g., ^{135}Cs and ^{129}I) are assumed to be released into the groundwater from every fuel element instantaneously.

3. Dissolution of the uranium oxide fuel is assumed to control further radionuclide release from the fuel. This rate is determined by the solubility of the uranium oxide and the rate of transport of uranium away from the fuel surface.

4. The redox conditions at the fuel surface are assumed to be sufficiently reducing to result in UO_2 or U_4O_9 being thermodynamically stable.

5. A redox potential gradient may exist, with the potential at the fuel surface (within the UO_2/U_4O_9 stability field) being greater than that in the buffer/backfill (controlled by Fe(II)/Fe(III) redox reactions). This would cause diffusion-precipitation coupling that could increase the fuel dissolution rate.

6. Uranium, Np, Pu, Tc and Th are assumed to precipitate in the near-field when their solubilities are exceeded. Their subsequent transport from the vault to the geosphere is then governed by the solubilities of the precipitates and transport rates under vault conditions.

The basis for these assumptions, as well as a detailed description of the model, is found in the primary reference on the vault model (Johnson et al. 1994).

Alternative approaches for developing used-fuel dissolution models have been described. For example, Shoesmith and Sunder (1992) described an oxidative dissolution model based on electrochemical studies of UO_2 dissolution. This approach allows the dissolution rate to be estimated for a broad range of redox conditions, and has been extended to degrees of oxidation below the U_3O_7 range. Using this model and the results of recent experiments on the effects of alpha radiolysis of water on oxidative dissolution of UO_2 (Sunder and Shoesmith 1992), we have concluded that oxidative dissolution of UO_2 would be unimportant beyond a period of approximately 60 a. The alpha activity of used fuel becomes comparable to that of a rich uranium ore, such as that at Cigar Lake, after approximately 10^5 a. Studies of this natural analogue of used fuel illustrate that, under the reducing conditions in the deposit, uraninite (UO_2) has experienced very little dissolution during the 10^9 a since its formation. The similarities between used fuel and such natural analogues indicate that a similar chemical stability can be inferred in the long term for disposal of used fuel in a vault in granitic rock (Cramer 1994).

Werme et al. (1990) have used measured dissolution rates of used LWR fuel as a basis for predicting long-term dissolution rates. On the basis of measurements of the ^{90}Sr release rate from used fuel under oxidizing and reducing conditions at 25°C, they have estimated both the rates of release of radionuclides from a failed container of used fuel and the fraction of the fuel matrix altered (dissolved) as a function of time. For a container lifetime of 1000 a, and oxidizing conditions, they estimate that approximately 10% of the fuel matrix would be dissolved within the first 10 000 a. Using the same approach for reducing conditions, they estimate that the quantity of fuel dissolved within the first 10 000 a would be approximately 1%. Such direct extrapolation of dissolution rate data from short-term experiments is unlikely to be an appropriate approach for modelling long-term dissolution, because the intense gamma-radiation field, which has been shown to cause oxidative dissolution of UO_2, would have diminished to an insignificant level within several hundred years (Shoesmith and Sunder

1992). A discussion of the implications of these various modelling approaches with respect to the extent of dissolution of used fuel after disposal and how they might affect dose estimates is presented in Chapter 7 of Johnson et al. (1994).

2.3 SOLIDIFIED FUEL-REPROCESSING WASTES

2.3.1 Introduction

As an alternative to direct disposal of used fuel, AECL has investigated the option of the disposal of solidified (immobilized) wastes that could be generated if Canada decided, at some time in the future, to reprocess its used CANDU fuel. The reprocessing option is not being pursued in Canada, as it is not currently economically viable for CANDU fuels; however, reprocessing and recycling of fissile material is currently the policy of a number of other countries, such as France, the United Kingdom and Germany. The purpose of reprocessing is to remove fissile material (e.g., ^{239}Pu or ^{235}U) in the fuel that could be used to fabricate new power-reactor fuel. AECL has demonstrated the methodology and technical feasibility for the solidification and disposal of these wastes in a glass or glass-ceramic waste form, and has developed methodologies for characterizing these waste forms.

This section briefly summarizes commercial-scale technologies available for the reprocessing of used nuclear fuel, as well as glass and glass-ceramic fabrication technology for the solidification (vitrification) of the high-level reprocessing waste. The low- and intermediate-level wastes arising from reprocessing, the volumes of wastes arising from reprocessing, and the potential impact of future changes in the fuel cycle are discussed briefly. A more detailed description of these subjects is presented in Appendix A.

From the early 1950s to about 1962, AECL demonstrated, by means of small-scale laboratory experiments, that high-level radioactive wastes from reprocessing nuclear fuel could be safely solidified (vitrified) in an aluminosilicate glass waste form (Merritt and Parsons 1964). Further research on waste form and solidification technology development was carried out when the Canadian Nuclear Fuel Waste Management Program (CNFWMP) commenced in 1978. Studies were initiated on borosilicate glasses, aluminosilicate glasses and titanosilicate glass-ceramics as potential waste forms for deep geological disposal. However, in 1987, it was decided that sufficient work had been carried out at the laboratory and small scale to demonstrate both the feasibility of engineering processes for vitrified waste-form production and the suitability of borosilicate glasses and alternative waste forms for high-level waste vitrification. Further research and development would only be required if a decision were made in the future to reprocess CANDU fuels.

The objectives of the waste immobilization project were to develop waste forms and process technologies for the production of glass and glass-ceramic waste forms for the immobilization of high-level liquid reprocessing wastes, and to characterize the physical and chemical properties of these waste forms under the conditions appropriate for disposal in a geological environment typical of the plutonic rock of the Canadian Shield.

For the purposes of defining a typical high-level waste stream, the well-proven Purex technology, used in commercial fuel-reprocessing facilities in France, Japan and the U.K., was chosen as a reference process. For the purposes of demonstrating vitrification technology, the AVM (Atelier de Vitrification de Marcoule) process, currently used in commercial fuel-reprocessing plants in France, was chosen as an example of existing technology for high-level waste solidification in glass, and elements of the AECL process development work were based on this technology.

In choosing waste-form materials for investigation, one of the most important considerations is the potential durability (dissolution resistance) of the material when contacted by aqueous solutions (groundwaters) in a disposal-vault environment. Three materials were chosen for development and evaluation as waste forms: borosilicate glasses, based on compositions in the Na_2O-B_2O_3-SiO_2 system; aluminosilicate glasses, based on compositions in the Na_2O-CaO-Al_2O_3-SiO_2 system; and titanosilicate glass-ceramics, based on compositions in the Na_2O-Al_2O_3-CaO-TiO_2-SiO_2 system. Borosilicate glasses were chosen because of their international acceptance as a waste form; aluminosilicate glasses were chosen on the basis of the early waste solidification experience at AECL. The titanosilicate glass-ceramics are an AECL product that have the potential to offer higher durability towards aqueous dissolution in a granitic disposal vault than borosilicate glasses, although they may be more technically complex to produce. There is a fundamental difference between the dissolution properties of glasses and glass-ceramics. Glasses are amorphous (i.e., they contain no crystalline phases), and thus a chemical equilibrium cannot be established between their dissolution products in solution and the solid glass phase. Glass-ceramics, on the other hand, contain a crystalline phase(s) that can establish a thermodynamic equilibrium with their dissolution products, leading to inhibition of dissolution when solution saturation is reached.

2.3.1.1 Technology for Reprocessing Used Nuclear Fuel

International strategies and options for reprocessing and recycling used fuel have been summarized in an International Atomic Energy Agency report (IAEA 1987). The Purex aqueous process (Bebbington 1976) is used in major commercial fuel-reprocessing plants in France and the U.K. for the recovery of plutonium from used fuel, and this process has reached a high level of technical maturity. Commercial fuel-reprocessing facilities have been in operation at Sellafield (formerly Windscale) in the U.K. since 1952; at Marcoule, France, since 1958, and later at La Hague; and at Tokai-Mura, Japan, since 1977. The U.S. has a number of facilities for reprocessing defence-reactor fuels for their defence weapons program, and they have demonstrated commercial fuel reprocessing at facilities in West Valley, NY.

The aqueous Purex process involves chopping the used UO_2 fuel, dissolving it in a nitric acid solution, and extracting more than 99.5% of the U and Pu using an organic solvent extraction process. The U and Pu are then chemically separated and purified for recycling into new reactor fuel. The recovered U may be sent to an enrichment plant for fabrication of enriched (several wt.%) UO_2 fuel, while the Pu may be used to fabricate mixed-oxide U-Pu fuels. The nitric acid waste solution contains virtually all the stable and radioactive fission products and the remainder of the actinides

(Cm, Am, Np, etc.), and it is this solution that constitutes the high-level waste (HLW) stream that requires solidification. A hypothetical HLW stream composition for reprocessed CANDU fuel was calculated (Smith et al. 1987) at the reference fuel burnup of 685 $GJ \cdot kg^{-1}$ U assuming a Purex extraction efficiency of 99.5% for U and Pu. The elemental inventories were converted to an equivalent oxide composition, since the majority of elements would be present as oxides in a vitrified waste form (Table 2-3). As discussed in Appendix A (Section A.2), a fission product loading in the waste form of 6% was recommended (on the basis of vault thermal analysis) for wastes arising from reprocessing the reference CANDU fuel.

2.3.1.2 Process Technology for the Vitrification of Reprocessing Waste

The solidification of HLW from reprocessing involves incorporating the waste into a stable host matrix such as borosilicate glass. Over the last 30-40 a, the nuclear industry has researched and developed a number of waste forms for solidifying reprocessing wastes. In 1978, a U.S. Department of Energy (USDOE) review panel (Alternative Waste Form Peer Review Panel 1979, 1980, 1981; Hench et al., 1984) recommended that borosilicate glass should be the preferred waste form for U.S. defence wastes. Other

TABLE 2-3

COMPOSITION OF HIGH-LEVEL PUREX REPROCESSING WASTE STREAM*

Element Oxide	wt.%	Element Oxide	wt.%
UO_2	43.28	TeO_2	0.99
NpO_2	0.26	Sb_2O_3	0.02
PuO_2	0.17	SnO_2	0.10
Am_2O_3	0.66	In_2O_3	<0.01
Cm_2O_3	<0.01	CdO	0.12
La_2O_3	2.31	Ag_2O	0.18
CeO_2	4.67	Pd	2.24
Pr_2O_3	2.13	Rh	1.12
Nd_2O_3	7.5	RuO_2	4.73
Pm_2O_3	0.05	TcO_2	1.84
Sm_2O_3	1.76	MoO_3	8.15
Eu_2O_3	0.18	ZrO_2	7.57
Gd_2O_3	0.15	Y_2O_3	0.86
Tb_2O_3	<0.01	SrO	1.38
BaO	2.87	Rb_2O	0.56
Cs_2O	4.06	SeO_2	0.12

* CANDU Bruce Fuel, 685 $GJ \cdot kg^{-1}$ U burnup, reprocessed after 10-a cooling and with 99.5% (U + Pu) extracted (calculated from Smith et al. 1987). Element masses have been converted to element oxide mass where appropriate.

countries (e.g., France, U.K., Japan) have also chosen borosilicate glasses as a waste form for commercial reprocessing wastes. The prime reasons for the choice of borosilicate glasses for permanent geological disposal are their low fabrication temperatures (<1150°C), their high resistance to aqueous dissolution, and the technical maturity of the glass fabrication process. A comprehensive international overview of the development and current status of solidification processes, and research on glasses and other alternative waste forms based on crystalline or ceramic products, can be found in a review entitled "Radioactive Waste Forms for the Future" (Lutze and Ewing 1988).

The borosilicate glass vitrification process used at the Marcoule reprocessing facility in France is known as the AVM process (it has also been adopted at another facility in La Hague and in the U.K. at Sellafield). Other countries have chosen similar glass fabrication technologies (Appendix A). In this process, the liquid HLW stream is fed to a rotary calciner (rotating heated drum) where the liquid is evaporated to leave a solid waste residue of nitrate salts, which can then be denitrated by heating to leave a solid mixture of oxides (calcine). The vitrification process involves combining this calcine with crushed borosilicate glass and heating the mixture in an induction-heated refractory (metal) pot to temperatures above 1000°C to melt the glass. The waste oxides dissolve in the melt, which is then poured into a metal container (about 50 cm in diameter and 1 m high, containing about 360 kg glass) and allowed to cool. The waste oxides are thus homogeneously distributed (~11-13 wt.%) throughout the solidified glass as part of the glass structure. The containers are then sealed and stored in concrete-shielded areas. Before permanent disposal in any waste vault, the containers could be sealed inside a corrosion-resistant outer container. A conceptual design for a CANDU reprocessing-waste container based on the AVM process and the AVM container geometry is discussed in Chapter 3 (Section 3.5.4.5).

During reprocessing, a number of other volatile off-gas waste streams and low- and intermediate-level liquid and solid waste streams are generated that could also require solidification. The technologies available for off-gas abatement and potential waste forms for the immobilization of these gaseous nuclides and solids are discussed in Section 2.3.7. The volumes of wastes arising from reprocessing are discussed in Sections 2.3.8 and 2.3.9.

2.3.1.3 Canadian Research on Vitrification Process Technology

From 1958 to 1960 AECL demonstrated, on a small scale, the production of radioactive aluminosilicate glasses. In this process, the aluminosilicate glass-making materials were mixed together with radioactive nitric acid waste from reprocessing experiments at the Chalk River Laboratories (CRL) to form a slurry. This mixture was then melted in small batches in clay crucibles under remote (radiation-shielded cell) conditions at temperatures up to 1350°C to produce fifty 2-kg radioactive glass blocks. These tests demonstrated the viability of producing aluminosilicate glasses as a vitrified waste form for reprocessing wastes. The glass blocks were later used in an in situ burial test in a sandy aquifer at AECL's Chalk River site. The release of radionuclides from these blocks into the aquifer has been monitored since 1958 (Section 2.3.2.3; Appendix A, Sections A.2, A.5); the results to 1976 are described in detail by Merritt (1976) and more recent monitoring studies are described by Killey et al. (1990). To fabricate full-scale aluminosilicate glass waste forms suitable for encapsulation in the conceptual reprocessing-waste container, considerable process development work would be required, since conventional glass melting technology used for borosilicate waste glasses may not be appropriate for production of these aluminosilicate glasses with higher melting temperatures. Low-temperature fabrication methods, such as sintering or sol-gel techniques, or melting techniques such as the induction-heating process used in the AVM facility, are potentially viable technologies that could be studied for aluminosilicate glass production on a larger scale.

Research in the CNFWMP on processes for HLW solidification in borosilicate glasses has concentrated on establishing and demonstrating, on a small scale, the necessary engineering technology for the pretreatment and vitrification of liquid reprocessing wastes. These technologies included calcination of simulated (non-radioactive) liquid HLW, borosilicate glass vitrification using a joule-heated electric melter (Figures 2-13 and 2-14), and off-gas technology to deal with the recovery of Kr and volatiles from the process stream (see Appendix A, Section A.2). The experiments demonstrated the continuous production of a simulated calcined waste; its subsequent incorporation into a borosilicate glass at concentrations up to 15 wt.% fission-product loading, using a joule-heated glass melter (in a joule melter, a pool of glass is kept molten by the resistance heating of a current passed between electrodes immersed in the melt (Sridhar 1985)); casting into metal containers; and the abatement of Kr and NO_x off-gases from the melter and calciner. A small laboratory-scale joule-heated melter was also used to demonstrate the production of titanosilicate glass-ceramics (containing up to 15 wt.% simulated waste (Section 2.3.2.4; Appendix A, Section A.6)) at melting temperatures up to 1350°C (Hayward et al. 1988).

Summary

Internationally, the technologies for reprocessing used fuel and for solidification (vitrification) of reprocessing wastes in borosilicate glass are practised on a commercial scale. These technologies are mature and demonstrate the viability of producing large-scale borosilicate glass waste forms suitable for permanent disposal. Small-scale engineered facilities at AECL demonstrated an integrated waste solidification process, consisting of liquid-waste calcination, volatile off-gas recovery, and the production of non-radioactive borosilicate glasses and titanosilicate glass-ceramics containing simulated reprocessing wastes using joule-melting technology. The production of aluminosilicate glasses containing radioactive reprocessing wastes was demonstrated using a batch crucible melting technology.

If any of these processing technologies were to be applied to the solidification of potential reprocessing wastes from used CANDU fuel in the future, the process would have to be matched to a selected waste form. If a borosilicate glass were selected, the technology for production is well established. If glasses with higher melting temperatures, or if glass-ceramics were selected, some redesign of the existing technology and the development of more corrosion-resistant melter construction materials would likely be

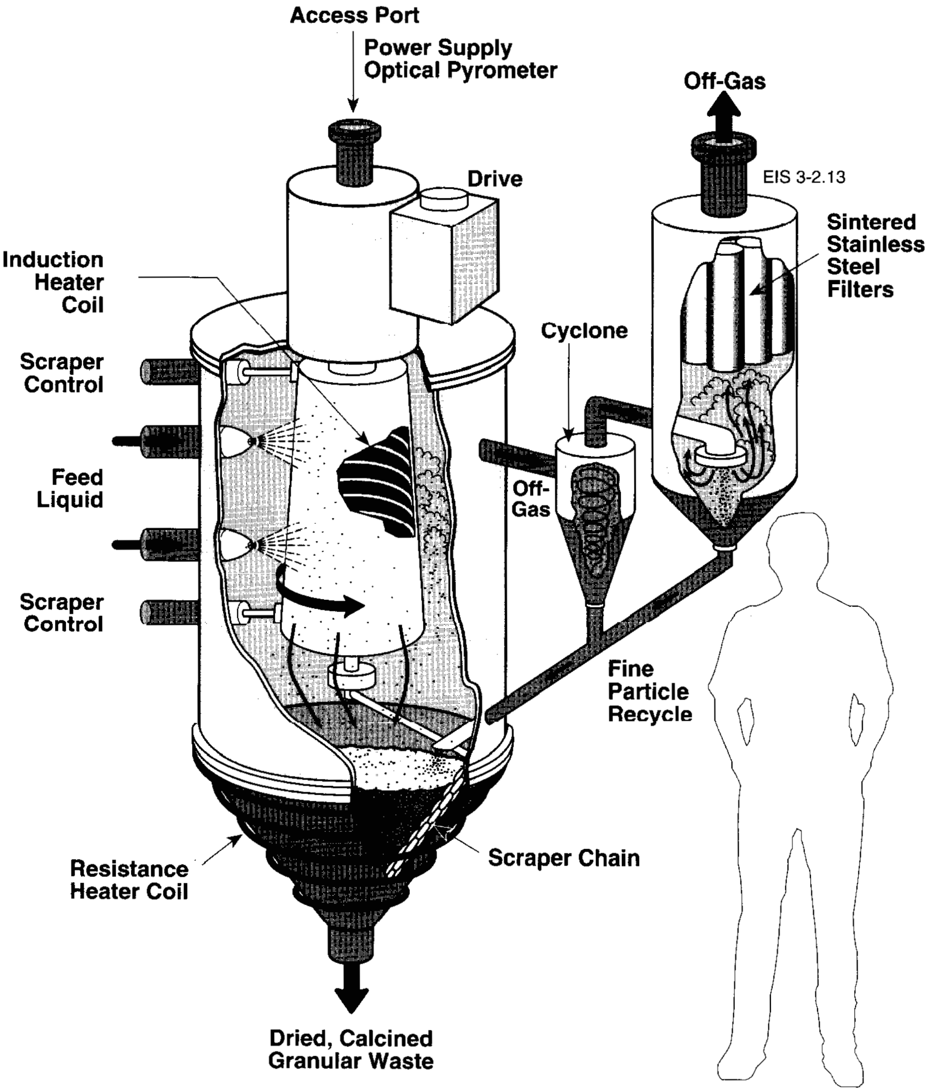

FIGURE 2-13: Schematic Diagram of Whiteshell Roto-Spray Calciner

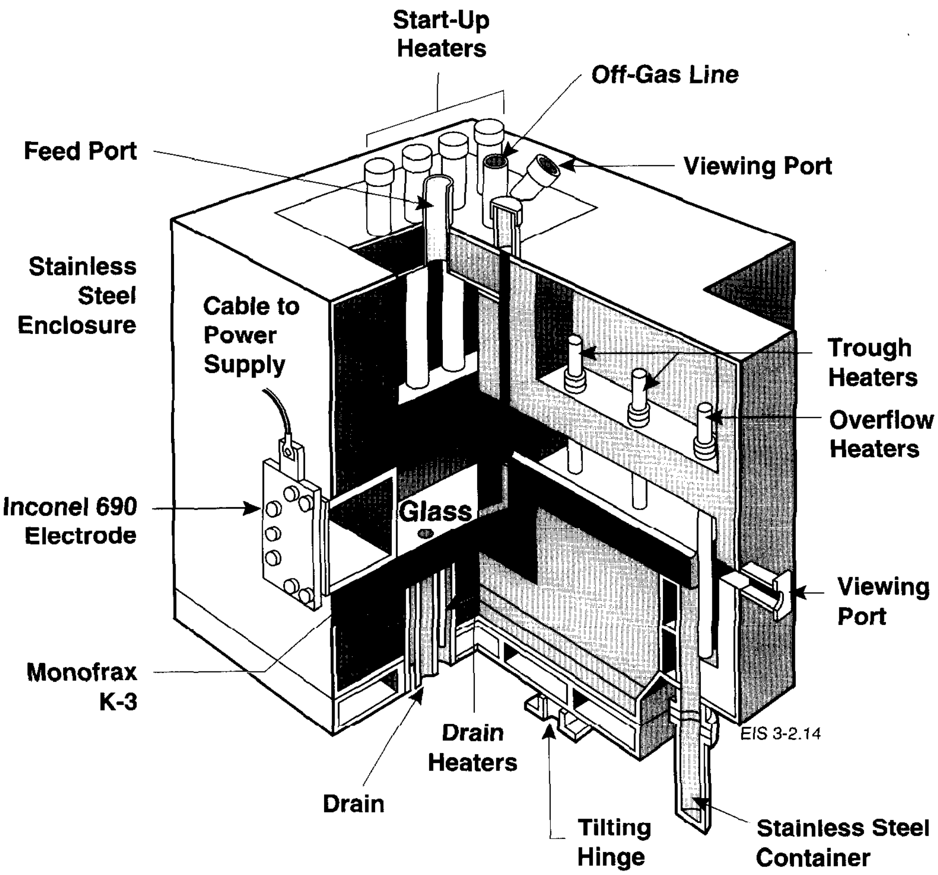

FIGURE 2-14: Schematic Diagram of the Whiteshell Joule Melter

required. In addition, considerable process optimization would be required and the technology would need to be tested on a larger scale before a full-scale commercial facility could be constructed. Since the basic technologies for glass production are well established internationally, the experiences of facilities operating in other countries, as well as any advances in the technology, could be taken into consideration in any future plant design.

2.3.2 Waste-Form Characterization

The primary objectives of the waste-form development and characterization work at AECL were to identify compositional regions for the three selected materials (borosilicate glass, aluminosilicate glass and sphene-based (titanosilicate) glass-ceramics) that would be the most appropriate for use as a high-level waste form for vitrification of CANDU reprocessing wastes. (Most international work has focused on waste forms for LWR reprocessing wastes.) Another objective was to establish the characterization methodology that could be applied if fuel reprocessing were adopted and if a product and process for waste immobilization were selected and optimized. The characterization studies focused primarily on the evaluation of waste-form durability under disposal conditions and the determination of dissolution mechanisms. Physical properties of importance to waste-form fabrication and disposal were also investigated (viscosity, electrical conductivity, phase constitution, etc.).

Various groundwaters, ranging from deionized water and low-ionic-strength surface groundwaters to the high-ionic-strength groundwaters typical of those found at a depth of 500 to 1000 m in granitic rock of the Canadian Shield (Gascoyne 1986) were studied to investigate their effect on durability. Other factors that could potentially affect the dissolution behaviour of the waste form were also studied. These included studies of the effects of various components of the disposal system (metal container, clay buffer, granite rock), as well as the effects of radiation-induced structural damage to the waste form and radiation-induced changes to the groundwater chemistry (radiolysis).

Optimization studies to determine the "best" glass or glass-ceramic composition were not carried out in this research phase, since this type of study would be undertaken only when fuel recycling was seen to be a viable option and when the most appropriate technologies for reprocessing CANDU fuel and solidifying the reprocessing wastes were chosen.

2.3.2.1 Chemical Durability of Silicate Glasses

The most important parameter to be considered when developing glasses for solidification of reprocessing waste is durability towards aqueous dissolution. The dissolution behaviour of borosilicate glass waste forms has been extensively studied both internationally and by AECL, and there are several general conclusions that can be drawn from these studies (Lutze 1988; Appendix A, Section A.4.1). The factors that are most important in determining glass durability are the glass composition; the contact solution composition, pH, flow rate and temperature; the composition and rate of formation of alteration layers; and both solid-state radiation and solution radiolysis effects.

In general, high-silica-content (45 to 70 wt.%) glasses and glasses with high Al_2O_3 content have exhibited the highest durabilities. Glass dissolution rates increase with increasing temperature, as solubilities of glass constituents also generally increase. Glass dissolution rates are highest in deionized water (used in many comparative dissolution tests), whereas the constituents of groundwaters might promote the formation of alteration layers that can lead to decreased dissolution rates. Also, in a closed (or low flow) system, dissolution rates are initially high as glass constituent ions dissolve into an undersaturated solution. However, the dissolution rate decreases with time as the solution becomes "saturated" with glass dissolution products (particularly silica), and becomes limited by the rate at which ions can diffuse through the hydrated surface layer on the glass or by the dissolution rate of silica from the glass surface. In a flowing system, the dissolution rate increases with increasing flow rate; but at sufficiently high flow rates, the dissolution rate eventually becomes constant, limited by the rate at which the glass surface can dissolve. Dissolution rates are not appreciably affected by pH in the range 3 to 9, but increase markedly above pH 9.5 as a result of the increased solubility of silica. Static (or very low flow) granitic groundwaters with a pH of ~8.5 would be the most probable scenario for a breached reprocessing-waste container surrounded by a clay buffer in the Canadian conceptual waste vault.

There is no reason to anticipate that the dissolution process should cease when the solution becomes saturated with glass dissolution products. As mentioned previously, glasses are an amorphous material, and thus, unlike crystalline phases, they are unable to establish a thermodynamic equilibrium with a solution that is saturated with glass dissolution products. Glasses would continue to dissolve, but their dissolution rate could be significantly reduced if there were an alteration phase on the glass surface that would provide a diffusional barrier to the release of glass (and waste) constituents. Ions, such as Fe^{3+}, Mg^{2+} and Ca^{2+} in the groundwater or leached (preferentially dissolved) from the glass, would promote the formation of alteration phases on the glass surface. These might inhibit glass dissolution by acting as a diffusional barrier or they might form crystalline alteration phases on the surface that could attain a chemical equilibrium with the solution, thereby potentially reducing the glass dissolution rate.

Waste ions in the glass would, in general, be released congruently as the glass dissolved into solution (although incongruent or preferential ion release might occur during the initial leaching stage (first few weeks to months)). Highly insoluble waste ions might concentrate or precipitate at the glass surface as dissolution proceeded, and their dissolution rate would be limited by their solubility. Redox potential in solution, while being able to affect the speciation of waste ions dissolved into solution, has not been found to have any major effect on glass dissolution rates.

Radiation effects on the release of radionuclides from a waste form have been reviewed by numerous authors (Tait 1993; Appendix A, Section A.4.1). The radiation effects can stem from both self-irradiation damage (solid-state damage) and radiolysis of groundwater adjacent to the waste form. The evidence indicates that solid-state damage is unlikely to enhance the dissolution rate of glass waste forms by more than a factor of two to three even 10^6 a after disposal. Radiolysis effects (chemical changes in solution as a result of irradiation) might enhance the dissolution rate of glasses by up to a factor of about five; however, these effects are greatest for gamma radiation and are pronounced only at radiation fields of about 100 to 1000 times greater than those anticipated for a glass waste form containing 6 wt.% fission products. Since the gamma-radiation field would decrease by about five orders of magnitude during the first 500 a after emplacement (a period during which the container is designed to remain intact), gamma radiolysis is not anticipated to be of any long-term consequence to waste-form dissolution.

2.3.2.2 Canadian Studies on Borosilicate Glass

Studies on simple borosilicate glasses ($Na_2O-B_2O_3-SiO_2$ system) have confirmed that high-silica-content glasses (greater than 70 mol% SiO_2, i.e., >5 mol SiO_2 on Figure 2-15) exhibit the highest dissolution resistance. Dissolution rates, over 30 d in deionized water at 100°C under static conditions, were ~10^{-9} $kg \cdot m^{-2} \cdot s^{-1}$ (Harvey and Jensen 1982). This compares with long-term (months to years) dissolution rates of 10^{-9} to 10^{-11} $kg \cdot m^{-2} \cdot s^{-1}$ for more complex borosilicate nuclear waste glasses

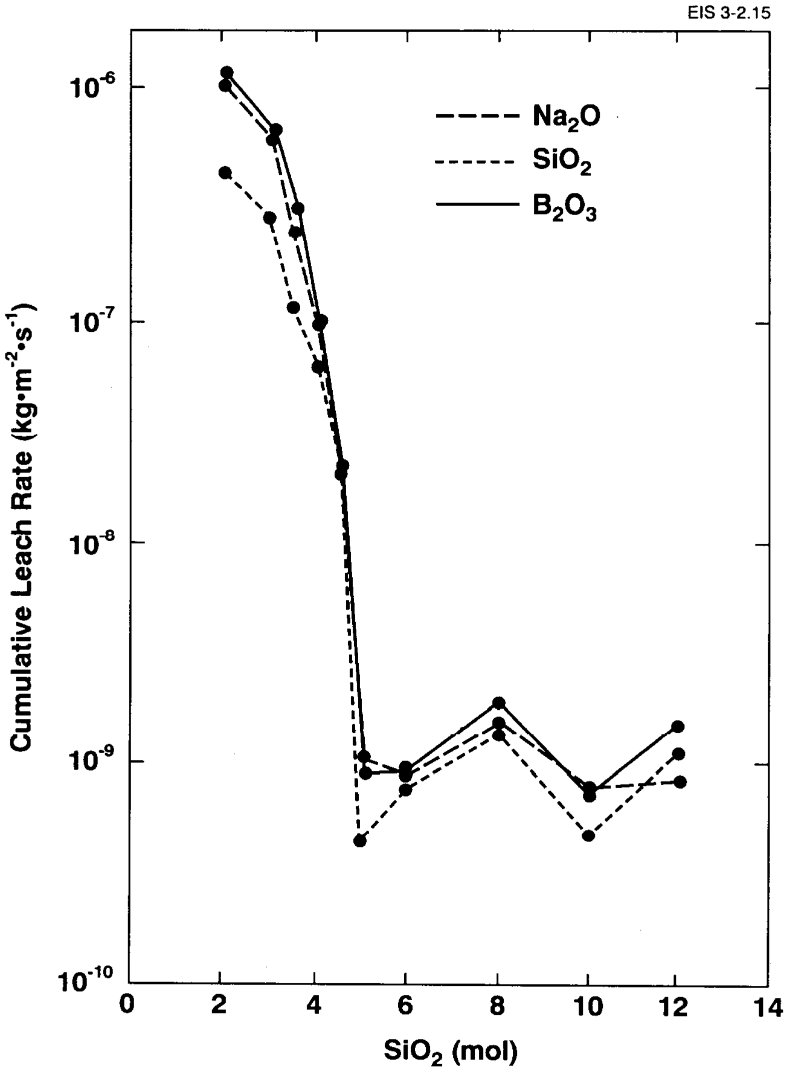

FIGURE 2-15: Thirty-Day Cumulative Leach Rate for Glasses with Composition $Na_2O \cdot B_2O_3 \cdot xSiO_2$

under similar leaching conditions (Lutze 1988). These simple borosilicate glasses dissolved by a first-order dissolution mechanism (the concentration of species in solution increased linearly with time) in the initial stages. The dissolution rate decreased as the solution became saturated with silica (Harvey 1983). High silica content and the addition of components such as Al_2O_3, Fe_2O_3 and ZnO were identified as factors that could increase the durability of the glass and decrease the glass dissolution rate (Appendix A, Section A.4.2).

Although it is recognized that physical factors, such as crystallization or phase separation in glasses, could potentially affect waste-form performance through the formation of less durable phases, these processes would need to be specifically investigated for the optimization of any waste form. No optimization of glass composition was carried out in this program, since the waste form would need to be tailored and optimized for any specific reprocessing technology, waste-stream composition and site-specific disposal conditions.

The physical properties important to waste-form fabrication (thermal conductivity, electrical resistance, viscosity, and mechanical properties) were also determined for a variety of glasses. Although not of primary importance in determining waste-form performance, these properties would need to be investigated fully to determine fabrication parameters for any specific waste form that might be chosen. These properties for glasses are more fully discussed in Appendix A, Section A.4.3, and by Lutze (1988).

2.3.2.3 Canadian Studies on Aluminosilicate Glasses

Aluminosilicate glass compositions were investigated by AECL in the late 1950s as a potential waste form for immobilizing small volumes of liquid waste from fuel-reprocessing experiments (see Section 2.3.1.2 and Appendix A, Section A.5). These glasses were based on compositions in the Na_2O-CaO-Al_2O_3-SiO_2 system. The laboratory dissolution rate for these glasses was measured to be 1.2×10^{-12} to 6.2×10^{-12} $kg \cdot m^{-2} \cdot s^{-1}$, which is about an order of magnitude more durable than typical borosilicate glasses. Their high dissolution resistance is attributed to the high alumina and silica content in this glass. In 1960, twenty-five 2-kg blocks of glass were buried in a sandy soil aquifer on the Chalk River site. The release of radionuclides from these blocks to the aquifer was monitored and the results indicate a dissolution rate (based on ^{90}Sr release over 15 a) of $\sim 5.8 \times 10^{-15}$ $kg \cdot m^{-2} \cdot s^{-1}$ (Merritt 1976). Assuming the ^{90}Sr release rate is representative of the bulk glass dissolution rate, we estimate it would take $\sim 10^7$ a to completely dissolve each 2-kg glass block. Although a wide variety of fission products and actinides were present in the glass blocks, only ^{137}Cs, ^{90}Sr, ^{155}Eu, ^{154}Eu and ^{241}Am were detected in the aquifer release plume over the last 30 a (Merritt and Parsons 1964, Merritt 1976, Killey et al. 1990). The low dissolution rate for the Chalk River glass can also be attributed in part to the low ambient temperature of the aquifer (6 to 9°C). Solution saturation and the formation of alteration products on the glass surface that inhibit diffusion have also been suggested as factors to account for the low dissolution rate (Arneson et al. 1986, Harvey and Litke 1984, Walton and Merritt 1980, Tait et al. 1986).

A number of dissolution studies have been conducted on both active and inactive aluminosilicate glasses (Harvey and Jensen 1982, Tait and Mandolesi 1983, Harvey and Litke 1984, Arneson et al. 1986). Presaturation of the leachant solution, by leaching a powdered, inactive aluminosilicate glass of a similar composition, was found to strongly inhibit continued glass dissolution of the subsequently leached active glass specimen (Figure 2-16). The addition of simulated waste was found to have little or no effect on the dissolution rate.

2.3.2.4 Canadian Studies on Titanosilicate Glass-Ceramics

A glass-ceramic is a partly crystalline/partly amorphous material that is prepared by slowly reheating a solid glass or slowly cooling a glass melt to a temperature region where the growth of microcrystalline phases within the glass can occur. With a good understanding of the kinetics of crystal nucleation and growth, as well as the effects of changes in the initial composition of the glass precursor, one can tailor the composition of the final glass and crystalline phases to produce the desired glass-ceramic product.

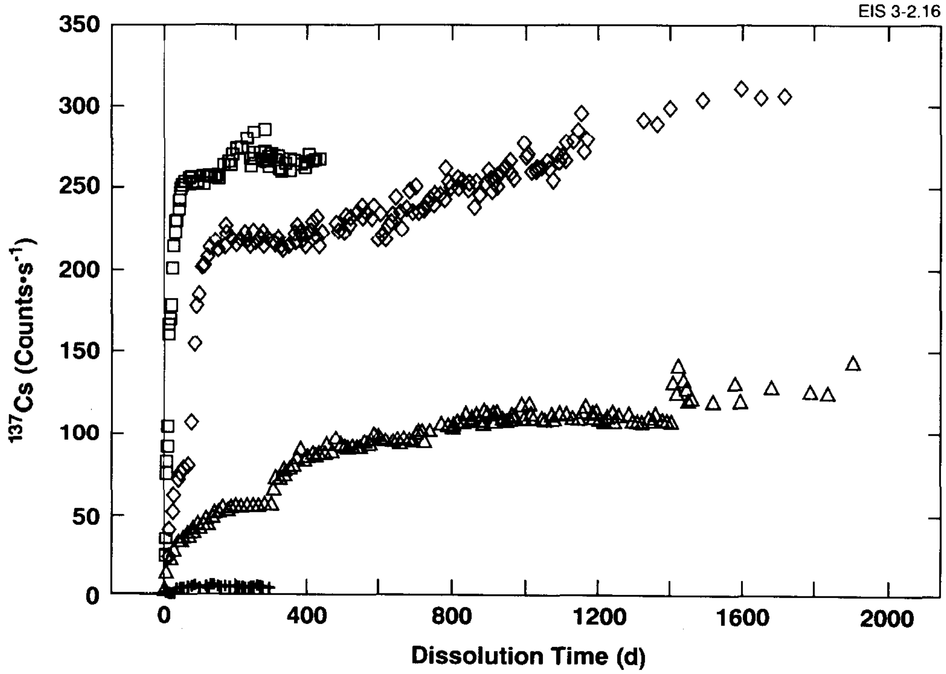

FIGURE 2-16: Release of ^{137}Cs from Chalk River Glass at 100°C Using the Prototype Sealed Leach Test Apparatus. □ Glass in deionized water (DIW); + the same glass in DIW previously saturated with dissolution products; ◇ glass replaced in DIW; △ glass in standard Canadian Shield saline solutions.

Titanosilicate glass-ceramics were investigated as a waste form because a crystalline phase is more thermodynamically stable than a glass of the equivalent composition, and may therefore be more resistant to aqueous dissolution (Appendix A, Section A.6). Unlike a glass, a crystalline phase may establish a thermodynamic equilibrium with dissolved products in solution, which could inhibit further dissolution (Hayward 1988).

Glass-ceramics based on the crystalline mineral sphene ($CaTiSiO_5$) are an AECL product tailored to accommodate wastes typical of a Purex reprocessing waste stream and to be specifically compatible with the granitic rock geochemical environment of the Canadian Shield. Comprehensive reviews of the international candidate ceramics for HLW immobilization (Hayward 1982, 1987, 1988) indicated that a glass-ceramic in the Na_2O-Al_2O_3-CaO-TiO_2-SiO_2 titanosilicate system would be most appropriate for the Canadian waste disposal concept.

Compositions based on the mineral sphene were chosen because sphene is commonly associated with granitic rock formations and has been found to have withstood natural alteration and weathering processes in granite for millions of years. Thermodynamic calculations indicate that sphene is stable towards aqueous dissolution in the Ca-Na-Cl groundwaters of the Canadian Shield. Observations on naturally occurring sphene showed that it incorporates a wide range of impurities in its crystal structure, including Th, U, and the rare-earth elements, and should thus incorporate most of the waste ions in a reprocessing waste. Elements not incorporated by the crystalline phase should be readily incorporated in the glass phase of the glass-ceramic.

Hayward (1988) demonstrated the production of sphene-based glass-ceramics containing discrete sphene crystals (cylindrical crystals about 1-5 μm in length and 0.1-0.2 μm wide) within a continuous Na_2O-CaO-Al_2O_3-SiO_2 aluminosilicate glass phase (Figure 2-17). Studies on sphene-based glass ceramics containing up to 15 wt.% simulated waste indicated that the rare-earth ions (simulants for the actinides) were preferentially incorporated into the sphene phase and that no other significant crystalline phases were formed.

The aqueous dissolution properties of the glass-ceramic were found to be a complex function of the dissolution of the glass phase and the crystalline sphene phase. Release from the glass phase was kinetically controlled, in a manner similar to borosilicate glasses, whereas release from the sphene phase was thermodynamically controlled. The main aqueous dissolution reaction of sphene produces solid rutile (TiO_2) (or anatase, a TiO_2 polymorph) and orthosilicic acid in solution:

$$CaTiSiO_5 + 2H^+ + H_2O \rightleftarrows Ca^{2+} + TiO_2 + H_4SiO_4 \quad .$$

The equilibrium constant, K, for this reaction is

$$K = [Ca^{2+}][H_4SiO_4]/[H^+]^2 \quad (\log K = \log([Ca^{2+}]/[H^+]^2) + \log[H_4SiO_4]).$$

It was determined that sphene stability was promoted by high Ca^{2+} and low H^+ solution concentrations over a temperature range from 25 to 150°C.

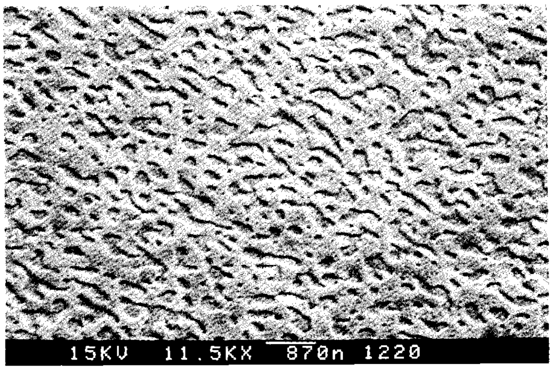

FIGURE 2-17a: Scanning Electron Micrograph Showing Phase-Separated Titanosilicate Glass

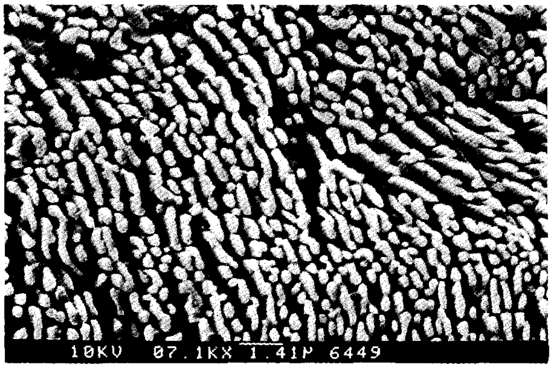

FIGURE 2-17b: Micrograph of Crystallized Sphene Glass-Ceramic Showing Rod-Like Sphene Crystals in an Aluminosilicate Glass Matrix

Groundwater in a granitic environment would fulfill these conditions, and would thus be expected to promote sphene stability. Dissolution experiments on a synthetic crystalline sphene phase indicated that once thermodynamic equilibrium is established between sphene and TiO_2, dissolution essentially ceases. It was also found that the aluminosilicate glass phase may eventually "passivate" by the formation of alteration layers and should exhibit dissolution rates comparable with those of sphene. Initial dissolution rates of the glass phase at 100°C were $\sim 5 \times 10^{-10}$ $kg{\cdot}m^{-2}{\cdot}s^{-1}$. These results are comparable with those observed from dissolution studies on the sphene glass-ceramic; they support the contention that the component phases of the glass-ceramic dissolve independently, and that radionuclide release from each phase would be proportional to the relative ion concentration in each phase. The effects of radiation (both solid-state and solution radiolysis) on the dissolution of the glass-ceramic, sphene and naturally occurring sphene mineral have been shown to be inconsequential (Hayward 1988).

2.3.3 Performance Under Disposal Conditions

The previous sections have indicated that the dissolution rate of borosilicate and aluminosilicate glasses and titanosilicate glass-ceramics is significantly reduced when the aqueous solutions become saturated with glass dissolution products or when the solution can establish a thermodynamic equilibrium with a crystalline phase such as sphene. Long-term (1 a) dissolution experiments conducted on the three candidate waste forms in the presence of clay, granite, and container materials indicated that the presence of the engineered barrier materials had no major detrimental effects on the dissolution behaviour of the waste forms. This observation may in part be attributable to the buffering of the pH at ~8.5 and the silica-saturated solution conditions (Tait 1986), which may be beneficial to the long-term performance of these waste-form materials.

2.3.4 Alternative Waste Forms for HLW Solidification

Alternative waste forms, such as Synroc (synthetic rock), tailored ceramics, TiO_2, monazite and FUETAP (formed under elevated temperature and pressure) concretes, have been studied in other international programs, and the research on these materials is reviewed by Lutze and Ewing (1988). Synroc, a synthetic multiphase crystalline (ceramic) material developed in the Australian program, is of particular note internationally. It has been recognized by the USDOE Alternative Waste Form Peer Review Panel (Hench et al. 1984) as the "official alternative waste form" to borosilicate glass. Synroc is composed of four TiO_2-based mineral phases that are found to persist in many natural geochemical/geological rock formations (Ringwood et al. 1988). Dissolution tests on this material have indicated a high resistance towards aqueous dissolution, particularly in hydrothermal solutions ($T > 100°C$). The dissolution rate in deionized water decreases rapidly with time to 10^{-11} to 10^{-12} $kg{\cdot}m^{-2}{\cdot}s^{-1}$. The dissolution mechanisms of Synroc are complex and are the subject of ongoing studies (Smith et al. 1992).

The technology for Synroc fabrication is necessarily more complex than for borosilicate glasses; however, its production has been successfully demonstrated using pilot-scale facilities (Ringwood et al. 1988). Specific Synroc formulations have been tailored that could accommodate a wide variety of reprocessing waste-stream compositions (high U and high Al, defence wastes, etc.). Specific tailoring of the mineral assemblages would be required to ensure compatibility with the specific groundwater and disposal environments being considered.

2.3.5 Modelling Waste-Form Dissolution

Considerable effort has been expended internationally to develop mathematical models to predict the dissolution behaviour of glass waste forms beyond the time frame of normal laboratory experiments. Models have been developed that take into account solid-state diffusion, solubility, dissolution and diffusion rate constants, mass transfer coefficients, solution saturation, precipitation, pH, temperature, solution flow rate and the formation of alteration layers on the glass surface (Appendix A, Section A.9). The predictions from these models have been compared with results from actual dissolution measurements on simulated and radioactive waste glasses. Agreement has been good, although the results indicate that further developments in the models are required.

Model development in the CNFWMP has considered dissolution conditions ranging from static to flowing leachants, saturation effects, and the formation of alteration layers that can inhibit dissolution by providing a diffusional barrier to release. The glass dissolution models are broadly similar to those used to describe used-fuel dissolution (Johnson et al. 1994) and have been verified through comparison with actual glass dissolution data from experiments lasting several years (Harvey, in preparation(b)).

Diffusion-based models have also been used to describe the long-term (20 a) dissolution rate of radionuclides from the Chalk River aluminosilicate-glass in situ burial experiment (Harvey and Litke 1984), as have non-equilibrium migration models (Walton and Merritt 1980, Melnyk et al. 1984). Because of the low dissolution rates observed in this burial test, the long-term (>500 a) predictions of these models are difficult to verify, since the rates would require very long observation times to validate the model. Validation studies would need to be carried out at much higher temperatures to gain any confidence in extrapolated dissolution rates. Internationally, it is recognized that the long-term kinetics and temperature dependence of glass dissolution are not yet well understood and will require further experimental studies to validate the various glass dissolution models that have been developed (Lutze 1988).

2.3.6 Natural Analogues

The observed weathering of naturally occurring glasses, such as volcanic (basalts and rhyolites) and meteoric glasses (tektites), has the potential to provide kinetic and thermodynamic information on long-term (millions of years) dissolution behaviour in glasses. A number of these studies have been conducted and are summarized by Ewing and Jercinovic (1987). This information provides evidence for the genesis of metastable and stable glass-phase alteration products arising from natural weathering processes. These data have been used with some success in several thermodynamic equilibrium studies (Jantzen and Plodinec 1984, Jantzen 1986) to correlate glass dissolution rates with the free energy of hydration of constituent ions in the glass. Grambow et al. (1986) have had some success in using a chemical speciation and mass transfer code to model the sequences of alteration products. These studies could ultimately be used to validate models predicting the long-term dissolution rates of waste glasses.

2.3.7 Low- and Intermediate-Level Waste Forms

Although the CNFWMP has focused on HLW solidification, it is recognized that fuel reprocessing would generate low- and intermediate-level waste (LLW and ILW) streams that might require solidification before disposal. These include off-gases, such as ^{3}H, ^{14}C, ^{85}Kr and ^{129}I, as well as undissolved fuel hulls and dissolver residues, ion-exchange resins, incinerator ash, and various other solid and liquid wastes. Internationally, solid reprocessing wastes, such as the fuel hulls, are immobilized in cement and stored at the facility. Ion-exchange resins used for liquid waste-stream treatment, and filters used to remove iodine and other radioactive isotopes from off-gases, are either stored, or immobilized in cements or bitumen before storage. Considerable work has been done internationally on technologies for the capture and immobilization of the radionuclides from reprocessing off-gas waste streams and the immobilization of solid and liquid process wastes. Summaries of these technologies can be found in a series of reviews by Taylor (1990a,b,c, 1991) and in Appendix A, Section A.11.

The disposal strategies being adopted internationally for LLW and ILW, both from reprocessing and reactor operations, are either deep underground disposal or shallow land burial, or a combination of the two (Clelland et al. 1989). Sweden, for example, has an operational disposal facility for reactor operational wastes in the bedrock under the Baltic Sea (Hedman et al. 1989, Clelland et al. 1989). Strategies for waste treatment, conditioning, waste-form characterization and disposal of LLW and ILW have been discussed in a recent symposium (IAEA 1989). Many of the new developments in these programs have concentrated on waste volume reduction, both at the source and in the processing of the waste form for eventual disposal, particularly in countries currently relying on interim storage (Clelland et al. 1989). Charlesworth and Howieson (1989) have presented an overview of the AECL LLW and ILW management program and Canadian LLW and ILW management policies. These international characterization, immobilization and disposal programs are, however, beyond the scope of this document.

2.3.8 Volumes of Waste Arising from Reprocessing

The reprocessing of used CANDU fuel could be viewed as a method to reduce the volumes of radioactive wastes that would require disposal relative to the direct disposal of used fuel. To make such comparisons, it is necessary to estimate the total volume of wastes generated from a reprocessing strategy, which would include all low-level, intermediate-level and high-level wastes. These would include the Zircaloy sheaths, liquid and solid process wastes, volatile off-gases, the separated uranium stream and the liquid high-level waste stream. Harvey (in preparation(a)) has compared the predicted total waste volumes arising from Purex reprocessing of used CANDU fuel with data available from existing reprocessing facilities in France, the U.K. and the U.S.; he found them to be similar for equivalent waste loadings in the waste forms (see also Appendix A, Section A.12).

The total volume of the containers of solidified reprocessing wastes (LLW, ILW, HLW) arising each year from reprocessing 63 400 used CANDU fuel bundles has been calculated (Harvey, in preparation(a)) to be ~1038 m^3 (Table A-4, Appendix A). This could be reduced to ~854 $m^3 \cdot a^{-1}$ if the separated uranium waste stream were considered to be a resource and enriched for use as new fuel. Direct disposal of the same amount of fuel without reprocessing would generate ~880 containers per year with a total volume of ~622 m^3 (72 bundles per container, 0.707 m^3 per container, based on the reference container design described in Section 3.5.2.2), and thus there would be no reduction in the total volume of wastes requiring disposal as a result of reprocessing. With further developments in technology, such as compaction of Zircaloy hulls instead of cementation, and vitrification of LLW, the volume of low- and intermediate-level wastes could be reduced from about 746 $m^3 \cdot a^{-1}$ to about 135 $m^3 \cdot a^{-1}$.

The total volume of vitrified high-level waste (nitric acid fission-product waste stream) would be ~107 $m^3 \cdot a^{-1}$ (6 wt.% fission-product oxide loading), representing ~206 containers (0.522 m^3 per container) (Harvey, in preparation (a)). Although this volume is smaller than that generated from the direct disposal scenario, the total amount of radioactive, heat-generating fission products present is the same. The heat generated per vitrified-waste container would be about a factor of four higher than the used-fuel containers. To maintain the same average temperature in the disposal vault and the same container skin temperature (~100°C), these vitrified-waste containers would require a wider spacing than the used-fuel containers. The vault volume required for disposal is thus directly related to the radioactive fission-product content of the waste containers. Thus a disposal vault for used CANDU fuel would be approximately the same size as one for vitrified waste if the same maximum container surface temperature constraint was applied.

2.3.9 Advanced Fuel Strategies and Effects on Volumes of Wastes Arising from Fuel Reprocessing

2.3.9.1 Alternative Fuel Cycles

Aside from potential future increases in steam-generation efficiency, the fuel economy of a reactor can be improved by using advanced fuel strategies based on slightly enriched uranium (1.2 wt.% ^{235}U); recovered uranium (U recovered from reprocessing LWR fuel or direct use of LWR fuel in a CANDU reactor; ~1 wt.% ^{235}U); or mixed-oxide fuels, such as Pu/U or Th/U (see Section 2.2.8). These cycles, using enriched fuels, would be operated at higher burnups, which would enhance the fuel economics over the natural U cycle (Moeck et al. 1989). The implementation of these fuel cycles could have a potential impact on the volumes of waste requiring disposal.

The electrical energy produced from a fuel is proportional to the fuel burnup. Increasing the fuel burnup would also proportionally increase the amount of fission products and actinides in the fuel. In an enriched fuel, there would be more fission products (and energy) produced per fuel bundle. This would result in a decrease in the volume of fuel discharged per kilowatt of electrical energy. However, the increase in fission-product concentration per bundle would result in a higher heat generation per bundle. Consequently, in considering the direct disposal of these fuels, either the fuel would need to be cooled longer (50-100 a) or the disposal containers would have to be spaced more widely apart in the vault to maintain a maximum temperature of ≤100°C at the container surface. Thus, although there would be a reduction in the volume of fuel waste from an enriched-fuel reactor for a given electrical output, the size of the vault would be proportional to the fission-product content (heat) in the fuel. As a result, for an equivalent amount of electricity generated, the size of a vault for the disposal of CANDU fuel would be similar to that required for disposal of enriched fuel, although the number of containers required would be greater for CANDU fuel.

2.3.9.2 Nuclear Transmutation

Nuclear transmutation is an alternative technology being investigated in several international programs for the potential management of nuclear fuel wastes. This technology involves the use of reactors or proton accelerators (Venneri et al. 1993) to generate a high flux of neutrons that would be used to bombard separated actinide and fission-product wastes. Absorption of the neutrons transmutes (transforms) long-lived radioactive isotopes in the waste to shorter-lived isotopes or stable elements. This technology requires that the fuel first be reprocessed and specific species chemically separated to provide the appropriate conditions for transmutation. Ramspott et al. (1992) conducted an evaluation of separation and transmutation technology as part of the U.S. disposal strategy. This study concluded that transmutation is not an alternative to the geological disposal program in the U.S., and that there are no cost or safety incentives to introduce transmutation into the high-level waste management strategy. Also, the process is primarily aimed at actinide transmutation, leaving the high-heat (^{137}Cs, ^{90}Sr) and long-lived fission-product wastes (^{129}I, ^{99}Tc, ^{14}C) in the liquid waste stream, which would require solidification and geological disposal. The latter are the major contributors to long-term risk, because of their limited sorption during groundwater transport in geological environments. The conclusions by Ramspott et al. (1992) were based on their judgement that the risk from radioactivity from a disposal vault is very low and that removal and transmutation of the actinide products would not significantly reduce this risk. The total volumes of waste for disposal using a transmutation strategy may not be significantly different from those arising from conventional reprocessing of used fuel, and the levels of low- and intermediate-level wastes would increase with the additional isotope separations required for transmutation. Ramspott et al. concluded that although the actinide inventory that would go to a disposal facility could be greatly reduced by transmutation, the total number of containers of reprocessed waste destined for the waste vault would not be much different from the number of used-fuel waste containers. Transmutation strategies are also discussed in the EIS (AECL 1994a).

2.3.9.3 Alternative Reprocessing Technologies

New developments in the area of chemical reprocessing could potentially reduce the total volume of wastes requiring disposal. These improvements involve "dry" or pyroreprocessing of UO_2 fuels and are in the research and development stage (Selvaduray et al. 1979, Hoyt and Rhee 1979, Ramspott et al. 1992). These processes could reduce or eliminate the wet chemical separation steps and the volumes of processing chemicals required, and could thus lead to significant reductions in volumes of low- and intermediate-level process waste streams. There would be no reduction, however, in the volume of separated uranium waste that would be contaminated with fission-product wastes and would require disposal in an underground vault.

3. CONTAINERS FOR NUCLEAR FUEL WASTE DISPOSAL

3.1 INTRODUCTION

This chapter describes the main elements of the research and development program conducted to develop containers that might be used for the disposal and long-term isolation of CANDU nuclear fuel waste. It reviews studies conducted on container design, construction and testing, and investigations on candidate materials for container construction. Sections 3.2 to 3.4 review engineering considerations that affect the choice of an appropriate container design, including a review of the related experience in other countries, and how these were applied to develop container options for the disposal of CANDU fuel waste. An initial,[6] brief discussion of materials for container construction is presented in Section 3.4.2 to review the rationale on which materials choices were narrowed for subsequent engineering studies.

The program adopted to evaluate a number of candidate container options is described in Sections 3.5 and 3.6. The development studies for container manufacture and inspection and for alternative container concepts demonstrate that considerable flexibility exists for choosing a container design for disposal. This program culminated in an assessment of structural performance and manufacturing attributes that was used to define a reference container option for the design of the surface and underground facilities for the engineering study for a conceptual used-fuel disposal centre described by Simmons and Baumgartner (1994).

Section 3.7 reviews the corrosion characteristics, under disposal conditions, of a range of potential construction materials studied internationally. The range of proposed disposal environments in different countries is reviewed and the corrosion properties of a wide range of materials are discussed. The suitability of these materials is then critically evaluated with emphasis on their suitability to Canadian conditions. Finally, recommendations are made regarding which materials represent acceptable options under Canadian conditions.

It is emphasized that structural performance, design and fabrication studies give us confidence that container failures can be expected to occur only as a consequence of corrosion. The possibility of failures due to structural overload or long-term time-dependent materials deformation behaviour can be eliminated through prudent design based on a sound understanding of stress-dependent materials behaviour in conjunction with a knowledge of materials degradation processes.

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[6] Materials for the construction of containers are described in greater detail in Section 3.7.

3.2 CONTAINER DESIGN CONSIDERATIONS

The design of containers for the disposal of nuclear fuel waste is affected by a number of factors. This section presents a discussion of these factors and how they influence the design approach.

The design exercise begins by considering the objects and/or material that the container must accommodate. As discussed earlier, two forms of nuclear fuel waste are possible: wastes from fuel reprocessing (such as vitrified high-level wastes), or unreprocessed used-fuel bundles. The selection of one of these options would influence the volume and dimensions of the container, because of differences in decay-heat output and the size and shape of the waste forms.

In jurisdictions that opt for the direct disposal of unreprocessed used fuel, it may be necessary to adopt a strategy that allows for flexibility in either container geometry or the quantity of fuel that can be loaded into the container. For example, in the United States both pressurized and boiling light-water reactors (PWRs and BWRs)[7] are used, and the respective fuel assemblies differ in dimensions, construction and enrichment. Consequently, a number of variations in both the internal design of the container and the quantity of fuel to be loaded into it have been proposed (Nelson et al. 1989). If the fuel is enriched, criticality considerations may affect the quantity that can be loaded into a container.

The decay-heat output of the waste will influence how much waste can be accommodated in each container without causing excessive waste-form and/or container-shell temperatures. It can also influence the internal structure of the container, particularly if it is intended that any residual space (following installation of the waste into the container) is to be filled with a packed or cast material. Such a material must be able to adequately transfer the heat to the external shell so it could be transferred to the other engineered barriers that surround the container and, subsequently, be dissipated into the disposal medium.

The period for which the container is to provide isolation (i.e., the containment target) will influence both the selection of materials for the container shell and the shell thickness. Cameron (1982) presented a discussion of four possible containment targets:

1. ~10 a, which would represent a system in which the container was intended only as a simple package for safe handling and transfer of the waste to the disposal vault, with no claim made for subsequent containment;
2. 300-500 a, representing containment for the period during which most high-activity fission products would decay and the radiotoxicity of the waste (used fuel or fuel-reprocessing waste) would be greatly reduced;

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[7] Collectively, called LWRs.

3. ~20 000-50 000 a, during which the temperature in the disposal vault would approach the ambient temperature and after which chemical processes, such as leaching and dissolution, and physical processes, such as diffusion, would tend to slow significantly; and

4. indefinite (>100 000 a) containment.

The first of these containment targets is technologically simple to achieve and would require neither materials durability research nor manufacturing development. The 300-500 a target would allow containers to be manufactured either from relatively inexpensive metals, with a thickness that would provide sufficient corrosion allowance, or from highly corrosion-resistant metals for which the corrosion allowance, and therefore the container-shell thickness, could be significantly reduced (see also Sections 3.4.2 and 3.7). Designing for the very long term containment targets could be approached by developing either thick-wall metal containers or containers manufactured from non-metallic materials, for example, ceramics, that would be essentially inert in the disposal environment.

Containers designed to provide a significant period of waste isolation (300-500 a or more) may eventually be subjected to loading in the disposal environment. For example, in the case of disposal in a vault constructed at depth in plutonic rock, eventual resaturation of the vault with groundwater would subject the container to hydrostatic pressure on its outer surface. In conjunction with this load, a container surrounded by a clay buffer would experience additional loading from the swelling of the clay in the presence of water. Thus, the container must be designed to maintain the integrity of its outer shell for the required isolation period under such loading, bearing in mind that corrosion would gradually, and possibly non-uniformly, reduce the shell thickness.

Where disposal was conducted in a medium that deforms plastically under continual stress (for example, salt formations), the container would eventually be subjected to lithostatic loads. In plutonic rock, the ability of the rock to deform plastically at depth, prior to fracture, is virtually nil (Pusch and Hökmark 1992). Therefore, in a disposal vault constructed in plutonic rock and with buffer around the container, lithostatic loads would not be transmitted to the container (see also Section 3.4.3.5).

The loads that a container would experience in the disposal vault are quite different from those it might experience prior to disposal. In the vault, loading would be non-cyclic and would be exerted over either the entire container surface or on broad areas of it. During manufacture, the container must be sufficiently strong to withstand the more localized loads it may be subjected to during normal fabrication and handling with sufficient factors of safety to ensure that the target lifetime would not be reduced by overstress of any part of the containment envelope.

Wherever possible, the container design should incorporate features that would facilitate its manufacture, inspection and handling, without compromising the containment capability. Ease of container handling and emplacement are essential to ensure smooth conduct of the disposal operation and to reduce or eliminate the risk of dropping or overturning the container.

The vault design also influences container design. If the containers are to be transported underground down a shaft or ramp and thereafter by transport vehicles, they must be of a size, weight and geometry that could be accommodated and handled readily in the confines of the vault passageways. Technological restrictions on, for example, shaft-hoist lifting capacity, underground vehicle capacity or size of emplacement borehole that could be drilled (where borehole emplacement of the container was selected) would affect container design.

In disposal media where eventual resaturation of the vault with groundwater can be expected, the selection of materials for container manufacture would be influenced by the anticipated groundwater chemistry, particularly for the case of metal-shell containers. A discussion of various disposal media being evaluated internationally and their potential groundwater chemistries is presented in Section 3.7.

The gamma-radiation field emitted from a container could cause radiolysis of the groundwater near the container, which could produce oxidizing and reducing chemical species. This effect could be decreased by constructing containers with shells that are sufficiently thick to provide substantial radiation shielding, or by surrounding the waste form within the container with a shielding material, for example, cast lead. Such containers would also reduce the shielding in operations equipment (e.g., in the container-handling flask) that would be required to protect personnel within the vault during the waste-emplacement period. However, they would be more difficult and costly to manufacture, inspect and handle.

The availability of materials proposed for the manufacture of containers must be considered in the design process. This might include present and projected reserves of the materials, current and projected demand and production capabilities, present and future materials costs, and how any or all of these factors might be affected by the quantities that would be required for large-scale nuclear waste disposal. Another important factor could be whether long-term supplies might have to be derived principally from foreign countries where there might be a potential risk of supply interruption because of political or economic instabilities.

In addition to these technical factors, other considerations may influence design approaches. Examples of such considerations include the requirements of regulatory authorities, public perceptions of the environmental acceptability of a particular design, existing laws, cultural traits, political factors, etc. Consequently, it is inevitable that the approach of individual countries to the development of the specific constituents of their waste management systems, such as the design of a waste-disposal container, will be unique.

3.3 CONTAINER DESIGN IN OTHER COUNTRIES

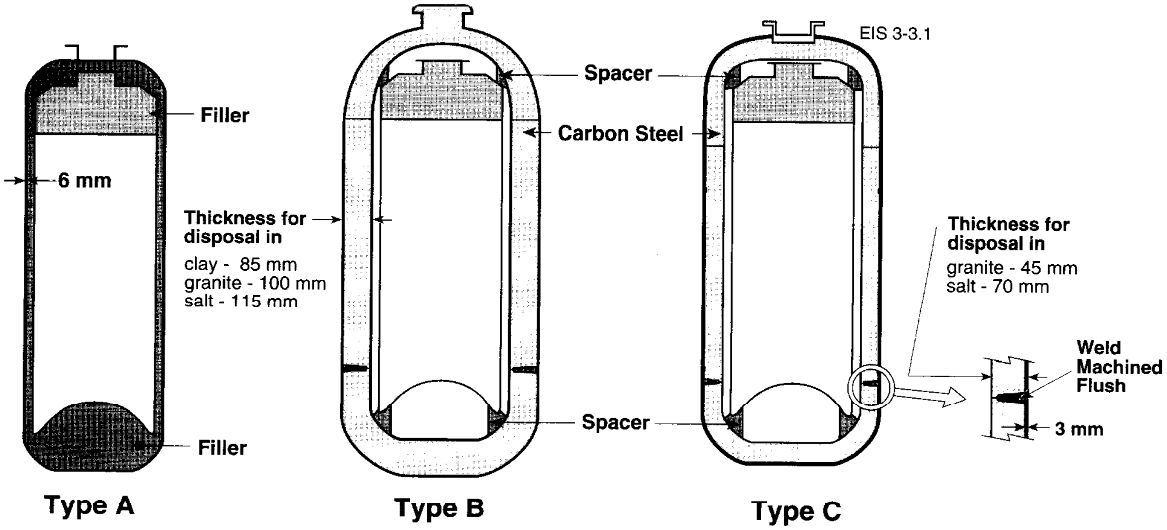
Throughout the Canadian container-development program we have monitored, and exchanged information with, major programs in other countries to ensure that an awareness of design principles used elsewhere was maintained. This has also ensured that technological advances (e.g., in fabrication, inspection, materials studies) were identified in a timely manner for possible application to the Canadian concept for radioactive waste disposal. Thus, we are confident that the approaches adopted by our program are in concert with worldwide developments. Sections 3.3.1 to 3.3.5 present a brief overview of studies in a selection of countries with significant container-development programs. Section 3.3.6 broadly reviews the general approach being adopted in a number of other countries.

3.3.1 Commission of the European Communities

In the program of the Commission of the European Communities (CEC), the reference waste form is vitrified fuel-reprocessing waste. The target containment period is 500 to 1000 a. Three disposal media relevant to Europe have been considered: granite, clay and salt formations. In initial studies (Ove Arup and Partners 1985, 1986), three types of container (see Figure 3-1) were selected for further detailed analysis:

1. Type A, a thin-walled, corrosion-resistant metal shell with lead or cement grout surrounding the vitrified block;

2. Type B, a thick-walled carbon-steel shell (no filler); and



Internal Diameter of All Containers 500 mm

FIGURE 3-1: Container Designs Under Study by the Commission of the European Communities

3. Type C, a thinner carbon-steel shell, plated externally with corrosion-resistant metal.

In Types A and C, the corrosion-resistant metal could be either commercially pure titanium, a titanium-palladium alloy, or Hastelloy C4, a proprietary nickel-chromium-molybdenum alloy.

Studies within the CEC program include detailed stress analyses of each of these concepts for each disposal medium (Ove Arup and Partners 1986, 1989, 1990).

3.3.2 Germany

In Germany, the reference waste form is vitrified fuel-reprocessing waste. The reference disposal medium is a domed salt formation. Vitrified wastes would be cast into single-shell, stainless steel containers that would be stacked into 300-m-deep boreholes drilled into the floor of the disposal vault. The container would be cylindrical, and about 0.43 m in diameter (Closs et al. 1989). The stainless steel shell would be 5 mm thick, with the vitrified waste providing the required resistance to the lithostatic pressure of the salt formation at the vault depth. This pressure is expected to be reestablished following closure of the vault. Each borehole would accommodate 236 containers (Bechthold et al. 1987).

The reprocessing of some types of fuel has been determined to be not economically justifiable. This includes thorium-containing fuel from the German high-temperature reactor (HTR) program, which is in the form of spheres about 60 mm in diameter, as well as some LWR fuel.

The principal goals of the German disposal program for unreprocessed fuel are to minimize radiation exposure to operations personnel during packaging and emplacement of the waste, to minimize the generation of secondary wastes arising from packaging procedures, and to provide a minimum container lifetime of 500 a (Bechthold et al. 1987). To meet these requirements, concepts for self-shielded containers holding unmodified LWR fuel assemblies have been developed (Nuclear Energy International 1990, Papp et al. 1990). For example, the currently preferred container design (designated the POLLUX cask, Figure 3-2) for the disposal of LWR fuel is multilayered: it employs a compartmentalized inner container holding either intact LWR fuel assemblies or dismantled assemblies and their structural components. The inner container is installed within a steel overpack (possibly with a corrosion-resistant layer of Hastelloy C4). This, in turn, is covered by a neutron-shielding layer and, finally, a cast-iron gamma-shielding overpack. The entire package is about 5.5 m long, 1.6 m in diameter, weighs about 65 Mg and holds up to 8 PWR fuel assemblies. For disposal, this container would be laid on the floor of an emplacement tunnel in the disposal vault. It is also potentially suitable for interim storage and transportation of the used fuel.

As a backup concept for LWR fuel disposal, a smaller container called the POLLUX canister (430 mm in diameter, 1.34 m long with a 50-mm-thick stainless steel shell), intended for stacking in 300-m-long boreholes, is also under consideration. In this case, the fuel would be sectioned into

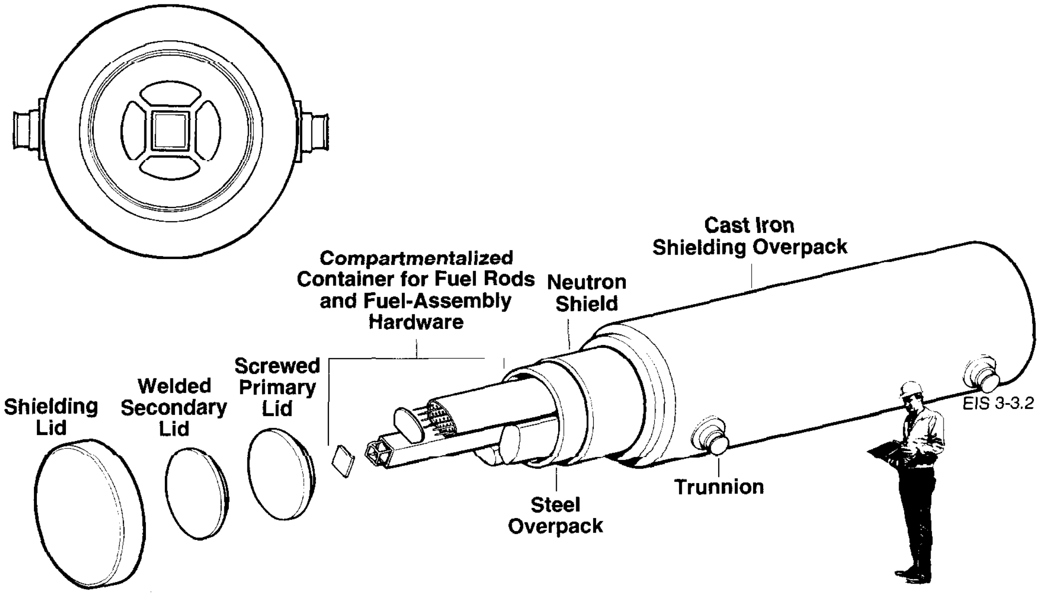


FIGURE 3-2: POLLUX Cask Accommodating Eight PWR Fuel Assemblies

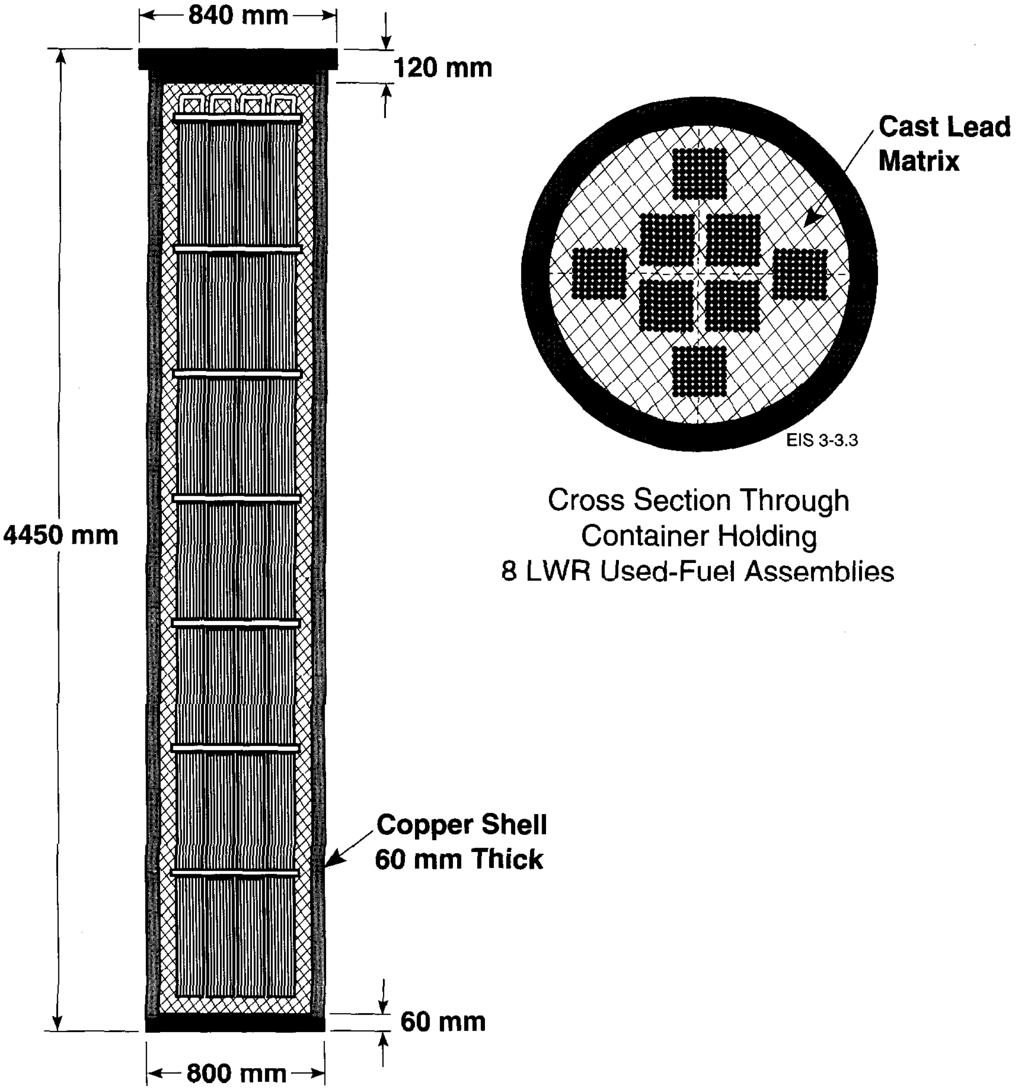
~1-m lengths for placement into the container, which has sufficient capacity to hold about the equivalent of one half a PWR fuel assembly.

For the disposal of spherical HTR fuel, a modified POLLUX cask and a stainless steel, long-borehole-emplacement container (1.08 m long, 0.7 m in diameter with a 50-mm-thick shell) are under study.

3.3.3 Sweden

In Sweden, the Stipulation Act of 1977 requires that a reactor owner must demonstrate that either high-level reprocessing waste or used fuel can be disposed of with "absolute safety." The implications of this somewhat imprecise requirement have influenced the design of containers in the Swedish program.

In the Swedish program, the ability of the container to provide a very long term barrier was considered to be important. Consequently, the option of a thick-wall container manufactured from high-purity copper was selected for detailed study (SKBF/SKB 1983). The containers are intended to accommodate full-length PWR and BWR fuel assemblies. A container design with a 60-mm-thick welded-copper shell and a cast-lead matrix was used for the Swedish program's safety analysis (SKB 1992a) (Figure 3-3). In subsequent studies (SKB 1992b, 1993), a design called the Advanced Cold Process container was selected as the reference for the Swedish disposal concept. Although still under development, this design incorporates a copper shell ~50 mm thick and an inner, carbon-steel shell of similar thickness to provide structural support to the copper shell (Josefson et al. 1992) (Figure 3-4). Residual



Cross Section Through
Container Holding
8 LWR Used-Fuel Assemblies

FIGURE 3-3: Container Design Used in Swedish Program Safety Analysis

space within the container, following loading with used fuel, may be filled with a particulate material.

Within a disposal vault mined in crystalline rock, each container would be deposited in a borehole and surrounded by compacted bentonite-clay buffer. It was concluded that gamma radiolysis of the groundwater would be insignificant because of the shielding provided by the thick container shell, and that, on the basis of the current understanding of the corrosion behaviour of copper in the anticipated groundwater environment, the time required to penetrate the container shell might approach several tens of millions of years. Thereafter, the slow dissolution and leaching of the fuel, the

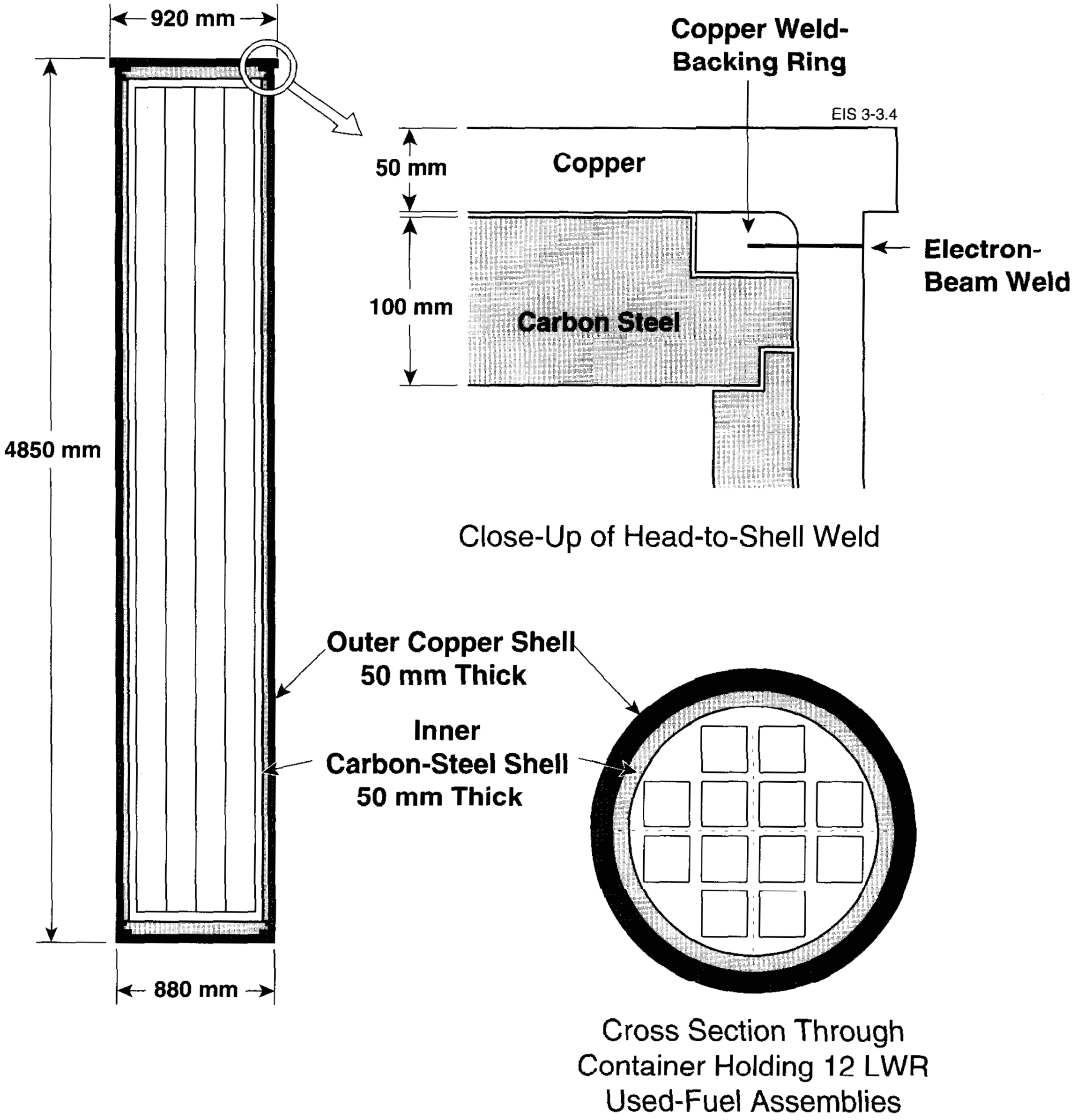


FIGURE 3-4: Swedish Program Advanced Cold Process Container

other engineered barriers placed around and near the container (buffer and backfill), and the slow movement of the groundwater would serve both to further retard the movement of radionuclides into the environment and to dilute their concentrations (SKBF/SKB 1983, SKB 1992a).

3.3.4 Switzerland

In 1978, the Swiss Government passed legislation similar to that of the 1977 Swedish Stipulation Law. The (Swiss) National Cooperative for the Storage of Radioactive Waste (NAGRA) was commissioned by Swiss electric utility companies to conduct studies into, and give evidence of, safe waste management and disposal.

The reference waste form is vitrified reprocessing waste. Crystalline bedrock and impermeable clays or other sediments are being considered as host media. A NAGRA report (NAGRA 1985) summarizes studies conducted on a conceptual disposal vault for purposes of safety calculations. For those studies, the reference disposal medium was granitic rock in which a mined disposal vault was located at a depth of 1200 m. The container is intended to provide complete isolation of the waste until the short-lived fission products have decayed and the period of elevated temperature in the disposal vault has passed, for which a minimum container lifetime of 1000 a was selected. In the disposal vault, the container is emplaced horizontally in a mined tunnel and is surrounded by compacted bentonite-clay buffer.

The NAGRA reference container for vitrified reprocessing waste is shown in Figure 3-5. The shell is made of cast steel with a minimum thickness of 150 mm (at the hemispherical heads). The design is intended to minimize radiation dose at its outer surface, aid handling and reduce groundwater radiolysis after emplacement. Following emplacement of the waste into the prefabricated shell, the container lid would be pressed into, and welded to, the container body. The welded joints would be inspected by ultrasonic and gas-leakage methods.

3.3.5 United States

Yucca Mountain, Nevada, was identified in 1987 as the potential site for the first disposal vault for U.S. high-level nuclear waste. The vault would be located in volcanic tuff, several hundred metres above the water table. The reference waste form is unreprocessed used LWR fuel. The design goal for the engineered barrier system (meaning the container plus the waste form) is to ensure "substantially complete containment" of the waste for up to 1000 a after vault closure, and thereafter, the yearly release of any radionuclides from the engineered-barrier system must be less than 10^{-5} of the inventory calculated to exist 1000 a after vault closure (the "controlled-release period"). The controlled-release period has been set at 10 000 a following vault closure (Cloninger et al. 1989). The waste is to be retrievable for up to 50 a after emplacement begins.

A conceptual waste package for used fuel is shown in Figure 3-6, along with two possible arrangements for PWR fuel. Candidate container materials are still under study; examples include copper, Alloy 825 (a high-nickel alloy) and a 70% copper-30% nickel alloy (Frei and Dayem 1989). Although both horizontal and vertical emplacement have been considered, the reference case envisages single containers placed in vertical boreholes with a 50-mm air gap between the container and the borehole liner (Figure 3-7).

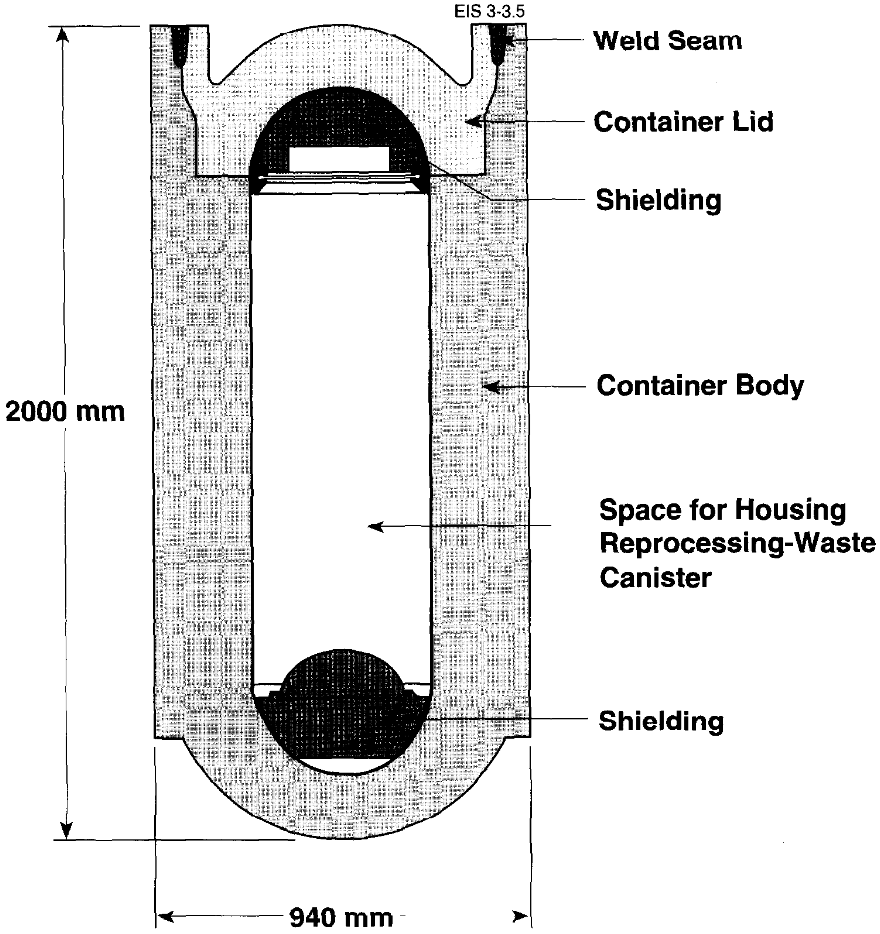


FIGURE 3-5: The NAGRA Reference Cast Steel Container for Disposal of Vitrified High-Level Waste

Since significant groundwater ingress into the disposal vault is not anticipated, containers would not be subjected to hydrostatic loads. The environment within the boreholes is expected to be primarily hot humid air, and most of the containers would remain at a temperature above the boiling point of water for about 300 a. Thus, container-design studies are focused primarily on the investigation of materials that will resist corrosion under these conditions and on reliable methods of container manufacture and inspection.

Also under consideration is a multiple-purpose container called the Multi-Purpose Canister (MPC). In the MPC concept (USDOE 1993, Bowser et al. 1993), a number of used-fuel assemblies would be placed within a metal container and the container would then be sealed at a nuclear power station. The container would be placed within a steel overpack for

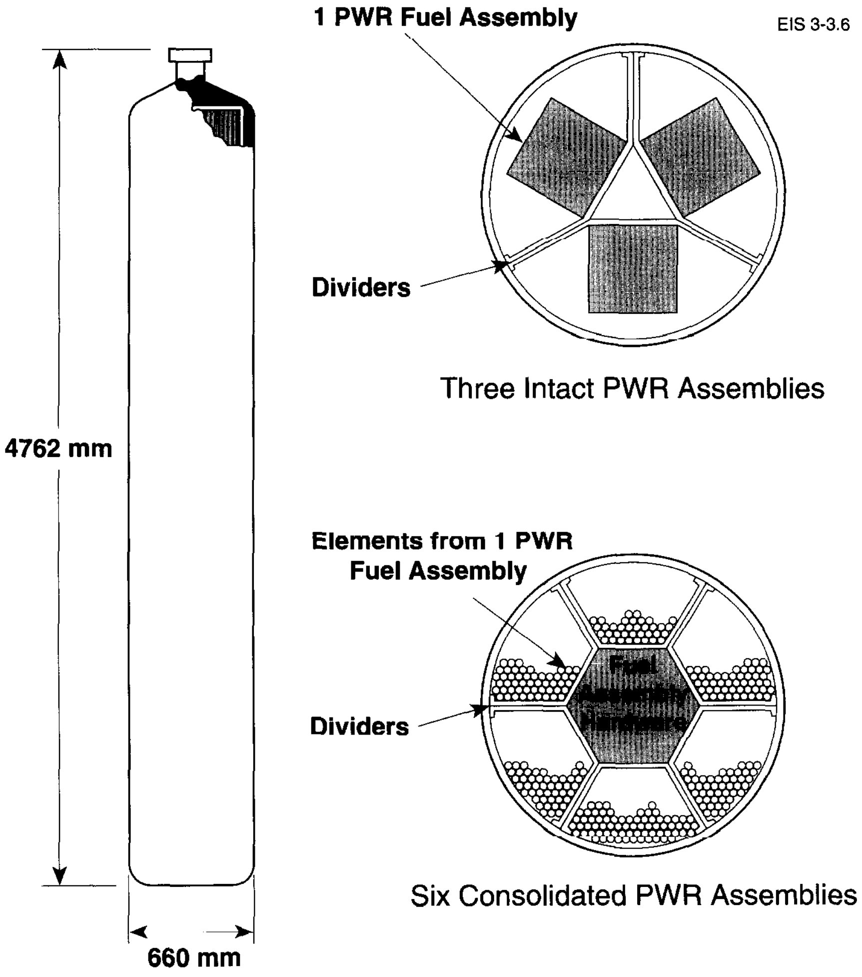


FIGURE 3-6: U.S. Used-Fuel Container Concept

transportation to either an interim-storage facility or a disposal-vault site.

At an interim-storage facility, the container would be removed from the transportation overpack and stored in a steel or concrete structure. At a disposal site, the container (following its removal from the transportation overpack) would be placed inside another metal container suitable for disposal. By eliminating the handling of individual used-fuel assemblies between a nuclear power station, interim-storage site and final-disposal vault, the MPC offers the potential to simplify handling operations, reduce radiation exposure to operations personnel, and reduce low-level waste generation.

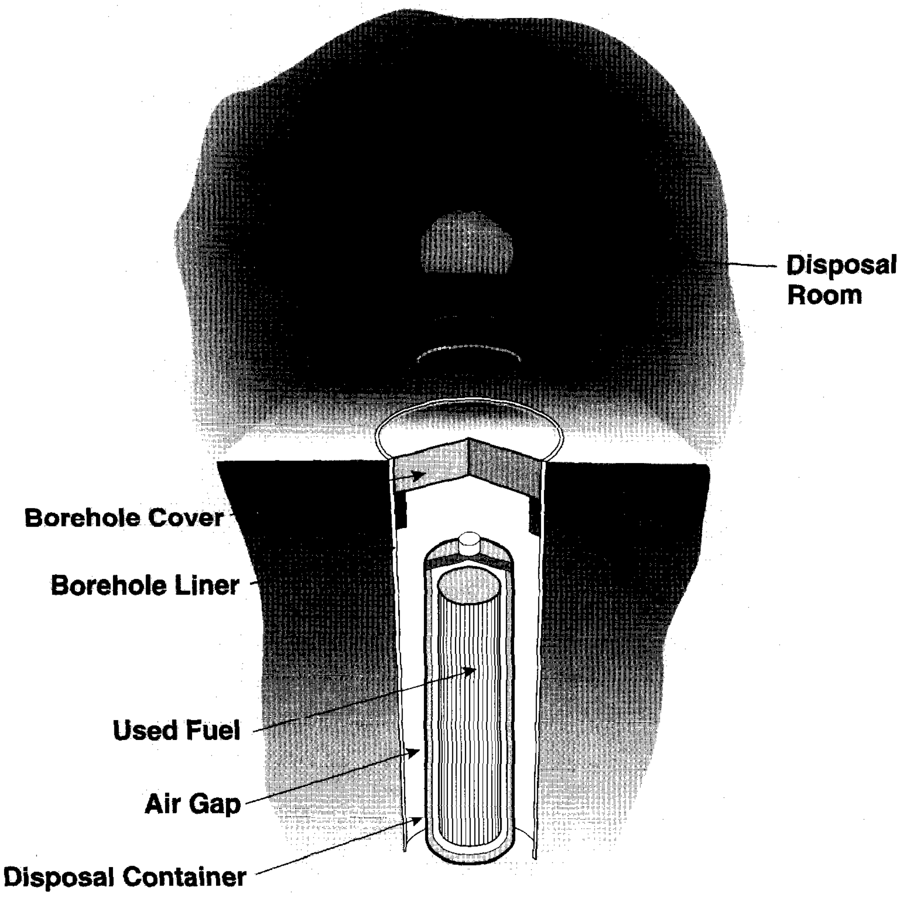


FIGURE 3-7: Conceptual U.S. Container-Emplacement Methodology for a Tuff Disposal Environment

3.3.6 Other Countries

Other countries with programs to investigate high-level radioactive waste disposal include Belgium, Finland, France, Japan and Spain. The Belgian program is primarily investigating the potential for disposing of vitrified reprocessing waste in clay deposits. The Finnish program is closely aligned with Swedish investigations into the disposal of unreprocessed used fuel in granite, using copper-shell containers. In France, four prospective geological media have been considered for the disposal of vitrified reprocessing waste: clay, granite, shale, and salt formations. In Japan, vitrified reprocessing waste would be stored for 30-50 a prior to disposal in a suitable geological formation, as yet to be identified. In

Spain, granite, clay, and salt formations are being investigated for the disposal of both unreprocessed used fuel and vitrified reprocessing waste.

3.4 DESIGN BASIS FOR CONTAINERS IN THE CANADIAN PROGRAM

3.4.1 Introduction

The Canadian nuclear fuel waste disposal concept is based on a multiple-barrier approach in which the combination of engineered barriers and the geological medium would ensure isolation of radionuclides from the biosphere until they have decayed and become diluted to the extent that human health and the environment would be protected. Early in the program, various targets for isolation of the waste within disposal containers were considered, and a minimum of 500 a was suggested (Cameron 1982). As is apparent from the discussion in Chapter 2, this choice relates to the relatively rapid decrease in radioactivity of the waste (by a factor of 100 000) in the first 500 a. In the interval between 500 and 10^6 a, the radioactivity of the waste decreases only by a further factor of 100 (see Section 2.2.4). Therefore, the focus of the container-design program has been to provide isolation during the period when the waste is most radioactive, i.e., for at least 500 a. However, the provision of longer-term containment has also been included as a key objective in the development studies. Therefore, many of the design considerations for containers having a 500-a minimum lifetime also pertain to containers having longer lifetimes.

In considering the design specifications for a container, five broad principles have been used as a guide. Some of these derive from the generic, non-site-specific mandate of the program in Canada. These principles are as follows:

1. Structural: containers should be designed to withstand short-term handling loads and long-term loads during disposal.
2. Fabrication: containers should be amenable to manufacture and inspection to ensure that the highest-quality product possible is produced.
3. Chemical stability: containers should be resistant to various modes of degradation, principally corrosion.
4. Technical feasibility: the designs and materials used for containers, and the operational activities necessary for their manufacture and emplacement, should be technically feasible with available technology or with reasonably achievable developments.
5. Flexibility: the approach to designing containers should be flexible so that a range of design options are available to accommodate potential constraints on vault design that might be imposed by the characteristics of an actual disposal site.

3.4.2 Container Materials Considerations

It is expected that, in the absence of failure by structural overload, the container lifetime would eventually be limited by corrosion or other localized degradation processes (Nuttall 1983). The corrosion/degradation process most likely to cause container failure would depend on the nature of the container material, its mode of construction (e.g., location of residual stresses, quality of welded joints) and the environment to which it was exposed.

To achieve very long container lifetimes (>100 000 a), the use of ceramic or vitreous materials, which can be produced with very high chemical stability, could be considered. Extensive investigations on the potential use of these materials have been conducted in the Canadian program (Onofrei et al. 1985). These studies, and those conducted in other programs (see Section 3.5.4.4) have shown that while the non-metallic materials considered have excellent corrosion resistance, to develop the ability to ensure that a container could be fabricated with high integrity would require extensive research. Also, the ability to accurately predict the potential for crack growth in ceramic containers under loading is not well developed. Consequently, the principal focus of materials studies for the construction of disposal containers has been on the use of metals. A similar conclusion was reached in the Swedish nuclear waste management program (SKB 1989a).

The ideal container would be one fabricated from a metal that is thermodynamically stable in water and hence does not corrode in the disposal environment. As discussed by Marsh (1982), only gold appears to meet this criterion (for oxidizing waters), but for the obvious reason of expense, its use is not feasible. The alternative is to fabricate containers from metals or alloys that, when used at an appropriate thickness, have a corrosion rate sufficiently low to ensure that penetration does not occur during the required containment period. Two classes of material may be used:

1. Corrosion-allowance materials possessing a slow, but measurable, corrosion rate. Such materials (e.g., iron and carbon steels, copper) are usually relatively cheap, but a substantial container thickness could be required. They tend to be thermodynamically unstable in water (Fe) or oxygenated water (Cu) and are expected to corrode uniformly and, hence, predictably.

2. Corrosion-resistant materials possessing very low corrosion rates. Such materials (e.g., stainless steels, titanium alloys, nickel-based alloys) are more expensive, but only a thin-walled container may be required for corrosion purposes. These materials are generally passive; i.e., they are protected from corrosion by the presence of a protective surface oxide. However, breakdown of this film can render them susceptible to localized corrosion processes, such as pitting, crevice corrosion or stress-corrosion cracking. Such processes are not readily predictable.

Generally, corrosion-allowance and corrosion-resistant materials can be categorized according to their position in the galvanic series, the former being located toward the active end of the series, the latter toward the noble end, as shown in Figure 3-8 for potentials measured in seawater (Hack 1987).

Two materials were chosen for evaluation in the Canadian program: the corrosion-resistant ASTM[8] Grade-2 titanium; and the corrosion-allowance material, oxygen-free copper. Some studies of the corrosion-resistant nickel-based alloys, Inconel 625 and Hastelloy C276, and the Grade-12 titanium alloy have also been undertaken and, for Grade-12 titanium, are continuing.

Both Grade-2 titanium and oxygen-free copper have the advantage of being compositionally and microstructurally simple compared with the alternatives. Since both are relatively pure, single-phase materials, it is extremely unlikely they would either undergo phase transitions that might enhance corrosion susceptibility under disposal-vault conditions, or form complex unstable structures as a consequence of mechanical and thermal treatments, such as cold working or welding.

As a corrosion-allowance material, copper has the advantage over the irons and steels of being stable in water containing no oxidants. As a consequence, its corrosion would not produce potentially large quantities of hydrogen, which may have uncertain impacts on vault performance, and its uniform-corrosion rate would be determined predominantly by the concentration of oxidants within the vault. Since vault redox conditions are expected to become anoxic with time, its uniform-corrosion rate would be much lower than the corresponding rates for iron and steels.

Many of the advantages of the corrosion properties of titanium alloys, compared with other corrosion-resistant categories of materials (stainless steels and nickel-based alloys), have been reviewed by Nuttall and Urbanic (1981). The protective oxide film of these alloys is strongly adherent and chemically stable over a wide range of pH, including acidic solutions known to be aggressive to other corrosion-resistant materials. This enduring passivity makes titanium and its alloys very resistant to uniform corrosion in saline solutions to temperatures as high as 260°C, and leaves it susceptible to very few modes of localized corrosion (Schutz and Thomas 1987). In fact, titanium appears to be very resistant to pitting and stress-corrosion cracking, two localized processes known to affect the corrosion performance of stainless steels and nickel-based alloys (see Sections 3.7.4.3 and 3.7.4.4).

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[8] American Society for Testing and Materials.

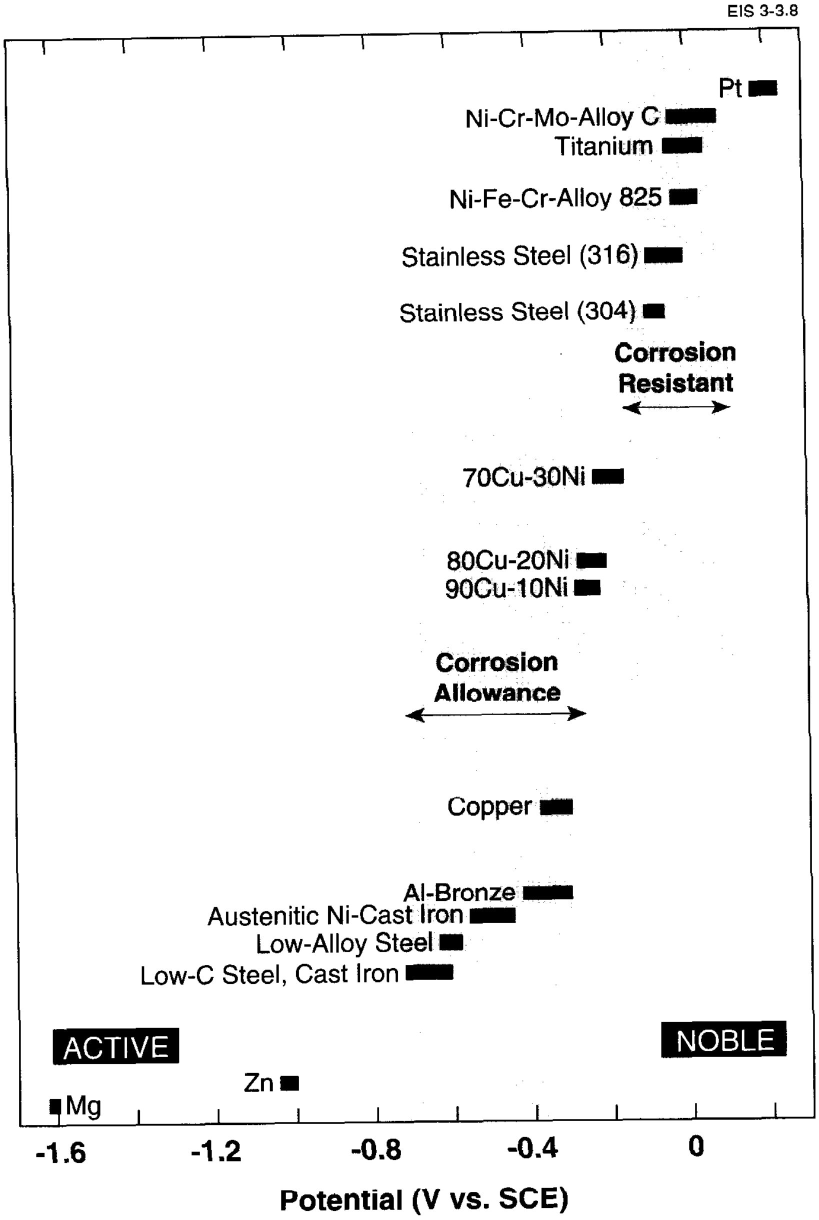

FIGURE 3-8: Galvanic Series for Seawater (after Hack 1987)

3.4.3 Engineering Considerations Applicable to Containers for the Canadian Program

3.4.3.1 Waste Form

The principal waste for disposal in the current Canadian program is unreprocessed, natural-UO_2 fuel in the form of CANDU fuel bundles.[9] Because the diameter and length of the vast majority of CANDU fuel bundles is the same (See Figure 1-1), and the bundles are short, considerable flexibility is available in the design of containers for disposal. Since CANDU bundles can be assembled into a number of efficient packing arrangements, conditioning and consolidation procedures that could introduce complications, such as the generation of secondary solid and gaseous wastes, are not necessary. Therefore, the focus of the program has been on the containment of intact fuel bundles. Since the UO_2 in CANDU fuel is of natural enrichment, there is no need to consider criticality in container design. Calculations that demonstrate the substantial degree of subcriticality for a container design that holds 72 CANDU fuel bundles are presented by McCamis (1992).

3.4.3.2 Quantity of Waste

The volume of used-fuel arisings that is to be disposed of is a consideration in the development of a nuclear fuel waste management strategy, of which one component is container design. Table 3-1 (OECD 1987) lists actual and projected quantities of annual used-fuel arisings for a selection of countries with major nuclear power programs. These data show that, in terms of discharged fuel mass, the arisings in Canada are comparable to those of countries with much larger nuclear generating capacities, such as France, Japan and the United States. This is because of the nature of the CANDU natural-uranium fuel cycle, for which the amount of fuel discharged per unit of energy generated is several times that of fuel cycles that employ enriched fuel.[10] Such projections of used-fuel arisings are useful for assessing and forecasting the required container production rates for the operational life of a used-fuel disposal centre. Container designs can then be developed to facilitate the production process, while incorporating those features essential to maintaining the container performance goals during disposal.

3.4.3.3 Container Temperature

In the short term, the surface temperature of the container would be governed primarily by the heat output of the contained fuel, which in turn is a function of the fuel burnup and the length of time that it is stored

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[9] Advanced fuel cycles that would employ slightly enriched uranium, or recycling to increase fuel burnup and reduce used-fuel arisings, are currently under study at AECL (Green et al. 1988; see also Sections 2.2.8 and Appendix A, Section A.13).

[10] However, the radionuclide inventory produced per unit of energy generated is approximately the same for all fuel cycles.

TABLE 3-1

ANNUAL USED-FUEL ARISINGS AND INSTALLED GENERATING CAPACITIES OF VARIOUS COUNTRIES (OECD 1987)

Country	1985[1]	1986[1]	1990[2] (Mg U)	1995[2]	2000[2]	Installed Nuclear Electricity Generating Capacity (GW(e))[3]
Belgium	97	140	140	130	160	5.5
Canada	1420	1500	2000[4]	2100	2100	14.0
Finland	65	65	68	68	68	2.3
France	300	640	1000	1220	1400	56.9
Germany	360	430	608	608	608	22.4
Japan	650	960	860	1370	1690	32.0
Spain	160	210	250	300	340	7.1
Sweden	238	296	250	250	250	9.8
Switzerland	85	85	85	85	110	3.0
United Kingdom	950	933	1007	725	375	11.7
United States	1200	1400	2000	2100	2100	99.8

[1] Actual

[2] Estimated

[3] Source: AECL (1993). These data are valid as of 1991 December 31.

[4] Increase between 1986 and 1990 was expected to arise from startup of the Darlington station, which actually occurred later.

prior to disposal. For 10-a-cooled CANDU fuel at the reference burnup of 685 $GJ \cdot kg^{-1}$ U, the heat output per bundle is about 5 W, a rate per kilogram U that is about 25% of that of LWR fuel irradiated to typical LWR burnups and cooled for the same period (Oak Ridge National Laboratory 1988). In the longer term, the temperature would be controlled by the heat loading of the disposal vault, the vault design (e.g., whether single- or multiple-level), the ratio of excavated to unexcavated area and the density of emplacement of containers within the disposal rooms (Cameron 1982). In initial studies it was assumed that the temperature at the container/buffer interface would be set at about 150°C. Subsequently, a lower value of 100°C was specified for the engineering study for a conceptual used-fuel disposal centre (Simmons and Baumgartner 1994); this change was based on the judgement that crevice corrosion rates in Grade-2 titanium might become unacceptably high at temperatures significantly above 100°C. Furthermore, this would avoid the mineralogical alteration of bentonite that might occur at temperatures above 100°C.

3.4.3.4 Container Geometry

Based on initial studies of conceptual disposal-vault designs (Acres Consulting Services 1980a,b), two possible container-emplacement methods were proposed. In one, the containers would be placed into boreholes excavated in the floor of each disposal room. In the other, the containers would be placed on a prepared bed of buffer material within the room, followed by buffer and backfill emplacement around the containers. To accommodate both emplacement options, three approximate reference container geometries were defined (Cameron et al. 1983) (Figure 3-9). All are cylindrical and were designed to achieve efficient fuel packaging. The TEC-I (Trench Emplacement Container, Mark I)[11] design is based on two layers of 36 bundles, and the TEC-II design is based on four layers of 18 or 19 bundles. The BEC-I (Borehole Emplacement Container, Mark I) design uses arrays of seven fuel bundles stacked in six layers. The configuration of the fuel bundles within the container would be achieved by installing the bundles in tubes that would be held together to form a "basket." This would simplify the loading of the fuel into the container and maintain the positioning of the bundles within it.

Scoping calculations have shown (Gray and Cheung 1986, Cheung et al. 1987) that the rate of radionuclide release to the geosphere from containers emplaced in boreholes would be similar to that from containers placed in-room, and that borehole emplacement would be preferable for operational considerations, including worker safety (see Section 4.7.1). To minimize disposal operations, resource use and costs, it is desirable to use a container with as large a capacity as possible, while retaining the option of borehole emplacement. The TEC-II container fulfills both these requirements. The diameter of borehole required to accommodate the container and a 0.25-m-thick annulus of buffer would be ~1.24 m. Since this borehole size is likely to be within readily developable capabilities of hard-rock mining technology, the TEC-II geometry was selected as the reference for the conceptual engineering study for a used-fuel disposal centre (Simmons and Baumgartner 1994).

3.4.3.5 Structural Loading

The principal structural requirement for the container is that it must withstand the hydrostatic pressure that would develop from the reestablishment of the water table. At a vault depth of 1000 m, the hydrostatic pressure would be about 10 MPa. Any additional pressure, for example, that caused by swelling of the buffer, must also be considered. It has been shown (Dixon et al. 1986) that swelling of the reference buffer material could impose a further 1.0 to 2.5 MPa pressure on the container.

Should nearby or distant seismic activity result in rock movements within the vault, the container would be cushioned by its surrounding of clay buffer, which would deform plastically, thereby distributing and dissipating loads arising from the rock movement. Baumgartner (1992) has assessed two possible types of localized rock movements for their potential to cause failure of a container surrounded by buffer within a borehole. Neither of

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[11] At the time these nomenclatures were developed, the in-room emplacement option was referred to as "trench emplacement." For continuity and ease of reference, the "TEC" nomenclature was retained throughout the development program.

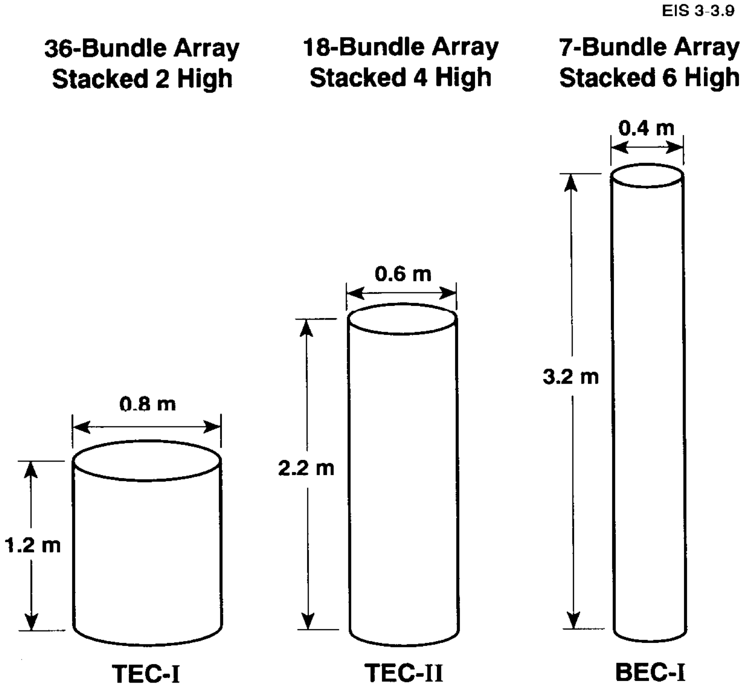

FIGURE 3-9: Basic Geometries of Fuel-Isolation Container Designs

the localized rock movements would impose significant loads on the container. During characterization of a plutonic rock mass as a potential site for disposal, large-scale faults that might be susceptible to movement as a result of seismicity or glacial loading or unloading would be readily identifiable. Depending on the characteristics of the fault, the plutonic rock mass containing it might either be rejected as a site for nuclear fuel waste disposal, or the disposal vault might be located at an appropriate distance from the fault to ensure that there would be no risk to container integrity from large-scale rock movement.

3.4.3.6 Manufacturing Considerations

The development of an engineered component must include consideration of a number of factors relating to its future production. These include

- the required duties and performance life of the finished component;
- required quantities and rates of production;
- quality control (QC) requirements, including inspection;
- manufacturing and QC constraints, e.g., whether some operations might have to be performed remotely or behind protective barriers to ensure worker safety;

- the reliability of, and historical experience with, proposed manufacturing and QC procedures, including acceptability according to regulatory criteria;
- the size of the component, and equipment needed to construct and handle it;
- whether new manufacturing and/or QC procedures might have to be developed;
- materials resource requirements; and
- cost.

All of these factors were included in the fabrication and inspection development studies for disposal-container options in the Canadian program; details are presented in Section 3.5.3. Fabrication and inspection considerations were also important in the selection of a reference container design for the engineering study for a conceptual used-fuel disposal centre (Simmons and Baumgartner 1994). Section 3.5.5 presents a discussion of the influence of these and other parameters in that selection.

Design features that would facilitate the emplacement of the container into, and retrieval from, the disposal vault during the vault operational period were considered. Wherever possible, design simplicity was adopted to ensure ease of container manufacture and inspection and to facilitate the design of other components that must interface with the container.

For the manufacture of test prototypes and for fabrication development studies, and in the absence of codes specific to the fabrication and inspection of nuclear fuel waste disposal containers, currently recognized engineering codes have been used, both in direct application and as design guides for good engineering practice. These include the use of ASTM standards for materials specification and procurement (ASTM 1993a,b), and the ASME[12] Boiler and Pressure Vessel Code, Sections III, V, VIII, IX and XI (ASME 1986a,b,c,d,e,f,g) for container design, fabrication and inspection.

Despite the most rigorous inspection procedures, manufacturing experience has shown that defective components can occasionally evade detection. For the postclosure assessment case study, an estimate of the frequency of initially defective containers was required. Experience with present-day manufactured components and fabrication and inspection techniques, combined with mathematical failure-analysis models, was used to provide such an estimate. The results of this reliability analysis are presented in Section 3.5.3.8.

Throughout the container development program, safety considerations that could affect the primary mission of the containers, i.e., that they must provide at least 500 a of isolation of the used fuel, have been accorded

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[12] American Society of Mechanical Engineers.

greater significance than container production costs. Nevertheless, where different systems employing alternative materials and/or manufacturing and QC procedures can equally achieve the primary objective, relative cost is a valid parameter for system comparison. Section 3.5.5.12 discusses relative costs in greater detail.

Container concepts other than those designed with a single, corrosion-resistant shell have also been considered for the disposal of unreprocessed used fuel. These include

- a dual-wall container employing a corrosion-resistant shell surrounding an inner, structurally supportive carbon-steel shell; and
- a concrete container potentially suitable for storage, transportation and disposal.

The dual-wall container concept was studied to determine if such a design could provide improved manufacturing and long-term structural durability characteristics over the single-shell concept. The integrated concrete container was investigated to build upon the excellent experience with dry fuel storage in Canada, accumulated both through its commercial implementation and during joint studies with Ontario Hydro (Wasywich and Frost 1988), and to examine the potential for cost benefits arising from a fully integrated storage, transportation and disposal system (Freire-Canosa 1982). Details of the results of these studies are presented in Section 3.5.4

3.5 CONTAINER DEVELOPMENT STUDIES FOR THE CANADIAN PROGRAM

3.5.1 Introduction

Two metal-shell container designs have been studied (Cameron et al. 1983, Nuttall et al. 1983):

- stressed-shell designs, in which the corrosion-resistant shell is the only structural member resisting externally applied loads; and
- supported-shell designs, in which a thinner shell (but of sufficient thickness to meet the corrosion durability requirement) is internally supported against external loading.

In the stressed-shell concept, design considerations include methods of manufacture, inspection for quality control (particularly at welded joints, where it would be necessary to determine if any embedded flaws were present), and short- and long-term structural durability.

In the supported-shell concepts, the same design considerations apply; however, fabrication and inspection of the welded joints could be facilitated by the use of thinner materials, which would require fewer weld passes and in which embedded flaws could be detected more readily. The outer shell could be internally supported against external loading either by supportive members attached to the shell's inner boundary or by a material that could be compacted or cast into the residual space within the container after the fuel was installed. However, the attachment of supportive members to the inner surface of the shell would greatly increase and complicate manufacturing and QC procedures. Consequently, our studies have focused on the use of the following materials to fill supported-shell containers:

- an inexpensive particulate (such as industrial glass beads, or sand) that could be compacted into the free volume of the container;
- a low-melting-point metal (such as lead) cast into the container and around the fuel bundles; and
- internal structurally supportive members to which the stresses could be transferred by a compacted particulate.

Early in the development studies, it was concluded that the most credible approach to developing and evaluating container designs was to carry out a program that included fabrication and inspection technology development, prototype fabrication, structural proof testing, and structural-performance modelling. This would allow

- the development and demonstration of fabrication and inspection techniques required for production,
- direct measurement of the structural performance of candidate container designs,
- the opportunity to test the validity of structural-performance predictions obtained from computer modelling and stress analysis, and
- evaluation of the sensitivity of the structural behaviour of various container designs to tolerances in their design specifications.

3.5.2 Structural-Performance Investigations

3.5.2.1 Stressed-Shell Container

Design and Construction

The 72-bundle-capacity stressed-shell container (Figure 3-10) was the first design investigated. Initial studies focused on determining the necessary shell and head thicknesses needed to meet short-term structural performance requirements under the external pressures that would ultimately develop during disposal (Crosthwaite et al. 1982). These studies clearly indicated that it would be less preferable to use flat heads because of the very thick sections required for adequate strength. Instead, semi-elliptical heads, which offer the same strength for less material thickness, were selected.

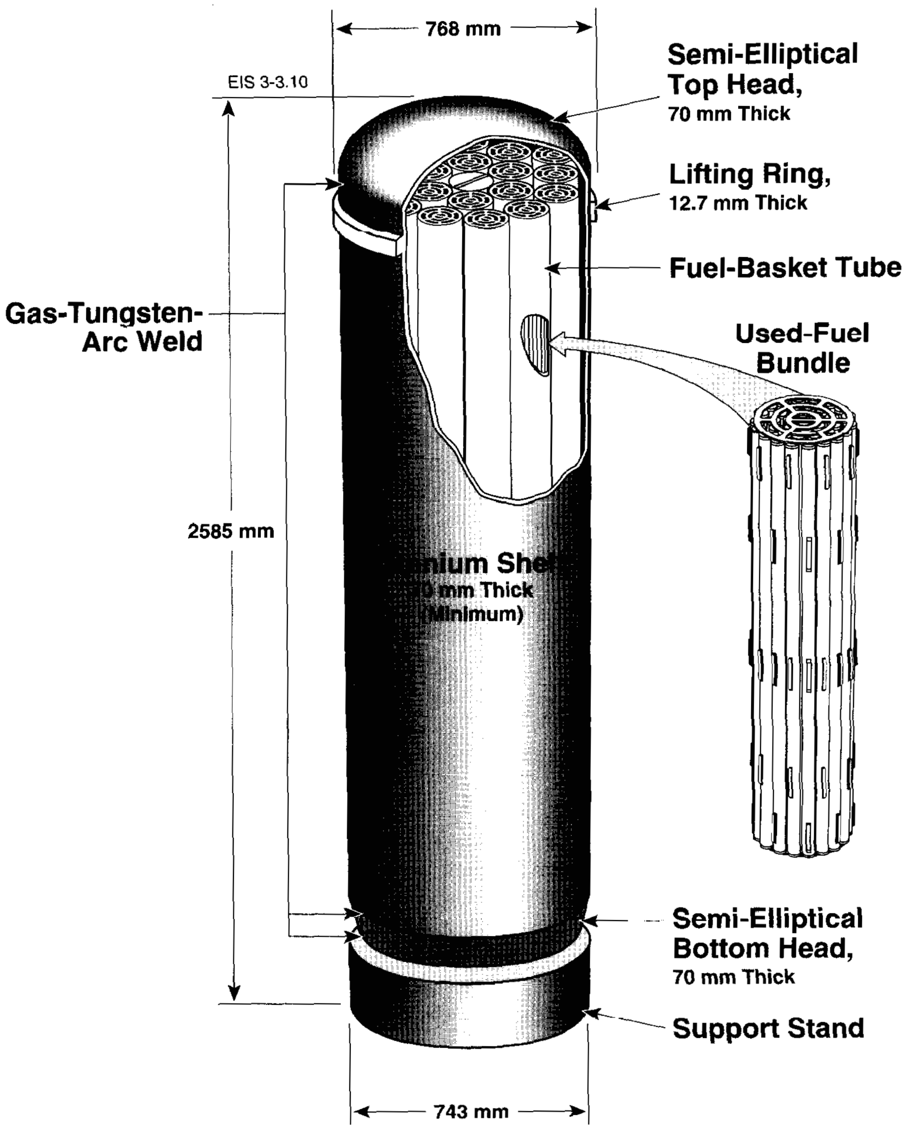

FIGURE 3-10: Titanium Stressed-Shell Fuel Disposal Container

A full-scale prototype container of TEC-II configuration was designed with a factor of safety of 2.0 against collapse, rather than the 3.0 to 4.0 provided by the ASME Boiler and Pressure Vessel Code for vessels constructed for industrial uses (i.e., where human activities would be in proximity to the stressed vessel). The prototype was constructed from 316L stainless steel, although this material would have sufficient corrosion durability only under very benign groundwater-chemistry conditions. This material was selected so that the structural-performance testing program could be launched and experience gained without the imposition, at that time, of the higher costs and greater fabrication difficulties associated with more corrosion-resistant materials. Furthermore, the primary test objectives, i.e., to gain structural-performance testing experience and to determine the accuracy of a pretest structural-performance prediction using a computer model, were independent of the container-shell material selected, as long as the material's mechanical properties data could be well defined. Such was the case for 316L stainless steel, which is widely used in industry.

Although the maximum container-surface temperature during disposal has been established at 100°C for the engineering study for a conceptual used-fuel disposal centre (Simmons and Baumgartner 1994), the structural-performance investigations on candidate containers were designed to be conducted at temperatures up to 150°C, to ensure an appropriate degree of conservatism in the tests.

Because facilities to test the prototype under hydrostatic pressures typical of those anticipated in a disposal vault were not available in Canada at that time, testing was conducted in a laboratory in the United States; however, these tests could only be conducted at room temperature. To maintain a factor of safety of 2.0 against collapse in the tests, the container-shell thickness was reduced from the required 50 mm at 150°C to 28.6 mm at 20°C.

The prototype was designed with a plate and pipe structure within its bottom head, which, in a production container, would support baskets containing used fuel. No fuel baskets were installed, however, since their presence would not affect the onset-of-collapse pressure for this type of container.

The prototype was constructed of seam-welded 316L stainless steel pipe and hot-formed semi-elliptical heads, which were joined to the shell by multiple-pass gas-tungsten-arc (GTA) welding. Full details are presented by Crosthwaite et al. (1982).

Tests and Analyses

A pretest structural-performance analysis was conducted using the commercially available BOSOR 5 computer program (Bushnell 1976), which uses an iterative, finite-difference method to determine the stresses in, and collapse pressure for, axisymmetric structures. Materials properties input data to the program were derived from tensile tests conducted on samples taken from the pipe. The program predicted the collapse pressure for the container, the collapse mode and the elastic/plastic response of the shell under increasing pressure.

Following its construction and inspection, the prototype was extensively instrumented with strain-measurement gauges and subjected to gradually increasing pressure until the container shell collapsed. Collapse occurred at 18.96 MPa, within ~3% of the predicted value, 19.51 MPa. Comparison of the shell-deformation data obtained during the test (prior to shell collapse) with the structural analysis predictions indicated that reasonable agreement was obtained for those locations of the shell that incurred maximum compressive strain. It was concluded that BOSOR 5 was acceptably accurate for predicting the deformation, collapse pressure and collapse mode of a stressed-shell container, on the basis of short-term mechanical properties of the shell material. However, it was clear that the effects of material creep could play an important role in the container's long-term structural behaviour.

Subsequent Studies of Stressed-Shell Designs

Subsequent theoretical analysis of the effect of creep on the long-term structural behaviour of a TEC-II geometry stressed-shell container manufactured of Grade-2 titanium revealed that, under 10-MPa external hydrostatic pressure at 100°C, the container shell's tendency to continuously deform and eventually collapse by buckling would be very dependent on the creep rate of the shell material (Hosaluk et al. 1987). These studies further indicated that a titanium-shell thickness of ~70 mm would be required to provide a 500-a creep-buckling lifetime. Such a thickness would introduce extensive fabrication and inspection difficulties plus severe economic penalties, particularly during mass production. Therefore, it was concluded that the TEC-II, titanium stressed-shell container was unlikely to be a practical option for used-fuel disposal. Depending on its type and method of manufacture, the strength of pure copper can be similar to or significantly less than that of titanium. Consequently, the concept of a stressed-shell container fabricated entirely of titanium or copper was dropped from further consideration. However, the concept of a carbon-steel stressed-shell container protected by a corrosion-resistant overpack has been retained as a possible alternative (see Section 3.5.4.2).

3.5.2.2 Packed-Particulate Container

Design and Construction

The packed-particulate container was the first supported-shell concept investigated. In this design (Figure 3-11), a thin, corrosion-resistant metal shell is internally supported by a granular material that is compacted by vibration into the residual space after loading the used fuel (Mikasinovic and Hoy 1982). The internal fuel basket is designed to provide a convenient means of loading fuel bundles into the container and retaining them in place during particulate compaction. For the packed-particulate container, the basket is constructed of a circular array of

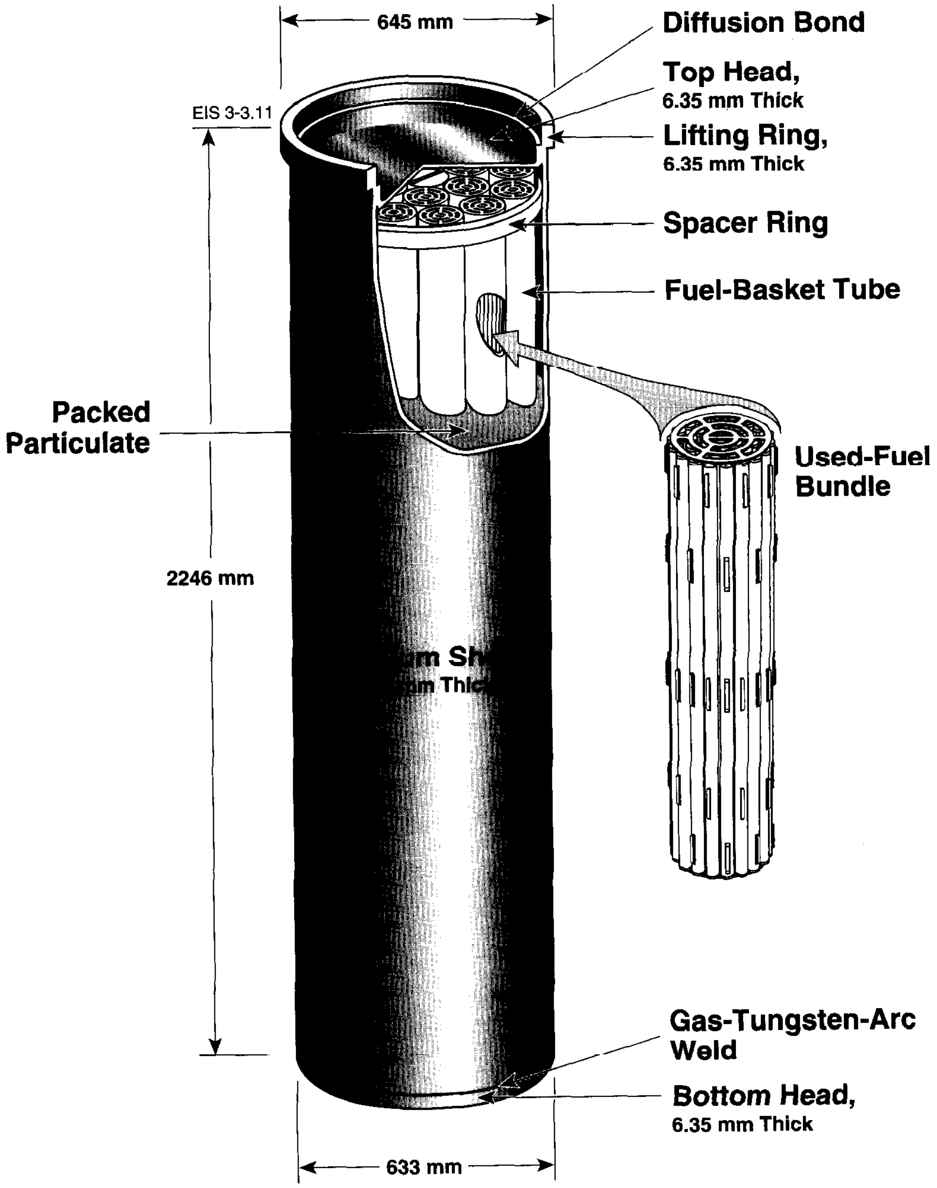

FIGURE 3-11: Titanium-Shell, Packed-Particulate Fuel Disposal Container

19 carbon-steel tubes,[13] 18 of which are of 108-mm inside diameter and 3.2-mm wall thickness. The tubes are tack-welded together at the top and are attached by welding to a bottom ring-and-spoke structure. For handling purposes, the central tube has a thicker wall and retains no fuel bundles. Thus, the container is designed to hold 72 used CANDU bundles, with 4 stacked in each of the 18 thinner-wall tubes. The tubes remain open-ended and are not intended to provide structural support to the shell. The ring-and-spoke structure transfers the weight of the fuel evenly to the bottom head.

A full-scale prototype was constructed to investigate the short-term structural behaviour of the design. The cylindrical part of the shell was constructed of welded, 4.76-mm-thick[14] Grade-2 titanium plate. The bottom head was constructed of 6.35-mm-thick spin-formed plate, which was GTA-welded to the cylindrical body. The top head was of 4.76-mm-thick spin-formed plate, also GTA-welded to the cylindrical body. Each head was stress-relieved by heat treatment in vacuum prior to its attachment to the shell. In the prototype, simulated fuel bundles were inserted into the outer ring of the tubes that make up the fuel basket to partially simulate the contribution that the bundles make to the stiffness of the compacted particulate.

A program was conducted to identify a suitable particulate material for compaction into the container (see Section 3.5.3.5). Of the materials selected for study, tests indicated that industrial glass beads ~1 mm in diameter were the preferred choice. The particulate was compacted by vibration into the container on a large shaker table, after which the top

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[13] Following penetration of the container shell, groundwater contact with the carbon-steel fuel basket would, as the steel corrodes, lead to the generation of free hydrogen (Johnson et al. 1994). Should future analyses determine that significant hydrogen generation is undesirable, the carbon-steel basket could be replaced by one constructed of fired clay, which would not generate hydrogen, or a metal, such as stainless steel, with a much lower corrosion rate than carbon steel. The basket of the packed-particulate container is not intended to provide internal support to the shell; it is required only to retain the fuel bundles in position during the container-loading and particulate-compaction procedures.

A one-bundle-long hexagonal array of extruded and fired clay tubes (Figure 3-12), of only slightly smaller diameter than would be required to accommodate CANDU fuel bundles, was produced to demonstrate the feasibility of manufacturing a ceramic fuel basket (Humphries 1990).

[14] During the design phase for the packed-particulate container, structural analyses had shown that the cylindrical shell would have adequate strength at a thickness of 4.76 mm; therefore, the prototype was constructed from this size of plate. Subsequent studies showed that a thickness of 6.35 mm would be preferable to provide the required corrosion allowance to meet the target container lifetime; see Section 3.5.6.

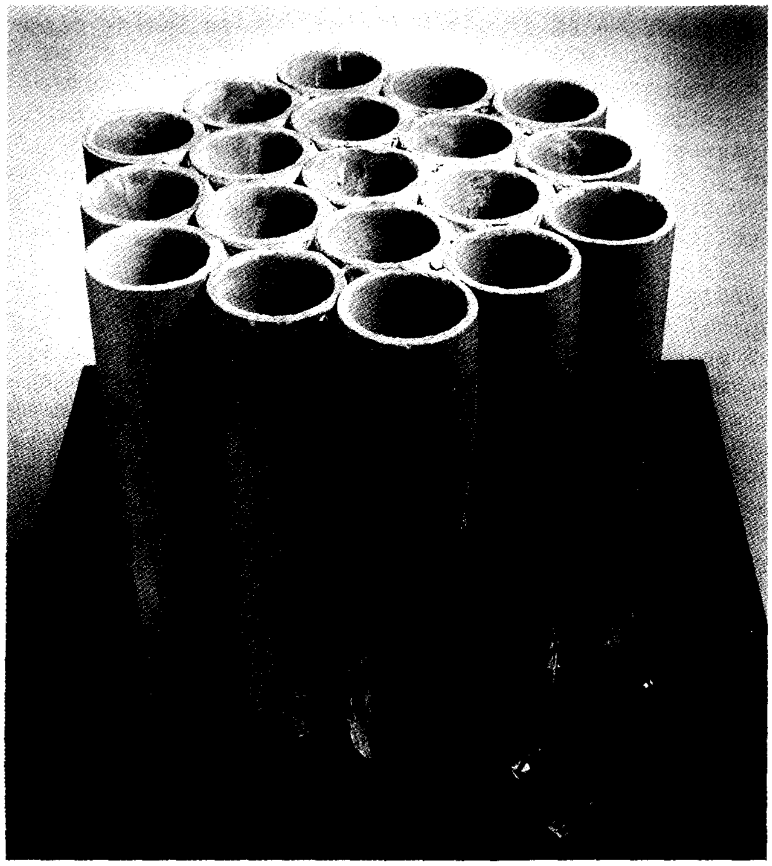

FIGURE 3-12: Near-Full-Scale Fuel Basket Manufactured from Fired Clay

head was welded on. Compaction of the particulate was conducted at Ontario Hydro in Toronto, and after the top head was welded in place the container was shipped to the AECL Research Whiteshell Laboratories for testing.

Testing and Analysis

The structural testing program on the supported-shell container designs was conducted in the Hydrostatic Test Facility (HTF) at the Whiteshell Laboratories.[15] The HTF is a large, carbon-steel pressure vessel in which instrumented test prototypes can be subjected to pressures up to 11 MPa at temperatures up to 200°C. Penetrations in the vessel allow the passage of instrumentation lines from the test prototype to data-acquisition equipment located outside the vessel (Figure 3-13).

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[15] Construction of the HTF was undertaken, following testing of the stressed-shell container prototype in the U.S., to provide the CNFWMP with in-house testing capabilities.

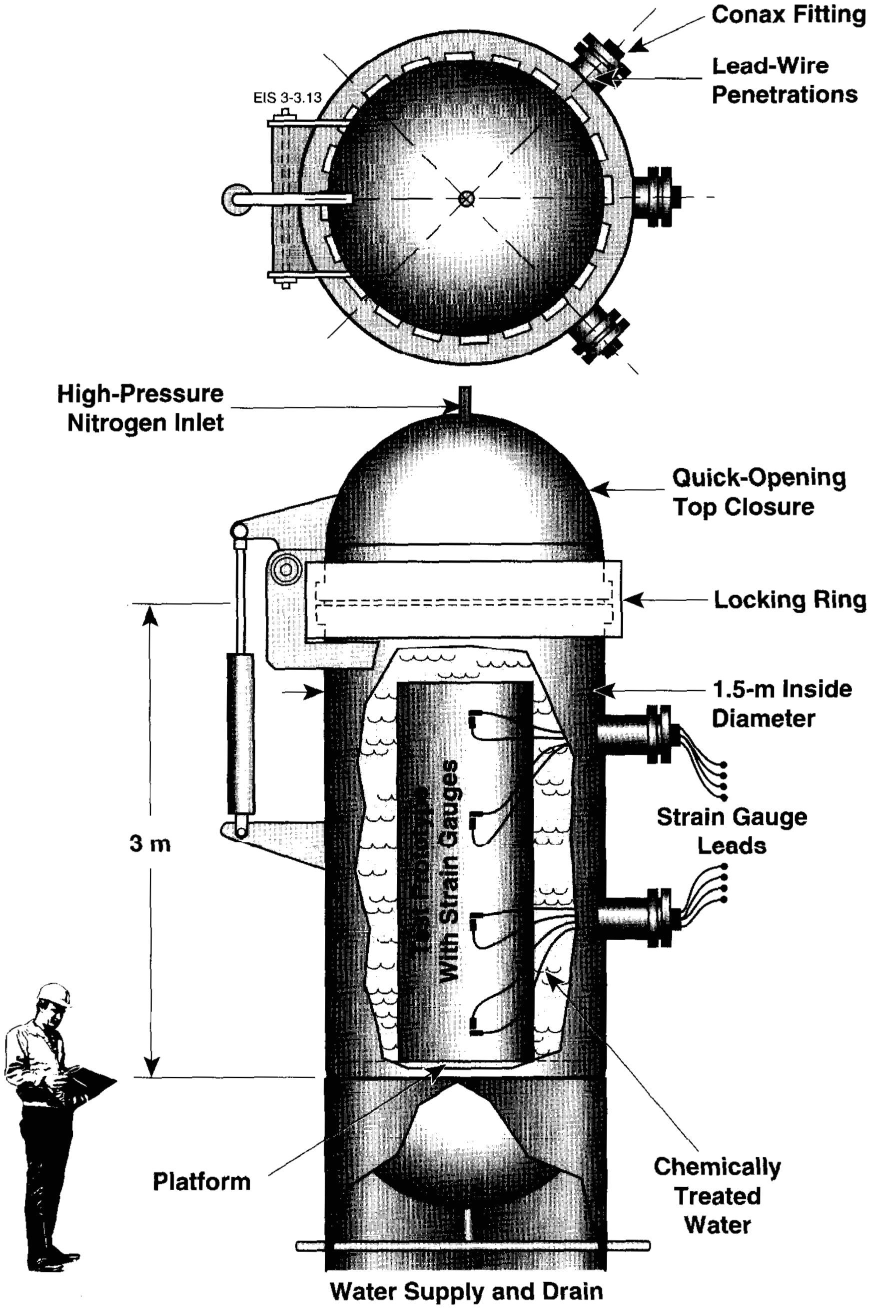

FIGURE 3-13: Whiteshell Laboratories Hydrostatic Test Facility

Because there was little previous world experience to draw upon for techniques to protect strain gauges from water ingress at pressures up to 10 MPa at 150°C, it was necessary to develop the technology independently (Russell 1983, Hosaluk 1985a). These development programs were successful in producing cost-effective strain-gauge instrumentation techniques that were used to monitor shell deformation during the testing of six container prototypes in the HTF.

In the test sequence performed on the packed-particulate container, conducted at up to 10 MPa at 150°C, the prototype was tested first in its as-received condition; only small deformations of the cylindrical portion of the shell occurred.[16] In two subsequent tests, the container was resubjected to these test conditions after artificial packing defects were introduced by removing some of the particulate. In the first of these tests, 0.2 L was removed; in the second, a further 0.8 L was removed. Although the shell deformed substantially adjacent to the packing voids, it was not breached by rupture or tearing (Teper 1987a, Teper and Reid 1989). During all tests, shell deformation was recorded by the strain gauges attached to the container surface.

The results of the test program were compared with those of finite-element analyses to demonstrate the adequacy of the analytical method and to provide confidence in any analyses that might be conducted at conditions beyond the scope of the tests (Teper 1987b, 1988, Teper and Reid 1989). In general, the code predictions of container-shell deformation were in good agreement with the recorded deformations. Comparisons of the predicted and measured deformations for the tests in which packing voids were introduced showed some variation at lower pressures, but were very similar at pressures above 5 MPa. It was concluded that the analytical method was acceptably accurate in predicting container response. Where discrepancies occurred, their causes were identifiable and indicated directions that could be pursued to achieve improvements in the analytical model.

Subsequent to the hydrostatic testing program, the packed-particulate container prototype was refurbished, to restore it to near its pretest condition, and subjected to a series of drop tests. The objective was to determine the container's durability under accident conditions in which a fully loaded container might be inadvertently dropped, either along the fabrication line at a used-fuel disposal centre or into a borehole within the disposal vault (Teper 1991).

In these tests, the container (loaded with steel bundles to simulate fuel bundles) was subjected to progressively higher drops, flat onto its base,

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[16] During transportation of the prototype from Toronto to the Whiteshell Laboratories, the glass-bead particulate within the container appeared to have settled further, causing an ~1% increase in its compacted density. This resulted in a gap forming between the top head and the top of the particulate, estimated from test results to have been ~14 mm in width. During an initial, low-pressure test conducted at 1 MPa and 20°C, the top head deformed downward through this gap until it recontacted the particulate. Details are presented in Teper (1988).

onto an unyielding surface from heights ranging from 0.1 m to 4.0 m (six drops total). Following each drop, the container was inspected to determine the extent of damage. Following the final (4 m) drop, the maximum permanent circumferential strain in the shell was less than 0.12%, and no shell rupture had occurred. Because this strain was, in fact, cumulative from all six drops, and the use of an unyielding impact surface is the most conservative test condition possible, it was concluded that the inadvertent dropping of a container into a borehole (where the impact surface, sand and compacted buffer material, would have considerably more shock absorbency than the tests' impact surface) would not result in damage that would impair subsequent retrieval of the container for return to the surface facilities for reinspection.

Summary, Packed-Particulate Container

The results of the design, fabrication and inspection, and structural testing and analysis program conducted for the packed-particulate container demonstrated both the feasibility of the concept and its tolerance to manufacturing defects and handling accidents. Development of the deformation and stress analysis program to correlate with the experimental observations has also been successful and is serving as the basis for future analyses of more complex and longer-term container-loading situations, in which the effects of materials creep and stress-relaxation behaviour on structural performance will be investigated (see Section 3.5.2.5).

3.5.2.3 Structurally Supported Container

Design and Construction

The structurally supported container design (Figure 3-14) employs a thin, corrosion-resistant shell that is internally supported by an array of sealed carbon-steel tubes containing the used-fuel bundles. In this container, the tubes are designed with sufficient thickness to support the external pressure on the shell, which is transferred to the array of tubes by a compacted particulate material. Details are provided by Cooper (1981).

From the design study, a TEC-II container configuration that holds 76 fuel bundles was developed. The basket consists of a hexagonal array of nineteen 8-mm-thick carbon-steel tubes, each containing four fuel bundles. The tubes are prefabricated with a press-fit seal plug in the bottom end and are similarly sealed at the top end after the fuel bundles have been installed.

A full-scale prototype was designed and constructed for structural-performance testing by Bristol Aerospace Limited (Hosaluk 1985b, 1986, Hosaluk et al. 1992). The container shell was constructed of 6.35-mm-thick Grade-2 titanium, which, at the time of construction of this prototype, was more readily available than the 4.76-mm-thick plate that had been used to construct the packed-particulate container prototype. After the sealed basket was installed in the shell, the residual spaces were filled with compacted glass-bead particulate and the top head was GTA-welded to the shell. No simulated fuel bundles were installed in the prototype because,

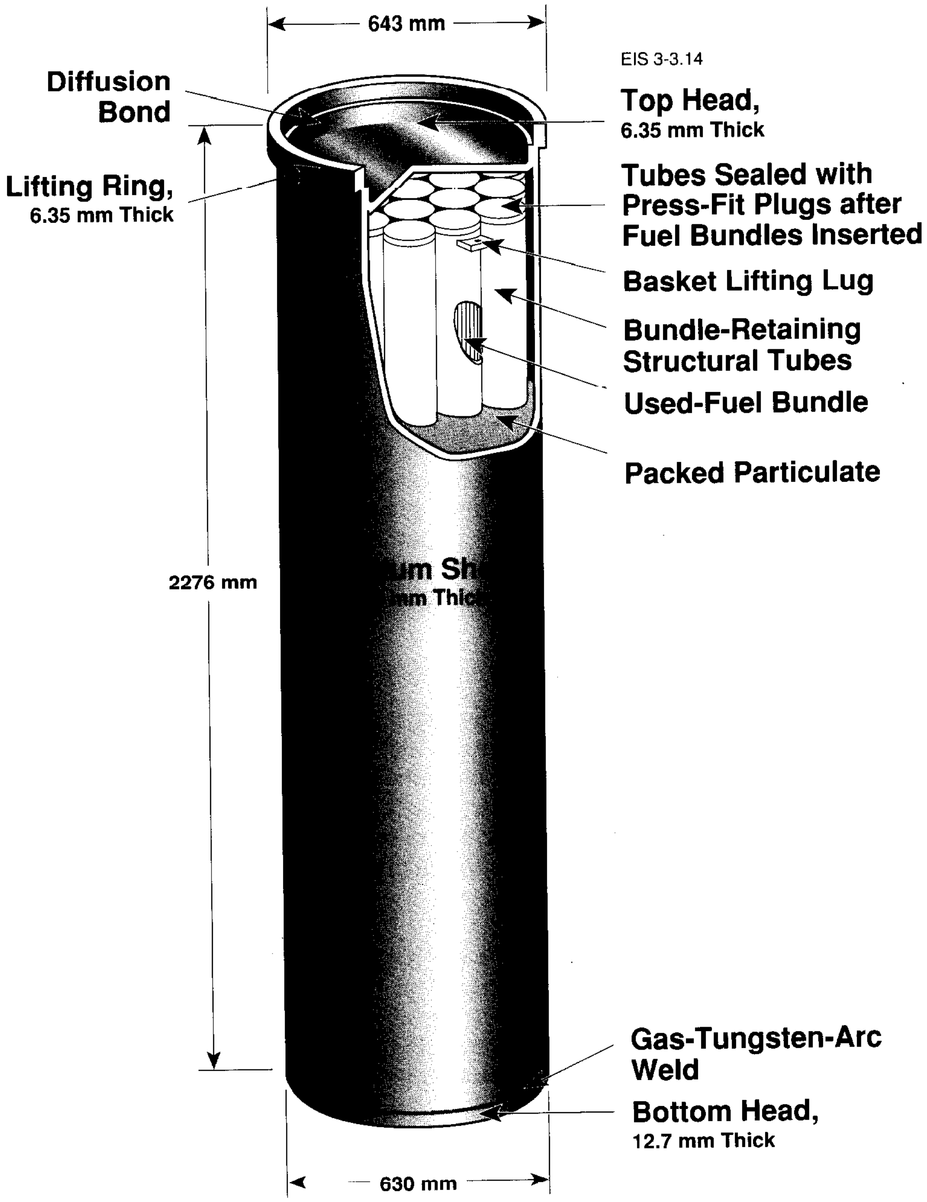

FIGURE 3-14: Titanium-Shell, Structurally Supported Fuel Disposal Container

when enclosed within the sealed tubes, they would not contribute to the support provided by the basket. As in the case of the packed-particulate container prototype, filling and compaction of the prototype with glass-bead particulate were conducted at Ontario Hydro, Toronto. Final assembly fitting (and welding of the top head to the shell) was conducted by Bristol Aerospace Limited following transport of the compacted container from Toronto to Manitoba.

Testing and Analysis

Prior to testing, a finite-element structural-performance model was assembled to predict the prototype's behaviour under the proposed test conditions. The analytical results were subsequently compared with the experimental data obtained from the test program conducted in the HTF.

The prototype was instrumented with strain gauges and subjected to a test sequence in the HTF similar to that conducted for the packed-particulate container, culminating in test conditions of 10 MPa at 150°C. When fully packed, the prototype was extremely rigid under loading: no plastic deformations of the shell were recorded. Two litres of particulate were then removed and the prototype was retested at 10 MPa and 150°C. As in the test conducted on the packed-particulate container, the shell adjacent to the artificial packing defect deformed severely, but did not rupture. Details are presented by Hosaluk (1985b) and Hosaluk et al. (1992).

The levels of stress predicted by the computer model to occur at various locations on the shell, under the test conditions, ranged from 5 to 170% higher than those calculated from the test data. Therefore, the analytical model would be conservative if used in future design and development work on the structurally supported container concept. Grover (1991) analyzed these discrepancies and concluded that their principal cause was a number of simplifications used in the model, the main one being the reduction of the computational time required for the analysis by using a two-dimensional axisymmetric model. Revised assessment of the container's structure has indicated that it is of sufficient complexity to warrant analysis by a three-dimensional model. Future development of the structurally supported container concept would, therefore, require that such conservatisms in the structural-performance analysis be addressed.

Summary, Structurally Supported Container

The design, fabrication, testing and analysis program conducted for the structurally supported container showed that it, too, was a viable design concept.

3.5.2.4 Metal-Matrix Container

Design and Construction

In the 72-bundle-capacity metal-matrix container (Figure 3-15), a cast, low-melting-point metal or alloy is used to provide support to the container shell. The cast metal surrounds the fuel bundles and forms a layer about 25 mm thick between the outer bundles and the shell. Following

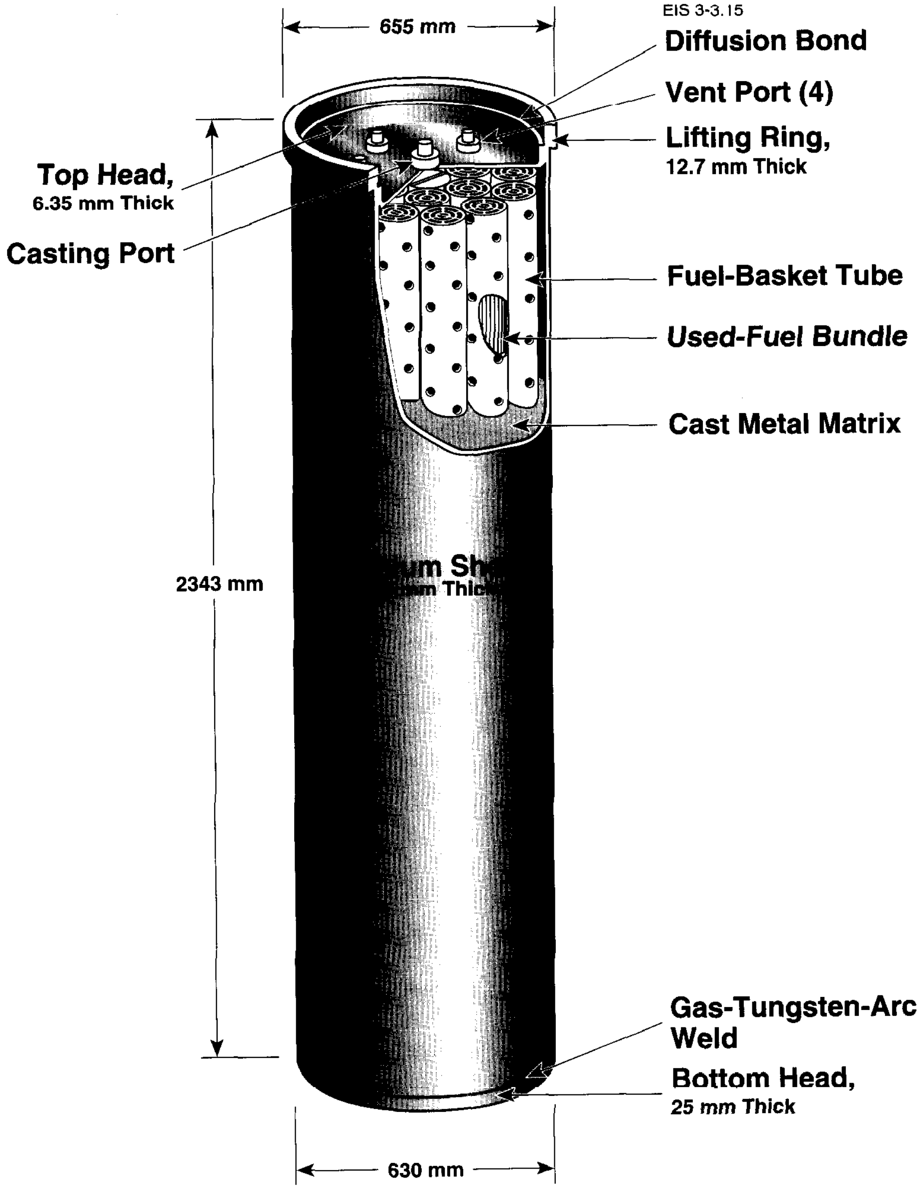

FIGURE 3-15: Titanium-Shell, Metal-Matrix Fuel Disposal Container

studies conducted on a number of candidate materials (see Section 3.5.3.6), 99.9% pure lead was selected as the preferred casting metal.

Because the weight of a full-scale prototype (~7 Mg, without dummy fuel bundles) could not be accommodated in the HTF, the structural testing program for this concept was conducted on half-scale prototypes. To ensure that the structural behaviour of the half-scale prototypes would be the same as that of the full-scale container, the same ratios of overall length/diameter and diameter/shell thickness were maintained. When cast with lead, each prototype weighed ~0.9 Mg, which could be accommodated in the HTF.

The principal design considerations for the metal-matrix container are the assessment of handling stresses and the development of matrix-casting procedures. It is desirable that the cast matrix be as void-free as possible, to ensure that the shell is adequately and uniformly supported. In contrast to the assembly procedure for the packed-particulate and structurally supported containers, the top head is welded to the shell directly after the basket containing used fuel is placed into the shell. Then the matrix is cast into the container through a port in the head. The air in the container that is displaced by the cast matrix escapes through several other ports arranged around the casting port. When the matrix solidifies and cools, the casting and air-venting ports are sealed with welded-in plugs. This fabrication procedure ensures that the final closure weld will not become contaminated by the proximity of the cast matrix.

Four half-scale models of TEC-I[17] design, designated MM1 to MM4, were constructed for testing in the HTF. MM1, MM2 and MM3 were manufactured with deliberate artificial voids in their matrices, so that the structural behaviour of an imperfectly cast container could be studied. MM4 was cast with a void-free matrix so that the structural behaviour of a container free of defects could be established as a reference. The MM1 shell was constructed from seam-welded 316L stainless steel; the other prototypes were made using seam-welded Grade-2 titanium (Crosthwaite 1985). MM1 was cast using commercial foundry techniques; MM2-MM4 were cast using techniques evolved from the casting-development program. The shell and head welds were made by GTA welding. Since the principal objective of the structural tests was to investigate the extent of the support provided by the matrix to the shell, no fuel baskets or simulated fuel bundles were installed in the half-scale prototypes. All test models were instrumented with strain gauges and dimensionally inspected prior to testing.

Testing and Analysis

The test sequence for all four container models consisted of initial short-term pressure cycles at 50 and 100°C, followed by more protracted tests at 10 MPa and 150°C (Crosthwaite 1985, Hosaluk and Barrie 1992a,b). Despite the presence of severe artificial defects in the cast matrices, such as a central void (MM1), a void between the matrix and the shell (MM2), and a void between the top of the matrix and the top head (MM3, see Figure 3-16),

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[17] See Section 3.4.3.3 for the meaning of this designation.

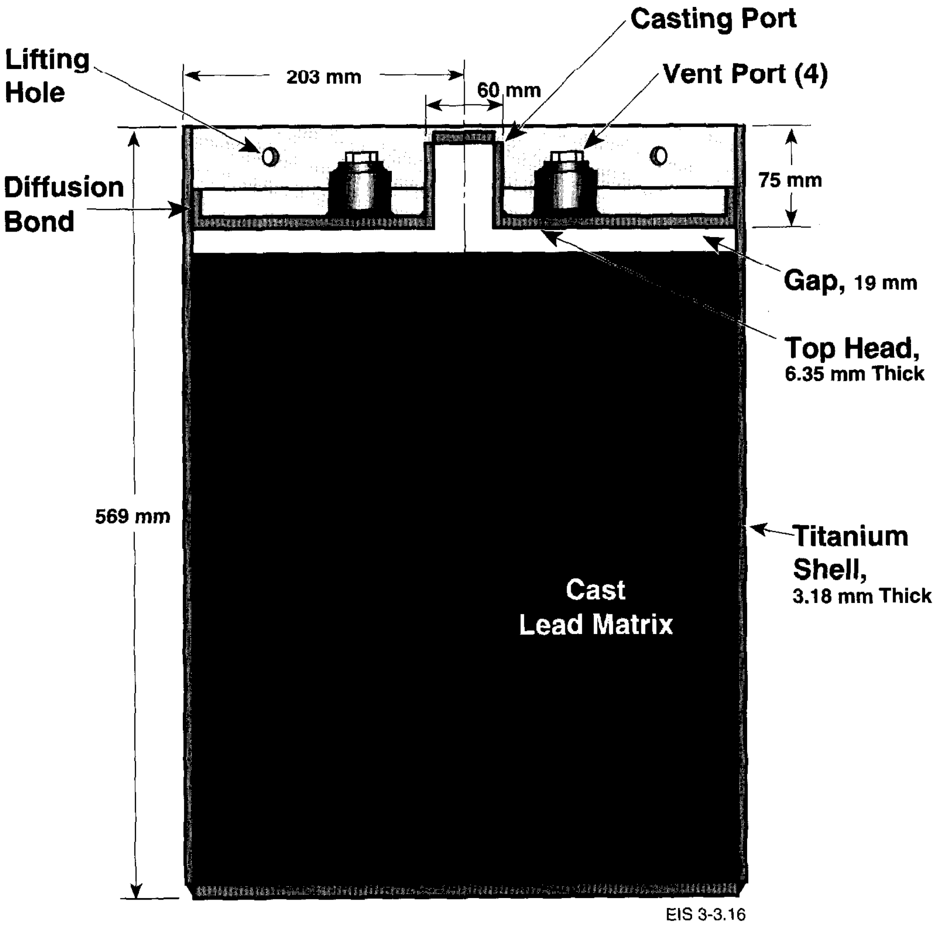

FIGURE 3-16: Metal-Matrix Test Container (MM3)

all of which resulted in extensive overall and localized shell deformations, no shell rupture occurred in any model. Data from the test conducted on MM4 (void-free) indicated that, following a small, generally inward deformation of the shell, which resulted from the presence of a solidification-shrinkage gap of ~0.5 mm between the matrix and the shell, the structure became a monolithic solid, and no further deformation could occur under hydrostatic loading conditions.

The structural deformation data acquired from the hydrostatic test on MM3 was used to develop a two-dimensional, finite-element structural-performance computer model (Grover 1988a,b). To date, qualitative agreement has been obtained between the model's predictions and the experimental results, including most of the shell deformations observed in the tests. Where discrepancies occurred, their causes, and directions to be pursued for improving the model, were identified.

Summary, Metal-Matrix Container

The design, fabrication, testing and analysis programs conducted for the metal-matrix container showed that this concept also was a viable option. The extensive data obtained from the testing of the four prototypes, in particular MM3, are being used as the basis for the development of more detailed finite-element computer models that, ultimately, will be applicable to a variety of internally supported, thin-shell container concepts (Grover 1988a,b).

3.5.2.5 Summary, Structural-Performance Studies

The principal conclusion from the structural-performance testing and analysis program on the various thin-shell container designs was that all were structurally durable, even with internal support deficiencies. No definitive argument for the selection of a reference design for the engineering study for a conceptual used-fuel disposal centre was possible solely on the basis of demonstrated short-term structural behaviour. Additional factors had to be considered; these are discussed in Section 3.5.5.

Design studies have been conducted (Ko and Hosaluk 1987) for a metal-matrix container with a copper shell (Figure 3-17) and have begun for a copper-shell packed-particulate container, as part of a continuing development program. Preliminary results from the latter indicate that the copper-shell, packed-particulate container concept is also a potentially viable option.

Analysis of the properties of container components that can influence long-term structural durability are an essential constituent of both the current and future programs. These include short- and long-term mechanical properties of materials, such as creep and stress-relaxation behaviour. Work is under way to define these properties, through experimental programs on copper and titanium in collaboration with Ontario Hydro and through information exchange with other programs, notably those being conducted in Sweden (Henderson et al. 1992). Ultimately, the results of these studies would be used as input data for long-term structural-performance models for containers and for design optimization studies.

3.5.3 Fabrication and Inspection Technology Development

3.5.3.1 Introduction

The container development program has included studies and development of the processes and procedures that would be required to manufacture used-fuel containers on a production basis using, where required, remote-operation techniques. These include

- welding techniques for corrosion-resistant materials,
- closure-weld inspection techniques,
- leak-detection techniques,

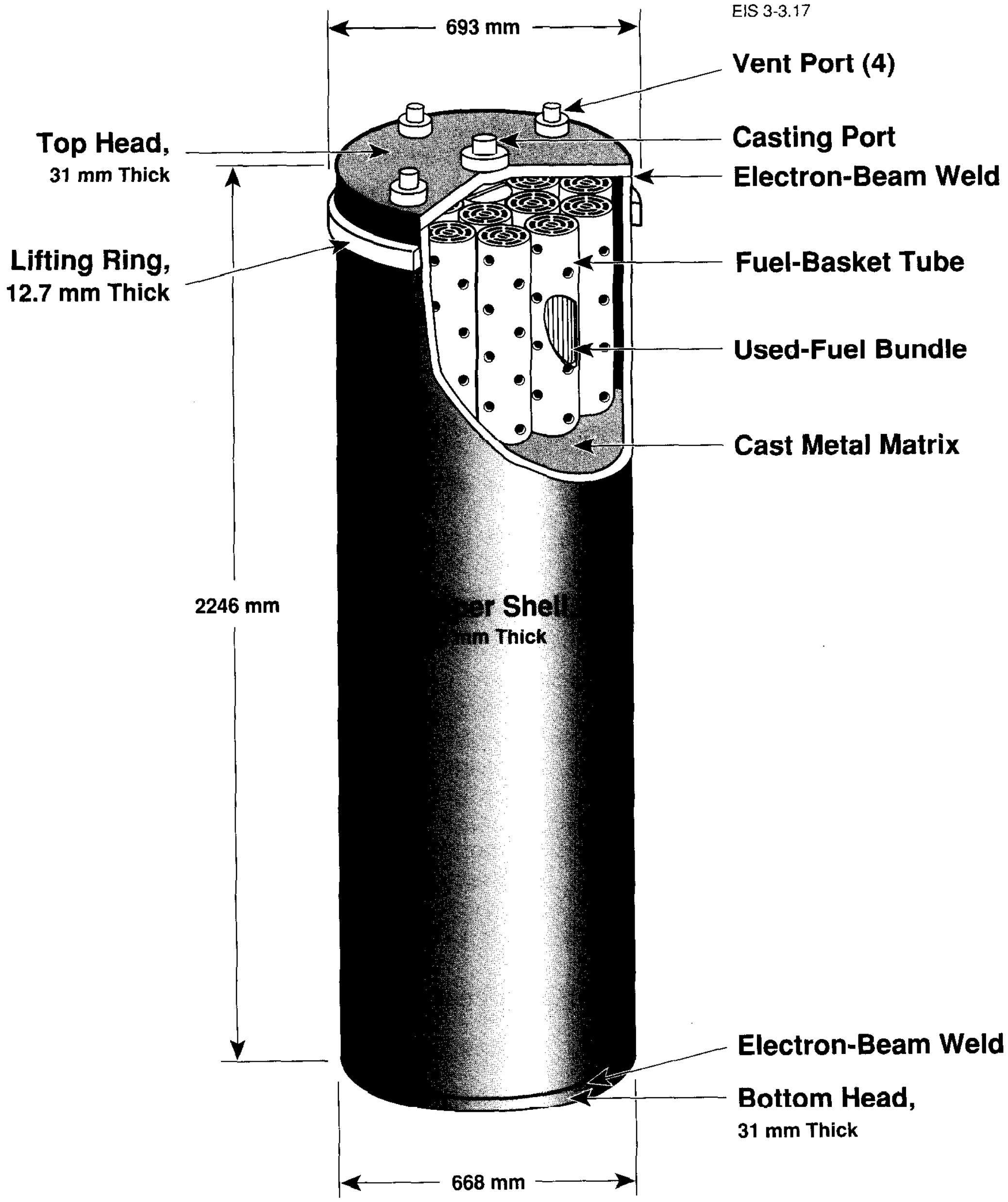

FIGURE 3-17: Copper-Shell, Metal-Matrix Fuel Disposal Container

- identification of suitable particulate materials and development of packing techniques for the packed-particulate and structurally supported containers,
- metal-matrix container fabrication development and matrix-performance studies,
- other fabrication considerations, and
- reliability analyses.

These are discussed in Sections 3.5.3.2 to 3.5.3.8.

3.5.3.2 Welding Techniques for Corrosion-Resistant Materials

In the molten state, such as during welding, titanium and its alloys react readily with, and become embrittled by, contaminants such as hydrogen, oxygen and nitrogen. Therefore, a prime requirement of a weld-development program for titanium is the identification of limits for these contaminants, as well as the means of excluding them from the weld zone (Lawson and Dolbey 1983).

Processes based on electrical-resistance welding are attractive for remote joining because the equipment is simple, rugged and accurate. Where bonding can be achieved by atomic diffusion, rather than melting, the risk of contamination and metallurgical changes, such as grain growth, can be minimized.

Copper has a high thermal conductivity, which rapidly conducts heat away from the intended weld joint. The problem is aggravated when thick sections must be joined, because this increases the available heat sink. Like titanium, the molten copper metal is reactive with air; if reactions are allowed to occur, they can severely degrade weld-joint quality. Consequently, copper joints must be made either by using rapid localized heat input in the absence of a surrounding atmosphere (e.g., electron-beam welding), by preheating the components to be joined so that a gas- or flux-shielded heat source can be used, or by employing joining techniques in which an alloy is formed at the joint interface (e.g., brazing).

In practice, processes that involve preheating the container, which includes brazing, are undesirable, since this would also heat the used-fuel bundles, possibly leading to their degradation. As well, the corrosion performance of brazed joints is potentially inferior to that of joints made in unalloyed copper.

Welds in used-fuel disposal containers must meet certain quality requirements (Lawson and Dolbey 1983):

1. The container must not leak after closure welding.
2. The probability of defects that might cause perforation by fracture during handling and emplacement, or as a result of in-service stresses, must be acceptably small.

3. There must also be an acceptably small probability of defects that could lead to premature perforation of the shell by localized corrosion, or other delayed failure mechanisms.

4. The depth of the weld must not be less than the nominal container wall thickness.

Several processes were selected for investigation in the welding development program. For titanium containers, GTA and electron-beam (EB) welding, and resistance-heated diffusion (R/D) bonding were selected; for copper containers, gas-metal-arc (GMA) and EB welding were investigated. In particular, effort was focused on methods of performing the final head-to-shell container-closure weld, which, at a used-fuel disposal facility, would have to be done remotely.

<u>Gas-Tungsten-Arc Welding</u>

In GTA welding, a weld preparation is usually made between the edges of the two components to be joined, such that a groove is formed between them that can accept the weld material (see Figure 3-18). An electrical arc is struck between a non-consumable tungsten electrode (connected to a low-voltage, high-current power supply) and the weld junction, which creates a localized region of intense heat that melts the material that will form the weld junction. A rod or wire (called the "filler") of (usually) the same material as that of the components to be joined is fed into this region and fuses the junction together. Because the molten weld-pool can be susceptible to detrimental processes (such as rapid oxidation) until it solidifies, the procedure is conducted either with a flow of protective, inert shielding gas over the pool, or in an enclosure purged of air and flooded with inert gas.

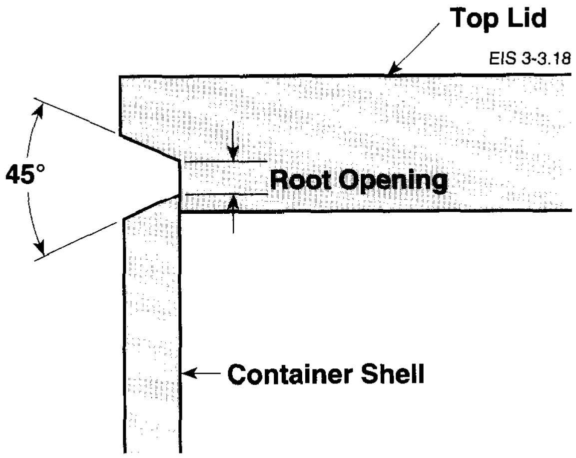

FIGURE 3-18: Weld Preparation Design for Assembly of Final Container Closure by GTA Welding

GTA welding requires that the weld pool be kept within the confines of the weld preparation. The maintenance of a line of weld along a desired path is called "seam tracking." In the case of large welds, multiple passes, each depositing a line of weld material, are required. Each pass requires seam tracking to ensure the desired weld path is maintained. Automatic seam-tracking technology has been a subject of intensive study in recent years, particularly in production industries, and many new and highly accurate techniques have been developed. A GTA final-closure weld in a used-fuel disposal container would require automatic seam tracking.

Electron-Beam Welding

In EB welding, the contacting edges of the mating surfaces of the two components to be joined are presented to a focused beam of electrons with a power density sufficient to melt the material of the components. The procedure is within a class of welding processes termed "autogenous," meaning that no weld filler is used. EB welding must be done under high vacuum, and, because of the narrowness of the focused beam, precise seam tracking is essential. With well-adjusted weld parameters (e.g., beam power, welding speed), extremely high grade welds can be achieved with a minimum of disruption to the grain structure and materials properties of the parent metal located on either side of the weld. This procedure is particularly attractive for joining materials with a high thermal conductivity, in which weld quality can be diminished when conventional welding techniques are attempted.

Gas-Metal-Arc Welding

Gas-metal-arc welding is similar to GTA welding, except that the electrical arc is struck between the components to be welded and an electrode that is continuously melted, and therefore consumed, to become the weld-fill material. Again, a flow of inert shielding gas over the molten weld pool can be used to prevent excessive oxidation. In some applications, the electrode contains both the weld material and a flux compound that floats on top of the weld pool and further protects the weld during the solidification and cooling period. As in GTA and EB welding, GMA welding requires seam tracking for remote-fabrication or automated production applications.

Resistance-Heated Diffusion Bonding

Resistance-heated diffusion bonding is particularly attractive for adaptation to remote applications because the procedure requires no seam tracking. Instead, the bond is made by applying pressure, between two rollers, to the surfaces to be joined and then passing a high electrical current across the rollers and thus through the location of the intended junction. With the correct combination of bonding variables (e.g., electrical current, pressure, time), the pressed-together surfaces fuse, but without undergoing any material melting (metallographic examination of a high-quality R/D bond often reveals little or no distinction between the microscopic structure of the bond and the parent material at either side of it). The rollers are then indexed to a new position that is preset to slightly overlap the previous one. The bonding procedure is repeated until a continuous line of bonded surface is obtained. Figure 3-19 shows the

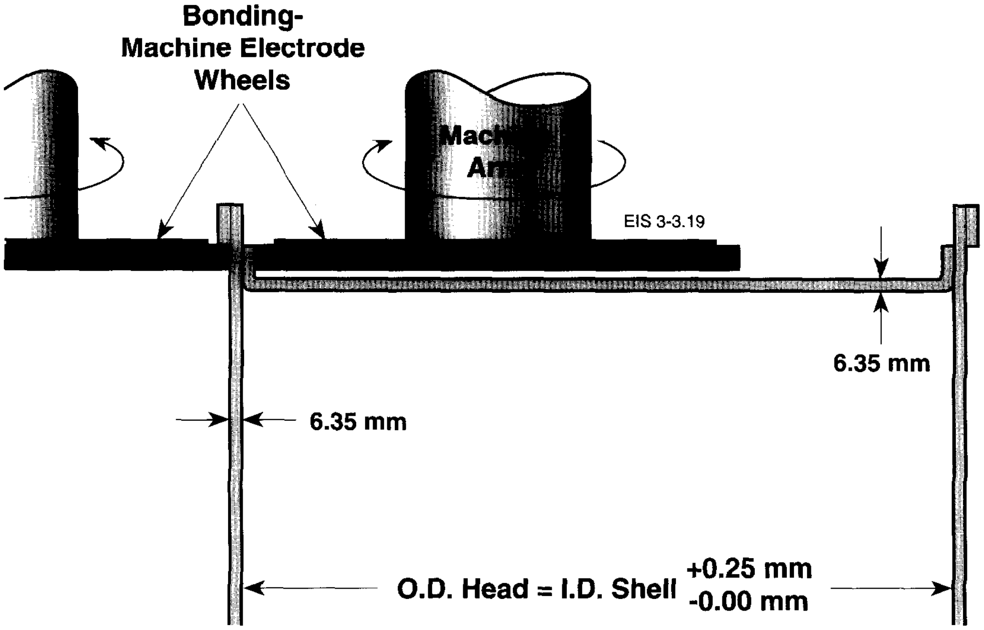

FIGURE 3-19: Joint Design for R/D Bonding of Head to Shell, Showing Position of Bonding-Machine Wheels

configuration of an R/D bonded joint designed for the MM3 test prototype described in Section 3.5.2.4 and illustrates how the bonding equipment was used to make the joint. Figure 3-20 shows the outer surface of the MM3 shell, following the bonding procedure.

Welding Program Results

Our program has shown that all three procedures that were investigated (GTA and EB welding and R/D bonding) are likely to be suitable for the production of high-quality welds in titanium (Maak 1986a, Maak and Moles 1986). In GTA welding, a pulsed-current technique (called P-GTA welding) produced the best results. It was demonstrated that sound quality GTA closure welds could be made successfully in one-third-scale thin-shell container mock-ups using a mechanized system and multipass welding (Maak and Galloway 1988). Although mechanized P-GTA welding can be used for the final closure welding operation, the technique required continuous operator surveillance at the welding station (i.e., to adjust the welding-torch position along the groove and to adjust welding parameters for changes of weld-joint fit-up). A state-of-the-art automated P-GTA welding system, equipped with a laser sensor system for real-time seam tracking has been developed at Ontario Hydro. With the use of this automated P-GTA welding system, sound closure welds can be made in thin-wall titanium containers reliably and remotely without the need for operator surveillance.

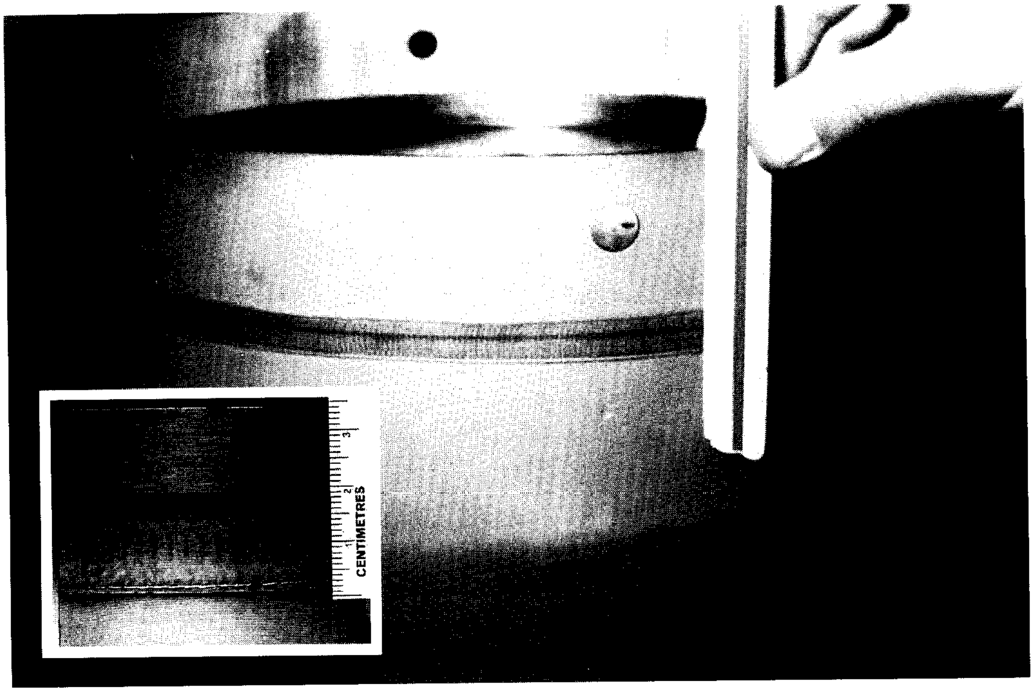

FIGURE 3-20: Post-Bonding Appearance of Titanium Shell Outer Surface Following Head-to-Shell Closure by R/D Bonding. Example shown is for MM3 half-scale test container. Inset shows bond sample dissected from container after testing.

Because it is a high-energy-density process, EB welding is attractive for welding thick titanium. The energy required to weld a joint with a given thickness is considerably less than that required by conventional arc-welding processes; this minimizes distortion and the size of the heat-affected zone near the weld region. However, closer weld-joint fit-up is required for EB welding than for arc welding. For thin titanium, EB welding appears to have no distinct advantages over GTA welding or R/D bonding. Therefore, it is considered to be more applicable to thicker-shell containers.

Resistance-heated diffusion bonding was shown to be particularly attractive for the final closure weld because the process is simple, rugged, and requires neither seam tracking nor inert-gas shielding. In addition, sound welds can be made over a wide range of bonding parameters (e.g., electrical current, roller speed (Maak and Cooper 1985)). It has also been shown that all bonding parameters can be dynamically recorded during the bonding process. This provides a permanent record of the bonding process for quality assurance and analysis. Large-scale demonstrations of the procedure have been achieved, including the preparation of a 300-mm-diameter bonded ring (Figure 3-21) and the MM3 half-scale metal-matrix container prototype (Figure 3-16). In the structural-performance test on the MM3 container, no evidence of tearing or disruption of the bonded joint could be found, despite extensive tensile deformation of the bonded region (see Figure 3-22).

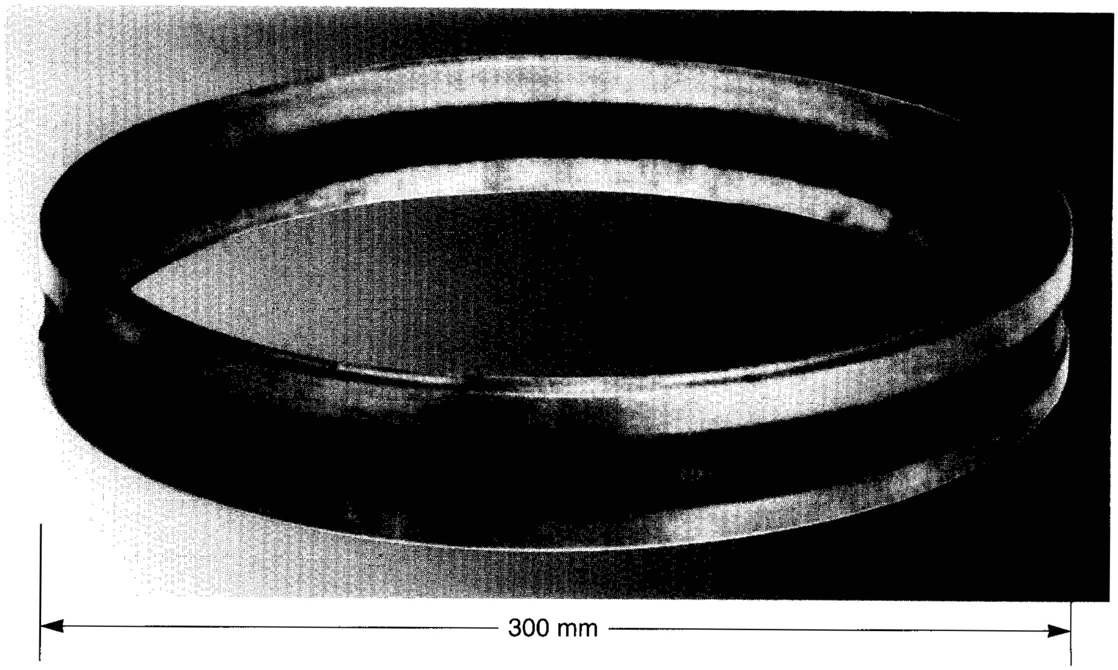

FIGURE 3-21: Titanium R/D Bonded Ring Mock-Up

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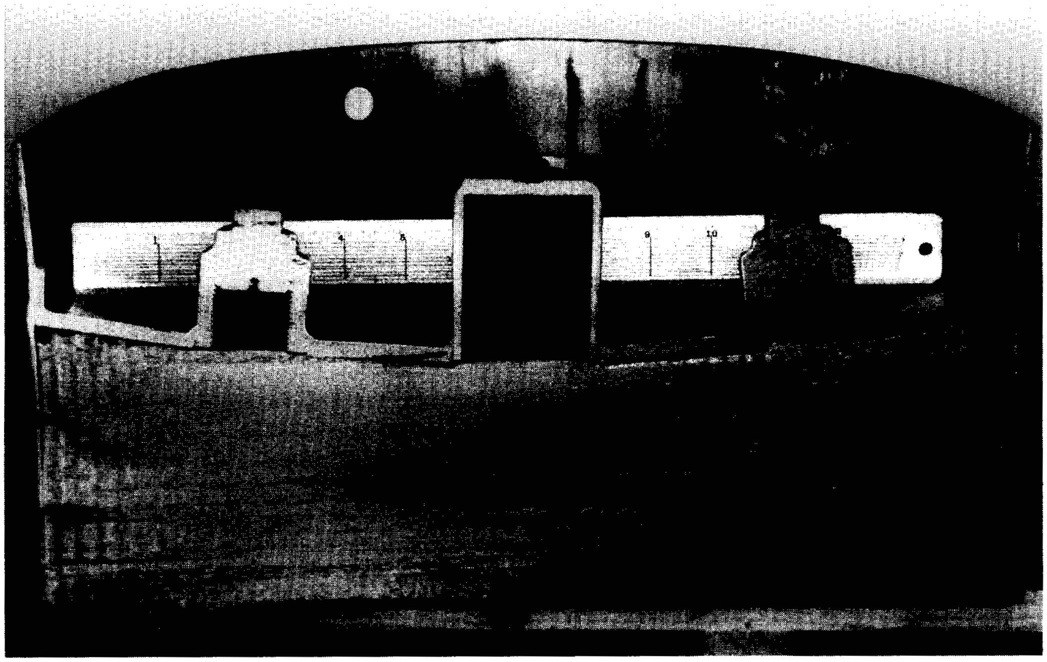

FIGURE 3-22: Post-Test Appearance of Dissected Top Head of MM3 Half-Scale Lead-Matrix Test Container, Showing Good Condition of the R/D Bonded Joint

The principal component of the R/D bonding method that remains to be fully developed is a proven procedure to ensure that good bonding can be accomplished to the edge of the mating head-to-shell components. A program to develop an acceptable edge-bonding process achieved partial success by demonstrating that edge bonding was possible; however, further work is needed to identify processes that can, with confidence, be used to produce good quality edge bonds with a high degree of reproducibility. From the results of the preliminary work conducted to date, this appears to be a readily achievable technology.

Preliminary GMA welding trials conducted on oxygen-free electronic (OFE) copper[18] showed that preheating 25-mm-thick copper plates up to 600°C was desirable (Maak 1982). Further studies on electrolytic tough-pitch (ETP) copper[19] indicated that appropriate preheating appeared to have the most significant effect on weld quality. Preheating to 400-600°C combined with welding currents of 500-600 A produced sound welds in 25-mm-thick copper plates. To reduce the possibility of developing porosity in the weld zone, it was recommended that future studies on this process, if any, be conducted on oxygen-free copper (Galloway and Maak 1987).

Extensive studies have been conducted into the feasibility of using EB welding for the final closure of copper containers (Maak 1984a,b, 1986b,c, 1988). These studies have demonstrated that single-pass EB welds, with full-depth penetration, can be made in 25-mm-thick ETP and OFE copper plates, and in small-scale container mock-ups. From these studies, appropriate designs of container-closure heads for EB welding and a preferred operating envelope of beam power and welding speed for 25-mm-thick OFE copper were specified.

Test results have shown that OFE copper exhibits better welding characteristics than ETP copper. Electron-beam welds in OFE copper can be made over a wide range of beam-power and welding-speed combinations. They display satisfactory mechanical properties without excessive gas porosity, large cavities or cracking. Because of the relatively high level of dissolved oxygen in ETP copper, EB welds in this material are more susceptible to the formation of porosity, and sound welds can only be made using a narrow range of parameters. Small cavities are sometimes observed in the root (bottom) of the weld in copper EB welds, but are considered to be inconsequential because they are embedded deep in the container shell and have no significant effect on the quality of the weld joint. Surface defects are promoted by high-beam-power/high-welding-speed combinations and appear to be the limiting factor in welding-parameter selection. Figure 3-23 shows

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[18] ASTM material designation number according to the Society's Unified Numbering System (UNS): C10100. The chemical requirements for OFE copper (according to ASTM Specification B 170) are that the minimum copper content shall be 99.99% and that the maximum oxygen content shall be 0.001%.

[19] UNS C11000. The chemical requirements for ETP copper (according to ASTM Specification B 5) are that the minimum copper content shall be 99.90%. No specific oxygen content is specified.

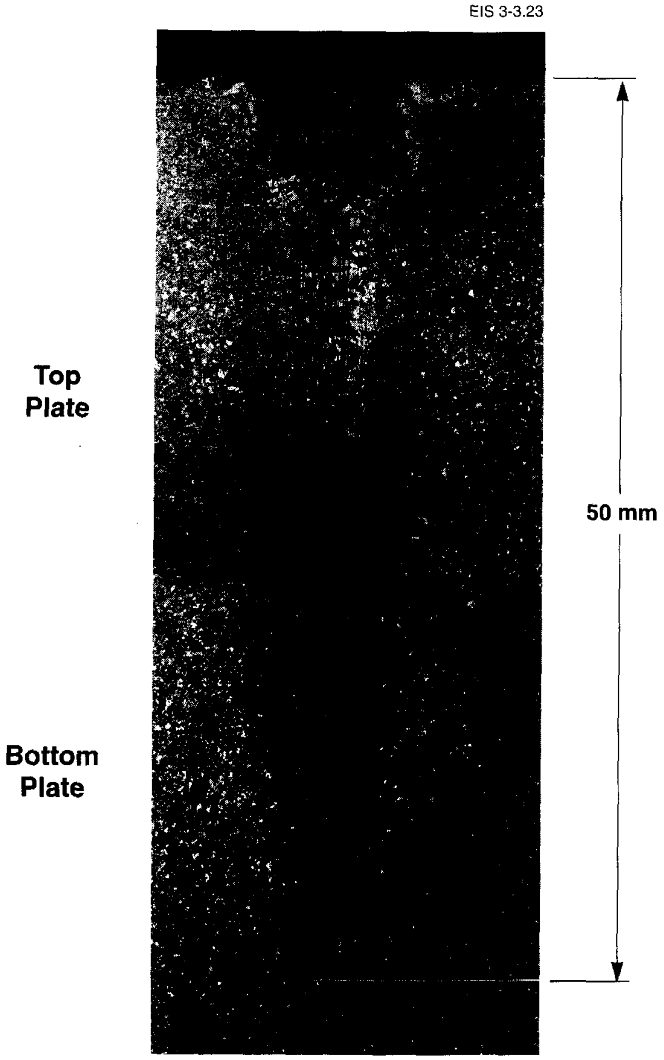

FIGURE 3-23: Example of High-Quality Electron-Beam Weld Produced in OFE Copper

an example of a high-quality EB weld in OFE copper produced in the development program.

In summary, test results show that OFE copper is clearly preferred to ETP copper for applications involving EB welding, and that high-quality welds can be achieved at depths of penetration ≥25 mm.

Similarly satisfactory results have been achieved in the Swedish copper-welding development program (Sanderson et al. 1983). Those studies demonstrated the feasibility of EB welding a container lid up to 100 mm thick. The results were similar to those in the Canadian program: welds made in

OFE copper[20] were free of major defects, whereas welds made in copper with higher oxygen content showed a greater tendency to contain porosity.

Summary, Welding Studies

Our fabrication-development program has demonstrated the viability of a number of procedures to weld both titanium and copper and, in particular, to perform the final closure weld, which would have to be done by remote techniques. Completed and current studies and those in other national programs have indicated that such welds can be produced with a high degree of reliability, with adequate strength.

3.5.3.3 Closure-Weld Inspection Techniques

Since the final (top) head-to-shell closure weld would have to be inspected in the presence of a radiation field, conventional radiographic techniques are impractical because the photographic film would be exposed to high-intensity gamma and X-radiation. Suggestions for using this used-fuel radiation field to produce the radiographic plates were judged to be impractical: firstly, the radiation-field strength from each container would almost always be different from that of other containers, because of differences in the burnups and cooling times of the used fuel they contained; and, secondly, the wavelength and energy spectrums of used-fuel radiation fields are extremely heterogeneous (industrially, radiographs are produced using radiation sources with narrow wavelength and energy bands). Consequently, the development of techniques to assess the quality of the final closure weld has focused on ultrasonic inspection (UI).

The basic inspection criterion would be that any detectable defect that, because of its size and/or location, reduced the required corrosion allowance or diminished the mechanical integrity of the container shell below that required for the container to have a minimum 500-a lifetime would be cause for rejection of the container for disposal. Such defects might, if possible, be repaired to restore the required integrity of the shell. One of the objectives of the inspection-development program has been to attempt to define, for UI, the practical limits of detectable defect size.

In accordance with recommendations from a scoping study conducted in the early stages of the program (Chen 1981), the interrogation of welded joints used to form the shell would be supplemented by helium leak testing. Failure to pass both inspections would result in rejection of the container. Rejected containers would be returned to the fabrication line for either weld repair (followed by reinspection) or, if necessary, disassembly of the shell and reencapsulation of the waste.

Ultrasonic waves (for non-destructive examination purposes, defined as sound waves in the frequency range from 1 to ~25 MHz with wavelengths of 5 to 0.1 mm) propagate with specific, definable characteristics through solids. If, during their passage through a material, they encounter an

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[20] In the Swedish program this is called "OFHC" (Oxygen-Free High Conductivity) copper.

anomaly, for example, a void or an inclusion, they may be partly reflected back to the ultrasound source, partly reflected at an angle to the line of the incident beam, partly attenuated, partly refracted, or be subject to some combination of all these effects. These phenomena, in particular reflection and attenuation, are used to determine the presence of a variety of flaws in metal components.

In ultrasonic inspection, a beam of ultrasound is generated by an ultrasonic probe and transmitted through the material to be inspected. In the single-probe technique, the sound-emitting probe is manufactured to serve also as a receiver for any signals that may be reflected by flaws within the component under inspection. This is also called the "pulse-echo" technique. If the ultrasonic beam is directed at right angles to the surface of the material, the technique is called the "normal-beam, pulse-echo" method. Another method, in which the beam is directed at an angle into the material surface, is also used.

In the attenuation technique, a separate sound-receiving transducer is placed on one side of the component under inspection, and the sound-emitting probe on the other. As the two are traversed in parallel across the component, the strength of the received signal is monitored and recorded. A reduction in signal strength may mean that the incident beam has been attenuated by the presence of a flaw. Other sophisticated UI techniques exist, and the advent of modern, computerized data-acquisition and -interpretation procedures has greatly improved their speed and accuracy.

Samples made from welds in candidate container-shell materials were subjected to tests designed to determine how amenable each material was to the use of ultrasound for inspection (Moles et al. 1987). These tests showed that Grade-2 or -12 titanium exhibited essentially isotropic behaviour; i.e., they caused little skewing of the ultrasonic beam, which could make interpretation of the reflected or transmitted signal difficult, or lead to erroneous results. In contrast, commercially pure copper exhibited significant anisotropy in the form of beam skewing and spreading. It was concluded that either grade of titanium should present few ultrasonic inspection problems; however, further UI development work might be needed for copper.

In subsequent work (Maak and Moles 1986), titanium R/D bonds containing a variety of deliberate defects (e.g., deliberately non-bonded regions and embedded contaminants, such as paint and grease spots, glass-bead particulate and thin nickel-chromium or tungsten wires) were examined ultrasonically. All tests used high-frequency (25 MHz) probes for high resolution, and water coupling between the probe and sample. Best results were obtained using the normal-beam pulse-echo technique. In general, all defects were readily detectable, including tungsten wires of 0.127-mm diameter, which implies that a container-closure leak path of this width would be detectable in an R/D bonded joint. Although it is possible that smaller defects may be detectable, it appears from current work that defects of this size may be near the lower limits of detection by UI. As previously noted, helium leak testing would also be used during container inspection, to ensure that any through-wall defects below this very small UI detection limit were identified.

Similar results have been obtained for GTA welds containing deliberate defects (Moles 1986a). In these tests, UI was used successfully to detect defects, such as lack of bonding (due to either grease contamination in the weld, poor mating of parts or poor weld-bead placement) and a tungsten inclusion in the root weld.

In other work (Moles 1986b, Maak 1988) it has been demonstrated that, for the proposed EB weld design for a copper container, UI should not present significant problems, despite copper's anisotropic characteristics for ultrasonic waves. Factors contributing to this conclusion include the use of a small (25 mm) weld thickness and the ability to employ longitudinal (rather than shear)-type ultrasonic waves for inspection, which have been shown to be less susceptible to beam skewing. Ultrasonic inspection of copper EB welds has indicated that relatively large cavities (width and length ≥ ~0.8 mm) and areas with a high density of small gas pores (with diameters ≥ 0.3 mm) could be detected by the pulse-echo technique. It was concluded that copper EB welds were, in principle, inspectable by UI and that the weld design developed for the program was well suited to this type of inspection.

Additional corroboration of the potential for reliable inspection of copper containers was obtained from work in Sweden, in which focused ultrasonic beams were used to detect small defects (down to 2-mm diameter) in copper EB welds and in thick (64-100 mm) copper blocks and copper-container mock-ups (SKBF/SKB 1983, Sanderson et al. 1983).

Work was also undertaken in our program to investigate how well UI could be adapted to remote technology. A simulated top-closure joint consisting of two 4.76-mm-thick rings joined by R/D bonding was constructed (see Figure 3-21). During fabrication of the ring, deliberate defects (areas with lack of bonding and inclusions of glass fibres, tungsten wires, grease, titanium oxide and zirconium oxide paste, mica shims, oxidized titanium strips and double-sided tape) were introduced at various locations around the joint circumference. The ring was inspected using an ultrasonic transducer mounted on a PUMA 560 industrial robot (Figure 3-24). The ultrasonic waves were transmitted from the transducer to the ring through a water jet.

In initial trials it was demonstrated that while the system was capable of detecting the defects, the procedure was too slow to be practical and also suffered from certain inaccuracies and operational difficulties. These problems were addressed through modifications to the robot-control software, system hardware and inspection procedures, resulting in considerable improvement. The modified system was capable of detecting artificial through-joint defects created by tungsten wires 0.127 mm in diameter that had been embedded in the joint during the bonding process (Piercy et al. 1989). Although the inspection procedure remained rather slow, strategies to increase speed were identified which, in combination with more sophisticated equipment and foreseeable advances in robotic technology, would ensure that a reliable and practicable inspection system could be

EIS 3-3.24

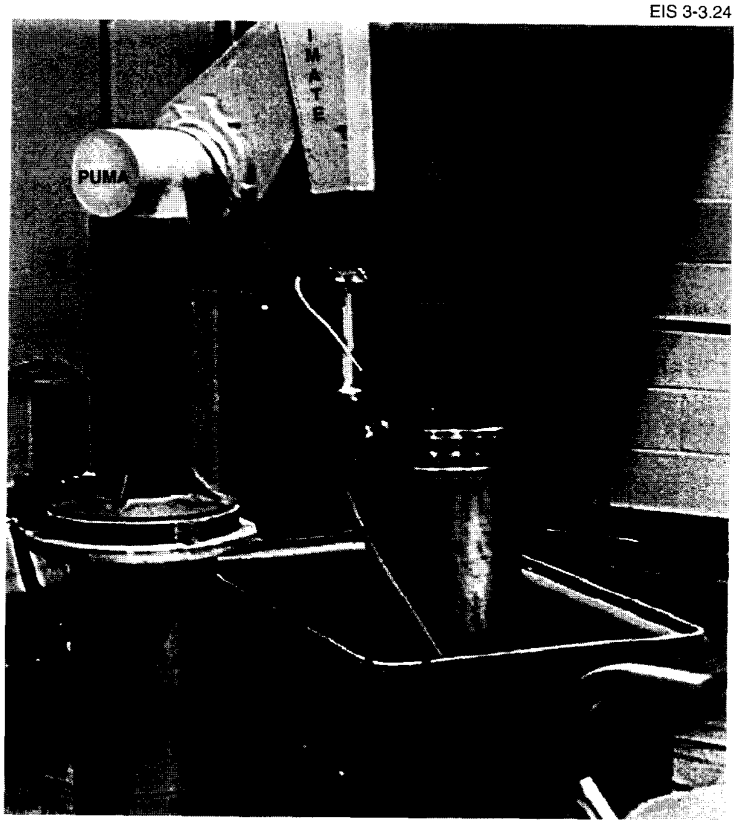

FIGURE 3-24: Inspection of R/D Bonded Titanium Ring by Water-Jet-Coupled Ultrasonic Transducer Mounted on an Industrial Robot

developed for a large-scale container-production facility. For example, Moles and Chan (1991) have assessed weld-inspection equipment capabilities and estimated that, even using currently available technologies, the time needed to inspect a full-size container-closure weld could be reduced from several hours to about one hour.

In other studies in the inspection-development program, an evaluation has been conducted of an advanced technique that uses a pulsed laser as an ultrasonic source, thereby eliminating the requirement for water coupling between the source and the weld joint (Taylor et al. 1989). In addition to the development of faster inspection procedures, future studies would include the establishment of a set of standards for the remote-inspection procedure and for rejectable flaws.

In summary, the results of the weld-inspection development program have shown that there is no fundamental impediment to the use of ultrasonic techniques to determine the integrity of the final closure weld.

3.5.3.4 Leak Detection Techniques

After inspection of the final closure weld by UI, the entire container would be subjected to a leak test to ensure that no through-wall defects had gone undetected (Simmons and Baumgartner 1994). Appropriate methods for conducting leak tests were reviewed and compared for accuracy, reliability, ease of remote application, and whether or not deliberate penetration of the container shell would be required to conduct them (Varian Associates Inc. 1980, American Society for Nondestructive Testing and American Society for Metals 1982).

Of a number of methods available, leak testing using helium and a mass-spectrometer detector is the most accurate. One procedure that offers the potential for adaptation to the inspection of fuel-waste containers is the "pressure-vacuum" method. In this method, helium can be introduced into a defective container by externally pressurizing the container in a helium-filled chamber. The container is then transferred to a vacuum chamber connected to a helium mass-spectrometer leak detector. If a leak is present, helium will escape from the container into the chamber and be detected. The technique is commonly used in manufacturing processes where highly accurate leak testing is required. Future optimization studies would include determination of appropriate techniques to adapt this procedure to the specific requirements of fuel-waste disposal containers.

3.5.3.5 Identification of Suitable Particulate Materials and Development of Packing Techniques for the Packed-Particulate and Structurally Supported Containers

The basic requirement for compacted particulate is that, for the packed-particulate container, it should provide structural support to the container shell; in the structurally supported container, it should transfer the external load on the shell to the inner support structure. Therefore, the compacted particulate should be free of major voids. It should be possible to compact the particulate to a high density so that its tendency to settle would be minimized and, during compaction, it should not tend to adhere to surfaces or generate excessive dust that would require extensive clean-up in the head-to-shell weld region.

Following eventual penetration of the container in the disposal vault, the interaction of the groundwater with the particulate should neither result in the production of chemical species that would increase the dissolution and/or leaching rate of the used fuel, nor impair the function of the buffer.

From initial screening studies, twelve candidate particulate materials were selected for study (Teper 1987c). Subsequent investigations included tests to determine how easily each material could be compacted by vibration, how readily it flowed into small voids or gaps, if it generated dust during compaction, and its creep behaviour under loading. From these tests, the candidate materials were reduced to three, one of which, glass beads of 1-mm average diameter, generated the least amount of dust during compaction and produced the highest bulk modulus of elasticity in the compacted state. Glass beads were therefore selected as the filler for the packed-particulate and structurally supported container prototypes.

Compaction investigations demonstrated that horizontal, sinusoidal vibration of the container at a frequency of 50 to 90 Hz at a peak-to-peak acceleration of 39.3 $m \cdot s^{-2}$ would achieve a satisfactory compacted density. It was recommended that compaction periods as long as practicable be used, but not less than 15 min.

The probability of internally isolated voids existing within glass-bead particulate following compaction was shown to be virtually nil. Rather, the most probable type of defect would result from incomplete filling of the container with particulate: after the container lid was welded on, a gap would exist below the lid. To ensure that this would not occur, a particulate metering device would be included in the fuel-packaging line at a used-fuel disposal centre (Simmons and Baumgartner 1994).

Tests have been conducted using typical Canadian Shield groundwaters to determine the chemical durability of glass-bead particulate and its compatibility with other components of the engineered barriers system, such as the bentonite-clay buffer. It was recommended that the glass used to manufacture the beads be of a high-silica, low-sodium formula. This would provide good chemical durability and ensure that any dissolution of the beads, following eventual penetration of the container, would not produce an alkaline solution, which could adversely affect fuel durability and/or buffer performance. Mechanical properties tests on high-silica beads have shown that their structural characteristics are very similar to those of the lower-silica beads that were used in the fabrication of the packed-particulate and structurally supported container prototypes.

3.5.3.6 Metal-Matrix Container Fabrication Development and Matrix-Performance Studies

Casting Techniques and Additional Barrier Studies

In containers employing a metal matrix, the matrix is intended to provide structural support to the container shell, and hence it should be free of major defects, such as shrinkage voids. During casting, the molten metal should neither chemically react with the corrosion-resistant shell nor otherwise reduce the thickness of the corrosion barrier. Similarly, interactions with the zirconium-alloy fuel sheath should be minimal to ensure that the fuel elements are not damaged. Following solidification of the cast matrix, chemical stability between the matrix and the container shell should persist.

The casting process should be conducted at as low a temperature as possible in order to reduce the preheating requirements of the container and its contents, decrease the possibility of promoting thermal-stress defects in the used-fuel sheath material, and shorten the solidification period, during which chemical interactions between the matrix and the used-fuel sheath material and/or the container shell are more likely. Finally, the cast matrix should not provide an additional source of contamination to the environment, following disposal (see also Section 3.5.5.7).

The casting procedure required to produce high-integrity metal-matrix containers is potentially complex and would have to take into account the following factors:

- the fuel bundles have different thermal properties than the matrix;
- the interstices between the fuel elements that make up the bundle are narrow, which could restrict matrix flow during casting and cause imperfections;
- the casting operation would have to be done remotely; and
- the containers are relatively large, and therefore poorly designed casting and cooling techniques could lead to large shrinkage cavities.

Studies were conducted to determine the chemical compatibility of various candidate metals and alloys possessing suitably low melting points for casting with the candidate container-shell materials and with the zirconium-alloy fuel sheath (specifically, lead, zinc and aluminum, and lead-antimony, aluminum-silicon and aluminum-copper alloys). Coupons of the container materials and Zircaloy-4 (Zr-4) were immersed in baths of the molten casting materials for various time periods, and the extent of the reaction at the coupon surfaces was examined (Mathew and Krueger 1990a). The results indicated that lead, zinc, lead-antimony and aluminum-7 wt.% silicon reacted least with the coupons; these materials were therefore assessed further to compare their casting characteristics. From this assessment (Mathew 1986), pure lead or zinc were recommended as the preferred casting materials. Specific advantages of these materials over the other candidate metals and alloys included a low tendency for gas porosity, a low susceptibility to shrinkage defects, and an absence of both solute segregation problems and any tendency for hot tearing. The subsequent development of techniques to produce high-quality castings focused principally on lead, which has the lower melting point.

To minimize major casting defects, such as those caused by shrinkage, cooling of the cast molten matrix by withdrawing heat solely from the base of the container (unidirectional cooling) had been recommended originally (Mathew 1986). However, because a full-scale metal-matrix container would contain a considerable volume (~400 L) of cast metal, the time required to completely solidify the cast metal by unidirectional cooling would result in long interaction times between the molten matrix, the Zr-4 fuel sheath and the container shell. Furthermore, in a production environment such as that at a used-fuel disposal centre, extended solidification times could cause considerable process-line difficulties. Therefore, an alternative technique, multidirectional cooling, was developed to increase the solidification rate while maintaining the casting's quality (Mathew and Krueger 1986). In this procedure, heat is withdrawn from both the bottom and the sides of the casting at a controlled rate. Initially, the development program consisted of theoretical analysis (the assembly of a finite-element heat-conduction model to predict the advance of the solidification front through the casting), experimental verification and small-scale metal-matrix container fabrication (Mathew and Krueger 1987a, 1990b). The subsequent phase of the work was directed toward fabricating considerably larger experimental prototypes by scaling up the procedures that had been developed.

The casting development program culminated in the production of the MM2, MM3 and MM4 half-scale container prototypes for the structural testing program. Dissection of two of these containers, following hydrostatic testing, confirmed that each had been cast free of unintentional defects within the body of the matrix. The successful production of these prototypes, each of which contained ~800 kg of lead, offers convincing evidence that the procedures developed in the laboratory to cast high-integrity metal matrices could be readily adapted to a production process.

The metal-matrix container design offers the prospect of extended isolation of the fuel from the disposal-vault groundwater, following eventual penetration of the container shell. A series of investigations was conducted to determine the corrosion durability of cast matrix metals in the vault environment. Experiments were conducted on coupons of lead, zinc and aluminum-7 wt.% silicon alloy to determine the corrosion resistance of these materials in a selection of oxygenated granitic groundwaters with dissolved oxygen contents ranging from 8 to 410 $mg \cdot L^{-1}$ (Mathew and Krueger 1987b). Although these high oxygen concentrations are not representative of Canadian Shield groundwaters found at depth, they were selected for these initial studies to examine the dependence of the matrix corrosion rate on dissolved oxygen. From these studies, it could be shown that the corrosion resistance of the materials increased in the order zinc, aluminum-7 wt.% silicon, lead. Subsequent studies were conducted at the lower oxygen concentrations more representative of deep groundwaters.

The results of the compatibility, casting development and corrosion evaluation tests suggested that, of the candidate materials investigated, lead had the greatest potential for use in the metal-matrix container concept. Its particular advantages include a low melting point, low susceptibility to casting defects and good resistance to corrosion in Canadian Shield groundwaters. The corrosion studies were extended to include investigations of the effects of galvanic corrosion on the durability of lead (Mathew and Krueger 1989). The objective was to investigate the dependence of the corrosion rate, in the presence of bentonite clay/sand buffer and Grade-2 titanium, on three groundwater variables: dissolved oxygen content, temperature and ionic strength. From the test data, a mathematical expression for the overall lead corrosion rate was derived as a function of the three variables. With this expression, and making conservative assumptions, it was calculated that the additional used-fuel isolation period that a 25-mm-thick lead layer could provide to a perforated, titanium-shell disposal container in a disposal vault constructed in plutonic crystalline rock in the Canadian Shield would be at least 3500 a (Mathew and Krueger 1991).

Because of the very low concentration of dissolved oxygen anticipated to prevail in the groundwater within the disposal vault, consideration has been given to the possibility of even slower corrosion of a lead matrix, following perforation of the container shell. Some similarities exist between the observed corrosion behaviour of lead and that of copper, in the presence of oxygen. The argument for the long lifetimes of copper, particularly in the absence of oxygen, is based on extensive experimentation over a period of 8-10 a (see Section 3.7). Since no similar scope of experiments has been done for lead, it would be highly speculative to predict the corrosion behaviour of lead in the absence of oxygen without an extensive, thorough investigation of the processes that might occur (e.g., pitting and galvanic corrosion).

In addition, unlike copper, lead is likely to be thermodynamically unstable with respect to water in pore-water solutions similar to those likely to be found in a disposal vault. Therefore, lead would continue to corrode in the absence of oxygen, although at a slow rate (Pourbaix 1973). In the absence of more detailed work at this time, it is difficult to assert that a lead matrix would provide very much longer protection of the used fuel from contact with groundwater. Localized effects, such as galvanic corrosion of the lead in a perforated container, would require much more investigation to remove uncertainties about the nature and rates of the processes involved.

Matrix Inspection Techniques for Metal-Matrix Containers

It is assumed that, for quality assurance purposes, it would be necessary to inspect the cast matrix of the metal-matrix container. Two methods have been studied: ultrasonic inspection (UI) and inspection by neutron-beam attenuation.

Ultrasonic techniques were shown to have limited ability to detect voids located at depth within a cast-lead matrix (Schankula 1990, Mathew and Krueger 1985). Because a beam of ultrasound can penetrate into the matrix only where shell/matrix bonding exists, the presence of voids behind a non-bonded region can easily remain undetected by UI. Furthermore, lack of bonding at the shell/matrix interface has been shown to be a normal feature of lead-matrix containers and, from the evidence of the tests conducted on the half-scale prototypes (Section 3.5.2.4), to have negligible effect on the container's structural performance. When intimate shell/matrix contact was present, voids 6 mm in diameter at a depth of 25 mm within the matrix were detectable. However, the detection of defects less than 5 mm from the matrix/shell interface proved to be difficult, principally because of ultrasound reverberations between the shell and the matrix.

Because of the limitations of ultrasonic methods, an alternative technique employing a beam of 14-Mev neutrons was investigated (Montin et al. 1987). The neutron beam was produced in a Walton-Cockcroft accelerator and passed through cast-lead specimens containing voids of known dimensions. The attenuation of the neutron flux by the casting for a given neutron source-to-detector path was measured with a neutron detector coupled to a photomultiplier tube with the necessary electronics to amplify and count the light pulses.

In the tests, the casting was probed with the neutron beam for a fixed time interval (generally 10 to 30 s), during which the neutrons that reached the detector were counted. If a void were present in the path of the beam, the neutron count over a given time would be greater than it would be if no void were in the path. The measured differences in neutron flux could be used to determine the void size.

The experiments showed that voids could be detected in both small (150-mm diameter) and large (400-mm diameter) lead castings. The smallest void detected was cylindrical in shape, 75 mm long and 12 mm in diameter, but no absolute detection limit was determined. From the results of the structural tests conducted on the half-scale metal-matrix containers (Section 3.5.2.4), it would appear that this void size is well below that which might have a significant impact on structural integrity. With further development, it appears certain that this technique could be used to develop a reliable void-detection procedure for metal-matrix containers.

Summary, Metal-Matrix Development Studies

The program conducted to identify suitable metals for casting into the metal-matrix container design and to develop casting techniques that would ensure that a void-free matrix could be produced demonstrated that these objectives can be achieved. Pure lead appears to be the most suitable metal for this application; similar conclusions were reached in studies of metal-matrix containers conducted in Sweden (SKB 1992a).

Corrosion studies on lead in the presence of titanium, which were conducted over a range of temperatures and in groundwater compositions that encompass Canadian disposal conditions, indicate that a 25-mm-thick layer of lead would further retard access of groundwater to the used fuel for up to 3500 a. Of the two matrix-inspection techniques investigated, inspection by neutron-beam attenuation is the more promising for detecting voids within solidified lead.

3.5.3.7 Other Fabrication Considerations

Shell Body and Heads

The shell bodies of all titanium prototypes used for short-term structural-performance testing were constructed of GTA seam-welded plates. This was the most readily available fabrication procedure for the development program, and the test results have demonstrated that containers made of seam-welded plate have good structural durability. However, for an optimized container design, this procedure would not necessarily be the preferred choice, particularly for large-scale manufacturing efficiency. Other industrial manufacturing processes are feasible, such as deep drawing, extrusion, centrifugal casting, and forging (for the top and bottom heads). Investigations of such procedures for container manufacture would include studies of microstructure, mechanical properties, corrosion behaviour and materials properties in the head-to-shell weld region.

None of the shells of the full- and half-scale test containers were heat-treated to relieve residual stresses, and the test-program results provided no evidence that any such stresses, if present, had any effect on the containers' short-term structural behaviour. In the packed-particulate container prototype, the top and bottom heads were manufactured by spin-forming. These heads were stress-relieved by heat treatment in vacuum at 540-590°C for 30 min. This procedure could also be applied to a prefabricated, seam-welded container shell; however, from current evidence, it does not appear to be required.

The tolerance of seam welds, in thin-shell titanium containers, to manufacturing defects was demonstrated in the hydrostatic tests conducted on the structurally supported container (Section 3.5.2.3). During pretest inspection, several of the shell-assembly welds were discovered to have rejectable defects. It was decided that the welds would not be repaired so that the effects of structural loading on them could be determined. Post-test examination (Maak 1986d) revealed that none of the defective welds had failed, and that even where extreme material deformation had occurred during the packing-defect test, there had been no loss of weld integrity.

For copper-shell containers, the shell could be manufactured either from EB-welded plate or by deep drawing, extrusion or casting. In U.S. studies (Stein et al. 1988) it was concluded that, for copper and copper-alloy containers, an integral seamless lower unit made by extrusion (i.e., combining both the shell body and lower head) had potential performance advantages, but was also very costly. In contrast, less costly welded construction may meet U.S. requirements.

Container Internal Atmosphere Following Final Closure Welding

The internal atmosphere within a titanium-shell container fabricated with an R/D bonded final closure weld would be air at normal atmospheric pressure. For a GTA-welded closure, the welding procedure would likely be conducted in an inert-gas atmosphere to ensure the highest quality weld; therefore, the internal atmosphere of the container would be the inert gas selected for the welding, at near-atmospheric pressure. Teper (1988) determined that for an increase in temperature within the container from 20°C (the assumed temperature during its construction) to 109°C (the average temperature within the container during disposal), the maximum tensile stress in the shell due to the resulting pressure increase (~0.06 MPa) would be below 60% of the yield stress of titanium[21] at the maximum shell temperature (100°C) during disposal.

The internal atmosphere of containers manufactured by EB welding would be air at low pressure (0.7 Pa or lower (Blakeley (1983)) because the procedure must be conducted in a vacuum chamber.

Inspection of the Prefabricated Container Components

During fabrication of the container shell, all welds, except for that used to complete the final head-to-shell closure, could be inspected by a number of techniques. These include radiography and ultrasonic inspection, both of which are widely used in industry. These types of material-inspection techniques are commonly referred to as "volumetric" techniques because they

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[21] The yield stress of titanium at 100°C is about 215 MPa.

can be used to inspect for flaws both at the surface and within the material substrate. Surface inspection techniques, such as liquid-dye penetrant, are sometimes used to supplement volumetric inspection. Any appropriate surface-inspection technique and at least one volumetric technique might be used to inspect prefabricated container-shell components, junctions (such as seam welds used to construct the cylindrical section of the shell from plate) and the bottom head-to-shell weld.

Residual Stresses in the Sealed Container

Residual stresses can remain in metal components that have been machined, cast, ground, formed or welded (in the latter because of cooling and shrinkage of the molten weld pool). In addition, residual stresses can occur around accidental dents, gouges, etc., introduced during manufacture or handling. Where high residual stresses persist, the application of further load can, if sufficiently large, cause the local stress to exceed the yield point of the material, leading to deformation or, possibly, failure of the component. Residual stresses can also lead to premature failure by promoting brittle fracture or localized corrosion in susceptible materials. The magnitude, direction, and distribution of residual stresses resulting from manufacturing procedures will often depend on the mechanical fabrication conditions and/or welding procedures, the degree of weld-joint restraint and weld geometry.

In some materials, residual stresses can be relieved by raising the temperature of the manufactured component for an appropriate period of time. For materials that react with the atmosphere at the stress-relieving temperature, the procedure is conducted in either vacuum or inert gas. As noted previously, heat treatment in vacuum was applied to the spin-formed heads used in construction of the prototype packed-particulate container. However, it is not always possible or desirable to subject the finished component to heat treatment, particularly where the required stress-relief temperature may risk damaging other parts of the component, or, in the case of a used-fuel container, its contents.

For commercially pure titanium, the recommended heat treatment to relieve stress is about 590°C for 30 min (Allen 1969). Welded copper is not normally heat-treated; such treatment is usually applied to cold-worked copper to restore ductility and softness.

As described earlier, GTA welding and R/D bonding have been evaluated for the final closure of thin-shell titanium containers. The GTA procedures employ relatively low welding current and, thus, low heat input, which can assist in minimizing the size of residual stresses. R/D bonding is a solid-state process and no melting occurs during bonding; therefore, the residual stresses generated by this procedure may be significantly less than those that may develop during fusion-welding processes. However, some residual stresses can arise in R/D bonded joints as a result of the deformation of the components when they are compressed together during bonding.

Structural-performance tests have been conducted on prototypes of the packed-particulate, structurally supported and metal-matrix containers, which were constructed using primarily GTA welding and, in one case, an R/D bond. Following their construction, no visible distortions were observed in these prototypes near any of the welded regions. As described previously, the results of tests conducted on all prototypes, even in the presence of severe, artificially induced defects in the internal support medium, demonstrated the short-term robustness of the container-shells' joints; the presence of residual stresses, if any, had no effect on the short-term structural performance of the containers.

As a result of material creep, the magnitude of residual stresses would likely be reduced with time. Nevertheless, to ensure satisfactory performance of titanium containers over the long term, the potential effects of residual stresses on the shell require further investigation. This could involve study of such factors as the magnitude, direction and distribution of residual stresses resulting from various mechanical and working operations, using analytical and experimental approaches. If, for example, it was determined that the maximum allowable residual stress was below the material's characteristic yield strength, some modification of the container-manufacturing and handling processes might be required. Such investigations would form part of a future optimization program.

As yet, no prototype copper-shell container has been constructed in the Canadian program. In the Swedish program, the extent of residual stresses in 100-mm-thick copper containers constructed by both welding and hot isostatic pressing[22] has been considered (SKBF/SKB 1983). By stress relieving, the starting material, i.e., the empty container and the lid, could be rendered stress-free prior to filling and sealing. However, during hot isostatic pressing (and subsequent cooling) the compaction of the copper powder, together with the differences in thermal expansion between the copper and the fuel assemblies, would produce residual stresses in the container surface. These stresses would be sufficiently large to plastically deform the copper. Calculations showed that, following this deformation, the container would have residual circumferential tensile stresses of 45-105 MPa and axial stresses of about 120 MPa, which is well below the ultimate tensile strength of both fully annealed copper (~225 MPa) and cold-drawn copper (~450 MPa).

In the case of a welded copper container, residual stresses can arise in and near the final closure weld. It was assumed that these stresses would be sufficiently large to deform the copper plastically in the weld zone and that the size of the subsequent residual stresses would be comparable to those obtained in hot isostatic pressing.

In confirmation studies conducted for the Swedish program in the United Kingdom (Sanderson et al. 1983), a near-full-scale mock-up of the proposed

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[22] A container-fabrication procedure that was considered early in the Swedish program, but which is no longer a preferred process. It involves filling the residual space in the container with copper powder or granules (after installation of the used fuel), followed by the attachment of a lid and compression of the entire component at high temperature and pressure to form a monolithic copper block surrounding the fuel.

(at that time) 100-mm-thick container closure weld was EB-welded and then investigated for residual stresses by experimental techniques. The measured residual stresses lay in the range from -32 MPa (i.e., compressive) to +36 MPa (tensile), well below the yield strength of the material (~160 MPa).

Since the proposed shell thickness is only 25 mm in the conceptual design of a copper-shell metal-matrix container for the Canadian program, it is reasonable to assume that residual stresses generated in the closure-weld region would not exceed those determined for the 100-mm thickness investigated in the Swedish program.

In summary, residual stresses would likely be present in both titanium- and copper-shell containers, resulting from the various welding and mechanical fabrication operations. In the absence of an optimized container design, detailed analyses of such stresses are, at present, premature. In future studies, such analyses would form part of the optimization process, from which appropriate manufacturing procedures, designed to minimize residual stress formation, could be developed.

Finished Container

Following fabrication and inspection, the container would be transferred to either temporary storage or to the disposal vault. In these transfer operations, the possibility exists that the container might be accidentally struck against a rigid object, or dropped. Generally, any unusual event of this nature would require that the finished container be reinspected for damage. If the damage were severe enough, the used fuel would be removed from the container and placed in another.

3.5.3.8 Reliability Analysis

Studies were conducted to determine the proportion of containers that would have initial perforations or be liable to early failure because of near-through or through-wall defects that had not been detected by inspection (Doubt 1984). The studies also examined

- the incidence of low failure rates and their relevance to container longevity;
- the likelihood that partial through-wall defects could perforate the container before or shortly after emplacement, and estimates of the distribution of defects in the material;
- the usefulness of reliability analysis techniques for estimating the reliability and life of fuel-waste containers; and
- other approaches to estimating the distribution of container longevity and failure versus time.

The principal finding of the study was that the proportion of containers that could be expected to be initially perforated or liable to early failure, as estimated from experience with present-day structures, appears to be between 1 in 1000 and 1 in 10 000. These values are used in the postclosure assessment case study (Johnson et al. 1994).

3.5.4 Other Container Concepts

3.5.4.1 Introduction

Sections 3.5.1 to 3.5.3 describe disposal containers and the techniques that might be used in their manufacture and inspection that have been investigated in considerable detail. In this section, other disposal-container concepts are described that have not, as yet, received a similar level of detailed investigation for their application in the Canadian program. These other concepts were examined to incorporate flexibility in our approach to container design and to demonstrate that other container concepts are possible for the disposal of nuclear fuel waste. Flexibility of approach is considered necessary to ensure that design options could be developed should other parameters in the disposal concept change in future (for example, the specific characteristics of the disposal site), or if the potential economic advantages of integrated fuel storage, transportation and disposal options could be realized. The following container concepts were investigated:

- a dual-wall stressed-shell container (the specific design studied was the Ontario Hydro iron-based stressed-shell (IBSS) container, similar in concept to the Swedish Advanced Cold Process container described in Section 3.3.3);
- an integrated or multipurpose container suitable for storage, transportation and possibly disposal, similar in concept to the U.S. Multi-Purpose Canister described in Section 3.3.5 (the specific design studied was the Ontario Hydro Dry Storage Container (DSC));
- ceramics for long-life containers; and
- a fuel-reprocessing-waste (FRW) container.

The principal investigations of the IBSS and DSC containers were conducted by Ontario Hydro. Ceramic and FRW containers were studied by AECL.

3.5.4.2 Iron-Based Stressed-Shell Container

In the IBSS container concept, a carbon-steel shell is surrounded by a corrosion-resistant overpack (Figure 3-25). The shell provides structural support against external loading, similar to the stressed-shell container described in Section 3.5.2.1, and the corrosion-resistant overpack prevents access of groundwater to the shell for the required isolation period. Seventy-two used-fuel bundles would be retained in a basket manufactured from 19 carbon-steel tubes, 18 of which would hold bundles. The overall geometry is of TEC-II configuration: the steel shell would be made from

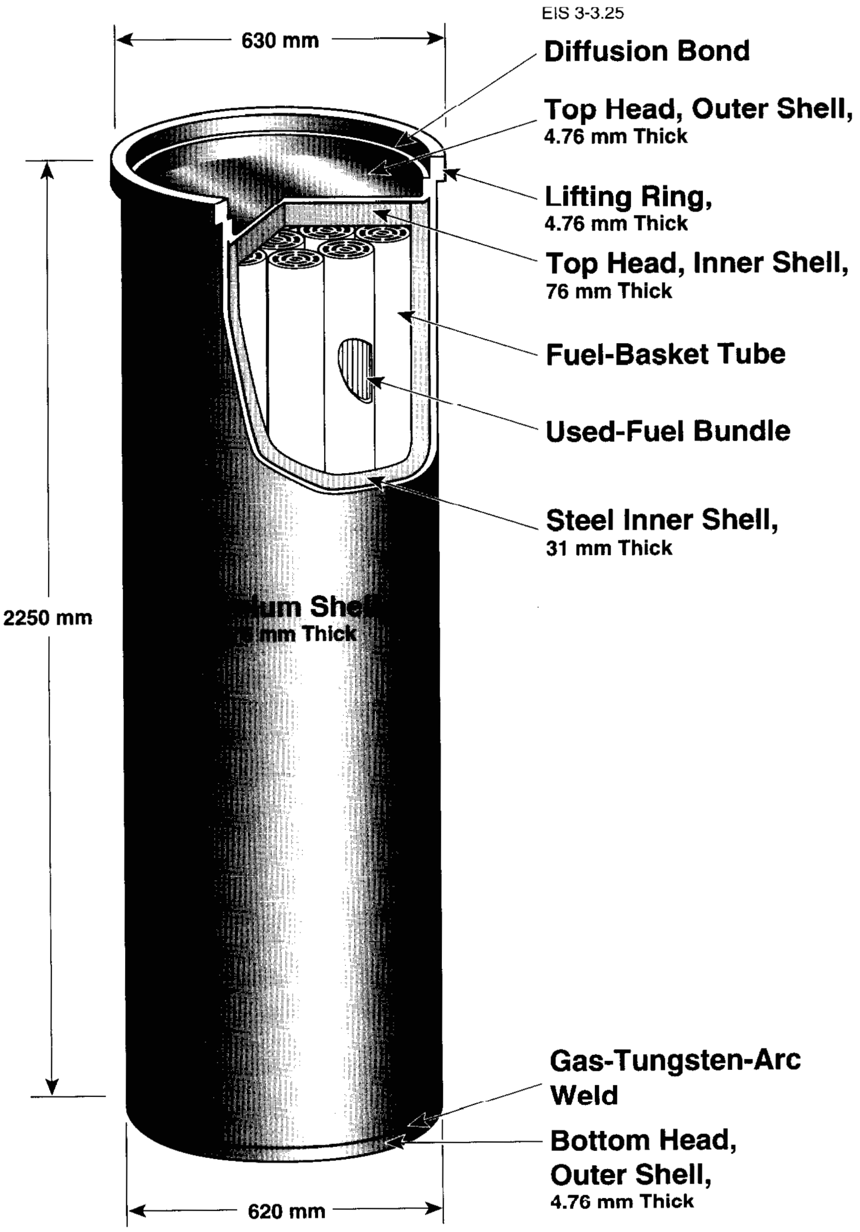

FIGURE 3-25: Titanium-Clad, Iron-Based Stressed-Shell Container

24-in. Schedule 80 pipe[23] and the corrosion-resistant overpack from Grade-2 titanium plate rolled to a cylinder to fit over the steel shell. The inner basket would be made of steel tubing of 110-mm outside diameter and 3.2-mm wall thickness. The steel shell would be closed with a press-fit steel plug and, possibly, sealed with a weld around its periphery.

Work to date on this concept has included the preparation of a detailed design and the completion of a structural-performance analysis of the container shell under uniform external pressures up to 13 MPa[24] at 100°C. Both the steel shell and its titanium overpack were analyzed for stress distribution, tendency for short-term buckling and for long-term creep-induced buckling. While material stress distribution and resistance to short-term buckling appear to be acceptable, a reliable prediction of the design's creep-buckling response would require further work and a more accurate definition of carbon-steel creep properties at 100°C.

The results of the program to date indicate that the IBSS concept may be a viable alternative to the thin-wall supported-shell designs; however, additional investigations, including the construction and structural testing of a prototype, would be required to confirm this indication. A decision on whether to pursue further development of this concept would depend on the results of assessments of the effects, within the vault, of the generation of free hydrogen by the corrosion of carbon steel (see also Section 3.5.2.2).

3.5.4.3 Dry Storage Container

Ontario Hydro has investigated the use of concrete containers for interim dry storage, transportation and possible disposal of used fuel (Freire-Canosa et al. 1986, Frost 1992). Dry storage of used fuel in DSCs has been proposed by Ontario Hydro as a cost-effective and timely solution to fuel storage, compared with constructing additional water-pool storage facilities. The DSC has features that allow the container to be loaded with fuel underwater. If the DSC were also licensed for transportation, the fuel handling steps between storage and transportation could be eliminated. If it was feasible to use the DSC for disposal as well, it would eliminate fuel handling at the disposal site. Such a fully integrated system (i.e., storage, transportation and disposal) offers the prospect of cost savings over one in which repeated fuel handling would be required.

Preliminary work focused on the development of cementitious materials with high strength and durability. Several sulphate-resistant, high-strength/high-density concretes were produced and used to construct scale-model DSCs for thermal and structural testing. These tests supported the technical feasibility of the DSC concept for storage, and it was recommended that it be included in future assessments of used-fuel management options.

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[23] American Standards Association designation for pipe manufactured of commercial wrought steel with an outside diameter of 24 in. (610 mm) and a wall thickness of 1.22 in. (31 mm)

[24] 10-MPa hydrostatic pressure plus 2.5-MPa buffer-swelling pressure (Section 3.4.3.5), rounded off upward for conservatism.

Following these preliminary studies, Ontario Hydro built and tested two prototype containers. The container design is shown in Figure 3-26; they are made from high-density concrete, are cylindrical in shape and have capacity for 384 CANDU used-fuel bundles held together in four storage modules that contain 96 bundles each. The storage modules, containing the fuel bundles, are loaded into the DSC in a used-fuel storage pool at a reactor site. Each container is designed with an inner liner and outer shell made of steel. The outer shell can be easily decontaminated once it has come into contact with the storage pool water. After the container is loaded with fuel, a lid is securely bolted onto it and the container is retrieved from the pool. Prior to storage, the container is drained, vacuum-dried via built-in draining and drying attachments, and decontaminated.

At Pickering nuclear generating station, various tests were carried out to demonstrate the practicability of loading and unloading the fuel. A long-term demonstration program to assess the leak tightness and thermal and radiological performance of the two fully loaded prototypes during storage is under way (Ontario Hydro 1989).

Following the success of the initial tests, the concept was optimized to improve storage and transportation performance. The shape was changed to a rectangular configuration that conforms more closely to the geometry of the fuel-storage modules, making more efficient use of space (Figure 3-27). Other changes included an increase of the wall thickness from 480 mm to 550 mm and a reduction of the gross loaded mass from 70 Mg to 63 Mg. A new closure design uses a welded, rather than bolted, system. Outer packaging, consisting of foam impact limiters on each end and steel armour that encases the DSC (not shown in Figure 3-27), was introduced to facilitate safe transportation in the event of accidental impacts of the container.

Extensive analyses have been carried out to determine the ability of the containers, with outer packaging, to withstand normal and accident conditions of transport. Both impacts and fire conditions were analyzed.

A structural testing program based on IAEA[25] requirements for the transportation of "Type B" packages, was then conducted with half-scale prototypes in outer packaging. These tests consisted of

- a 9-m drop test of the container onto its top corner, and
- two 1-m drop tests of the container onto a rigid, perpendicularly mounted steel pin at the top lid centre and at the side flange.

All of these tests were successfully passed by the scale models according to IAEA requirements for maintenance of integrity and shielding. Helium leak testing also confirmed the leak tightness of the package. The results of these tests and analyses are being used to obtain transportation licensing for the DSC.

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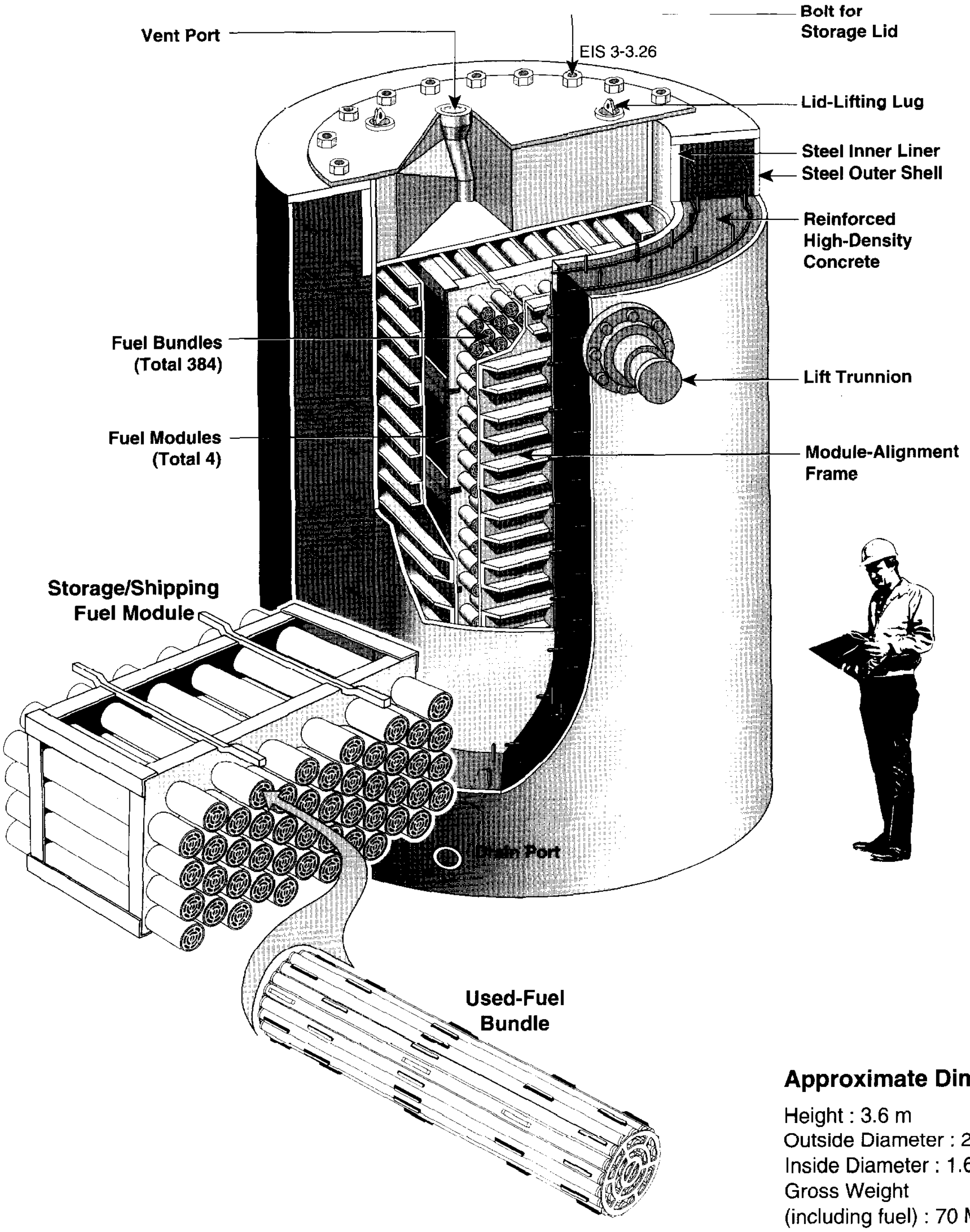
[25] International Atomic Energy Agency.



Approximate Dimensions:

Height : 3.6 m
Outside Diameter : 2.6 m
Inside Diameter : 1.6 m
Gross Weight
(including fuel) : 70 Mg

FIGURE 3-26: Ontario Hydro Dry Storage Container, Original Cylindrical Design

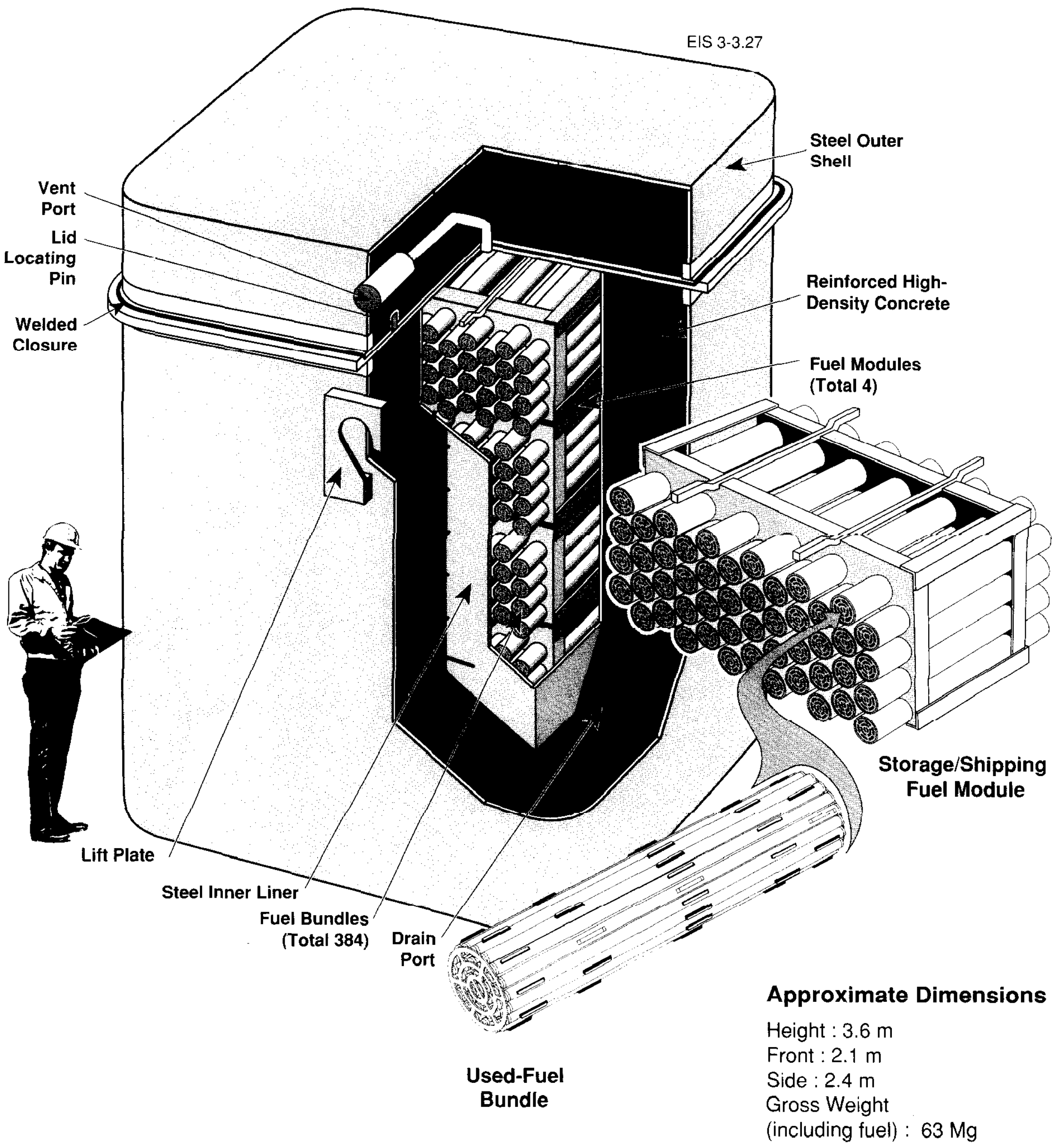


FIGURE 3-27: Ontario Hydro Dry Storage Container, Rectangular Design

More recently, Ontario Hydro has applied for a license to store used fuel in rectangular DSCs on a commercial scale at its Used-Fuel Dry Storage Facility located at Pickering Nuclear Generating Station (NGS).

Future work will focus on the suitability of the concept for disposal (Boag and Williamson 1992). Specific issues to be addressed would include corrosion of the steel liners, hydrogen generation due to steel corrosion, and structural performance of the DSC under disposal-vault conditions.

3.5.4.4 Ceramics for Long Container Life

To achieve very long container lifetimes (>100 000 a), the use of ceramic or vitreous materials, which can be produced with very high chemical stability, could be considered. Extensive investigations on the potential use of these materials have been conducted in the Canadian program (Onofrei et al. 1985, 1986a,b; Burnett et al. 1985). Although the non-metallic materials considered have excellent corrosion resistance, achieving the ability to ensure that a container could be fabricated with high integrity would require extensive further development. Furthermore, the potential for delayed cracking of manufactured components is not only considered to be a material property, but is also highly dependent on the manufacturing technology. It is also a statistically related phenomenon, and observations of specimens from small-scale manufacture may, to some extent, not be relevant for the assessment of the probability of delayed fracturing in full-size containers (SKB 1989a).

It was concluded that further work on the durability of ceramic materials for containers would only have relevance if linked with the full-scale fabrication of containers from such materials. For these reasons, further work on ceramic materials for containers was suspended, although work on concrete for other engineered barriers (grouting, seals, etc.) was continued at AECL, and concrete development for the DSC was continued at Ontario Hydro.

3.5.4.5 Fuel-Reprocessing-Waste Container

Although, at present, the reference waste form for disposal in the Canadian program is irradiated CANDU fuel bundles, the container designs investigated could be readily adapted to fuel-reprocessing waste immobilized in a corrosion-resistant medium, such as glass or glass-ceramic, if it were decided at some future date to reprocess CANDU fuel. To demonstrate this, a container design for vitrified reprocessing-waste disposal was developed (Hosaluk 1992a,b,c; Baumgartner et al. 1993), based on the titanium-shell packed-particulate container design for used fuel (Figures 3-28 and 3-29). The FRW container is designed to retain a stainless steel canister containing 288 L of vitrified fuel-reprocessing waste and ~27 L of glass-bead particulate. The particulate provides internal support in the unfilled portion of the canister. The canister is a modified version of the French AVM canister, with twice the volume of the AVM design. The container fabrication procedures would be essentially the same as those required to construct a packed-particulate container for used fuel.

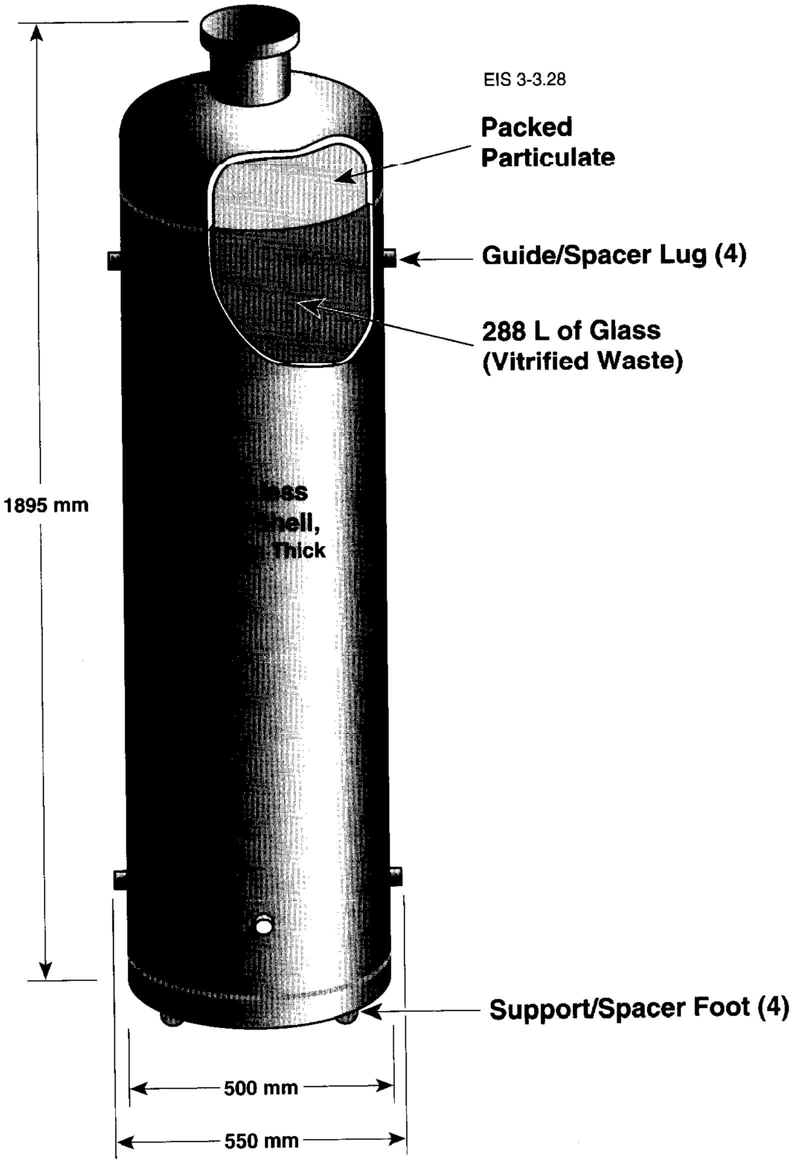


FIGURE 3-28: Vitrified-Waste Canister

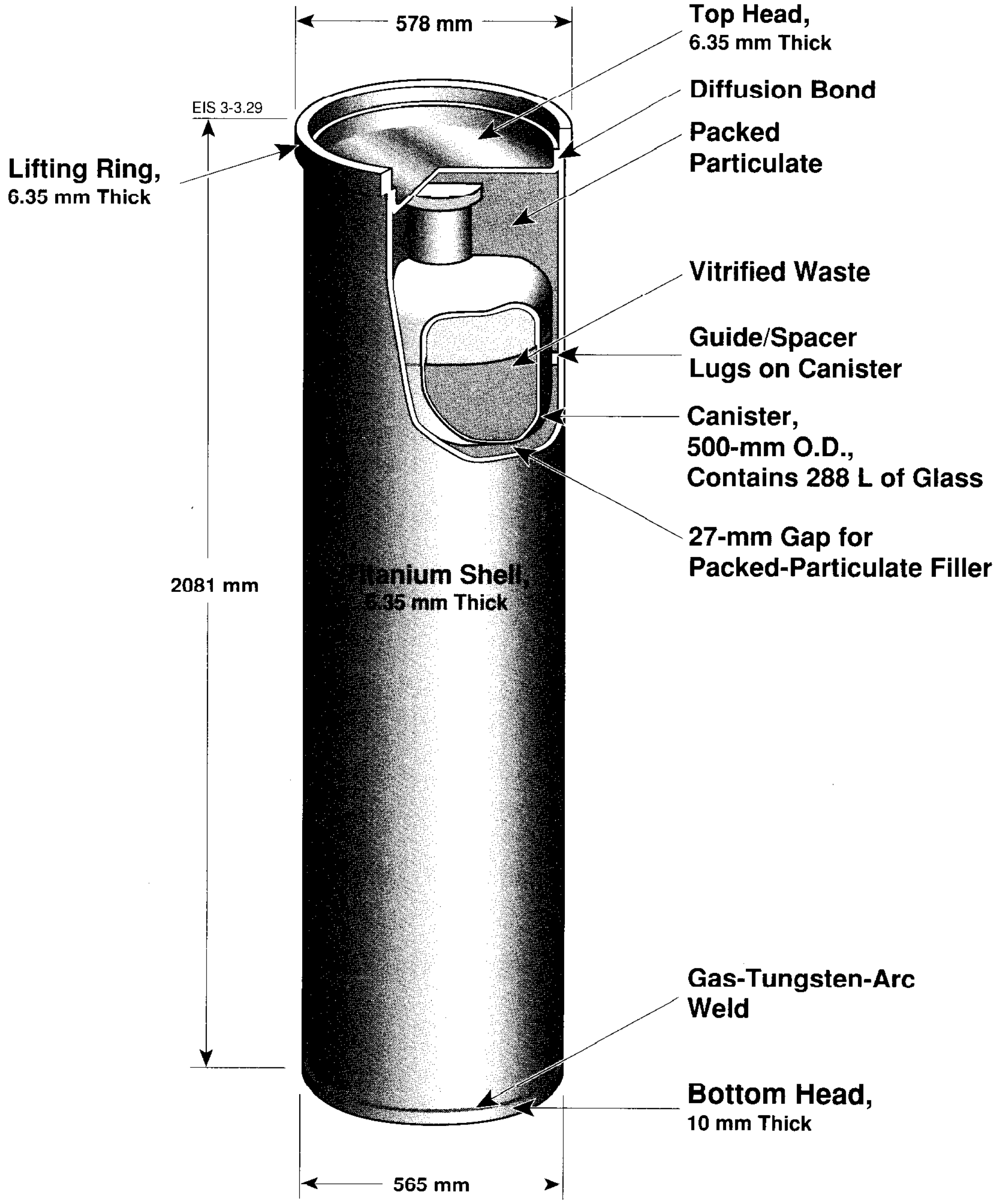


FIGURE 3-29: Titanium-Shell, Fuel-Reprocessing-Waste Disposal Container with Vitrified-Waste Canister

3.5.5 Selection of a Reference Container Design for the Used-Fuel Disposal Centre Study

3.5.5.1 Introduction

To be able to perform a safety analysis of the operation of a used-fuel disposal facility and to demonstrate the methodology of performing a long-term safety assessment of the Canadian disposal concept, it was necessary to develop a reference disposal facility design, including selection of the reference engineered barriers. This study, called a Used-Fuel Disposal Centre conceptual design, is described by Simmons and Baumgartner (1994) and was based on, and conducted according to, specifications outlined by Baumgartner et al. (1993). In those specifications, a specific container design is detailed for purposes of the Used-Fuel Disposal Centre study. It is stressed that this design concept is not intended to represent a final disposal-concept selection; rather, it provides a common basis to demonstrate the engineering aspects and the performance-assessment methodology that would be used to evaluate a disposal vault design proposed for implementation at an actual site.

Because the structural testing program conducted on the three candidate supported-shell container designs indicated no clear structural-performance advantage for one specific design, other factors were used to determine a reference container design for the Used-Fuel Disposal Centre engineering study and the postclosure assessment case study. These factors are listed below:

- ease of fabrication,
- ease of inspection,
- ease of repair,
- ease of handling,
- ease of emplacement into and retrieval from the reference disposal vault,
- chemical toxicity of the waste container construction materials,
- degree of self-shielding,
- ability to provide an additional barrier,
- temperature of the container during disposal,
- resource use, and
- cost.

These factors are discussed in Sections 3.5.5.2 to 3.5.5.12.

3.5.5.2 Ease of Fabrication

During its manufacture, the packed-particulate container would be subjected, on a shaker table, to a horizontal sinusoidal vibration of ~50-60 Hz with a peak-to-peak acceleration of 39.3 $m{\cdot}s^{-2}$ for periods of 15 min or more. Since the mass of a titanium-shell packed-particulate container, when loaded with used fuel and particulate, would be about 2800 kg, the shaker table would have to be large and mounted on robust support to withstand the dynamic forces generated. At a disposal facility, personnel, delicate equipment, key structural components, etc., would have to be isolated from these forces.

The durability of used fuel under vibration and impact has been extensively studied (Forest 1980, 1985). These investigations revealed that used CANDU fuel is robust: in impact studies, bundles withstood decelerations of 766 $m{\cdot}s^{-2}$ in the lateral direction and 1718 $m{\cdot}s^{-2}$ in the axial direction without damage. In endurance testing, irradiated bundles were subjected to extended periods (up to 23 h) of shaking at 21 Hz and 4.9 $m{\cdot}s^{-2}$ peak-to-peak acceleration, plus shorter (1 h) periods at 21 Hz and 29.4 $m{\cdot}s^{-2}$, which compares closely with the total dynamic loading in the proposed container-compaction procedure. The fatigue life of the bundles (i.e., the time lapse before the appearance of damage in the fuel sheath) under these conditions was 24 h, well beyond the approximately 15 min required to compact a fuel-waste container.

Since the integrity of titanium joints made by either GTA welding or R/D bonding is adversely affected by contamination, appropriate methods are required to ensure that no particulate adheres to the surfaces to be bonded. Therefore, for the final closure weld in particulate-supported containers, the surfaces to be joined would have to be thoroughly cleaned.

In the structurally supported container design, the fabrication procedures are similar to those of the packed-particulate container, except that the used-fuel-bundle basket is constructed of heavier-gauge pipes that are sealed with interference-fit plugs. Thus, the structurally supported design requires more fabrication procedures than the packed-particulate design.

For the metal-matrix container design, fabrication requires the casting of lead at >330°C to cast the matrix. At a disposal centre the melting facility would likely be located outside the shielded cell in which the fuel bundles would be loaded into the container, and the molten metal would be fed by conduit into the cell. A source of hot air would be required to preheat the container, basket and bundles. Prior to its discharge to the environment, this air would require monitoring for the presence of radionuclides and metal vapours, and appropriate filtration systems would be needed to ensure that any releases of these contaminants were maintained at acceptable levels.

The casting procedure would subject the fuel bundles to a high-temperature period, potentially promoting the release of some volatile radionuclides from any fuel elements with through-wall or incipient sheath defects.

Appropriate monitoring and filtration systems would be required to ensure that any releases were adequately managed.

Controlled cooling of the cast metal-matrix container to achieve a high-integrity matrix would require a substantial supply of water to the packaging cell. Monitoring and filtration of any discharge of water or water vapour from the cell would be required.

The surfaces to be bonded in the casting and venting ports in the top head of a metal-matrix container must be cleaned of foreign material (in this case, most likely to be matrix-metal spatter). Care would also be required to ensure that the welding process did not vaporize nearby matrix metal and contaminate the weld, particularly if the final closure were made by GTA or EB welding.

Of the three candidate supported-shell concepts, the metal-matrix design is the most complicated to make and requires the largest energy input. The structurally supported design is the next most complicated, followed by the packed-particulate design.

3.5.5.3 Ease of Inspection

The ultrasonic inspection procedure for the final closure weld is the same for all container designs, as is the helium leak-test procedure. As noted in Section 3.5.3.5, the probability of internally isolated voids existing within particulate-supported containers is insignificant, precluding the need to inspect the packed-particulate and structurally supported designs for such defects. Conversely, although reliable techniques have been developed to produce high-quality castings for the metal-matrix design, the existence of internally isolated voids remains possible. Inspection for such voids would have to be done by one of the techniques described in Section 3.5.3.6., probably by neutron-beam attenuation. This would require the use of sophisticated equipment (a neutron generator and associated electronic detection and data-interpretation hardware) and, quite probably, a lengthy inspection period.

3.5.5.4 Ease of Repair

At a disposal facility, if one or more rejectable defects (usually in the final closure weld) were detected, and an attempt at repair were judged to be practicable, the container would be transferred to a weld-repair station and a repair attempted. If a repair were either not possible or unsuccessful, the container would be disassembled and the basket of used fuel removed for transfer to a new container (Simmons and Baumgartner 1994).

The procedures to repair the final closure weld of all thin-wall supported-shell containers employing the same weld type would be the same. However, should fuel recovery for repackaging be necessary, this would be considerably easier for the packed-particulate and structurally supported designs than for the metal-matrix design. In the particulate-supported designs, the fuel basket could be recovered by cutting open the container and removing the particulate (either by vacuum hose or by draining). Recovery of the fuel basket from a metal-matrix container would require either that the cast matrix of the defective container be remelted or that the intact matrix/basket/fuel composite be removed from the defective shell for transfer to a special shell (i.e., slightly oversize to permit insertion of the casting). Remelting and recasting the matrix would subject the fuel bundles to additional high-temperature cycling, increasing the possibility of inducing sheath defects. Furthermore, the procedure would be both time- and energy-consuming. Transferring of the intact casting to an oversize shell would be preferable from an operational standpoint, provided analysis showed that satisfactory long-term structural performance of such a container could be achieved.

3.5.5.5 Ease of Handling

The lighter the waste package, the simpler and less costly the equipment required to manufacture and handle it. Examples of handling equipment include cranes, hoists, transport vehicles, trolleys and turntables, and their auxiliary components, such as drive belts, gear trains, buckets, holding bins, chains and hooks. Platforms and loading and storage areas (including the floors of water-filled storage bays) would have to be designed for the anticipated loads. The approximate masses of each supported-shell container design, loaded with used fuel, are as follows:[26]

- packed-particulate	2800 kg
- structurally supported	3400 kg
- metal-matrix (cast with lead)	8000 kg.

The fabrication of lead-matrix containers would require handling equipment and support structures with more than twice the static-load bearing capacity required for the manufacture of particulate-supported containers.

3.5.5.6 Ease of Emplacement into and Retrieval from the Reference Disposal Vault

All candidate containers were designed for handling and emplacement into a borehole within the disposal vault. A ring attached to the top end of the container (see Figures 3-10, 3-11, 3-14 and 3-15) would be grappled by a latching mechanism in the shielded cask used to transfer the container from the surface facilities to the vault for borehole emplacement (Simmons and Baumgartner 1994). One advantage of this system is that the latching mechanism would not have to be circumferentially oriented to a specific position to grapple the container.

Relative ease of container emplacement into, or retrieval from, the disposal vault would be affected primarily by container weight. Equipment required to handle a lead-matrix container would have to be constructed with more than twice the load-handling capacity of equipment for handling compacted-particulate containers.

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[26] Masses are for 6.35-mm-thick, titanium-shell containers.

If any corrosion of the shell occurred, its effect on the ease of retrieval of the container would be more profound for heavier containers, since part of the retrieval procedure would rely on the container shell having some measure of structural strength (Simmons and Baumgartner 1994).

3.5.5.7 Chemical Toxicity of the Container Construction Materials

Goodwin et al. (1987) have assessed the potential environmental impact, during disposal, of chemically toxic materials, including those proposed for container manufacture.

In the assessment analysis, stainless steel, Inconel, copper and titanium were included as container-shell materials; lead-5 wt.% antimony and zinc were included as cast matrices. The results of the analysis, when applied to the candidate container designs in this assessment, showed that only lead, as would be used in a lead-matrix container, presented a potential source of chemical toxicity. For the time frame of the analysis (10^7 a), the probability that lead concentrations would exceed acceptable limits in the biosphere, based on chemical toxicity, was very low. Therefore, use of the lead-matrix container for disposal would present a finite, but low, risk as a source of chemically toxic elements from the disposal vault.

3.5.5.8 Degree of Self-Shielding

The effectiveness of the gamma-radiation shielding provided by equal thicknesses of different materials is approximately proportional to their respective densities. At a density of 11.34 $Mg \cdot m^{-3}$, lead is at least 5.6 times as dense as vibrationally compacted glass beads (density up to 2.02 $Mg \cdot m^{-3}$). Therefore, the gamma dose rate[27] at the surface of a titanium-shell packed-particulate container, ~52 $Sv \cdot h^{-1}$, would likely be reduced by a factor of about five if cast lead were substituted for the particulate. This improvement in gamma shielding would be slightly offset by reduced neutron-radiation attenuation.

Downstream of a lead-matrix container production line, reduced levels of shielding would be possible for certain major facilities and components, e.g., in a temporary storage area for finished containers, and for the flask used to transfer containers into the vault for disposal. Conversely, more stringent occupational health- and safety-related procedures, and increased environmental protection measures would be required for the large-scale melting and casting operations required for the production of lead-matrix containers. In the absence of a detailed study, it is not clear whether any overall cost savings would be realized.

In the disposal vault, reduced radiation fields near each emplaced container would result in reduced production of molecular oxidizing species, such as H_2O_2 and O_2, by the radiolytic decomposition of groundwater. The role of such species on the rate of corrosion of the container shell and the UO_2 fuel is an area of extensive study in the Canadian program. Experiments have shown that, over the expected range of gamma-radiation fields and

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[27] Calculated for an assumed average bundle burnup of 1008 $GJ \cdot kg^{-1}$ U and 10-a cooling (Simmons and Baumgartner 1994).

groundwater compositions, there is no evidence of any increase in the rate of corrosion of titanium (Ikeda et al. 1989, Johnson et al. 1994).

When the container is eventually breached and flooded by groundwater, there may be radiolytic decomposition of this water, producing oxidizing species such as H_2O_2 and O_2. The concentrations of these species would depend on the time of container failure. The gamma-radiation field of 10-a-cooled fuel within a disposal container will decrease by a factor of about 10 000 during the next 500 a to a level where the concentrations of radiolytically produced oxidizing species near the container would be extremely low. When the container is breached, any oxidizing species in the water entering the container would be consumed in reactions with the internal structural materials (e.g., the fuel basket), the Zircaloy fuel sheath and the residual container-shell material. Following eventual failure of the Zircaloy sheath, the subsequent production of molecular oxidizing species would be largely a function of groundwater radiolysis by long-lived alpha-emitting radionuclides in the UO_2. The effects of alpha and gamma radiolysis on used-fuel dissolution have been discussed in Section 2.2.9.2 and by Shoesmith and Sunder (1991). Such radiolysis effects would be independent of the container materials used for disposal.

In summary, although the self-shielding characteristics of a lead-matrix container would be significantly greater than those of particulate-supported containers, there is no evidence that this would result in improved occupational health and safety, substantial cost savings at a used-fuel disposal centre, or a reduction in the corrosion rate of either titanium- or copper-shell containers in the disposal vault.

3.5.5.9 Ability to Provide an Additional Barrier

The current designs of particulate-supported containers do not include materials that would retard the movement of radionuclides. At present, it is assumed, for the purpose of modelling the release of radionuclides, that following penetration of the shell groundwater would immediately pass through the particulate and contact the UO_2. This is a conservative assumption because the Zircaloy sheath of the fuel elements (except for the few that had sheath defects at the time of disposal)[28] would prevent UO_2/groundwater contact for some time. However, the duration of this protection is uncertain; hence, in modelling the release of radionuclides from the fuel, it is assumed that the sheath provides no additional barrier to radionuclide release (Johnson et al. 1994).

In contrast, a lead-matrix container offers the prospect of achieving a minimum of 3500 a of additional isolation of the fuel (see Section 3.5.3.6).

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[28] The incidence of fuel-sheath failures in Canadian CANDU reactors is very low. To date, of those bundles irradiated, 99.9% have operated without failure.

3.5.5.10 Temperature Gradients Within a Container During Disposal

The container-surface temperature and maximum internal temperature of a titanium-shell lead-matrix container were calculated for the case of a 1000-m-deep disposal vault (Mathew 1985). The analysis indicated that the temperature gradient from the shell to the fuel would be very small (1-2°C) because of the high thermal conductivity of the lead matrix.

A similar analysis (Baumgartner et al. 1994) was conducted for a titanium-shell container compacted with glass beads and loaded with used fuel, using an assumed value of the radial coefficient of thermal conductivity for the container, combined with a sensitivity analysis of the effect of variations in the coefficient over a range that would encompass the actual value. The results indicated that the temperature difference between the container centre and outer shell would not exceed 10°C. Such a gradient is well below that from which significant thermomechanical stresses might be expected. As well, even this temperature difference is conservatively high, because only heat transfer in the radial direction was considered. Values of thermal conductivity of compacted glass beads used in the analysis were verified experimentally by Teper (1990). A mean value of $0.37\ W \cdot m^{-1} \cdot K^{-1}$ has been determined for high-silica glass of the type specified for the packed-particulate and structurally supported containers.

3.5.5.11 Resource Use

Two studies have been conducted to determine the availability of, and projected requirements for, non-renewable materials resources to construct containers on a production basis. In the earlier study (McConnell 1982), estimates were made of the requirements for a variety of candidate materials which, at that time, were considered to have potential for the construction of containers. Candidate shell materials included 316L stainless steel, Inconel 625, Grades-2, -7 and -12 titanium, and copper. Candidate container-filling (i.e., matrix) materials included pure lead, lead-5 wt.% antimony, aluminum-10 wt.% silicon and pure zinc. Of the candidate shell materials, it was concluded that only Grade-7 titanium might present supply problems.[29] Of the candidate matrix materials, only the lead-antimony alloy was considered to present potential supply problems, primarily because of the low production of antimony in Canada (although Western World resources and production of this metal are large).

When subsequent research identified titanium and copper as the candidate container-shell materials warranting further detailed consideration, and pure lead as the preferred candidate matrix material for the metal-matrix container design, an updated study (Grover 1990) of the future supply of, and demand for these materials was conducted. A brief description of the principal findings of this study follows. For completeness, the findings of the study relating to lead are included.

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[29] The reasons for the author's reservations about this alloy related primarily to considerations of world production of palladium and those countries possessing major economical reserves of that metal, which constitutes between 0.12 and 0.25 wt.% of the composition of Grade-7 titanium.

Titanium

Although the favoured ore for titanium-metal production is rutile (basically, TiO_2), in recent years, more than 60% of the world's supply of titanium metal has been produced from ilmenite ($FeTiO_3$). Canada is one of the principal world producers of ilmenite ore, most of which is exported to the United States and Europe. At present, Canada has no titanium-metal production capacity; however, industrial capability to fabricate metal into finished components does exist.

For a supported-shell container with a 6.35-mm-thick shell, the annual titanium-metal requirement at a disposal centre designed to dispose of 10^7 fuel bundles over a 40-a period would represent about 2.25% of U.S. production during 1988. It was determined from titanium-industry sources that this requirement would likely be too small to provide an incentive for the establishment of a metal-production plant in Canada.

Total proven world reserves are estimated to be about 26 x 10^7 Mg (titanium content). With static demand for titanium minerals beyond the year 2000 and no new economically recoverable discoveries, these reserves would last until 2110. If, based on historical trends, an annual growth in usage of ~1.5% is assumed, the reserves would last until 2075.

In addition to the proven reserves, there are (currently) uneconomic titanium resources throughout the world. These are estimated to contain about 43 x 10^7 Mg. Extraction of these resources would considerably extend titanium supply in time.

Copper

Canada is the fourth-largest copper producer in the world, and has an industrial infrastructure capable of processing refined copper into a variety of products, such as bars, plates, pipes and cable.

Based on the conceptual design of a copper container with a 25-mm-thick shell (see Section 3.5.2.5), the yearly copper requirements for a used-fuel disposal centre would represent about 1% of the production of refined copper in Canada. In the year 2000, total remaining world reserves of copper ore are projected to be 20 x 10^7 to 36 x 10^7 Mg. Beyond 2000, the balance between copper supply and demand may warrant increased monitoring as currently identified economical reserves are consumed and if, as is currently projected, demand continues to increase at about 3 to 4% per year. Some of the factors potentially affecting the future supply/demand ratio for copper include increased recycling of scrap metal, the development of new technologies to recover lower-grade ores and the development of recently inferred new deposits, including possibly substantial ocean resources.

Lead

Canada is the fourth-largest producer of primary refined lead in the world. Based on the conceptual design of the metal-matrix container described in

Section 3.5.2.4, the yearly lead requirements for a disposal facility would represent about 10% of the production of refined lead in Canada. As in the case of copper, the balance between lead supply and demand may warrant increased monitoring beyond the year 2000, when it is estimated that total world reserves will be about 8 x 10^7 Mg and demand for primary lead will be about 4 x 10^6 $Mg{\cdot}a^{-1}$. At present, about 35 to 50% of total world lead use is estimated to be met from "secondary" lead, i.e., lead that is recovered from scrap lead products (such as used automobile batteries) and lead-processing and lead-product manufacturing wastes and residues. Thus, diminishing primary lead reserves beyond 2000 may result in greater incentives for secondary lead recycling and for the development of nonconventional resources, such as inferred mineralized sediments, and nodules of the ocean basins and rift zones. Some estimates of these resources are placed as high as 15 x 10^8 Mg.

In summary, adequate titanium supplies appear to be available for the projected period of operation of a Used-Fuel Disposal Centre (2025-2065). The availability of economical supplies of copper and lead in this period is less certain; however, based on future demand projections, incentives to further explore and develop currently uneconomic reserves and to increase recycling are likely to ensure an adequate supply of these materials as well.

3.5.5.12 Cost

As noted in Section 3.5.3.6, safety considerations that could affect the primary mission of the container, i.e., that it must provide at least 500 a of isolation of the used fuel, have been accorded greater significance than container-production costs. However, where different systems employing alternative materials and/or manufacturing and QC procedures can equally achieve the primary objective, relative cost is a valid parameter for system comparison. An example of cost comparison, based on materials costs only, and using a specific candidate container design was prepared by Crosthwaite (1992) and is shown in Table 3-2. This analysis indicates that the cost of the container-shell material, per kilogram of contained uranium, using a copper container would be roughly twice that for disposal using a titanium container.[30]

Materials cost analyses for a copper-shell container employing an inner supportive steel shell similar to the Swedish Advanced Cold Process container design (Section 3.3.3, Figure 3-4) indicate that the cost per kilogram U contained could reach nearly C$18 (Crosthwaite 1992).

For the thin-wall, supported-shell container concepts described in Sections 3.5.2.2 to 3.5.2.4, further cost analyses have been performed, although rigorous cost estimates for each option have not been conducted. To date, the most detailed cost estimate has been produced for only the

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[30] Based on 1992 prices for copper and titanium plate of 25.4-mm and 6.35-mm thickness respectively. The structural strength of the thicker-shell copper container would be roughly equivalent to that of the thinner-shell titanium container.

TABLE 3-2

COSTS OF SHELL MATERIALS FOR TWO CONTAINER DESIGN OPTIONS

Container Design	Cost of Shell Material (C$)	Cost per kg UO_2 Contained[1] (C$)	Cost per kg U Contained[2] (C$)
6.35-mm titanium-shell, packed-particulate container (72 fuel-bundle capacity)	3800	2.45	2.78
25.4-mm copper-shell, packed-particulate container (72 fuel-bundle capacity)	7150	4.62	5.23

[1] Bruce fuel, 21.5 kg UO_2 per bundle
[2] Bruce fuel, 19.0 kg U per bundle

titanium-shell packed-particulate container. Nevertheless, it is possible to provide coarse estimates of the major cost components of all three supported-shell designs and to infer how particular design features would likely affect relative cost.

An analysis of the relative costs of the titanium-shell packed-particulate, structurally supported and metal-matrix containers has been completed by Crosthwaite (in preparation). The analysis considers materials and labour costs, but excludes consideration of the capital costs of equipment required at a used-fuel disposal centre for manufacturing and inspection. However, qualitative analyses are presented for costs that cannot currently be estimated. The results show that, for titanium-shell containers, the least costly would be the packed-particulate design, followed by the structurally supported container (~10% more expensive) and the metal-matrix container (~25% more expensive).

3.5.5.13 Selection of a Reference Container Design for the Used-Fuel Disposal Centre Study

On the basis of demonstrated short-term structural performance, and other factors discussed in Section 3.5.5, the titanium-shell packed-particulate container was selected as the reference design for the engineering study for a conceptual used-fuel disposal centre (Simmons and Baumgartner 1994). Of the three supported-shell container designs, the packed-particulate design appears to be the easiest to manufacture, handle and, if ever required, to retrieve from the disposal vault. It also appears to require the least materials resources and to be the least costly to construct.

Ease of inspection and repair, the degree of self-shielding, the ability to provide an additional barrier to radionuclide release, and internal temperature during disposal appear to be approximately the same for the packed-particulate and structurally supported designs.

The potential for chemically toxic contamination of the biosphere by the container construction materials does not appear to be significant for any of the three candidate container designs.

The metal-matrix design provides greater self-shielding, a lower internal container temperature and an additional barrier to radionuclide release. However, the first two of these factors are not likely to provide significant advantages in the packaging plant at a disposal facility, or in the vault during disposal. While very small temperature gradients can be anticipated through a metal-matrix container, they are not sufficiently steep through particulate-supported containers to warrant concern about thermomechanical stresses.

The principal advantage of the metal-matrix design is its ability to provide an extension to the fuel-isolation period of about 3500 a. However, current analyses (Johnson et al. 1994) show that a titanium-shell container with a wall thickness of 6.35 mm would adequately meet the required 500-a isolation objective, and that extensions of that period by several thousand years would not result in substantial further reductions in the eventual release of very long-lived radionuclides (Cameron 1982, Goodwin et al. 1994). In any case, were it to be determined in some future assessment that an extension of the isolation period provided by the container would be advantageous, comparison of several possible options would be undertaken, including, for example, further increasing the titanium-shell thickness, changing the shell material to copper, or using the metal-matrix design. Therefore, for the performance-assessment case study, the additional barrier provided by the metal-matrix design was an insufficient incentive for its selection as the reference container design.

3.5.6 Selection of the Container-Shell Material and Reference Shell Thickness

As discussed in Section 3.4.2, one corrosion-resistant material, Grade-2 titanium, and one corrosion-allowance material, oxygen-free copper, were selected for detailed evaluation as candidate container-shell materials. The decision to undertake a conceptual design for a disposal centre was made in 1984. As discussed in Sections 3.5.5.2 to 3.5.5.12, the experience gained in constructing prototype titanium-shell containers for the structural-performance studies described in Section 3.5.2, as well as other studies relevant to container fabrication and performance, led to the selection of the packed-particulate container constructed of titanium as the reference design for the Used-Fuel Disposal Centre study. Subsequent corrosion studies confirmed that the minimum container-lifetime target of 500 a would be met with this material, provided container temperatures did not exceed 100°C. This temperature maximum was based on the judgment that crevice corrosion rates might become unacceptably high at temperatures significantly above 100°C. Further discussion of the potential for crevice corrosion in titanium is presented in Section 3.7.4.5.

The specification for wall thickness for the titanium-shell packed-particulate container was based on the results of the following investigations. From initial analyses conducted for the packed-particulate container (Teper 1988, 1992), an evaluation was conducted to determine the minimum residual shell thickness below which it must be assumed that the container would perforate as a result of induced loading stresses under disposal-vault conditions. Analytical results[31] were used to define the criterion that the container would be assumed to fail when the through-wall strain at any location exceeded 5.3%, or when the container shell reached a condition of buckling instability. To determine the residual container-shell thickness below which a through-wall strain of 5.3% or buckling instability might occur, an engineering judgement was first made that this thickness might be about 2 mm. A finite-element structural analysis of a packed-particulate container with a uniform 2-mm-thick shell under 10-MPa uniform external hydrostatic pressure at 100°C (for comparison with the analyses conducted for the prototype tested in the HTF) was then conducted (Teper 1988). This analysis showed that, provided the container was well-packed (i.e., no gap between the top head and the particulate), a shell thickness of 2 mm over the entire container surface would still have sufficient strength to resist reaching a through-wall strain deformation of 5.3% and buckling instability under the container-loading conditions assumed for the analysis. Since the entire container surface could be reduced to a 2-mm thickness and still maintain sufficient structural strength against material failure, the size (i.e., area) of any crevice corrosion patch on the container shell is not a factor in the continuance of the mechanical integrity of the shell, provided the remaining shell thickness within the patch is ≥2 mm.

In summary, for a loading condition on the container of 10-MPa uniform hydrostatic pressure at 100°C, it was calculated that a 2-mm overall shell thickness would not result in mechanical failure of the shell. In fact, this thickness was recognized as likely to be conservative for these specific loading conditions. To maintain this measure of conservatism, the 2-mm thickness was selected as the reference residual thickness of the shell, at which further thinning of the shell by corrosion would be assumed to cause the container to fail by mechanical tearing of the material. In studies subsequent to this analysis, it was determined (see Section 3.4.3.5) that swelling of the buffer surrounding the container during disposal could add a further 1-2.5 MPa pressure on the container. Therefore, the decision to maintain conservatism in the residual-shell thickness specification was clearly justified. Future analysis would be required to determine a more precise residual shell thickness specification for maximum disposal-vault container-loading conditions (~12.5 MPa at 100°C); however, the calculations conducted to date indicate that the original engineering judgment that it would be ~2 mm was correct.

This (2 mm) specification, in conjunction with titanium crevice corrosion rates determined under the vault conditions assumed in the postclosure assessment case study (Johnson et al. 1994), indicates that for a container to meet or exceed a minimum lifetime of 500 a, the initial shell thickness

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[31] See Appendix B.

should be at least 6 mm. For titanium-shell containers manufactured from commercially available plate, the nearest product thickness is 0.25 in. (6.35 mm). Consequently, the reference titanium-shell packed-particulate container thickness was set at 6.35 mm.

3.6 SUMMARY

Sections 3.1 to 3.5 have reviewed the design basis for long-life containers for nuclear fuel waste disposal, drawing on our own research program together with the experience of other countries. In conjunction with concurrent studies of durable materials, it has been concluded that containers appropriate for meeting, and indeed exceeding, the minimum fuel-isolation objective of 500 a can be designed and manufactured. The latter has been demonstrated through the construction of full- and half-scale container prototypes for structural-performance testing.

It has been demonstrated that, with current technologies, a variety of techniques are available to fabricate and inspect containers that would meet the required performance objectives. While improvements in these technologies are virtually certain, and would be welcomed for gains in quality control and/or manufacturing efficiency, they are not essential for fuel-waste container manufacture.

For purposes of conducting an engineering study of a conceptual used-fuel disposal centre, a reference container design has been selected, taking into account the constraints of the study. Reference container selection was based on demonstrated structural performance and considerations relating to manufacturing, handling, resource use and projected performance during disposal.

Flexibility of design and choice of future container options has been demonstrated through the study of several other container concepts. In addition to the designs considered in the program to date, it is recognized that further options could be studied and that the process of developing a container design for actual disposal is one that would continue to be evolutionary.

3.7 THE CORROSION OF POTENTIAL MATERIALS FOR NUCLEAR FUEL WASTE CONTAINERS

3.7.1 Introduction

Since container failure by mechanical overload can be avoided by prudent engineering design and appropriate fabrication and inspection practice (Crosthwaite, in preparation), it is expected that the container lifetime will eventually be limited by corrosion or other localized degradation processes (Nuttall 1983). The corrosion/degradation process most likely to cause container failure will depend on the nature of the container material, the mode of container construction (i.e., location of residual stresses, condition of welds, etc.), and the environment to which the container is exposed.

Materials for engineered structures generally belong to one of two classes: corrosion-allowance or corrosion-resistant materials. The criteria by which materials are assigned to one of these classes and a general description of the differences in their corrosion properties have been given in Section 3.4.2 of this report. Of the candidate container materials, iron, carbon steels and copper can be classed as corrosion-allowance materials, whereas stainless steels, nickel-based alloys and titanium alloys are corrosion-resistant materials.

Great care must be taken when specifying the corrosion performance of materials over exposure periods of hundreds to thousands of years. Predictions of failure times and calculations of required corrosion allowances can be made only with a predictive model based on a sound and generally accepted mechanistic understanding of the corrosion processes involved. The establishment of such understanding requires an extensive experimental and modelling program; the approaches required in such a program have been discussed by Marsh (1988) and Shoesmith et al. (1989).

3.7.2 Disposal Environments

The geological formations being considered for nuclear waste disposal can be divided into three categories: crystalline rock (Canada, Sweden, Switzerland, U.K. and U.S.A.); salt deposits (U.S.A.,[32] Germany, Spain); and sedimentary deposits such as clay (Belgium). Before discussing the corrosion performance of candidate materials, we discuss briefly the various geological formations with respect to the factors likely to control corrosion of the container materials in these media. The discussions of the geochemical conditions in each of these environments are very brief, and the reader is encouraged to examine the references in each section for a more complete discussion of the conditions.

3.7.2.1 Crystalline Rock Environments

The disposal of waste 500 to 1200 m into a crystalline rock formation is an option under consideration in a number of countries. With the exception of the United States Yucca Mountain Project, where disposal would be in a tuff medium in an unsaturated zone above the water table, the proposed vaults would be in granite or granite-like formations, where prolonged contact with groundwater would be unavoidable. The option of disposal in a basalt formation in the United States has been discarded. A brief review of the conditions in the various proposed disposal environments follows. Despite the fact that neither basalt nor tuff environments are realistic options in Canada, corrosion data recorded under these conditions are included for comparative purposes.

Granitic/argillaceous formations

In these formations the containers would be placed in boreholes and backfilled with a series of buffer/backfill layers. The container would be

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[32] Refers to the potential disposal site for transuranic waste near Carlsbad, New Mexico.

subjected to a combination of hydrostatic and clay swelling pressures. Such pressures are expected to range from 10 to 30 MPa.

The groundwaters encountered would be anoxic (Johnson et al. 1994, SKB 1992a). Groundwater chemistry would vary with depth, with sodium and calcium carbonates predominating at shallow depths, and increasing concentrations of chloride and sulphate occurring at greater depths. Descriptions of groundwater compositions (Marsh 1982, Braithwaite 1987, Gascoyne 1988) indicate that chloride concentrations can vary from a few milligrams to many tens of thousands of milligrams per litre. The pH generally ranges from 5 to 9.

Prior to coming into contact with the container, the groundwater would be conditioned by diffusive passage through the buffer and/or backfill materials. The impact of a clay buffer on the composition of groundwater has been considered by a number of authors (Wanner 1987, Oscarson and Dixon 1989, Lemire and Garisto 1989). Apart from transitory increases in the levels of anions, such as sulphate and fluoride, the main impact would be a buffering of pH and a stripping of oxidants by reaction with oxidizable minerals within the buffer and backfill. Consequently, although oxic conditions may prevail initially, as a result of the trapping of oxygen when the vault was sealed, the reestablishment of anoxic conditions would eventually occur. How rapidly this occurred would depend on the amount of oxidizable material present and its rate of reactivity with oxygen trapped in the buffer. For conditions expected in a Canadian vault the time required for anoxic conditions to be established has been conservatively estimated to be ~300 a (Johnson et al. 1994).

Basalt formations

The potential disposal of waste 1000 m deep in the Grand Ronde basalt formation on the Hanford reservation in the U.S.A. has received considerable attention. While disposal at this site is no longer an option under active consideration, much of the corrosion data measured under basalt conditions is valuable in a much wider context. To facilitate discussion of these data, a brief description of basalt conditions is required.

As with crystalline rock formations, it is accepted that a disposal facility in basalt would flood with groundwater within tens to hundreds of years. This groundwater is not expected to be particularly saline ($[Cl^-] \leq 500\ mg \cdot L^{-1}$), and in the unperturbed environment, i.e., prior to excavation of the vault, conditions would be strongly reducing, with a pH ranging from 9 to 10. These elevated pH values are attributed to the hydrolysis of silicate minerals and/or silicate glass (Smith 1980).

Excavation followed by container emplacement and backfilling with a packing made from a mixture of crushed basalt (75 wt.%) and bentonite clay (25 wt.%) would lead to a number of significant changes in the chemical environment around the container. If the waste form to be disposed of was reprocessed high-level waste, temperatures as high as 250°C could be anticipated at the container surface (Braithwaite 1987). Such temperatures would cause a slow alteration of the basalt glass phase to illite and/or smectite clays and quartz. The effect of temperature on the dissociation of silicic acid would lead to a fall in pH to ≤6.0 at 250°C, and the production of sulphide from either dissolved sulphate ($\leq$200 mg$\cdot$L^{-1}) or pyrite could occur.

The redox conditions would be controlled by the geology of the site, and the oxygen trapped in sealing the vault would be consumed by reaction with the packing material and the rock. Data from high-temperature experiments on basalt rock/water and bentonite/water interactions suggest that anoxic conditions would be reestablished by the time groundwater reached the container, after a few hundred years (Smith 1980).

Tuff formations

A disposal facility has been proposed in a tuff formation site under a desert mountain, Yucca Mountain, in southern Nevada. The vault would be located 700 ft. above the water table and 300 to 1200 ft. below the surface of the mountain. The variations in these numbers are a result of variations in mountain topography (Kass 1990a). Such a location, in an unsaturated zone, and because of the fractured character of the tuff, would preclude the waste containers being inundated with groundwater until after their surface temperature fell below ~100°C (i.e., after almost 1000 a). A groundwater infiltration rate of ~5 L$\cdot$a^{-1} per container is considered a very conservative overestimate. However, whether dry or wet, the atmosphere in the vault would remain oxidizing over the lifetime of the containers, since the fractured nature of the tuff would not block the ingress of oxygen.

Initially, when temperatures would be high, corrosion would occur in a dry air atmosphere. As the temperature cooled, the containers would be exposed to moist air, and the impact of gamma radiolysis might produce nitrogen-bearing species, leading to the formation of moist ammonia and/or acidic vapours (Reed et al. 1990). However, since the radiation fields would have decayed to much lower levels (~1 Gy$\cdot$h^{-1}) by the time moist oxidizing conditions were established, such radiolysis effects are not expected to be major. Eventually, the containers would cool sufficiently to allow condensation, dripping, or the flow of water onto their surface (Reed et al. 1990). Under these last conditions, the corrosivity of the groundwater would determine the integrity of the containers. This water, as typified by the samples taken from the J-13 well (Ogard and Kerrisk 1984), has a neutral pH and a low ionic content. Chloride concentrations are not expected to exceed ~10 mg$\cdot$L^{-1} (Kass 1990a), but, because of the possibility of a series of wetting and drying cycles as the temperature cooled, some concentration of groundwater species might occur (Beavers et al. 1992). For this reason, chloride levels up to ~100 mg$\cdot$L^{-1} are considered possible.

3.7.2.2 Salt Deposits

The disposal of waste in salt deposits is an option under consideration in the United States, Spain and Germany. In the United States the Waste Isolation Pilot Plant (WIPP) facility near Carlsbad, New Mexico, is the proposed site for the disposal of transuranic wastes; in Europe, a salt dome at Gorleben in Germany is the proposed site for the disposal of nuclear fuel wastes. Since extensive salt deposits do exist in Canada, they could represent a potentially viable alternative.

Container materials are expected to be resistant to corrosion, provided the salt remained dry. However, dryness is difficult to guarantee, and corrosion in contact with hot brines is the most likely degradation process. According to Westerman et al. (1986), there are two main scenarios by which brine could contact the container in a salt deposit: the intrusion brine scenario and the inclusion brine scenario. While the compositions of brines from individual salt deposits may vary, these scenarios are general for all salt deposits (Westerman et al. 1986, Smailos et al. 1986a). In the first scenario, brine is assumed to form by dissolution of salt in water intruding into the vault. The source of this water could be an aquifer lying just above the salt deposit. Such intrusion brines would reflect the gross composition of the salt deposit and, hence, would be primarily halite-saturated sodium chloride brines. However, the most likely source of brine would be the brine-filled inclusions present in the salt, which could migrate to the container surface under the influence of the thermal gradient existing in the vicinity of each waste package (Westerman et al. 1986).

These inclusion brines exhibit compositions very different from those of intrusion brines because of their ability to concentrate the more soluble species present in the deposit, such as magnesium. Their chloride concentration is very high, in the range from 190 000 to 270 000 $mg \cdot L^{-1}$. The hydrolysis of magnesium, present in inclusion brines (Q-brine and Z-brine in Germany (Smailos et al. 1986a)) at levels up to 85 000 $mg \cdot L^{-1}$, leads to acidification, especially at higher temperatures. At the initial temperatures anticipated for the disposal of reprocessed high-level waste (~250°C in the U.S.A., ~200°C in Germany), pH values as low as 2 are possible.

3.7.2.3 Sedimentary Deposits

Two types of sedimentary deposits have been considered as potential sites for a waste disposal facility; sub-seabed sediments and clay formations. While seabed disposal is no longer an option under consideration, the presence of clay deposits in Canada make these formations potential disposal sites. There are many aspects of disposal in clay that are common to vaults in other formations, where backfilling with clay provides a barrier to radionuclide transport. In Belgium, disposal is being investigated in the Boom clay formation at Mol, and the conceptual design for a repository envisages waste containers placed in holes or galleries excavated out of the clay formation (Casteels et al. 1985). If these holes were lined for stability, the most probable environment contacting the container would be humid air contaminated with volatile organic and inorganic compounds released from the clay.

The composition of this moisture would depend on temperature (Casteels et al. 1980), but would generally include species such as HCl and H_2SO_4, which could produce acidic condensates on the container surface. At higher temperatures ($\geq$150°C), sulphur compounds would be the main products governing the corrosiveness of the atmosphere. The presence of SO_2 in the moisture and gases escaping from the clay would arise mainly from the presence of pyrite in the clay and the chemical reaction of this pyrite with water vapour (Dresselaers et al. 1982).

If the borehole was unlined, corrosion might occur in direct contact with clay. The corrosiveness of this environment would depend on a number of clay characteristics: electrical resistivity, pH, redox conditions, chemical composition, moisture content, and biological activity. Many of these factors have been discussed (Dresselaers et al. 1982, DeBruyn 1990). Under equilibrium clay conditions the pH is around 9 to 10, and redox conditions are reducing. On aeration, however, the pH falls to around 3 at room temperature as a result of the decomposition of carbonates. As demonstrated by DeBruyn (1990), using a combination of Eh and pH measurements, neutral to alkaline reducing conditions are reestablished over a period of a few months.

Finally, it is possible that the containers might come into contact with an aqueous environment caused either by the release of interstitial water from the clay or by the intrusion of water from overlying aquifers present in formations above the clay formation. The interstitial waters present in the Boom clay formation are essentially sulphate-bearing, and the intrusion waters, typified by Antwerpian groundwater, are generally neutral and contain relatively small amounts of anions ($[Cl^-] = 36\ mg \cdot L^{-1}$; $[F^-] = 817\ mg \cdot L^{-1}$; $[HCO_3^-] = 188\ mg \cdot L^{-1}$; $[NO_3^-] = 6\ mg \cdot L^{-1}$).

3.7.3 Factors Controlling Corrosion Processes

To compare the corrosion behaviour of various materials under different vault conditions, it is necessary to discuss the common controlling parameters. These parameters are the redox conditions within the vault, the surface temperature of the container, the presence and concentration of aggressive species within the groundwater or vapour atmosphere, and the structure and properties of the container material.

3.7.3.1 Redox Conditions

Redox conditions within the vault would be determined initially by the air and other oxidants trapped within the buffer/backfill medium. For longer exposure periods, conditions would be controlled by the amount of oxidant transported into the vault either by air flow (tuff) or groundwater transport (other formations) and by the products of water radiolysis. For sealed vaults in deep saturated geological formations, the transport of oxidant into the vault would not be significant, and the original slug of trapped oxidant would be consumed, at least partially, by reaction with oxidizable minerals within the buffer/backfill. Thus, conditions within the vault would eventually become anoxic if it were not for the effects of water radiolysis.

The concentration of oxidants produced radiolytically would be determined by the dose rate of gamma radiation to the environment. Other forms of radiation (alpha, beta) would not penetrate the container. The gamma dose rate would be determined by the concentration and decay rate of the various radioisotopes within the waste form and would be attenuated by the presence of packing materials within the container as well as by the nature and thickness of the container wall. For high-level reprocessing waste encapsulated in glass, the radioisotope inventory would be determined by the age of the waste and the amount loaded into the glass. For used fuel, it would be determined by the type of fuel, its power rating and extent of in-reactor burnup, and the length of time since it was discharged from the reactor.

For a given type of waste (used fuel or high-level reprocessed waste) the maximum radiation dose rate would be lower for containers constructed from thick-walled corrosion-allowance materials and higher for containers constructed from thin-walled corrosion-resistant materials. Thus, dose rates <0.5 Gy·h^{-1} are expected for the Swedish thick-walled copper (6 cm) container (used fuel) (Lundgren 1982) and the Swiss shielded cast-shell (15 cm) container (high-level reprocessed waste) (Knecht and McCombie 1990). By contrast, the 0.64-cm-thick Grade-12 titanium container (high-level reprocessed waste) tested in the VIPP project would allow a maximum dose rate of close to 10^3 Gy·h^{-1}. In relation to these values it should be noted that the maximum dose rate at the surface of the Canadian reference container (used fuel) is expected to be ~50 Gy·h^{-1} (Johnson et al. 1994). This container is constructed from ASTM Grade-2 titanium (wall thickness 6.35 mm) and is filled with a packed particulate (Section 3.5.2.2).

3.7.3.2 Temperature

The decay of radionuclides produces significant amounts of heat; this would lead to an initial increase and subsequent decrease in the surface temperature of the containers. The maximum temperatures achieved, and their decrease with time, would be controlled by (i) the activity levels within the waste form; (ii) the thermal conductivities and diffusivities of the surrounding buffer, backfill and geological materials; and (iii) the geometry of emplacement of containers within the vault.

3.7.3.3 Groundwater Composition

Given the wide variety of proposed disposal environments internationally, it is not surprising that groundwater compositions would be substantially different for the various proposed disposal-facility concepts. The groundwater constituent of most concern is probably chloride ion, since this is one of the most aggressive in initiating localized corrosion. However, any groundwater species directly involved in the corrosion process could adversely affect the corrosion rate, either by accelerating active dissolution or by causing passivation and leaving the material potentially susceptible to localized corrosion processes.

3.7.3.4 Comparison of Vault Corrosivities

Often a material's vulnerability to various corrosion processes can be expressed in terms of two summary diagrams: (i) a potential-pH diagram, which summarizes the redox conditions under which a material may be subject to active or localized corrosion processes; and (ii) a susceptibility diagram, which plots the combination of temperatures and chloride concentrations under which a material is susceptible to a specific localized corrosion process. Since the redox conditions for most vault scenarios are not well defined, it is difficult to compare vault environments in terms of redox condition and pH; one can only say that, with the exception of tuff environments, most would eventually be anoxic. However, it is possible to produce a comparative susceptibility diagram. In Figure 3-30, the range of chloride concentrations anticipated in the various proposed disposal facilities are plotted against the range of container-surface temperatures for the associated waste-form packages. The chloride concentration ranges for each environment represent the ranges obtained by analysis of groundwater samples or reported as being achievable as a result of concentration processes. The temperature ranges represent the range from the maximum temperature, achieved for most waste packages after a few years, to that after ~1000 a of disposal. Susceptibility to localized corrosion is expected to increase from the bottom left-hand to the top right-hand corner of Figure 3-30. This is based on the general observation that the initiation of localized corrosion occurs at lower temperatures for higher chloride concentrations. Uniform-corrosion processes might be expected to be more dependent on temperature than on chloride concentration. From this diagram, the wide range of temperatures and salinities for the various disposal concepts is evident. Of the granitic environments (4 to 7 in Figure 3-30), the anticipated Canadian environment is potentially the most corrosive, with maximum salinities close to those in sea sediments (8, Figure 3-30). The relatively benign nature of clay environments (2, Figure 3-30) and the extreme aggressiveness of salt deposits are also clearly apparent in this diagram.

3.7.4 Container Materials

A wide variety of metals and alloys have been studied as potential container materials. For the purposes of comparison they can be divided into the following categories: iron and carbon steels, copper and copper alloys, stainless steels, nickel-based alloys, and titanium and titanium alloys. In the following sections we review the work done in each of these categories. In many cases the studies are incomplete, and modelling, where attempted, has often been very rudimentary and based on simple extrapolations of corrosion rates measured over short exposure periods.

3.7.4.1 Iron and Carbon Steels

Thermodynamically, iron is unstable in water and its corrosion in a vault would involve (i) the coupling of metal dissolution with one or a combination of the cathodic reactions; (ii) proton reduction, water reduction; or (iii) the reduction of dissolved oxidant (e.g., oxygen). Hence, the corrosion of irons and steels would proceed at a rate determined by, among other factors, the pH and redox conditions within a vault. Over the relevant pH range (5 to 9), iron would react directly with oxygen-free water to produce either Fe^{2+} or $Fe(OH)_2$. At temperatures above approximately 60°C, Fe_3O_4 as opposed to $Fe(OH)_2$ is the expected corrosion product.

The impact of oxygen on the corrosion rate is difficult to predict and would depend on the composition of the exposure environment. Generally, oxygen accelerates corrosion under aggressive conditions (acidic, active), but induces passivation in environments where the ratio of passivating to aggressive ions is favourable. The latter effect is favoured in environments containing passivating ions, such as borate, phosphate and carbonate. A more detailed review of the uniform-corrosion properties of iron has been given by Marsh and Taylor (1988).

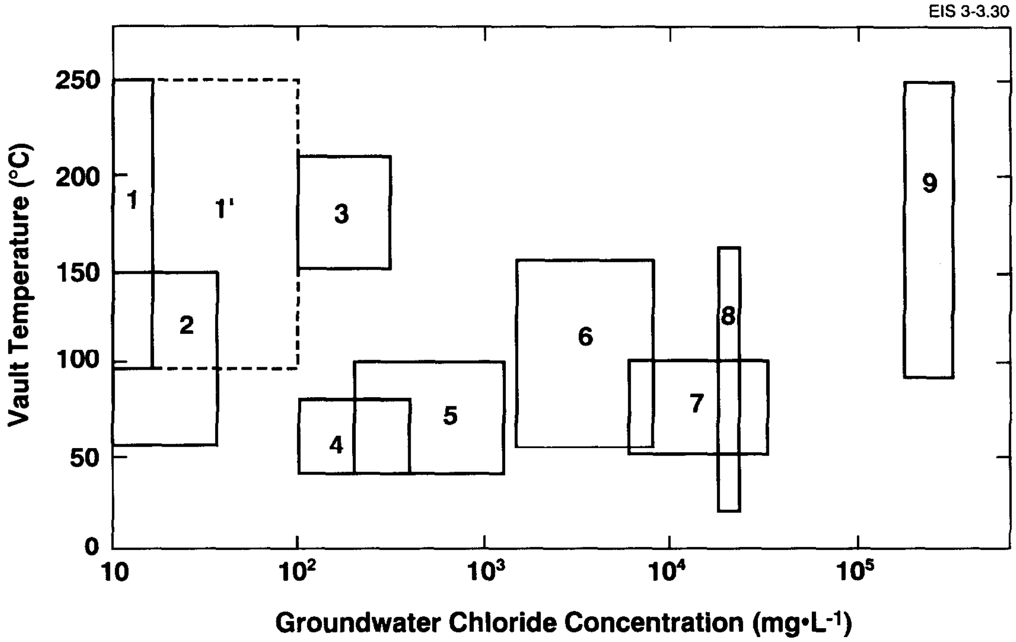

FIGURE 3-30: The Range of Chloride Concentrations Anticipated in Various Waste Vaults as a Function of the Container-Surface Temperatures for the Associated Waste-Form Packages.
1 - Tuff (U.S.A.) (Ogard and Kerrisk 1984, Stahl 1990);
1'- tuff with groundwater concentrated by a factor of 10;
2 - clay (Belgium) (Casteels et al. 1980);
3 - basalt (U.S.A.) (Brehm 1990b, Braithwaite 1987);
4 - granite (Sweden) (SKBF/SKB 1983);
5 - granite (U.K.) (Marsh et al. 1983);
6 - granite (Switzerland) (NAGRA 1984);
7 - granite (Canada) (Shoesmith et al., in press);
8 - sea sediment (Braithwaite and Molecke 1980, Marsh et al. 1987a);
9 - salt (U.S.A., Germany) (Braithwaite 1987, Smailos et al. 1986a).

Since iron and steels are corrosion-allowance materials, the required wall thickness for containers is expected to be large, making the relative cheapness and ease of fabrication of these materials major advantages. A further advantage is provided by the large database of published information on their corrosion under a wide variety of conditions.

The irons and steels tested as potential container materials can be divided into a number of categories:

1. Carbon steels, either as-cast or forged. They possess simple microstructures, well-characterized corrosion properties and are

easy to fabricate. The carbon content is generally low (<2%), and other elements are generally present as only minor impurities (<1%).

2. Cast irons. These materials contain more than 2% carbon and 1% silicon. Their low material costs and ease of manufacture make them the least expensive engineering material. The microstructures of cast irons are generally more complex than those of steels, and the silicon content controls, to a large extent, the fate of carbon. When the silicon content is low, iron carbides form, whereas at high silicon contents the carbon separates as graphite nodules. The presence of graphite or carbides does not generally exert a big effect on the corrosion resistance, although graphite may act cathodically with regard to the metal matrix.

3. Alloyed cast irons. Silicon, at levels between 3 and 14%, is the most important alloying element used to improve the corrosion resistance of cast irons; it promotes the formation of strongly adherent surface films. Formation of such films requires time, and, consequently, initial corrosion rates are often high. For high silicon contents (approaching 14%) there is a risk of low strength and ductility. High-silicon cast irons are the most universally corrosion-resistant alloys available at moderate cost.

4. Low-alloy steels. These steels exhibit mechanical properties superior to those of ordinary (unalloyed) carbon steels as a result of the addition of alloying elements, such as chromium, nickel and molybdenum. Total alloy content can range from 0.5 to 1% up to levels just below those of stainless steels (iron-based alloys containing ≥10.5% chromium). These alloying additions enhance corrosion resistance in moderately corrosive environments, but in severe environments the alloys seldom function better than the ordinary carbon steels. The higher the alloy content the more susceptible the steel becomes to localized corrosion. The 2Cr1Mo and 9Cr1Mo low-alloy steels have received most attention as candidate container materials.

Uniform corrosion

The corrosion of several of these iron-based materials has been studied under a wide range of vault conditions. Many of these studies must be considered incomplete since either the exposure periods were too short to establish a steady-state corrosion rate value, or there are insufficient data as a function of time to determine the form of the corrosion kinetics or the impact of specific factors on the rate. In the following discussion, corrosion rates are generally compared at a temperature of 80 to 100°C, a temperature range covering the anticipated maximum surface temperatures of containers in a Canadian vault. With the exception of tuff conditions, vault environments are expected to be reducing, or at least anoxic. Under these conditions, corrosion would be supported by the reduction of water. With two exceptions, the corrosion rates for anoxic conditions are in the range from 1.7 to 14.6 $\mu m \cdot a^{-1}$; Simpson (1984) and Knecht and McCombie (1990) have assumed 10 $\mu m \cdot a^{-1}$ to be a conservative rate for the granitic conditions expected in a Swiss waste vault.

Corrosion rates (for reducing conditions) outside this range are either for synthetic groundwaters typical of granitic conditions in the U.K. (Marsh et al. 1986a), where rates as low as 0.1 $\mu m \cdot a^{-1}$ are obtained, or for exposure to inclusion brines containing large concentrations of Mg^{2+}, where rates >30 $\mu m \cdot a^{-1}$ were obtained (Smailos et al. 1986b, 1988, 1989; Schmitt et al. 1984). The very low rates obtained in granitic waters may be attributable to the low ionic strength of these waters; the concentration of anions likely to form protective films (e.g., HCO_3^-) is well in excess of the concentration of aggressive anions such as Cl^-. The presence of large concentrations of Mg^{2+} in inclusion brines causes both a decrease in pH as the temperature increases and a change in composition and structure of the corrosion-product film. Both of these factors could contribute to the higher corrosion rates. In the absence of a significant concentration of Mg^{2+}, concentrated brines are no more corrosive than the much less saline granitic and basaltic waters.

Corrosion rates increase with increases in oxygen concentration. These increases are moderate under granitic conditions (Simpson 1984) and in intrusion brines (Westerman et al. 1986). In the latter case the increase is only a factor of two or less for a thirtyfold increase in dissolved oxygen concentration. Under basaltic conditions at 150°C the corrosion rate decreases by approximately a factor of nine when the basalt/bentonite packing is introduced. This decrease can be attributed to the decrease in oxygen concentration as a result of its reaction with oxidizable species in the packing.

Of particular interest for Canadian conditions is the behaviour in clay. For carbon steel in direct contact with clay, Debruyn et al. (1991) obtained a corrosion rate of 7.7 ± 0.8 $\mu m \cdot a^{-1}$ (at 90°C). In these experiments the redox conditions were uncertain, but the observation of only Fe^{III}-containing corrosion products (γ-$Fe_2O_3 \cdot 2H_2O$) indicated that corrosion had occurred predominantly under oxidizing conditions. Once anoxic conditions had been reestablished, by reaction of oxygen with oxidizable species in the clay, much lower corrosion rates were obtained (~0.2 $\mu m \cdot a^{-1}$). Unfortunately, this last value was recorded at ambient temperature. Rates of 10 to 30 $\mu m \cdot a^{-1}$ were obtained by Honda et al. (1991) for carbon steel in aerated compacted bentonite saturated with synthetic seawater.

Consistent with the results of previous studies of corrosion behaviour (Metals Handbook 1987), the corrosion rates of low-alloyed steels and steels with high silicon content are lower than the rates for carbon steels and cast irons. This is true for clay, basaltic, intrusion brine, and oxidizing tuff environments. For a significant benefit of alloying to be achieved, the silicon and chromium contents need to be up to, or in excess of, ~15% and 9% respectively. At these alloying levels it is likely the materials function as film-covered, corrosion-resistant materials. By contrast, the differences in corrosion rates between cast and forged steels (Marsh et al. 1983) under granitic conditions, carbon steels with various carbon contents under basaltic conditions (Anantatmula et al. 1984), and as-cast and heat-treated mild steels (i.e., low carbon) in brines (Haberman et al. 1988) are insignificant. These marginal differences for various materials suggest that the interfacial and microstructural characteristics of these materials are not particularly important in determining uniform corrosion rates.

Apart from the general insensitivity of corrosion rates to microstructure and exposure environment, two other observations suggest that the buildup of corrosion products inhibits and eventually controls the corrosion rate: (i) the corrosion rates decrease markedly with time; and (ii) the rates do not increase substantially with temperature, and in the one environment in which they do (inclusion brines) (Westerman et al. 1986; Smailos et al. 1986b, 1988, 1989; Schmitt et al. 1984) the increase has been attributed to changes in the nature and protectiveness of the corrosion-product film. In many environments, particularly granitic (Simpson 1984) and basaltic (Brehm 1990a), the corrosion rates decrease at temperatures in excess of 100°C. For corrosion in compacted bentonite (Honda et al. 1991) the rate at 180°C was only two to three times the rate at 50°C. The films formed at low temperatures tend to be amorphous, clay-like and iron-containing compared with the more protective crystalline iron oxides (particularly magnetite) formed at higher temperatures. Also, the greater corrosivity of inclusion brines (high Mg^{2+}) compared with intrusion brines (low Mg^{2+}) (Westerman et al. 1986, Smailos et al. 1986a) has been attributed to the inhibition of magnetite formation in the presence of high Mg^{2+} concentrations (Westerman et al. 1986). The presence of clay and/or clay-like corrosion-product layers appears to lead to control of the corrosion reaction by transport of oxygen or dissolved iron. Thus, Honda et al. (1991) attribute a decrease in the corrosion rate with an increase in compaction density of bentonite to a decrease in the transport rate of oxygen to the corroding surface. Debruyn et al. (1991) and Miwa et al. (1992) observed concentration gradients for iron in the contacting clay. If transport in the corrosion product or surrounding clay layers is controlling the corrosion rate, then the observed insensitivity of corrosion rates to the microstructure of the materials is to be expected.

One supply of oxidant, available irrespective of the behaviour of the clay, is that produced radiolytically. The impact of radiation has invariably been studied under overtest conditions, i.e., at dose rates in excess of the maximum expected dose rate of 1 to 10^3 $Gy \cdot h^{-1}$ (see Section 3.7.3.1), and the corrosion rates generally increase (Marsh and Taylor 1988, Nelson et al. 1984, McCright and Weiss 1985, Westerman et al. 1982). An exception to this general rule is provided by the results of DeBruyn et al. (1991) who observed a decrease in rate for carbon steel in interstitial clay water (90°C) (free water equilibrated with oxidized clay) irradiated at 10^3 $Gy \cdot h^{-1}$. Studies on the impact of irradiation dose rate have been undertaken for corrosion in brines (Westerman et al. 1986, Smailos et al. 1986a) and in deaerated seawater (Marsh et al. 1983). For intrusion brines (low $[Mg^{2+}]$) at 150°C a significant impact of irradiation is observed at 10^3 $Gy \cdot h^{-1}$, whereas the effect of a dose rate of 20 $Gy \cdot h^{-1}$ is marginal, suggesting that dose rates lower than this value should exert no significant effect on the uniform-corrosion rate. Marsh et al. (1983) have observed similar increases in corrosion rates in deaerated seawater (at 90°C) in the presence of irradiation. For the highest dose rate

(1.5×10^3 Gy·h^{-1}), the corrosion rate is up to 15 times higher than in the absence of irradiation, whereas at the smallest dose rate (3 Gy·h^{-1}) the increase is barely discernible. These increases in corrosion rate cannot be solely accounted for by the production of oxidizing species, and Marsh has speculated that an irradiation-induced change in film morphology and protectiveness may also occur. It is possible that the decrease in corrosion rate observed by Debruyn et al. (1991) is attributable to the predominance of sulphate, as opposed to chloride, in his solutions (Haijtink 1985).

From these results we can conclude that a dose rate of ~3 Gy·h^{-1} represents a threshold value for an observable impact of irradiation on the corrosion of irons and carbon steels. Below this dose rate the effect on uniform corrosion is negligible. Thus, even for thin-walled containers with high initial dose rates, any effect of irradiation is unlikely to persist beyond 200 to 300 a, after which dose rates will be below this threshold value of ~3 Gy·h^{-1}.

Marsh and co-workers (Marsh et al. 1986a, Marsh and Taylor 1988, and Marsh 1990) have produced a model to predict the uniform-corrosion rates of carbon steels and, hence, to calculate the corrosion allowance required to give container lifetimes of 500 to 1000 a. The model is one-dimensional in form and considers the surface reaction rates and mass transport of reactants (O_2, H_2O, CO_3^{2-}, HCO_3^-, etc.) and corrosion products (Fe^{2+}, $Fe(OH)_2$, $FeCO_3$, H_2) for a carbon-steel surface contacting a low-permeability backfill.

Iron dissolution (as Fe^{II}) is assumed in the model to be activation-controlled and represented by a Butler-Volmer relationship, the standard equation relating reaction current to applied potential. Corrosion is driven by the cathodic reduction of water, the reduction of oxygen having been shown to be a transitory negligible effect. The groundwater flow in the surrounding rock is considered sufficient to maintain a constant concentration of reactants at the rock/backfill interface. The rate of reduction of radiolytically produced oxidants is assumed to be controlled by their rate of formation. A "worst case" estimate of the G-value equal to 2.8, based on tests in seawater, was used. This G-value is the yield of radiolytic species produced for each 100 eV of radiation energy absorbed and is estimated by assuming that the increase in corrosion rate over the corresponding inactive value is due solely to these species. An initial dose rate of 10 Gy·h^{-1}, attenuated by a container wall thickness of 100 mm and decaying with a half-life of 30 a, was assumed.

The electrochemical parameters required to evaluate the Butler-Volmer relationships were determined in 3% NaCl solution under conditions where the metal surface was bare. Consequently, the model does not take into account the experimentally observed retardation of corrosion resulting from the buildup of a corrosion-product film. Marsh is also of the opinion that their model overestimates corrosion rates, since it does not take into account the retarding effect of the accumulation of hydrogen at the container/backfill interface. Such a buildup would be expected to polarize the water reduction cathodic reaction and to suppress the radiolytic generation of oxidizing species.

Using the mean values of corrosion rate (obtained using mean values of the input parameters) gives calculated values ranging from 14.8 $\mu m \cdot a^{-1}$ at 20°C to 96.9 $\mu m \cdot a^{-1}$ at 90°C; the equivalent measured values are 2.1 to 2.2 (20°C) and 16.8 to 21.6 $\mu m \cdot a^{-1}$ (90°C). These values should be compared with the corrosion rate of 10 $\mu m \cdot a^{-1}$ used by the Swiss (Knecht and McCombie 1990) in calculating the required corrosion allowance for their container design. Their value of 10 $\mu m \cdot a^{-1}$ was a "conservative" value based on experimental measurements of corrosion rate.

Pitting

A literature survey by Marsh et al. (1986a) showed that pitting was possible in oxygenated environments. Using electrochemical methods they demonstrated the conditions under which carbon steels were susceptible to pitting and determined the rates of pit growth. By constructing a series of experimentally derived potential-pH diagrams, they showed that only saline waters with relatively high carbonate contents were likely to cause passivation and, hence, leave the material susceptible to localized corrosion (Marsh et al. 1986b, Marsh 1990). High-carbonate groundwaters are more likely at shallow disposal depths, or in groundwaters with relatively low salinities, such as those encountered in U.K. granitic groundwaters, or in clays (see Figure 3-30). For the more saline groundwaters with relatively low carbonate concentrations encountered in the Canadian Shield, such passive conditions appear unlikely.

Using the maximum pit depths obtained under electrochemical conditions (constant potential), Marsh (1990) and Marsh et al. (1983, 1986a, 1987b, 1988a) applied the extreme-value statistical analysis developed by Gumbel (1958) to predict the maximum penetration depth on an area equivalent to that of a container surface. According to this prediction a maximum penetration by pitting of 200 mm is to be expected in 1000 a.

Subsequently, Marsh (1990) and Marsh et al. (1987c, 1988a,b) produced a more realistic prediction of penetration. Since, for most vault environments there would be sufficient oxygen to maintain passivity for a limited time only, pitting would be limited to the period before the oxygen supply falls below that required to sustain the passive film. For the case of a tunnel-type disposal vault of the Swedish KBS[33] design (Marsh 1990), where the container is surrounded by a bentonite buffer similar to that proposed for a Canadian vault, they predicted that localized corrosion could be maintained for only about 125 a. Hence, extrapolation of pit growth rates need only encompass this period, not the 1000 a previously considered.

Using the full population of pit depths obtained in his electrochemical experiments, Marsh (1990) analyzed the pit size distribution statistically by attempting to fit these pit depths to a number of established statistical distribution functions. A maximum penetration of 160 mm was predicted, but, surprisingly, the data fitted an unlimited exponential distribution function, suggesting that very deep pits are a distinct possibility.

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[33] Kärnbränslesäkerhet (Swedish Nuclear Fuel Safety Project, sponsored by Swedish Nuclear Fuel Supply Company (SKBF))

Beavers et al. (1987) consider such a pit depth distribution to be an artifact of the electrochemical method used to grow the pits, and Beavers and Thompson (1987) have experimental evidence to show that the broadening of propagating pits would eventually lead to the degeneration of pitting into rough uniform corrosion.

The problems inherent in the use of electrochemical methods to grow pits are apparent when one compares the results of Marsh (1990) and Akashi et al. (1990). By using constant-potential conditions in his pit growth experiments, Marsh (1990) allowed the growing pits to draw sufficient electrochemical current to maintain indefinite growth. This is equivalent to allowing an unlimited supply of oxygen. This approach is clearly conservative since, under natural corrosion conditions, many factors, but especially a limited supply of oxygen, will limit pit growth. Using constant current conditions in electrochemical experiments, Akashi et al. (1990) attempted to simulate the localized corrosion of carbon steel for a condition of a constant rate of consumption of oxygen. They assumed that the amount of available oxygen was limited to that trapped around a container placed in its own borehole. Using a Gumbel distribution function they calculated a maximum penetration depth of 2.2 mm for a total population of 20 000 containers after 1000 a of emplacement. The value of this calculation is unclear, since corrosion supported by the reduction of water and the radiolytic production of oxidants is ignored. However, the contrast between the two predictions (160 mm and 2.2 mm) is a good indication of the conservatism inherent in Marsh's prediction.

Despite this conservatism, Marsh's prediction is the best available; he estimates a probability of 10^{-6} that any pit would exceed this calculated maximum value of 160 mm. More sophisticated modelling approaches to pitting have been undertaken but are still some way from meaningful predictions of container penetration rates (Sharland 1987, 1988; Marsh et al. 1986b).

Determination of corrosion allowance

To determine the required corrosion allowance it is necessary to consider both uniform corrosion and pitting. Over the estimated 125-a period of passivity, uniform corrosion would be negligible. If a containment period of 1000 a is essential, then a corrosion allowance in addition to the 160 mm needed to avoid failure by pitting in the first ~125 a is required. This allowance must guarantee that general corrosion would not cause the container to fail over the subsequent 875 a. Using his uniform-corrosion model for a temperature of 50°C (a time-averaged value for a U.K.-designed vault), Marsh (1990) calculated that an additional allowance of 227 mm would be necessary. Both these allowances are conservative, since the inhibiting effects of corrosion-product buildup are ignored and pit growth rates measured electrochemically allow continuous unlimited growth.

Most other attempts to calculate corrosion allowances include the inhibiting effect of corrosion-product buildup, since they are based on measured corrosion rates assumed to remain constant over the required container lifetime of 1000 a. The calculations are based on short-term measurements ranging from a few months to a year or two, and the continued buildup of corrosion product could lead to even lower rates after more extensive exposure periods.

Thus, Knecht and McCombie (1990) adopted a corrosion allowance of 50 mm for the Swiss reference container. This estimate was based on the assumption that the container would experience only uniform corrosion at a rate no greater than 10 $\mu m \cdot a^{-1}$. This rate represents the upper limit of corrosion rate measurements made over a period of a year or two under simulated vault conditions (NAGRA 1984).

Corrosion allowances under brine conditions are difficult to estimate. The measured corrosion rates vary markedly depending on temperature, brine composition (particularly the Mg^{2+} content) and radiation dose rates. If one accepts the rates measured by Smailos et al. (1986a, 1988, 1989) and Schmitt et al. (1984) for cast steels exposed to Q-brines (~27 wt.% $MgCl_2$) in the absence of irradiation, then corrosion allowances of ~30 mm (90°C) to 100 mm (170°C) are required for the containers to survive 1000 a. In the presence of a gamma-irradiation dose rate of 10^3 $Gy \cdot h^{-1}$, the corrosion rates are up to a factor of seven greater. However, for thick containers such dose rates are likely to be highly attenuated and it is unlikely corrosion allowances of up to 700 mm would be required.

Tests performed in WIPP salt brines (Westerman et al. 1986) indicate that corrosion allowances (for 1000 a) of 100 to 200 mm (90°C) and 1000 to 2000 mm (150°C) are required for containers to be protected against exposure to inclusion brines (up to 48 000 $mg \cdot L^{-1}$ Mg^{2+}). If exposure only to intrusion brines low in magnesium content is considered, corrosion allowances in the range from 15 to 25 mm would be sufficient. It does not seem reasonable to contemplate the construction of containers over 1000 mm in wall thickness. Under hot brine conditions it would appear more sensible to think in terms of a dual-wall container, with an outer shell of a material known to be corrosion-resistant to such environments. The philosophy behind the design of dual-walled containers has been outlined by Stahl (1990), primarily in relation to waste disposal in a tuff environment. In the German program, a dual-wall container utilizing a corrosion-resistant layer of Hastelloy C4 on a steel substructure (the POLLUX cask, see Section 3.3.2) has been designed for disposal in salt deposits where exposure to magnesium-containing brines (Q-brines) is anticipated (Einfeld and Popp 1988).

Stress corrosion cracking

Stress corrosion cracking (SCC) presents a particular problem because its rate of propagation is so fast it is not feasible to specify a corrosion allowance. According to Marsh et al. (1986a) and Marsh and Taylor (1988) it is necessary to demonstrate either (a) that the disposal environment would not promote this form of attack, or (b) that containers could be made effectively immune to the process. Different approaches have been taken by different investigators.

Marsh considers the challenge of proving that carbon steels would not fail by SCC under vault environments to be extremely difficult, because SCC agents might concentrate at susceptible sites on the container surface.

Consequently, he has concentrated on determining threshold stresses below which SCC cannot occur, and using these results as a basis for specifying stress-relief heat treatments to reduce the fabrication stresses to below this threshold.

On the basis of stress corrosion tests conducted by Parkins (1985) in sodium carbonate/bicarbonate solutions (a well-known SCC environment), a stress-relief heat treatment that reduced fabrication stresses to ~50% of the yield stress was deemed adequate to render a carbon steel container immune to SCC. Kass (1990b) has expressed doubts that such a procedure would be adequate. However, a thorough review of the factors that influence SCC, conducted by Beavers et al. (1984), justified Marsh's approach, concluding that stresses approaching yield are generally required for cracking to initiate, even where cracking agents are present at high concentrations. They concluded that an extensive experimental and modelling program would be required to assess the likelihood of SCC in waste disposal vault environments. The limited testing programs in bulk environments, such as those conducted for steels in brines (Pitman 1987, Westerman et al. 1986, Simpson 1989), are inconclusive. The prospect of successfully conducting such an extensive program is remote, justifying the efficacy of Marsh's approach.

Hydrogen production

In most assessments carried out to date, the effects of hydrogen production in a sealed waste disposal vault have received surprisingly little attention. Since uniform corrosion is expected to proceed under anoxic conditions, supported by water reduction, substantial amounts of hydrogen could be formed throughout the life of the vault. There are a number of potential consequences of such hydrogen production:

1. Embrittlement of the container could lead to its unpredictable early failure.

2. The buildup of a hydrogen pressure at the corroding surface could polarize the water reduction reaction, thereby decreasing the corrosion rate.

3. The hydrogen pressures could exceed the confining stress of the surrounding rock, leading to unpredictable physical changes in the vault structure.

Of these possible effects, only embrittlement has received much attention. Marsh and Taylor (1988) have calculated the fugacity of hydrogen required to bring the reaction

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2$$

to equilibrium at the container surface. From relationships between hydrogen partial pressure and the solubility of hydrogen in iron, they calculated that the maximum amount of hydrogen in iron even at 100°C would be only a fraction of a microgram per gram. The hydrogen embrittlement of iron has been studied extensively, and such modest hydrogen concentrations would be insufficient to cause embrittlement.

That relatively small amounts of hydrogen are absorbed by steels under vault corrosion conditions was demonstrated by Beavers et al. (1987), who determined the hydrogen contents of as-cast and wrought steels exposed to simulated basaltic groundwaters at 250°C. Even at such a high temperature the wrought steels absorbed only ~0.5 $\mu g \cdot g^{-1}$, compared with ~3 $\mu g \cdot g^{-1}$ for the as-cast steel. All of this hydrogen was picked up in the early stages of exposure, suggesting that an "equilibrium" level of hydrogen was rapidly achieved.

The effect of hydrogen overpressures on the corrosion of carbon steel has been studied in solutions expected in cementitious environments. Under active anaerobic conditions, Naish et al. (1991) observed a decrease in corrosion rate as the hydrogen overpressure increased (by a factor of 4 between 1 and 80 kPa). A similar decrease can be expected under high-level-waste disposal conditions. It remains to be demonstrated whether the active corrosion of steel would stop once the equilibrium pressure of hydrogen was achieved. Grauer et al. (1991) have measured the rate of hydrogen production in solutions typical of those expected in a Swiss waste vault (see Figure 3-30) as well as in solutions simulating cementitious environments. So far, the implications of a buildup in hydrogen pressure have not been rigorously analyzed in the Swiss program.

The hydrogen pressures achievable around a corroding steel container would be very dependent on the permeabilities of the surrounding buffer/backfill and rock materials. For deep disposal vaults the use of low-permeability materials, such as compacted bentonite clay, make it likely that substantial hydrogen pressures would build up. Using available thermodynamic data for the iron/water reaction and data for permeability of clays, Neretnieks (1985) calculated that equilibrium hydrogen pressures up to 1000 atm (101 MPa) could be expected. These calculations were made for corrosion rates ranging from 0.03 to 0.8 $\mu m \cdot a^{-1}$, values generally much lower than those anticipated. According to Neretnieks, such pressures are high enough for the formation of a capillary breaking layer that would stop corrosion by preventing water from contacting the iron.

Microbial corrosion

An assessment of the potential effects of microbial corrosion has been given by Marsh et al. (1986a, 1988a). Because of the lack of organic carbon in a deep granitic rock environment and the presence of high temperatures and radiation fields, they concluded that such effects are not likely to be significant. Even when all the most pessimistic assumptions are made, the total decrease in container wall thickness would be only ~13 mm. This calculation is based on an oversimplification of the activity of sulphate-reducing bacteria within a vault and, hence, is very conservative. Oscarson et al. (1986a), and more recently Stroes-Gascoyne and West (1994), have also concluded that microbial action within a waste disposal vault would be unlikely to adversely affect its performance.

Corrosion under Canadian vault conditions

The groundwaters expected in a Canadian vault could range from those that are relatively low in salinity, and therefore similar to other granitic waters, to those that are very saline, and hence similar to the brines encountered in salt deposits (Figure 3-30). However, even the most saline Canadian groundwaters contain no significant amounts of magnesium, and hence the high uniform-corrosion rates observed in inclusion brines are very unlikely under Canadian conditions, particularly since vault temperatures are not expected to exceed ~95°C. The very low rates of uniform corrosion observed by Marsh and Taylor (1988) (~0.1 $\mu m \cdot a^{-1}$) in low-chloride, high-carbonate groundwaters are unlikely under Canadian vault conditions, since groundwaters are high in chloride and low in carbonate and will not produce the passive surface films that probably accounted for these low rates.

With the exception of these two situations (high Mg^{2+} and passive surfaces), the corrosion rates under anoxic conditions similar to those expected to be rapidly established in a Canadian vault are from 1.7 to 14.6 $\mu m \cdot a^{-1}$ and are independent of chloride concentration. Lower rates are possible under anoxic conditions in compacted clay, but no appropriate measured values are currently available. If a dose rate of ~3 $Gy \cdot h^{-1}$ can be considered a threshold below which the effect of radiation on uniform corrosion is negligible, then any acceleration of corrosion due to radiolysis effects would likely be minor and short-lived under Canadian vault conditions, where dose rates would be <1 $Gy \cdot h^{-1}$ after ~100 a. For these reasons we would expect the corrosion rates to fall within this range of 1.7 to 14.6 $\mu m \cdot a^{-1}$.

The generally high chloride concentrations, coupled with relatively low concentrations of passivating anions in Canadian groundwaters, would maintain active conditions as opposed to the passive conditions required to sustain pitting. If pitting were to occur it would be more likely under less saline conditions, such as those in the Canadian reference groundwater, WRA-500, than in the more saline standard Canadian Shield saline solution (SCSSS).[34] In view of the results of Simpson and Vallotton (1986) on pitting in sulphate/chloride solutions, it is unlikely that the sulphate concentrations encountered in Canadian groundwaters would be sufficient to produce pitting conditions.

Consequently, it would be appropriate to apply the model developed by Marsh (1990) for predicting uniform-corrosion rates. Since the electrochemical parameters used in this model were measured in 3% NaCl they are appropriate for Canadian saline conditions. Application of this model would be conservative, as it was for U.K. conditions, because both the buildup of

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[34] The complete compositions of WRA-500 and the synthetic granitic groundwater designated SCSSS are given in Table 3-1a of Johnson et al. (1994). For the present discussion only the major anion concentrations are relevant. The respective concentrations of chloride, sulphate and bicarbonate in WRA-500 are 6000 $mg \cdot L^{-1}$, 1000 $mg \cdot L^{-1}$ and 50 $mg \cdot L^{-1}$, compared with 34 260 $mg \cdot L^{-1}$, 790 $mg \cdot L^{-1}$ and 10 $mg \cdot L^{-1}$ in SCSSS.

corrosion-product films and the polarizing effect of hydrogen on the water reduction reaction were ignored. Uniform-corrosion allowances in the range of 250 mm are predicted using this model. In the absence of a model that takes into account the impact of corrosion-product formation and/or transport limitations in compacted clays, this allowance is the best estimate available, but undoubtedly very conservative.

The two major effects that are not accounted for by any of the modelling approaches are SCC and the buildup of hydrogen pressure. At the low temperatures expected (<95°C), the concentrating mechanisms required to produce significant levels of anionic SCC agents are unlikely to occur. As suggested by Marsh and Taylor (1988) and Marsh (1990), the specification of a stress-relief heat treatment to reduce fabrication stresses to below the threshold value required for SCC appears to be the most appropriate course of action.

The implications of hydrogen production require a more considered analysis. The impact of a buildup of hydrogen pressure on the corrosion rate and on the stability and performance of the vault is unknown. Not only are such effects difficult to measure experimentally, they are also difficult to model with any certainty. These implications extend beyond the lifetime of the container, when prediction of the transport rates of radionuclides released from the fuel are required. To date, a rigorous analysis of the possible two-phase transport of radionuclides driven by pressurized pockets of escaping hydrogen gas has not been carried out.

Until a more thorough understanding of the effects of hydrogen production is available, it is difficult to recommend the use of iron or steel as a container material under the conditions in a Canadian vault. If such materials were to be used, then significant corrosion allowances (>200 mm) would be required. Such allowances are very conservative because of the highly conservative nature of the corrosion model used to predict them. A substantial experimental and modelling program would be required to predict more realistic corrosion allowances.

3.7.4.2 Copper and Copper Alloys

Copper and copper-based materials have been used by man since the Bronze Age (1600-400 B.C.), and much is known of their corrosion behaviour. There is a large number of copper-based alloys with a correspondingly broad range of properties. Copper and copper alloys are near the noble end of the galvanic series and, in seawater, only gold, silver, platinum, titanium and passivated stainless steels and nickel-based alloys are more noble (Shreir 1976). Pure copper is thermodynamically stable in oxygen-free water, and, indeed, metallic copper deposits are well known (Crisman and Jacobs 1982). Although copper will corrode in the presence of dissolved oxygen and other oxidizing species, the rate of corrosion is often low because of the formation of protective surface films. These films may be oxides, as in the case of domestic water pipes, or basic copper salts containing sulphate, carbonate, nitrate or chloride (e.g., the green patina on copper roofs). In addition, cuprous ions can be stabilized by complexation with anions and molecules, such as Cl^-, Br^-, I^-, CN^- and NH_3. The copper complex ions often play an important role in various corrosion processes.

All of the major nuclear waste management programs have considered using copper-based alloys as container materials (Table 3-3). Invariably, the alloys considered have been wrought copper alloys. There are seven groups of wrought copper alloys (CDA 1983): coppers, high copper alloys, brasses, bronzes, copper-nickels, nickel-silvers and special alloys. Of these groups, all but the brasses and nickel-silvers have been considered as candidate materials for waste containers.

The alloys with the highest copper content are known simply as the coppers and are designated C10100 to C15760 according to the UNS (Unified Numbering System). These alloys contain a minimum of 99.3 wt.% copper (including silver) and can be subdivided into three groups: oxygen-free, tough-pitch, and phosphorus-deoxidized coppers. All three alloy groups have excellent resistance to seawater corrosion and biofouling. The tough-pitch coppers contain about 0.04 wt.% oxygen and are susceptible to steam embrittlement (also known as hydrogen sickness) in hydrogen atmospheres at high temperature. For this reason, phosphorus is added as a deoxidizer, and the phosphorus-deoxidized coppers are designated as being either high- or low-residual-phosphorus alloys.

High-copper alloys (C16200 to C19600) are defined as alloys with between 96 and 99.3 wt.% copper and that do not fall into any other group. Small amounts of alloying elements, such as cadmium, beryllium and chromium, are added to produce high-strength materials. The corrosion properties of these alloys are similar to those of the coppers, and they are often used in applications at slightly elevated temperatures.

Historically, bronzes were alloys of copper and tin, but the name is also applied now to alloys containing aluminum and silicon. Phosphor bronzes (copper-tin-phosphorus) are stronger than pure copper and single-phase brasses, have high resistance to erosion-corrosion, and are more resistant to SCC than the brasses. Aluminum bronzes are highly resistant to erosion-corrosion and high-temperature oxidation. Moist ammoniacal environments may cause SCC of these alloys. Silicon bronzes (copper-silicon) are mechanically superior to the coppers with similar resistance to corrosion.

Nickel and copper form solid-solution alloys over the complete composition range. The copper nickels (C70000 to C72900) have nickel contents of between 2 and 33 wt.%, are more resistant than other alloys to acidic solutions, and are highly resistant to SCC. Alloy C71500 (Cu-30 wt.% Ni) is said to be the most corrosion-resistant of all commercial alloys (ASM Committee on Corrosion of Copper 1987).

Table 3-3 gives a summary of those national programs that have tested or proposed the use of copper-based materials, along with a brief description of the respective disposal environments. The corrosivity of these environments is compared in Figure 3-30. Coppers and high-copper alloys have been the most frequently considered. Both oxygen-free and phosphorus-deoxidized grades have been considered for use in granitic rock. In Sweden (Swedish Corrosion Institute 1983) and Canada (King and Litke 1990a) the two corrosion processes of most concern for oxygen-free copper are uniform corrosion

TABLE 3-3

NUCLEAR WASTE MANAGEMENT PROGRAMS WORLDWIDE CONSIDERING COPPER-BASED ALLOYS

Country	Geological Formation	Copper Alloy	Environment			Other	Comments
			Groundwater	Gamma Radiation	Temperature and Pressure		
Sweden	Granite	Oxygen-free high-conductivity UNS C10100	Dilute, HCO_3^--based water, pH 7-9	No	80°C Hydrostatic and clay swelling pressures (15 MPa max.)	Bentonite clay buffer material	10^6-a lifetime (Swedish Corrosion Institute 1978, 1983)
Switzerland	Crystalline Rock	Phosphorus-deoxidized copper	~10 $g \cdot dm^{-3}$ total dissolved solids; Cl^--, SO_4^{2-}-, CO_3^{2-}-based; reducing	No	155°C max. Hydrostatic and swelling pressures (30 MPa max.)	Bentonite clay backfill	1000-a target lifetime. Main emphasis on cast steel container (Simpson 1984)
Canada	Plutonic Rock, (Granite, Gabbro)	Oxygen-free electronic UNS C10100	Saline; 0.1-5 $mol \cdot dm^{-3}$ Cl^-, depending upon depth	Yes ~50 $Gy \cdot h^{-1}$ max.	100°C max. Hydrostatic (5-10 MPa) + swelling (~2 MPa)	Bentonite clay/sand buffer material	500-a minimum target lifetime; >10^6 a achievable
Finland	Granite	Oxygen-free high-conductivity UNS C10100	Fresh water				Similar to Swedish concept
U.S.	Salt	Oxygen-free high-conductivity UNS C10200 90Cu-10Ni UNS C70600 70Cu-30Ni UNS C71500	Brine	Yes			Westerman (1990)

continued...

TABLE 3-3 (concluded)

Country	Geological Formation	Copper Alloy	Environment			Other	Comments
			Groundwater	Gamma Radiation	Temperature and Pressure		
U.S.	Basalt	Oxygen-free electronic UNS C10200 Phosphorus-deoxidized copper UNS C12200 90Cu-10Ni UNS C70600	~1 $g \cdot dm^{-3}$ total dissolved solids, pH ~ 9.7	Yes 2 $Gy \cdot h^{-1}$ max.	170-225°C 9.4 MPa	Crushed basalt/ bentonite packing material	Program cancelled
U.S.	Tuff	Oxygen-free electronic UNS C10200; Be-copper UNS C17200; Mn- Zr-Cu-copper UNS C18100 Al-bronze UNS C61300 70Cu-30Ni UNS C71500	~10 $\mu g \cdot g^{-1}$ Cl^-, NO_3^-; ~20 $\mu g \cdot g^{-1}$ SO_4^{2-}; ~120 $\mu g \cdot g^{-1}$ HCO_3^-; oxidizing	10^2 $Gy \cdot h^{-1}$ max.	250°C max. Nominally atmospheric pressure	700 ft. above water table	300-1000 a target lifetime; UNS C17200 and UNS C18100 no longer under detailed investigation

and pitting. Before its cancellation, the basalt project in the U.S. was also studying environmentally assisted cracking of oxygen-free copper (C10200) and phosphorus-deoxidized copper (C12200) and the specific effects of gamma radiation on these alloys (Brehm 1990b). At one stage, the U.S. tuff program included two high-copper alloys (beryllium copper C17200 and a manganese-zirconium-chromium-copper alloy C18100) because of their improved high-temperature strength in comparison with the unalloyed grades (McCright 1985).

Only the various U.S. programs have considered the use of any other type of copper alloy. An aluminum bronze (C61300) and the 70Cu-30Ni alloy (C71500) are candidates for the tuff disposal vault. The aluminum bronze was selected because of its better resistance to oxidation than the pure coppers (Kass 1990a). This is an important consideration in an environment that is likely to be hot, dry, and oxidizing for the first several hundred years. The copper-nickel alloy was chosen because of its better resistance to all forms of aqueous corrosion. Copper nickels were also tested in the U.S. for their suitability in salt and basalt formations. The 90Cu-10Ni alloy (C70600) was included in both programs (Brehm 1990b, Westerman 1990) and the 70Cu-30Ni alloy was part of the salt formation program (Westerman 1990).

Uniform corrosion

Uniform-corrosion rates of copper-based alloys have been measured under conditions representative of many vault environments. Many of the measurements were used only to rank various materials during scoping studies, and no serious attempts were made to calculate container lifetimes. Rates vary from less than 1 $\mu m \cdot a^{-1}$ to 5 $mm \cdot a^{-1}$, but comparison of the data is often not possible because the experimental conditions vary considerably. However, a few general trends are apparent.

The corrosion rate increases with increasing concentration of oxidizing species. This trend is obvious from the data given by Braithwaite and Molecke (1980) for copper and 90Cu-10Ni in Salton Sea Brine A and seawater at 250°C. For copper, the corrosion rate increases from 70 $\mu m \cdot a^{-1}$ in deaerated brine to 1200 $\mu m \cdot a^{-1}$ in the same brine containing 600 $\mu g \cdot g^{-1}$ O_2. The equivalent figures for 90Cu-10Ni are 140 $\mu m \cdot a^{-1}$ and 400 $\mu m \cdot a^{-1}$ respectively. Even greater differences in the rates for the two alloys are observed in deaerated and oxygenated (1750 $\mu g \cdot g^{-1}$ O_2) seawater. This dependence on oxygen concentration is confirmed by corrosion rate measurements in aerated and deaerated saline solutions in the Canadian program (P.J. King et al. 1981, P.J. King 1985, Lam 1990). Work by F. King and Litke (1987) suggests that there is a logarithmic relationship between the corrosion rate and the oxygen concentration. Swiss researchers observed a higher corrosion rate for phosphorus-deoxidized copper in air-saturated (~6 $\mu g \cdot g^{-1}$ O_2) dilute granitic groundwater at 80°C (40 $\mu m \cdot a^{-1}$) than in the same solution containing 0.1 $\mu g \cdot g^{-1}$ O_2 (26 $\mu m \cdot a^{-1}$) (Simpson 1984).

The most thorough study of temperature effects on copper corrosion has been carried out in the Canadian synthetic granitic groundwater, WN-1, containing 6500 $\mu g \cdot g^{-1}$ Cl^- (P.J. King 1985, Lam 1990). In deaerated solutions the rate is higher at 150°C (24 $\mu m \cdot a^{-1}$) than at 75°C (1.4 $\mu m \cdot a^{-1}$). However, in aerated solution the trend is reversed, whilst in aerated or deaerated solutions containing sulphide the rates are similar at the two temperatures. A variation in oxygen solubility with temperature probably explains the maximum in the corrosion rate observed between 50 and 100°C (P.J. King 1985). In oxygen-saturated brine (Marsh et al. 1983), the corrosion rates of copper, 90Cu-10Ni and 70Cu-30Ni increase with temperature, from 22 to 150°C, despite the decrease in oxygen solubility.

Corrosion rates are expected to decrease with exposure time as a result of either the buildup of a corrosion-product layer or a decrease in the limited amount of available oxygen in the test (King and Litke 1987, 1990a). After several months, however, the corrosion rate has often achieved a steady-state value (Brehm 1990b). Instances of the corrosion rate increasing with time are probably due to changes in the mechanism, such as for 90Cu-10Ni in air-steam mixtures at 250 and 300°C (Brehm 1990b), or simply to experimental artifacts (Simpson 1984).

King and Litke (1990a) found a dependence of the corrosion rate of copper (C10100) in saline groundwater at 100°C on the specimen surface-area-to-solution-volume ratio, suggesting rate control by a transport process. Control by transport is even more likely for containers surrounded by compacted clay-based materials, and various workers have compared the rates of uniform corrosion in bulk solution with those in compacted buffer or packing material. Brehm (1990b) found that the presence of packing (1:3 sodium bentonite:crushed basalt) led to an increase in the corrosion rate of oxygen-free copper and 90Cu-10Ni in an air-steam environment at temperatures between 150 and 300°C. In highly compacted bentonite, copper exhibited a corrosion rate of 1 $\mu m \cdot a^{-1}$ at 140°C compared with a value of ~3 $\mu m \cdot a^{-1}$ in bulk solution after a similar exposure period (Simpson 1984). While these results indicate that the surrounding clay does influence the corrosion process, they do not clearly demonstrate the origin of this effect. In fact, studies of copper corrosion in many different soil types (Denison and Romanoff 1950, Romanoff 1957) yielded average corrosion rates varying by a factor of >50 (0.5 to 27 $\mu m \cdot a^{-1}$), but failed to establish any correlation between rate and soil type (Swedish Corrosion Institute 1978).

Various authors have measured corrosion rates with and without gamma radiation (Simpson 1984, King and Litke 1987, King et al. 1989, Brehm 1990b, Kass 1990a). Unfortunately, the results are generally inconsistent and unexplained. What mechanistic studies have been performed have been carried out at large dose rates ($>10^3$ $Gy \cdot h^{-1}$) (Glass et al. 1986). Irradiation has been found to result in both increases and decreases in the corrosion rates of copper. To explain a decrease in rate, Simpson (1984) suggested that the radiolytically produced reducing species were more electrocatalytic than the oxidizing radiolysis products under the conditions of his experiment (0.1 $mol \cdot L^{-1}$ NaCl and natural granitic groundwater; room temperature; 13.3 $Gy \cdot h^{-1}$). King and Litke (1987) and King et al. (1989) explained their lower corrosion rates in the presence of gamma radiation (0.97 $mol \cdot L^{-1}$ Cl^-; 150°C; 14 to 27 $Gy \cdot h^{-1}$) by the formation of a more compact and protective corrosion-product film. Brehm (1990b) also claimed that the presence of irradiation-induced changes in surface-film morphology affected the corrosion rates in air-steam tests at 150°C

(10^2 Gy·h^{-1}). However, in this environment, corrosion rates increased with radiation dose rate.

Glass et al. (1986) suggested that the anodic shifts in the corrosion potential of copper observed in the presence of radiation (tuff groundwater, 30°C) could be attributed to the production of species such as H_2O_2 and OH$^\cdot$. Unfortunately, these experiments were performed at dose rates of 3.3×10^4 Gy·h^{-1} and their relevance to situations involving lower dose rates is unclear.

The increase in corrosion rate of the 70Cu-30Ni alloy in wet steam environments at 95°C (10^3 Gy·h^{-1} for 5 000 and 10 000 h) (Kass 1990a) was tentatively attributed by McCright et al. (1987) to the formation of nitric acid or other acidic nitrogen oxides in the radiation field. Other radiolysis products were implied to be the aggressive species in dry steam at 150°C, but no explanation was offered for the higher corrosion rates of this alloy at 95°C in waters typical of those expected in a tuff formation ($[Cl^-] \sim 10$ μg·g^{-1}; $[SO_4^{2-}] \sim 20$ μg·g^{-1}; $[HCO_3^-] \sim 120$ μg·g^{-1}). The more uneven nature of the attack on 70Cu-30Ni compared with that on copper, and the tendency of the thicker oxide (CuO) film to spall in irradiated solutions, is a possible explanation (Yunker and Glass 1986).

The effect of gamma radiation on the corrosion behaviour of copper, 70Cu-30Ni and Al-bronze in moist air systems has been studied by Reed et al. (1990) and Reed and Van Konynenburg (1991). The corrosion rate of copper at 150°C was about 1.5 times higher in the presence of a radiation field (2×10^2 Gy·h^{-1}) (Reed and Van Konynenburg 1991). It was also higher than that of the other two alloys. The extent of corrosion increased with moisture content (dry air to 100% relative humidity) and temperature (90 to 150°C) for all three materials. At dose rates $\geq 7 \times 10^2$ Gy·h^{-1}, nitrate phases ($Cu_2NO_3(OH)_3$) were observed on the coupon surfaces. Alexandrov et al. (1987) also reported the formation of nitrate species on Cu coupons exposed to moist air at 37°C at a dose rate of 6.5×10^3 Gy·h^{-1}. These authors reported that the irradiated corrosion rate of ~3 μm·a^{-1} exceeded the unirradiated rate by about two orders of magnitude. However, they observed no effect of moisture content and concluded that NO_2 was the aggressive species. Corrosion was believed to result from a gas-phase oxidation process rather than a condensed water film on the metal surface.

Another possible oxidant for copper-based alloys is H^+ in the presence of the bisulphide ion (HS^-) (Swedish Corrosion Institute 1978) by the following reaction:

$$2Cu(s) + HS^-(aq) + H_2O(l) \rightarrow Cu_2S(s) + H_2(g) + OH^-(aq) .$$

Lam (1990) found that sulphide ions generally lead to an increase in the corrosion rate of copper in granitic groundwater. This increase has been attributed to the formation of a surface film that catalyzes oxygen reduction (Kato et al. 1984, de Sanchez and Schiffrin 1982). However, Syrett (1981) suggested that the porous cuprous sulphide film that forms on copper-nickel alloys in sulphide-polluted seawater affects the formation of the normal protective oxide film.

Microbial activity is a possible source of sulphidic species in a disposal vault, and it is claimed that the formation of copper sulphide in natural near-surface environments is indicative of microbially induced corrosion (MIC) (McNeil et al. 1991). In deeper groundwaters, i.e., at lower redox potentials, the potential-pH diagram for the Cu-H_2O-S^{2-} system suggests that it is possible to form chalcocite (Cu_2S), but not covellite (CuS), under a biofilm. Exposure of 99Cu (grade unknown), 90Cu-10Ni and 70Cu-30Ni to solutions containing sulphate-reducing bacteria (SRB) for four months produced black, porous corrosion products on all samples. The films formed on the 99Cu were nonadherent, whereas those formed on the two copper-nickel alloys were adherent. Various copper sulphide mineral phases were identified (McNeil et al. 1991).

Mechanistic studies of the uniform corrosion of copper have been carried out in Sweden (Swedish Corrosion Institute 1978) and Canada (King and Litke 1989a,b,c,d; Litke et al. 1992; King et al. 1992a,b), with the objective of producing long-term predictions of container lifetimes. In the Swedish program (Swedish Corrosion Institute 1978, 1983), of the possible oxidants within the vault, only dissolved oxygen and bisulphide ions were considered to be significant in causing corrosion of a copper container. Furthermore, it was assumed that the vault would be designed to minimize the quantities of these species reaching the containers (Swedish Corrosion Institute 1978), and that the rate of transport of oxidants through the compacted clay surrounding the container would be rate-controlling. On this basis it was concluded that for a 200-mm-thick container, the penetration resulting from uniform corrosion would be only 2.4 mm after 10^6 a (Swedish Corrosion Institute 1978).

On the basis of comparisons of weight losses with the total amount of available oxygen in his experiments (at 80 and 140°C), Simpson (1984) has claimed that oxygen transport is rate-controlling at low oxygen levels (0.1 $\mu g \cdot g^{-1}$), but that an interfacial reaction is controlling in air-saturated solutions. King and Litke (1987) found a logarithmic dependence of the corrosion rate on the initial oxygen concentration (0.1 to 6 $\mu g \cdot g^{-1}$) in synthetic granitic groundwater at 150°C, as opposed to the linear relationship expected for oxygen-transport control. In the presence of compacted buffer material, it is more likely that the interfacial reduction of oxygen would be transport-limited.

By studying the component electrochemical reactions of the overall corrosion process in aerated NaCl solution at rotating disc electrodes (RDE), King and Litke (1989a,b,c,d) concluded that the rate of uniform corrosion of copper containers would be controlled by the rate of the anodic transport step, i.e., the transport of dissolved copper away from the corroding surface. These studies were supplemented by corrosion tests under simulated disposal conditions (Litke et al. 1992; King et al. 1992a,b).

The anodic dissolution of copper in chloride solutions has been extensively studied (see for example King and Litke 1989b,c,d; Smyrl 1981; Moreau 1981a,b; Moreau et al. 1982; Deslouis et al. 1988a,b), and despite remaining uncertainties (Deslouis et al. 1988a) it is generally agreed that the rate-limiting anodic step is the transport of copper-chloro complex ions ($CuCl_2^-$, $CuCl_3^{2-}$) away from the electrode surface. Under natural corrosion conditions in the presence of dissolved oxygen, the anodic transport step is rate-limiting for the overall corrosion process (King and Litke 1989d). Measurements at lower oxygen concentrations suggest that oxygen transport becomes rate-limiting only at very low oxygen concentrations, <0.03 $\mu g \cdot g^{-1}$ (King et al. 1992b).

A series of corrosion tests has been carried out under simulated disposal conditions (Litke et al. 1992, King et al. 1992a) in which a disc of copper corroded whilst in contact with a column of compacted buffer material. At the end of each test, the copper concentration profile in the column of buffer was measured, and the mean corrosion rate was estimated from the weight loss of the coupon. A correlation was found between the corrosion rate and the rate of copper transport, suggesting that, as in the case of an RDE in oxygen-containing NaCl solution, copper transport is rate-limiting. In a series of irradiated tests the copper was observed to diffuse farther along the column of buffer than in other unirradiated experiments, but the corrosion rate was lower (Litke et al. 1992, King et al. 1992a). This somewhat unexpected effect is believed to result from a decrease in the extent of copper sorption by the clay. Sorption of copper on the clay drives the interfacial dissolution of copper but retards its migration through the buffer. Post-test gas analyses showed only small amounts of oxygen remaining at the end of the irradiated tests. Therefore, it is possible that in the irradiated tests copper dissolved as weakly sorbed Cu(I) species, e.g., $CuCl_2^-$, whereas in unirradiated tests containing plenty of oxygen, strongly sorbed Cu(II) species predominated. It is believed that the low $[O_2]$ rather than the presence of radiation caused the proposed change in Cu speciation.

Further evidence for slow copper transport comes from two Swedish studies. Hallberg et al. (1988) described the analysis of a bronze cannon that had been partly buried in clay sediments in the Baltic Sea for 310 a. The shapes of the copper concentration profiles through the clay sediments at various positions adjacent to the cannon were very similar to the ones found by Litke et al. (1992). In the second study, Hallberg et al. (1984) examined copper lightning conductor plates that had been buried in soil for 60 to 80 a. The copper concentrations in the soil were reported to decrease sharply with distance away from the plates, with no appreciable amounts of copper diffusing further than 3 cm.

Localized corrosion

The various copper-based alloys have varying susceptibilities to localized corrosion. In this review, emphasis is placed on the localized corrosion behaviour of the coppers (C10100 to C15760), with some mention of the susceptibilities of the other copper-based alloys.

In the predominantly anoxic conditions of a Canadian disposal vault, crevice corrosion of copper is unlikely to be a major concern (ASM Committee on Corrosion of Copper 1987). No evidence of crevice corrosion has been observed on creviced planar and U-bend specimens exposed to simulated Canadian disposal conditions at temperatures up to 150°C and for periods of up to 5.5 a (King and Litke, unpublished data 1990). Similarly, dealloying and long-term phase separation would be of no concern for pure coppers, but have been addressed in the U.S. where the use of 70Cu-30Ni and Cu-7 wt.% Al has been considered (Kass 1990a).

Pitting

Pitting of coppers in natural waters has been quite extensively studied, especially on copper pipes carrying potable water. Pitting of copper water pipes can be divided into two types (Campbell 1974). Type 1 pitting occurs mainly in cold water and is usually associated with a carbon film on the inner surface of the pipe. Campbell (1974) reports that increasing sodium, sulphate and dissolved oxygen concentrations increase the risk of pitting, whereas increases in the nitrate and chloride concentrations or the pH decrease the pitting propensity. Microbial action has been implicated in a form of copper pitting in Germany (Fischer et al. 1988) that shows similarities to the model for Type 1 pitting proposed by Lucey (1967). Type 2 pitting occurs in soft waters at temperatures above 60°C (Campbell 1974). Relatively little work has been done on the mechanism of Type 2 pitting, although Mattsson (1980) reports that a low pH (<7.4) and a low bicarbonate:sulphate ratio (<1) are required.

In general, pitting has not been a frequent occurrence in studies related to the disposal of nuclear waste. No evidence of pitting was observed in either basaltic groundwaters or air/steam environments (up to 300°C) (Brehm 1990b) or in granitic environments (up to 140°C) (Simpson 1984). However, Yunker and Glass (1986), in work for the tuff program, have reported pitting of two copper specimens (C10100) in an irradiated moist gas phase at 95°C; and Reed et al. (1990) observed pits on single 70Cu-30Ni and oxygen-free copper coupons exposed to gamma radiation in moist air (15% relative humidity) at 120 and 150°C respectively. Lam (1990) has reported pitting in a variety of environments using a synthetic Canadian groundwater known as WN-1. Pitting was reported in WN-1 solution with and without daily addition of sulphide, in aerated and deaerated solution, in the presence and absence of a gamma-radiation field and at temperatures of both 75 and 150°C. Many of these instances of "pitting" were thought to be no more than localized surface attack that would degenerate into surface roughening with time (Ives 1990).

These few occurrences make it difficult to unequivocally rule out the possibility of pitting, especially since studies of copper and copper alloys buried in various types of soil have also revealed instances of pitting. In an extensive study of the underground corrosion behaviour of structural materials in soils in the U.S., Romanoff (1957) reported pitting of copper, copper-silicon, copper-zinc and copper-nickel-zinc alloys. Swedish workers (Swedish Corrosion Institute 1978) could find no statistical correlation in the Romanoff data between the extent of pitting and soil characteristics, such as the electrical resistivity, pH and the presence of species like Na, Ca and Cl.

Despite this inability to correlate the extent of pitting with the soil conditions, it seems unlikely that pitting would be a major degradation mode under Canadian disposal conditions. High salinities are likely to maintain active conditions, and the oxygen concentration needed to maintain pit propagation would be limited. However, there are the unknown factors of sulphide formation, mineral deposit formation, and radiolysis, which might all induce localized corrosion.

Other localized effects

Hydrogen effects in coppers are associated with a type of corrosion known as "hydrogen sickness" (Gdowski and Bullen 1988, Mattsson 1980). In this process, hydrogen diffuses along grain boundaries and reacts with oxygen in the metal, which forms water that accumulates along the grain boundaries, creating cavities. This phenomenon has been observed in materials containing as little as 22 atomic parts per million (appm) oxygen, making it difficult to claim that even the purest of coppers (containing ~40 appm oxygen) is immune to this process, especially under vault conditions, where hydrogen could be generated by radiolysis or water reduction in the presence of sulphide. The best way to prevent embrittlement or cracking due to hydrogen is to use a deoxidized grade of copper containing elements such as zirconium, boron, phosphorus or magnesium. Hydrogen sickness is unlikely to be an issue in geological disposal in general and is of no concern in a Canadian disposal vault, where container temperatures would not exceed 100°C.

No evidence exists for the localization of corrosion in microstructurally altered sites in welds and the associated heat-affected zones. Modin and Modin (1983) concluded from an inspection of copper EB welds that pore-free welds should have the same corrosion resistance as the surrounding metal, and Simpson (1984) found no preferential attack on EB-welded phosphorus-deoxidized copper in synthetic granitic groundwater containing 0.1 $\mu g \cdot g^{-1}$ O_2 at 80 and 140°C.

Stress corrosion cracking

Classically, copper alloys are susceptible to SCC in ammonia- or ammonium-containing solutions (ASM Committee on Corrosion of Copper 1987). Farmer et al. (1988a,b) report that pure copper undergoes intergranular SCC (IGSCC) in non-tarnishing ammoniacal solutions, but undergoes transgranular SCC (TGSCC) in tarnishing solutions. TGSCC in ammonia-containing solutions also occurs on aluminum bronzes and, to a lesser extent, on copper-nickel alloys. In moist ammonia-containing solutions, phosphorus-deoxidized copper was found to be susceptible to SCC, whereas both tough-pitch and oxygen-free grades were not (Thompson and Tracy 1949). An inverse relationship was found between the time-to-failure and phosphorus content of the alloy. Escalante and Kruger (1971) found pure copper to be susceptible to SCC in cupric acetate solution but not in cupric sulphate.

Nitrite, remaining in the vault as a consequence of blasting operations or produced by the radiolysis of thin moisture films in contact with air, would appear to be the species most likely to cause SCC of copper containers (Pednekar et al. 1979). However, the assessment of Benjamin et al. (1988) on oxygen-free high-conductivity and phosphorus-deoxidized copper in nitrite solutions showed that cracking occurred only under naturally corroding conditions in aerated solutions at room temperature at nitrite concentrations greater than 0.1 $mol \cdot dm^{-3}$. Deaerating the solutions or increasing the temperature to 80°C reduced the susceptibilities of both materials. Aaltonen et al. (1984) observed TGSCC of oxygen-free copper in 0.3 mol·dm^{-3} $NaNO_2$. The crack was reported to initiate intergranularly and then propagate transgranularly. In the absence of SCC-inducing species, no SCC of pure copper has been observed in granitic groundwaters (Benjamin et al. 1988, Aaltonen et al. 1984, Simpson 1984).

If SCC of copper-based containers were to occur, it would seem most likely under the oxidizing conditions expected in a tuff formation, and an extensive literature survey of the SCC of copper alloys has been carried out in support of the tuff program (Farmer et al. 1988b). SCC seems unlikely in granitic environments because of the more reducing conditions and the absence of aggressive species.

Microbially induced corrosion

The microbiologically induced corrosion of copper and copper alloys is a well-documented phenomenon (Pope et al. 1989). In particular, the effects of sulphate-reducing bacteria and the corrosion of copper alloys in sulphide-polluted seawater have been extensively reported (McNeil et al. 1991, Videla et al. 1989, Syrett 1981, Pope et al. 1989 and references therein). Biofilm formation has also been implicated in the pitting of copper (Fischer et al. 1988, Chamberlain and Angell 1990).

Microbial activity in the compacted buffer material around a container should be more restricted than in surface or near-surface environments because of the relative lack of nutrients (Stroes-Gascoyne 1989); the small pore size of the buffer (Johnson et al. 1994); and the presence of elevated temperatures, gamma-radiation fields and high salinity. However, the possibility of some microbial activity cannot be excluded. Calculations based on conservative assumptions regarding the activity of SRB suggest that MIC could result in <1 mm of attack on copper containers under Swedish vault conditions (Werme et al. 1992) and up to 13 mm on carbon steel (Marsh and Taylor 1988). Given the similarities between the Canadian and Swedish disposal concepts, the extent of MIC for a copper container in a Canadian vault is likely to be closer to 1 mm.

Modelling corrosion behaviour

Assessments of the lifetimes of copper containers have been carried out for the Swedish and Canadian disposal concepts (Swedish Corrosion Institute 1978, 1983; Werme et al. 1992; King et al., in press; King and LeNeveu 1992). In both programs, uniform corrosion and pitting have been considered as possible failure processes. Despite the obvious similarities in the two disposal concepts, significant differences exist between the disposal environments. Swedish groundwaters are more reducing than those in the Canadian Shield, and contain significant quantities of sulphide (Werme et al. 1992). Consequently, sulphide (or, more correctly, H^+ in the presence of sulphide) has been considered the major oxidant in Swedish assessments, whereas in Canada the emphasis has been placed on dissolved oxygen.

In the various Swedish assessments, the rate of uniform corrosion was assumed to be limited by the rate of supply of oxidants. In their original assessment of a 200-mm-thick container, the Swedish Corrosion Institute

(1978) calculated that the penetration due to corrosion by dissolved oxygen and sulphide would amount to 2.4 mm after 10^6 a. In a subsequent analysis of thinner-walled containers (10, 60 and 100 mm thick), the effects of gamma radiolysis were considered in more detail, but were found to be significant (greater than 0.4-mm extra general attack after 10^6 a) for only the 10-mm-thick container (Swedish Corrosion Institute 1983). Pitting was treated using a pitting factor derived from an analysis of pit-depth data from long-term underground corrosion tests (Romanoff 1957) and from studies of archaeological bronze artifacts and buried objects (Bresle et al. 1983, Hallberg et al. 1984). Originally, a conservative pitting factor of 25 was adopted, although an upper limit is now believed to be five, with two being a "realistic" value (Werme et al. 1992). Consequently, for a combination of uniform corrosion and pitting, the lifetime of a copper container with a wall thickness of 60 mm or greater is predicted to be $>10^6$ a.

Two copper container failure models have been developed to predict the rate of container failure under Canadian disposal conditions (King et al., in press; King and LeNeveu 1992). Dissolved oxygen is taken as the oxidant for uniform corrosion and pitting because of the absence of sulphide in groundwaters typical of the Canadian Shield (Gascoyne and Kamineni 1992, Gascoyne 1989). In the first model, a conservative assessment of the rate of uniform corrosion, King et al. (in press) assumed that aerated conditions were maintained indefinitely and that, consistent with experimental evidence (King et al. 1992a, Litke et al. 1992), the rate of corrosion was limited by the diffusion of Cu(II) away from the container surface. These assumptions are conservative since the amount of oxygen available would be limited once that initially trapped in the pores of the buffer and backfill had been consumed. Nevertheless, based on a mathematical formulation of the mass transport conditions within the disposal vault, the lifetimes of 25-mm-thick copper containers were predicted to range from 30 000 to $>10^6$ a.

Pitting has also been included in the Canadian assessment of container lifetimes by using a statistical extreme-value analysis of the literature pit-depth data used in the Swedish assessment. The container lifetimes given above are based on a general corrosion allowance of 16 mm for a container wall thickness of 25 mm, and this analysis of pitting suggests that, even after 10^6 a, the probability that the deepest pit on a copper container would exceed the remaining 9 mm is less than 1 in 10^9 (King and LeNeveu 1992). Consequently, uniform corrosion would penetrate the 16-mm corrosion allowance before the total penetration due to the combination of uniform corrosion and pitting exceeded the full wall thickness of 25 mm. Consequently, for periods up to 10^6 a, failure would be by uniform corrosion, not pitting (King and LeNeveu 1992).

Recently, a more realistic second assessment was performed in which the evolution in environmental conditions around the containers is described by three distinct phases (Shoesmith et al., in preparation): an initial transient period during which the vault becomes saturated with groundwater; a subsequent period of relatively high oxygen concentration; and, finally, a long-term low-oxygen-concentration phase. Significant corrosion occurs only during the first two phases, since, in the long term, the oxygen concentration in the groundwater is too low (<10 ng·g^{-1}) to sustain any appreciable rate of corrosion. As a consequence of the limited quantity of oxidants, the combined penetration resulting from uniform corrosion and pitting is now estimated at <10 mm for periods up to 10^6 a.

Although slightly different approaches have been used in the Swedish and Canadian assessments, both studies predict very long lifetimes for copper containers. The most important factors in achieving indefinite containment are the lack of oxidants and the restrictive mass transport conditions that are common to both disposal concepts.

3.7.4.3 Stainless Steels

Stainless steels have been considered as candidate container materials in a number of disposal environments. These include (a) the hot and dry, but oxidizing conditions encountered in the U.S. Yucca Mountain tuff environments; (b) the hot, dry bedded-salt conditions anticipated in the WIPP facility; and (c) the non-saline groundwaters and humid clay atmospheres occurring in Belgium (Boom) clays.

A critical comparison of the physical metallurgy and corrosion properties of a number of kinds of steel, including ferritic, austenitic, martensitic, and precipitation-hardened, was carried out by Nuttall and Urbanic (1981). They concluded that low-carbon steels of the AISI[35] 300 series, particularly 316L, were the most appropriate for Canadian conditions, but added that steels with higher molybdenum content might be required to withstand saline conditions. Although originally recommended for further study, stainless steel received little attention in the Canadian program once high-salinity groundwaters were discovered in test drill sites.

According to McCright et al. (1987), the most important degradation modes for austenitic stainless steels are

- intergranular corrosion (IGC) processes caused by the formation of sensitized microstructures;
- corrosion and embrittlement processes caused by the transformation of metastable austenite to other phases; and
- localized corrosion processes resulting from aggressive, particularly oxidizing and saline, groundwaters.

These processes have been reviewed in detail in the tuff program (U.S.A.) (Fox and McCright 1983; Oversby and McCright 1984; McCright et al. 1987; Kass 1990c; Farmer et al. 1988a,c; Bullen and Gdowski 1988; Gdowski and Bullen 1988).

Since the disposal temperatures in a Canadian vault would not exceed 100°C and would, in fact, be below 70°C for times beyond 100 to ~200 a, sensitization and phase transformations are unlikely to be significant degradation modes. However, the highly saline environments anticipated in a Canadian

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[35] American Iron and Steel Institute

vault mean that the stainless steels would be susceptible to localized processes, such as crevice corrosion, pitting and SCC. This susceptibility to various modes of localized corrosion can be assessed from susceptibility diagrams (temperature vs. chloride concentration) of the kind shown for 304 stainless steel in Figure 3-31, reproduced from the report by Nuttall and Urbanic (1981). The temperature-chloride concentration envelopes define the conditions for initiation of the three forms of corrosion. The diagram was based on results obtained by Truman (1977) from long-term immersion tests in air-saturated solutions. Also shown are the results of electrochemical tests by Efird and Moller (1979). The two shaded areas in the figure define the conditions of temperature and chloride concentration anticipated in tuff (Yucca Mountain) and Canadian waste vaults. It is apparent from this figure that 304 stainless steel is susceptible to both crevice corrosion and pitting under anticipated Canadian vault conditions. It may also be susceptible to SCC, depending on the reliability of the envelopes determined by Truman (1977). In a tuff environment, this material may be a viable candidate, depending on whether the electrochemical results in Figure 3-31 are considered realistic or not. Increasing the alloy content of the steel improves the resistance to localized corrosion.

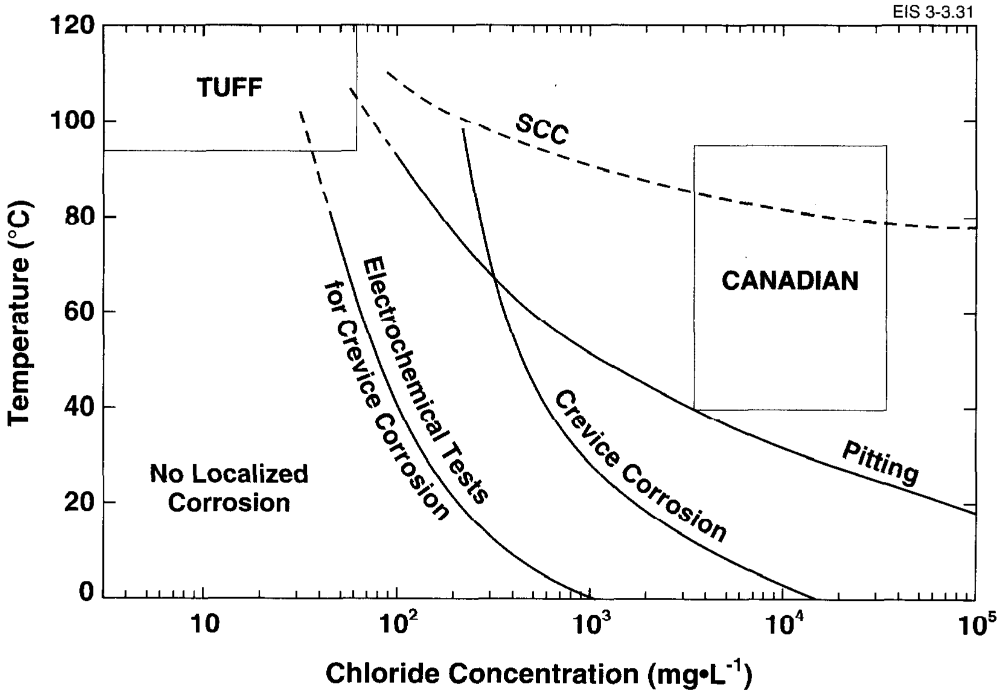

FIGURE 3-31: Localized Corrosion of Type 304 Stainless Steel in Water as a Function of Temperature and Chloride Concentration (from Nuttall and Urbanic 1981). The temperature ranges and chloride concentrations for potential U.S. and Canadian disposal environments are also shown.

The advantage is minor and insufficient to justify the use of 316L stainless steel in a Canadian vault environment. This susceptibility of stainless steels to localized corrosion processes is much higher than that of the alternative corrosion-resistant materials, nickel-based and titanium alloys. Hence, stainless steels are no longer considered viable materials for Canadian fuel waste containers.

3.7.4.4 Nickel-Based Alloys

Nickel is a more noble metal than iron but a less noble metal than copper, and a supply of oxidant is generally required for significant nickel corrosion to occur. However, nickel does possess the ability to protect itself by passivation, thereby reducing the corrosive effect of oxidizing conditions.

Because nickel is used to stabilize the austenitic (fcc) phase in some of the highly alloyed stainless steels, the boundary between these materials and the nickel-based alloys is rather diffuse. Nickel can accommodate large additions of alloying elements before encountering phase instabilities, making it possible to fabricate a large number of alloys that take advantage of the passive nature of nickel and the properties of the specific alloying elements. This compatibility offers the prospect of designing materials with corrosion resistance to a wide range of severe environments. As well, the formation of unique intermetallic phases can produce very high-strength alloys. A more extensive discussion of these properties is available (Friend 1980).

The nominal chemical compositions of a number of nickel-based alloys studied in various waste container programs is given in Table 3-4. Monel 400 is a nickel-copper alloy. Since copper has good resistance to corrosion by dilute non-oxidizing and non-aerated solutions of mineral acids, as a result of its nobility, its addition to nickel improves the alloy's resistance to these conditions. The known resistance of nickel-copper alloys to corrosion in seawater makes them worthy of consideration as container materials. The remaining materials in Table 3-4 are nickel-chromium-molybdenum alloys fabricated to combine the good performance of nickel-chromium alloys in oxidizing media with that of nickel-molybdenum alloys in reducing media.

Of the materials listed in Table 3-4, the three most studied as container options are Hastelloy C4 (favoured by the Commission of the European Communities (CEC)), Hastelloy C276 and Inconel 625. Experience with the Hastelloys C276 and C4 shows they remain bright for many years in marine environments, do not pit in seawater, and generally possess good corrosion resistance in oxidizing chloride solutions similar to those anticipated in many waste vaults. Their high molybdenum content increases resistance to pitting but can lead to the formation of molybdenum-rich intermetallics after heat treatment. Increasing the chromium content and decreasing the molybdenum content in Inconel 625, compared with Hastelloys C276 and C4, maintains the corrosion resistance under oxidizing conditions while improving corrosion resistance to a number of reducing acid conditions. Inconel 625's resistance to pitting in seawater and to corrosion in hypochlorites and oxidizing chloride conditions should make the material useful in

TABLE 3-4

NOMINAL CHEMICAL COMPOSITION (wt.%) OF CANDIDATE NICKEL-BASED ALLOYS

Alloy	Ni	Cr	Mo	Fe	Cu	Mn	Si	C	Other
Monel 400[a]	66.5	-	-	1.2	31.5	1.0	0.2	0.2	
Incoloy 825[a]	42.0	21.5	3.0	30.0	2.2	0.5	0.2	0.03	0.9 Ti
Inconel 600[a]	76.0	15.5	-	8.0	-	0.2	0.2	0.04	
Inconel 625[a]	63.0	21.5	9.0	2.5	-	0.2	0.2	0.05	4 Nb, 0.2 Ti
Incoloy 800[a]	32.5	21.0	-	44.0	≤0.75	-	≤1	0.08	0.38 Ti
Hastelloy C276[b]	59.0	15.0	17.0	5.0	-	-	-	-	4 W
Hastelloy C4[b]	68.0	15.6	15.4	0.5	-	0.22	0.05	0.006	0.11 Ti
Hastelloy C22[b]	54.0	21.0	13.0	4.0	-				
Hastelloy G30[b]	38.0	29.5	5.0	15.0	1.7				
Hastelloy B[b]	61.0		28.0	5.0		≤1	≤1	≤0.05	≤2.5 Co

Trademarks:
[a] Huntington Alloys, [b] Cabot Corporation

radiolytically decomposed saline solutions. Also, the relatively high niobium content makes this alloy resistant to intergranular corrosion by stabilizing the carbon content in the form of niobium carbides.

Nickel-based alloys have been considered as candidate materials in a wide variety of waste vault environments, including saliferous environments (Germany); tuff environments (Yucca Mountain); granitic and saline environments (Europe and Canada); and humid and wet clay environments (Belgium).

On the basis of studies on a wide range of potential materials, the CEC selected Hastelloy C4 as a reference material for further study in the wide range of geological conditions encountered in the waste vaults proposed by the various member nations (Haijtink 1986). In addition, some laboratories in Europe have tested other materials for comparison. Thus, Inconel 625, and to a lesser extent Inconel 600 and 800, have been studied in clay environments (Casteels et al. 1986); Hastelloy C276 and C4 have been tested in granitic environments (Plante and Helie 1986, Marsh et al. 1986c); and Hastelloy C4, C22, G30, Inconel 625 and Incoloy 800 have been tested under salt brine conditions (Smailos et al. 1986a,b; Vu Quang et al. 1986). The alloys C22 and G30 were studied mainly as a series with C4 in an attempt to determine the advantages/disadvantages of changing molybdenum and chromium contents. In the Canadian program, efforts have concentrated on Inconel 625 and Hastelloy C276 (Postlethwaite 1991), the two alloys recommended for study by Nuttall and Urbanic (1981).

Uniform corrosion

As expected for corrosion-resistant materials, uniform-corrosion rates for nickel-based alloys are very low. In clay, clay waters and humid clay atmospheres, rates are well under 1 $\mu m \cdot a^{-1}$ (Casteels et al. 1985, 1986). In fact, analyses of corroded specimens by Auger electron spectroscopy showed that corrosion was limited to the formation of surface oxide layers only, ~1 nm thick in clay, and <5 nm thick in humid clay atmospheres. In salt brines containing large concentrations of magnesium (Q-brines), the corrosion rate of Hastelloy C4 increased from ~0.02 $\mu m \cdot a^{-1}$ at 90°C to only 0.15 $\mu m \cdot a^{-1}$ at 170°C (Casteels et al. 1985, 1986).

A more extensive summary of rates is given by Postlethwaite (1991), including a summary of the rates obtained from industrial-plant corrosion tests in a wide variety of process brines. Much of these data are from the book by Friend (1980). Under deaerated conditions, rates are generally low (in the order of a few micrometres per year), but at high temperatures in aerated saline solutions rates are one to two orders of magnitude higher. Thus, the corrosion rates of Inconel 625 and Hastelloy C276 increased from <0.5 $\mu m \cdot a^{-1}$ under deaerated conditions to 480 and 150 $\mu m \cdot a^{-1}$ respectively under aerated conditions at 232°C in Salton Sea geothermal brines ($[Cl^-] = 140\ 200\ mg \cdot L^{-1}$; $[Mg^{2+}] = 27\ mg \cdot L^{-1}$). The state of aeration made no difference at 105°C in the same brine. Braithwaite and Molecke (1980) reported a similar effect of aeration in WIPP brine (Postlethwaite 1991) for Hastelloy C276 at 250°C, the corrosion rate increasing from 5 to 60 $\mu m \cdot a^{-1}$. A similar rate increase was observed in seawater at 250°C.

These large increases in corrosion rates can be attributed to transpassive dissolution under oxidizing conditions (Schmitt and Köster 1986, Vu Quang et al. 1986). The close proximity of the corrosion (E_{CORR}) and breakdown (E_b) potentials in Q-brine at 90°C (~300 mV) (Schmitt and Köster 1986) shows that only a relatively small change in the oxidizing environmental conditions is required to drive the corrosion potential into the potential region where film breakdown and transpassive dissolution or pitting occur. The threshold temperature for transpassive dissolution is ~55°C. This small safety margin for film breakdown (~300 mV) should be compared with that for titanium and titanium alloys, which is >2 V and often as high as 5 to 10 V under similar conditions (Schutz and Hall 1984).

Under Canadian disposal vault conditions the rapid achievement of anoxic conditions coupled with low temperatures would preclude the achievement of transpassive conditions. The very low rates obtained in clay are to be expected in compacted bentonite and, consequently, uniform corrosion of these nickel-based alloys should be insignificant.

Localized corrosion

Using a combination of electrochemical techniques and immersion tests, a number of alloys have been tested in a variety of environments.

In direct contact with clay and interstitial clay water, the nickel alloys Inconel 800 and Hastelloy B showed only minor uniform corrosion. However, when tested in humid clay atmospheres[36] at 50°C for 49 months, all surfaces were pitted (Casteels et al. 1985). Reaction appeared to start at grain boundaries as a result of the presence of large amounts of precipitates at these sites. Incoloy 800 was attacked under the salts produced by the successive drying and wetting of the surface, resulting in the crystallization of corrosive deposits. In such corrosive vapours, the wetting and drying cycles would periodically produce highly acidic and localized oxidizing conditions shown to be aggressive to these alloys.

Using an anodic polarization technique, Plante and Helie (1986) and Helie and Plante (1985) determined that the alloys C4, C276 and 625 were susceptible to crevice corrosion in granitic groundwaters at 90°C, and that this susceptibility increased greatly with temperature. There was little observable difference between the three alloys.

When tested for susceptibility to pitting in the same environments, these materials showed little evidence of being susceptible at 90°C, but very definite susceptibility at 170°C, even though the chloride concentration was an order of magnitude lower at the higher temperature. Polarization tests performed by Marsh et al. (1986c) in a series of granitic groundwaters indicated that C4 was only susceptible to pitting at 90°C when the groundwater contained HCO_3^- and F^-. This dependence of pitting susceptibility on the presence of anions other than chloride was confirmed by Vu Quang et al. (1986), who systematically studied the susceptibility to pitting based on the relative concentration of Cl^- to that of the anions HCO_3^-, CO_3^{2-} and SO_4^{2-}. Pitting was observed only at 90°C, provided the chloride activity was higher than a critical value determined by the activity of the other inhibiting anionic species.

From anodic polarization curves, Vu Quang et al. (1986) determined the susceptibility to pitting of the alloys C4, C22 and G30 in deaerated 3% sodium chloride and deaerated brines. They found that an increase in chromium and, to a larger extent, molybdenum concentrations had a beneficial effect in preventing pitting, in contrast to the smaller detrimental effects of increases in nickel and iron content. On the basis of this analysis, Hastelloy C22 exhibits the highest resistance to pitting, and, of the alloys under consideration, the higher molybdenum content of C4 and C276 should make them more resistant to pitting than Inconel 625.

In terms of salinity, potential conditions in a Canadian vault would straddle the range from low (i.e., WN-1, $[Cl^-] = 6460\ mg{\cdot}L^{-1}$) to high salinity (i.e., SCSSS, $[Cl^-] = 34\ 260\ mg{\cdot}L^{-1}$) (Figure 3-30). Carbonate

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[36] Composition of moisture (ppm): HCl, 4.9; H_2SO_4, 15 (see Table 1 in Casteels et al. (1985)).

concentrations are too low to exert any inhibiting effect on pitting by competitive adsorption, but it is possible that sulphate (1040 $mg \cdot L^{-1}$) could inhibit localized corrosion in WN-1. Such adsorption effects have not been considered in corrosion testing on alloys C276 and Inconel 625 (Postlethwaite 1991). Our work focused on electrochemical and immersion tests under a variety of temperature and chloride concentration conditions. The results indicated that C276 has a superior resistance to localized corrosion over 625. The susceptibility to crevice corrosion and pitting measured electrochemically was generally much worse than that observed in immersion tests, particularly for 625. Such discrepancies are common, and inevitably electrochemical tests are considered overly conservative (Nuttall and Urbanic 1981). The dilemma is whether the absence of crevice corrosion and pitting on immersion samples can be taken as proof that these processes would not initiate under those conditions. The electrochemical tests tell us that, once initiation has occurred, propagation is probable.

The resistance of C267 and 625 to localized corrosion decreased rapidly as the temperature was raised, as shown by the fall in passivation breakdown potentials to more active values (Postlethwaite 1991). At higher temperatures, this breakdown potential was independent of chloride concentration and alloy composition. However, for temperatures below 100°C neither material appears to be susceptible to film breakdown and, hence, localized corrosion, even in 20 wt.% NaCl. Provided we accept these immersion test results as opposed to the more conservative electrochemical results, then both C276 and 625 appear to be viable materials under Canadian disposal vault conditions. A critical temperature for film breakdown, of ~100°C under granitic conditions, should be compared with the value of ~55°C for C4 determined by Schmitt and Köster (1986) in Q-brine.

Influence of radiation

The impact of radiation has received only minor attention, even though many observations indicate that radiation effects are significant in a wide range of environments.

The effect of irradiation (8×10^3 $Gy \cdot h^{-1}$) on the uniform corrosion of Hastelloy C4 in granitic solutions (90°C) was beneficial; slightly thicker and more protective films were formed (Marsh et al. 1986c). However, irradiation can induce localized corrosion, provided the groundwater contains fluoride and carbonate. No convincing explanation was offered.

In the highly saline Q-brines at 90°C the impact of irradiation (10^3 $Gy \cdot h^{-1}$) on corrosion of C4 was more marked: the average corrosion rate (after >600 d) calculated from weight losses increased by a factor of ~10^2 (Smailos et al. 1986a). Most of this increased weight loss was attributable to localized corrosion, with pit depths and crevices penetrating up to 1000 and 100 μm respectively. This behaviour suggests that the oxidants formed radiolytically (e.g., H_2O_2, Cl_2^-) act as cathodic depolarizers, driving the corrosion potential up to and beyond the breakdown potential. This sensitivity of C4 to radiolytically produced oxidants was confirmed by Schmitt and Köster (1986), who studied the impact of added H_2O_2 and ClO^- on the corrosion potential (E_{CORR}) and the general form of the polarization curve. Peroxide concentrations as small as ~5×10^{-4} to 5×10^{-3} $mol \cdot L^{-1}$ shifted E_{CORR} by up to 200 mV.

For thin-walled containers filled with reprocessed waste, such high dose rates are achievable at sufficiently high fission-product loadings. However, in disposing of reference used CANDU fuel under Canadian vault conditions, dose rates would be much lower (~50 $Gy \cdot h^{-1}$) and the chances of generating sufficient oxidant (radiolytically) to drive $E_{CORR} > E_b$ are much lower. However, even at these lower dose rates Smailos et al. (1988) have shown that crevice corrosion and pitting can be initiated on Hastelloy C4 in brine solutions. Since no work on irradiation effects has been performed under Canadian vault conditions, the durability of nickel-based alloys remains unconfirmed under these conditions.

A major reason for preferring nickel-based alloys over stainless steels is their improved resistance to SCC, an asset attributed to their high nickel content. However, testing under geothermal brine conditions (high temperature, high salinity) showed that these alloys were susceptible to transgranular SCC, the cracking mode typical for non-sensitized austenitic alloys (Postlethwaite 1991, Ellis and Conover 1981, Cramer and Carter 1980).

Although slow strain rate tests on C4 under potentiostatic control in Q-brine (90°C) showed good resistance of C4 to SCC at potentials close to the free corrosion potential (Plante and Helie 1986), even a slight positive shift in potential (~50 mV) led to rapid cracking together with general dissolution. Since such small positive shifts in potential may be achievable (perhaps as a result of water radiolysis), SCC must be considered a possible failure mode in highly saline environments.

Also, SCC tests show that C276 could suffer from cracking at potentials close to the corrosion potential in granitic solutions, but not in argillaceous solutions (Plante and Helie 1986). Since the free corrosion potential of C276 in neutral media corresponds to the cracking domain in acidified solutions, it was concluded that cracking was possible if local acidification occurred, such as inside a crevice.

Even though Postlethwaite's results indicate that nickel-based alloys would not suffer localized corrosion under Canadian disposal vault conditions, where the maximum container temperature would not exceed 100°C (Postlethwaite 1991), it is difficult to recommend their use without further testing. The discrepancies between susceptibilities to localized corrosion determined from immersion tests and those determined electrochemically leave doubt as to whether or not such processes would occur. Also, the safety margin for film breakdown—the difference between the corrosion potential and the film breakdown potential—appears to be small in hot saline solutions, and remains undetermined for Canadian groundwaters. In the absence of a good understanding of the factors controlling crevice or pit propagation, the approach used to predict the long-term durability of titanium containers (Section 3.7.4.5) cannot be applied.

Also, irradiation has been shown to enhance localized corrosion. At the moment, it is not known whether a decreasing impact of irradiation with decreasing dose rate would leave these materials immune to radiation effects at the low dose rates expected after a few hundred years in a Canadian vault of the reference design.

Finally, the results of SCC tests show that Hastelloy C4 may be susceptible to SCC in granitic groundwaters of moderate salinity at temperatures around 90°C. Since Canadian groundwaters may be more saline and temperatures in excess of 90°C are anticipated, there is no guarantee that the untested alloys C276 and 625 would not be susceptible to SCC, particularly under acidified crevice conditions in a Canadian vault.

3.7.4.5 Titanium and Titanium Alloys

Titanium metal is unstable in air and water. However, because of the metal's high affinity for oxygen, a protective oxide film forms rapidly when a fresh metal surface is exposed to air or moisture. In fact, a damaged oxide film can generally reheal itself, provided traces (i.e., $\mu g \cdot g^{-1}$) of oxygen or water are present in the environment. The nature of this film remains essentially unaltered by traces of alloy impurities (e.g., Fe in Grade 2) or minor alloy constituents (e.g., Ni and Mo in Grade 12), making titanium and its alloys very resistant to uniform corrosion in water, natural waters and steam to temperatures in excess of 300°C. The typical contaminants expected in natural waters, such as iron, sulphide, sulphate and carbonate do not affect this resistance.

Of more relevance to titanium's viability as a container material is its resistance to corrosion in saline environments. Titanium alloys exhibit negligible corrosion in seawater to temperatures as high as 260°C (Schutz 1986, Schutz and Thomas 1987), and unalloyed titanium has been used for over 20 a in seawater applications, such as power generation, desalination and oil refining. Compilations of uniform-corrosion rates for Grades-2 and -12 titanium list the rate as nil (Schutz and Thomas 1987).

Like most passive metals and alloys, titanium alloys are susceptible to some localized corrosion processes. When discussing such susceptibilities it is necessary to distinguish between two classes of alloy:

1. alpha- or near-alpha-phase alloys used in industrial applications in which corrosion resistance is a primary requirement; and

2. alpha-beta-phase alloys developed for applications in which strength is a primary requirement.

Materials in the first class exhibit relatively few modes of degradation compared with those in the second class. In particular, while materials in class 2 may be susceptible to SCC in aqueous chloride solutions, those in class 1 are considered immune. Not surprisingly, the three titanium alloys considered as potential container materials, Grades 2, 12 and 7, (Table 3-5) belong to class 1. Further major advantages of these alloys are their apparent immunity to microbially induced corrosion and their very positive pitting potentials, which rule out the possibility of container failure by pitting. A more extensive justification for ignoring these processes has been given in Section 4.6 of Johnson et al. (1994).

Despite their excellent resistance to uniform and pitting corrosion, the use of titanium alloys in hot saline environments is sometimes limited by the fact they may undergo crevice corrosion. Crevices can form under adhering deposits, in metal-to-metal joints, such as poor welds, and at sites of severe mechanical surface damage, such as heavy scratches or gouges. All such sites are potentially available on container surfaces. Detailed reviews of the nature of the crevice corrosion of titanium alloys and the factors that affect it are available (Schutz and Thomas 1987, Schutz 1988), as are general discussions of the crevice corrosion process (Oldfield and Sutton 1978a, 1978b, 1980; Krueger and Rhyne 1982; Oldfield 1987; Sharland and Tasker 1988; Sharland et al. 1989).

Titanium alloys perform excellently in hydrogen-containing environments, since the surface oxide film is a highly effective barrier to hydrogen penetration. Nevertheless, hydrogen-induced cracking (HIC) of titanium alloys is a possibility, particularly with alpha and alpha-beta alloys, where excessive hydrogen uptake can induce the precipitation of titanium hydride in the alpha phase. The formation of hydrides can occur at quite low hydrogen contents ($\gtrsim$100 $\mu g \cdot g^{-1}$ according to Schutz and Thomas (1987)), since the terminal solubility of hydrogen in the alpha phase is low (~20 $\mu g \cdot g^{-1}$ at 300 K (Paton et al. 1971)). In fact, titanium hydride precipitates are commonly present in the commercially pure material.

Two forms of HIC merit consideration: general embrittlement, where extensive hydride formation is observed in the metal; and delayed hydride cracking (DHC) (sometimes referred to as sustained load cracking), where hydride formation at the tip of an advancing crack is the important criterion. This last mechanism is difficult to rule out even in the relatively low-strength Grade-2 alpha alloy, because of the presence of hydrides in the commercially supplied material.

The ASTM specified compositions of the three titanium alloys chosen as potential container materials are given in Table 3-5. Considering the above discussion, it is not surprising that the evaluation of these alloys has concentrated on their susceptibility to crevice corrosion and HIC.

TABLE 3-5

NOMINAL COMPOSITIONS (wt.%) FOR VARIOUS CANDIDATE GRADES OF TITANIUM

Grade	N*	C*	H*	Fe*	O	Mo	Ni	Pd
2	0.03	0.10	0.015	0.30	0.25			
7	0.03	0.10	0.015	0.30	0.25			0.2
12	0.03	0.10	0.015	0.30	0.25	0.3	0.8	

* indicates maximum values according to the specifications

According to Schutz and Thomas (1987), the resistance to crevice corrosion improves in the order Grade 2 < Grade 12 < Grade 7. Since hot, possibly acidic, highly saline environments are anticipated in vaults located in salt deposits, Grade 12 is the preferred material for containers in the WIPP brines in the U.S., and the even more resistant Grade 7 was evaluated for use in West German brines (Smailos et al. 1985) (see Figure 3-30). Under the more benign conditions anticipated in a Canadian disposal vault (lower temperatures, lower salinities, and non-acidic, Figure 3-30), Grade-2 titanium has been chosen as the reference material, with Grade 12 as an alternative option. The Grade-7 alloy was defined as one of the reference materials in a joint testing program undertaken by the CEC and has been tested in a wide range of environments, including salt brines, clays and saline granitic conditions.

Uniform corrosion

As part of the WIPP project, Braithwaite and Molecke (1980) and Molecke et al. (1981) measured the uniform-corrosion rates for Grades-2, -7 and -12 titanium in seawater and in concentrated brines at temperatures from 70 to 250°C. All three grades exhibited acceptable corrosion rates under both oxidizing (500 $\mu g \cdot g^{-1}$ O_2) and "reducing" (30 $pg \cdot g^{-1}$ O_2) conditions. Variations in redox conditions were unimportant except for Grade-2 titanium at 250°C in concentrated brine (~5 $mol \cdot L^{-1}$ Cl^-; up to 1.4 $mol \cdot L^{-1}$ Mg^{2+}), where the uniform-corrosion rate became extremely large (>3000 $\mu m \cdot a^{-1}$) under oxidizing conditions. At temperatures more representative of expected vault conditions ($\lesssim$100°C), the uniform-corrosion rates for all materials were very low (<0.1 $\mu m \cdot a^{-1}$).

Uniform-corrosion rates for Grade-7 titanium, and to a lesser extent Grade 2, have been measured in a variety of vault environments ranging from clay to salt brines as part of the CEC joint testing program (Smailos et al. 1985, 1986b; Casteels et al. 1985). Invariably, corrosion rates were $\lesssim$0.1 $\mu m \cdot a^{-1}$, and in most cases corrosion was confined to the formation of a very thin (~10 nm) layer of oxide.

In the Canadian program, measurements were made on many specimens exposed to a variety of unirradiated and irradiated environments, including solutions, buffer slurries, and compacted bentonite (Ikeda et al. 1986, 1990a). Exposure periods ranged from a few months to approximately 5 a at temperatures from 100 to 150°C; for Grade 2 exposed to SCSSS ([Cl^-] ~ 0.97 $mol \cdot L^{-1}$; 100°C; 4.5 $Gy \cdot h^{-1}$ ± 0.5 $Gy \cdot h^{-1}$), the corrosion rate decreased from ~0.25 $\mu m \cdot a^{-1}$ (8-month exposure) to ~0.05 $\mu m \cdot a^{-1}$ after 2 a. Even these rates are high when compared with those of Mattsson and Olefjord (1984), who studied the rate of oxide thickening on titanium specimens in water and embedded in bentonite. Since immeasurable amounts of titanium dissolved into solution, they equated the uniform-corrosion rate to the rate of oxide growth, and estimated that the oxide layer would be ~160 μm thick after exposure for 10^5 a. Corrosion to such a depth on a container wall would be negligible.

The effect of radiation has been tested on the uniform corrosion of both Grades-2 and -12 titanium in a wide range of environments of varying salinities, ranging from basaltic groundwaters (140 $mg \cdot L^{-1}$ Cl^-) (Westerman et al. 1982, Nelson et al. 1984) to brines (190 000 $mg \cdot L^{-1}$ Cl^-) (Braithwaite and Molecke 1980; Molecke et al. 1981), and at temperatures ranging from 90°C (brines) to 250°C (basaltic waters). Dose rates ranging from 10^2 to 10^5 $Gy \cdot h^{-1}$ were used. Unfortunately, none of these studies was particularly comprehensive. At combinations of high dose rate and high temperature, some increase in the uniform-corrosion rate of Grade 2 (by a factor of two to three) was observed. The impact on Grade 12 was minor. The results of Ikeda et al. (1990a) for both Grades 2 and 12 exposed to SCSSS ($[Cl^-] \sim 0.97$ $mol \cdot L^{-1}$) for periods up to 5 a at 100 and 150°C showed no measurable effect of irradiation. This minor impact of irradiation is not surprising in view of the results of Kim and Oriani (1987a,b), who showed that the film formed on Grade-12 titanium, after exposure to irradiated brine (1.5×10^3 $Gy \cdot h^{-1}$; 2 a; 25 and 108°C) was thicker, less defective and more protective than that formed in the absence of radiation.

Clearly, container failure as a result of uniform corrosion is highly unlikely, under even the most aggressive vault conditions. The one exception is the poor performance of Grade-2 titanium in oxidizing acidic brines (i.e., Mg^{2+}-containing) at high temperatures (250°C) (Braithwaite and Molecke 1980). For this reason Grades 12 and 7 are preferred in brine environments.

Crevice corrosion

The use of titanium containers is contemplated in three distinct environments for geological disposal of nuclear fuel waste: in salt deposits; in granitic rock surrounded by buffer/backfill materials, such as bentonite clay/sand mixtures; and in relatively shallow clay deposits. None of these environments is likely to support the conditions required for crevice corrosion, i.e., acidity within the creviced area and a supply of oxidant to support crevice propagation once initiation has occurred. The maintenance of acidic conditions would appear more likely in salt deposits, especially if high-temperature ($\gtrsim$200°C) inclusion brines (Mg^{2+}-containing) made contact with the containers. For containers surrounded by clay at lower temperatures ($\lesssim$100°C), i.e., the conditions anticipated for a Canadian vault, the prospects for initiating crevice corrosion appear poor. The clay buffer should maintain the pH of the pore water in the 7 to 9 range (Lemire and Garisto 1989), making it difficult to establish acidic conditions. Also, the buffer's ability to control redox conditions by the reaction of oxidants with oxidizable minerals within the buffer and backfill, and to impede transport of oxidants to the container's surface, would reduce the supply of oxidants required for extensive crevice propagation.

Despite these caveats, the possibility of crevice corrosion cannot be entirely ruled out. According to Schutz and Thomas (1987) and Schutz (1988), initiation does not occur at temperatures below ~70°C. However, for both salt deposits and Canadian granitic environments, chloride concentrations would be above those required for the initiation of crevice corrosion, and container surface temperatures would be >70°C over the early emplacement period when conditions would be oxic. Also, the results of Ikeda et al. (1990c, 1994) show that once crevice corrosion is initiated on Grade-2 titanium at temperatures greater than 70°C, its propagation can continue at temperatures as low as 30°C. This makes the study of the rate of crevice propagation an essential component of any program designed to determine the feasibility of using titanium alloys as waste container materials.

Since titanium is used as a construction material in many saline environments, its crevice corrosion has been widely studied and many of the important features have been discussed (Schutz 1988). Within the context of nuclear fuel waste management programs, the crevice corrosion of all three grades has been studied in Germany, the U.S.A. and Canada. Grade-2 titanium was ruled out as a candidate container material in salt deposits when it was found to exhibit extensive crevice corrosion in brine at 250°C (Molecke et al. 1981, Ruppen et al. 1981). In similar tests (Molecke et al. 1982), the performance of Grades 7 and 12 proved much more promising: no crevice attack was observed after 30 d of exposure in deaerated brine. This lack of crevice corrosion was apparently confirmed by the tests of Schutz and Hall (1984) but proved inconsistent with the findings of several other investigators (Ahn and Soo 1982a,b; McKay 1984, 1987; Stahl and Miller 1983).

It would appear that immunity to crevice corrosion, especially in hot brine environments, cannot be claimed even for the most corrosion resistant of titanium alloys, Grade 7. However, the extent of its propagation appears to be limited. For both salt deposits and Canadian granitic environments, the assumption that crevice corrosion can occur is conservative, since no crevices have been observed to initiate on Grade-12 specimens buried at the WIPP site (Molecke et al. 1988) and have been found only with artificially creviced samples of Grade-2 titanium under granitic conditions (Ikeda et al. 1989).

In the Canadian program, artificially creviced samples, often coupled to large uncreviced titanium specimens, were used to force initiation to occur and thus allow us to study the much more reproducible crevice propagation (as opposed to initiation) reaction using electrochemical techniques (McKay and Mitton 1985, Ikeda et al. 1986). Using such methods we studied the effect of various parameters on the rate of crevice propagation of both Grades-2 and -12 titanium. These parameters included

- the effect of temperature over the range from 30 to 150°C;
- the impact of oxygen concentration ranging from oxygen-saturated solutions to anoxic conditions;
- the impact of alloy impurities and microstructure, particularly on the crevice corrosion rate of Grade-2 titanium;
- the mode and depth of penetration within the crevice (using a combination of metallographic and image analysis techniques);
- the effect of varying the chloride concentration of the groundwater;
- the impact of irradiation; and

- the effects of welding.

The details of these studies have been published elsewhere (Ikeda and McKay 1985; Ikeda and Clarke 1986; Ikeda et al. 1986, 1990a,b,c, 1991, 1992, 1994; Ikeda and Shoesmith 1990; McKay 1987; McKay and Mitton 1985; Shoesmith 1990; Shoesmith et al. 1992, in press) and will only be summarized here.

Our studies found that Grade-2 titanium corrodes uniformly within the creviced area, and the rate of crevice propagation is predominantly determined by temperature and oxygen concentration. The rate of oxygen reduction on surfaces external to the creviced area appears to be rate-controlling, and the overall extent of crevice corrosion is determined by the amount of available oxygen. When the oxygen is exhausted, repassivation occurs. If sufficient oxygen is present, propagation continues at all temperatures down to ~30°C. In agreement with the results of Tsujikawa and Kajima (1991), the rate, and to a lesser extent the propagation, of crevice corrosion is dependent on the iron content of the material.

By contrast, Grade-12 titanium corrodes locally within the creviced area, and the extent and depth of penetration appear to be controlled predominantly by properties of the material, such as alloy content and phase composition, rather than by properties of the environment, such as oxygen concentration and temperature. The dependence of propagation rate on temperature is complex, suggesting that the relative importance of various kinetic steps changes with temperature. For temperatures below 70°C, the alloy appears to be immune to crevice corrosion. Above 70°C, the extent of crevice corrosion is not related to the amount of available oxidant.

Radiation appears to cause repassivation of crevices on Grade-2 titanium (Ikeda et al. 1990a). There is no evidence to suggest that radiation accelerates the crevice propagation rate. This is not surprising at the low dose rates used ($\sim 10^2$ $Gy \cdot h^{-1}$), since the concentration of oxidizing radiolysis products formed would be very low ($\ll 10^{-7}$ $mol \cdot L^{-1}$). Only within the restricted confines of the crevice, where the surface area of reactive metal would be very high compared with the volume of radiolytically decomposed solution, could such concentrations of radiolytically produced oxidants be expected to exert any influence. It is worth noting again that such dose rates (i.e., ~50 $Gy \cdot h^{-1}$) represent the maximum expected under Canadian vault conditions.

Immersion tests and electrochemical tests have been performed on welded specimens, and the effects of heat treatment, to simulate the weld heat-affected zone, on the crevice corrosion behaviour of Grade-2 titanium have been investigated. All of these studies show a decreased susceptibility; i.e., the microstructural changes induced by welding improve the material's resistance to crevice corrosion. The reasons for this improved performance are unclear, but the electrochemical results, coupled with results from transmission electron microscopy, suggest that the redistribution of beta-phase material is involved.

It is clear from these studies that, although crevice corrosion of titanium under waste disposal conditions might occur, its duration would be restricted. For the Grade-2 material, the time for which crevices propagate would be limited by the supply of oxygen, and the time period required to drive vault conditions anoxic would be critical. In a Canadian vault the consumption of oxidants is expected to take no more than ~300 a (Johnson et al. 1994). For Grade-12 titanium the duration of crevice propagation is controlled by the properties of the material and should not exceed ~120 a, the average time taken for container temperatures to cool to less than ~70°C. These periods of propagation undoubtedly represent conservative overestimates.

Hydrogen-induced cracking

Despite the fact that titanium alloys are widely and successfully used in hydrogen-containing environments and under conditions in which galvanic couples or cathodic charging causes hydrogen to be evolved on the titanium surface, it is difficult to demonstrate unequivocably that HIC would not be a long-term container failure mechanism.

Two forms of HIC appear possible: general embrittlement, where extensive hydride formation is observed in the metal; and DHC, sometimes referred to as sustained load cracking (SLC), where hydride formation at the tip of an advancing crack is the important phenomenon. Results indicate that neither Grade-2 nor Grade-12 titanium suffers from HIC at the hydrogen levels normally encountered in the as-received condition (Clarke et al. 1992). In tests using compact tension specimens precracked in fatigue, the fractures appeared extremely ductile, and the crack had to be continually pushed through the specimen by increasing strain. Consequently, in the absence of corrosion and hydrogen absorption, early failure as a result of SLC would not occur, and the retention of container integrity becomes a question of prudent engineering.

The determination of susceptibility to HIC and the time at which it might initiate on a waste container becomes a matter of establishing the combinations of stress and hydrogen concentration that leads to failure, whether the latter occurs by plastic collapse, hydrogen-induced slow crack growth or general embrittlement by hydride. At present, the stress distribution in a waste container subsequent to closure by welding and its variation throughout the lifetime of the container is not known. Consequently, it is prudent to assume that stresses would not relax with time after emplacement and that the time when HIC became possible on a container would be determined by the rate and extent of hydrogen absorption.

The slow strain rate tests of Clarke et al. (1992) showed that high stress intensity factors, independent of hydrogen content up to ~500 $\mu g \cdot g^{-1}$, were required to cause slow crack growth in both Grades-2 and -12 titanium. Slow crack growth was, however, no longer observed in either material above 500 $\mu g \cdot g^{-1}$, where fast cracking because of general embrittlement occurs. These observations are in agreement with the results of Schutz and Thomas (1987) and Sorensen and Ruppen (1985). The latter authors found no effect of hydrogen content up to at least 445 $\mu g \cdot g^{-1}$ for smooth specimens of Grade-12 titanium in both air and hot brine solutions (150°C). In fact, they observed only a minor impact on tensile properties of hydrogen contents as high as 975 $\mu g \cdot g^{-1}$. There is, however, evidence that the threshold value of hydrogen concentration at which the transition from slow cracking to fast fracture occurs is influenced by the detail of the microstructure, including texture introduced by the fabrication process.

A number of attempts have been made to measure the amount of hydrogen absorbed by titanium in environments relevant to waste vaults. Mattsson (1979) observed no measurable hydrogen absorption by Grade-2 titanium exposed to seawater for 300 d at 130°C. Hydrogen absorption has been observed at crevice corrosion sites where the metal is active and the environment acidic (Clarke et al. 1989). This observation is consistent with the electrochemical results of Phillips et al. (1972) in acidic solutions. Westerman (1988) analyzed the total hydrogen content of crevice-corroded Grade-12 specimens exposed for 15 months to concentrated brine (150°C), but found no enhanced hydrogen absorption compared with planar samples under the same conditions.

Other authors have observed increased hydrogen contents for Grade-12 titanium exposed to magnesium-containing brines characteristic of those anticipated in a salt repository. Westerman (1990) observed hydrogen absorption by Grade-12 titanium exposed to brine at 150°C in the presence of a radiation field (3×10^2 $Gy \cdot h^{-1}$). Absorption appeared to stop after 6 months when a total of ~30 $\mu g \cdot g^{-1}$ had been absorbed. The duration of the tests was 15 to 20 months. These levels were much lower than those quoted for as-received Grade 12 by Schutz and Hall (1984), who observed hydrogen contents ranging from 27 to 81 $\mu g \cdot g^{-1}$. In a similar neutral brine (pH 6.5 to 8.0), Kim and Oriani (1987a) observed hydrogen absorption (up to ~90 $\mu g \cdot g^{-1}$) over an exposure period of 2 a. The amount absorbed was only slightly greater at 108°C than at 25°C, and in both cases appeared to be levelling off with exposure time.

These results suggest that the passive film on Grade-2 titanium is a highly effective barrier to hydrogen penetration, as stated by Schutz and Thomas (1987), but raise doubts about the ability of the passive film on Grade 12 to totally protect the metal against hydrogen absorption. Consistent with a lower resistance of Grade 12 to hydrogen absorption is the observation of Schutz and Covington (1981) that the thermally formed oxide on Grade 12 does not provide as effective a barrier to hydrogen entry as that on Grade 2.

From this discussion it is clear that, if hydrogen levels sufficient to cause brittle fracture are to be achieved, then a substantial period of crevice corrosion accompanied by hydrogen absorption would have to occur. Thus, the two potential failure modes for titanium containers, crevice corrosion and hydrogen-induced cracking, are inextricably linked, and the rate and duration of crevice corrosion would determine the amount of hydrogen absorbed. The implications of this linkage have been discussed in some detail elsewhere (Ikeda et al. 1990a, 1994; Shoesmith et al. 1992, in press). As mentioned earlier, the duration of crevice corrosion would be limited by repassivation on both Grade-2 and Grade-12 titanium. However, it remains to be demonstrated whether sufficient hydrogen is absorbed during crevice corrosion to leave the material susceptible to HIC once repassivation has occurred. Once repassivation of crevices has occurred, hydrogen absorption would proceed at an extremely low rate, which would be related to the rate of uniform corrosion (Johnson et al. 1994). As discussed above, the hydrogen absorption rate under passive conditions may be somewhat higher for Grade-12 than for Grade-2 titanium.

To date, the cracking behaviour of both materials has been studied only at ambient temperature, and present understanding is based on the limited amount of published work on alpha/beta alloys that are known to be more susceptible to HIC (Boyer and Spurr 1978, Moody and Gerberich 1982, Lederich et al. 1982). The evidence of Boyer and Spurr (1978) for the Ti-6Al-4V alloy suggested that extremely high stress intensities would be necessary to produce even minor crack growth at temperatures above 20°C. If these data are accepted as applicable to both Grades-2 and -12 titanium, a conservative assumption especially for Grade-2 titanium, then HIC is unlikely to occur even in materials containing substantial concentrations of hydrogen until considerable cooling of the container has occurred. According to the results for Ti-6Al-4V, 20°C appears to be an upper temperature limit above which only failure by ductile overload would occur.

Modelling Container Failure

A model to predict the failure rate of Grade-2 titanium containers has been produced as a component of the vault model used to assess the performance of a reference disposal system in the Canadian program (Johnson et al. 1994). This model is based on the assumption that crevice corrosion would be the main failure mechanism, and that any containers that did not fail by this mechanism would fail by HIC. The use of Grade-2 titanium for the reference container does not necessarily mean that this grade of titanium is judged to be a more viable candidate than Grade 12. At present, the database for Grade 12 is insufficient to justify the necessary long-term extrapolations of corrosion behaviour. Since the extent of crevice corrosion would be severely limited with Grade 12, eventual failure would undoubtedly be by some other corrosion process, such as embrittlement. Until a firmer understanding of the processes of hydrogen absorption and HIC in Grade-12 titanium is obtained, prediction of container lifetimes remains difficult. By comparison, failure by crevice corrosion is the most likely mode of degradation for Grade 2. Since a good mechanistic understanding and a substantial database of crevice corrosion rates are available for commercially available Grade 2, a justifiable, if necessarily conservative, prediction is possible.

The model is based on the following assumptions, many of which are very conservative:

1. Crevice corrosion initiates rapidly on all containers.

2. Crevice corrosion is a chemical process controlled by temperature and redox conditions. The rate-controlling process appears to be the reduction of oxygen on surfaces external to the crevice.

3. There is always sufficient oxygen available for crevice corrosion to propagate indefinitely without repassivation.

4. The reference container material is a low-iron-content Grade-2 material, the Grade-2 material most susceptible to crevice corrosion.

5. Crevice propagation proceeds as a localized front ahead of a uniform-corrosion front. The localized front reaches a limiting depth and subsequently does not proceed faster than the general front. The depth of this localized front does not exceed the wall thickness reserved to guarantee the mechanical integrity of the container before the general front exceeds the corrosion allowance (see Section 3.5.6).

6. HIC is a low-temperature process and does not occur until containers cool to <30°C. The rationale for selecting this temperature has been discussed in detail in Sections 4.6.4 and 4.7.3 of Johnson et al. (1994).

7. Once containers cool to less than 30°C, failure by HIC occurs rapidly. This assumes that sufficient hydrogen absorption has occurred and that the residual tensile stresses in the container are large enough to drive the cracking.

8. Only a very small number of containers (~1 in 5000) fail rapidly (in ≤50 a) from defects undetected during inspection prior to emplacement.

9. Once failure occurs, the container provides no further protection against rapid ingress of water and subsequent leaching of the fuel.

The basis for these assumptions has been discussed in detail elsewhere (Johnson et al. 1994).

By analyzing the temperature distributions within the vault and distributing the crevice corrosion rates according to both their variation with temperature and their measured uncertainty, we have predicted the failure rate of containers for the reference disposal vault. Apart from a few containers that cool rapidly, and hence fail by HIC (~1 to 2%), the majority of containers are predicted to survive beyond 1000 a before failing by crevice corrosion. A very small fraction of containers («1%) crevice corrode slowly enough to eventually fail by HIC after a few thousand years. The details of this model as well as a discussion of the predictions have been given elsewhere (Johnson et al. 1994).

In summary, it can be concluded that titanium alloys are excellent candidates for container construction materials under a wide range of vault conditions. Although Grade 2 can be justified for the disposal of used fuel under granitic conditions when temperatures in excess of 100°C are very unlikely, it does not appear viable for the disposal of vitrified fuel-reprocessing waste with high fission-product loadings when contact with acidic brines is a possibility. Under these conditions, either Grade-12 or Grade-7 titanium would be preferable, since, for wall thicknesses of several millimetres, neither material appears capable of sustaining crevice corrosion over time periods long enough to cause container failure.

Despite this reservation, titanium alloys appear to be the best of the corrosion-resistant options, since they demonstrate much better resistance to localized corrosion processes than either the nickel-based alloys or the stainless steels. Unlike the nickel-based alloys they do not appear susceptible to enhanced corrosion in the presence of irradiation, even at dose rates as high as 10^3 $Gy \cdot h^{-1}$. On the contrary, radiation appears to assist the titanium alloys to maintain passivity, and thereby reduces their sensitivity to localized corrosion.

Titanium alloys also appear to have an advantage over other corrosion-resistant materials when welds are considered. Significant metallurgical changes can occur in complex multiphase alloys when they are subjected to the heat treatments associated with welding, both in the weld itself and in the surrounding heat-affected zones. Since Grades-2, -7 and -12 titanium contain so little alloy content and second phase, metallurgical changes during welding are minor and actually appear to improve corrosion performance.

More recently, the framework for a model that takes into account the limited propagation of crevices as vault conditions become anoxic has been outlined (Shoesmith et al., in preparation). Preliminary calculations using this model indicate that titanium container lifetimes of tens to hundreds of thousands of years can be achieved.

3.8 SUMMARY

The choice of an appropriate container for the disposal and long-term isolation of used-fuel waste is likely to be unique for individual countries. Differences between container design and choice of construction material arise from a number of factors, including the waste form for disposal, its characteristics and geometry, choice of geological disposal medium, the required isolation period, engineering considerations (including both the vault and container), regulatory requirements and public and cultural traits.

In the Canadian program, the container is required to isolate unreprocessed used CANDU fuel for a minimum of 500 a in a disposal vault constructed in crystalline plutonic rock of the Canadian Shield. In this disposal medium, commercially pure titanium and oxygen-free copper have been identified as the preferred materials for container construction, as a result of their chemical durability in the anticipated groundwater environment. The manufacturing considerations relevant to these materials, and the anticipated physical conditions that containers would be subjected to in the vault, have strongly influenced the approach to container design. For the conceptual engineering study for a used-fuel disposal centre and the performance-assessment case study, the method of container emplacement in the vault is within boreholes, with the container surrounded by a layer of clay-based buffer material. A cylindrical container, approximately 2.2 m high and 0.63 m in diameter, capable of retaining 72 CANDU fuel bundles, could be accommodated within each borehole with a 0.25-m-thick annulus of buffer.

This size of borehole is within the capabilities of current hard-rock mining technology.

At a vault depth of 1000 m, the container would be subjected to a hydrostatic pressure of ~10 MPa and an additional 1- to 2.5-MPa buffer-swelling pressure, following eventual resaturation of the vault with groundwater. To provide structural support to the container shell, a number of container design options have been considered, including designs with adequate container-shell thickness and designs incorporating methods for internal support for thinner-shell containers, such as a compacted particulate material or a cast-in-place metal matrix. Structural-performance experiments conducted on full- and partial-scale prototypes of these container options showed that thinner-shell containers with internal support were the preferred option.

A program to investigate and develop fabrication and inspection techniques has shown that existing technologies can be used as a basis for the production of high-quality containers. For titanium, GTA welding and resistance-heated diffusion bonding can be used to produce container-shell joints, in particular the final closure weld, that would have to be done using remote technology. For copper, electron-beam welding is the joining method of choice. Inspection of the final closure weld, which would also have to be done remotely, could be achieved using ultrasonic techniques. For titanium, it has been demonstrated that this inspection could be accomplished remotely, using industrial robotics.

For metal-matrix-supported containers, it has been demonstrated that lead is the preferred matrix and that casting techniques to ensure a void-free matrix could be developed. For particulate-supported containers, the preferred particulate material is industrial glass beads. Short-term structural performance tests conducted on full-scale container prototypes have demonstrated that glass-bead particulate can be compacted into the residual space within a container to provide adequate support to the shell. In ongoing studies, investigations of long-term structural phenomena, including material creep and stress-relaxation behaviour, are under way. The results of these studies would be applied to the container-design component in any future optimization endeavour.

Future advances in production technology are certain to increase both quality assurance and container-manufacturing proficiency; however, such advances are not essential to current capabilities to produce high-quality containers.

To demonstrate flexibility of approach in container design, several alternative concepts have been investigated. These include a dual-wall container employing an inner supportive shell; a concrete container for storage, transportation and possibly disposal; ceramic materials for container-shell construction; and a fuel-reprocessing-waste container. These concepts are indicative of the type and range of options that could be studied and developed in future stages of the program, should that be warranted.

On the basis of demonstrated structural performance and related manufacturing, handling, and long-term performance considerations, the packed-particulate container design was selected for the conceptual engineering study for a used-fuel disposal centre and for the performance-assessment case study. The reference container is constructed with a corrosion-resistant shell of 6.35-mm-thick ASTM Grade-2 titanium, is compacted with glass beads, and would accommodate 72 CANDU fuel bundles.

This container option is not intended to represent a final selection; rather, it provides a common basis for the safety and engineering analysis for a conceptual used-fuel disposal centre that is illustrative of the analyses that would be used to evaluate a disposal facility proposed for implementation at an actual site.

Of all the materials studied as candidates for nuclear waste containers, titanium alloys appear to be the best of the corrosion-resistant materials and oxygen-free copper the best of the corrosion-allowance materials for Canadian disposal conditions.

Of the alternative corrosion-resistant materials, the nickel-based alloys look promising, but only if the container is shielded to keep radiation dose rates low. Until the question of their susceptibility to pitting and transpassive dissolution in the presence of radiation is addressed more thoroughly, they cannot be recommended for use in constructing designs of thin-walled, unshielded containers. The alternative corrosion-allowance material to copper would be iron or carbon steel. While many of the features of these latter materials are attractive, the question of hydrogen production and its impact on the performance of a sealed vault remains unresolved. Consequently, despite the existence of a model capable of conservatively predicting the lifetimes of iron or carbon-steel containers, it is difficult to recommend their use.

Both Grade-2 titanium and oxygen-free copper are capable of providing containment for the 500-a minimum period required. For Grade-2 titanium it has been predicted that ~99% of the reference packed-particulate containers would fail between 1000 and 7000 a after emplacement. The great majority of these failures would be by crevice corrosion. The remainder would fail by hydrogen-induced cracking, a small fraction (~1%) failing by this mechanism before 1000 a. These containment times are estimated on the basis of a container wall thickness of 6.35 mm, a standard plate thickness that is commercially available.

These predictions come from a very conservative model (outlined in Section 3.7.4.5 under Modelling Container Failure) that is based on a number of extremely conservative assumptions. Of these, the assumption that there would always be sufficient oxygen available for crevice corrosion to propagate indefinitely without repassivation is the most conservative. More recent calculations, yet to be completed, which take into account the consumption of oxygen, lead to much longer lifetimes in the range of 10^4 to 10^5 a.

A major extension in container lifetimes is expected to be attainable by switching to the more crevice-corrosion-resistant Grade-12 alloy. For this alloy failure is expected to be by hydrogen-induced cracking, but, at present, a model to predict the times for failure by this mechanism is unavailable.

Studies in various countries have shown copper to be an ideal container material for the conditions expected in a Canadian disposal vault. The extent of uniform corrosion would be limited by the lack of oxidants and by the restrictive mass transport conditions within the vault. Pitting would be the only localized corrosion process of concern. Even if it is conservatively assumed that aerated conditions persisted in the vault, 25-mm-thick copper containers are predicted to survive for between 30 000 and $>10^6$ a. A more realistic assessment that takes into account the reduction of oxidant concentration with time suggests that, with the exception of initially defected containers, all containers should remain intact for 10^6 a.

4. VAULT SEALING

4.1 INTRODUCTION

Any method developed to dispose of nuclear fuel waste in crystalline rock would result in excavations that would require subsequent sealing to retard groundwater movement and associated contaminant transport. Depending on the vault design and the site-characterization techniques adopted, this might involve the sealing of vertical shafts, horizontal tunnels and disposal rooms, container emplacement boreholes, vertical and horizontal boreholes used for site characterization, and major fracture zones. This chapter describes the sealing strategies, the sealing materials proposed for use, and the engineering application of these materials.

The seals are only one of a series of barriers against radionuclide release in the multibarrier system that would form a vault for nuclear fuel waste disposal. The performance of the sealing materials and the effectiveness of the designs for individual sealing elements would depend on the interactions of the seals with other components of the vault. Three factors that have affected the selection of sealing materials and seal design have been waste characteristics, the size and type of waste containers, and the range of possible site characteristics. These factors are described in detail in Chapters 2 and 3 of this document and by Davison et al. (1994a) and Simmons and Baumgartner (1994). However, in view of their importance to seal design and engineering, Section 4.2 of this chapter focuses on aspects of the three factors that have significantly influenced sealing materials selection and seal design for the reference disposal vault. The layout of the vault would also influence seal design and engineering. Alternative configurations for a vault are described and discussed by Simmons and Baumgartner (1994). Insofar as these alternative vault designs influence the design of vault seals, the alternatives are briefly reviewed here in Section 4.3.

The reference design for a disposal vault, which has been developed for the conceptual engineering study for a used-fuel disposal centre and for the performance-assessment case study, is briefly reviewed in Section 4.4. This provides a foundation for the review of the seal design process (Section 4.5), sealing material properties (Section 4.6), and the presentation of seal designs (Section 4.7). It is emphasized that the seal designs are not optimized; thus, future developments might lead to significant changes that could affect the design of a vault and other engineered barriers.

The reader is referred to two other primary references to the EIS (AECL 1994a) that deal with the design and performance of engineered barriers. The first is the report describing the vault model for postclosure assessment (Johnson et al. 1994), which presents conceptual and mathematical models for the postclosure performance of engineered barriers in a disposal vault. Descriptions of the evolution of the hydrogeochemical conditions in the reference vault and models for radionuclide release and transport through sealing materials are included. The second primary reference, the report on engineering for a disposal facility (Simmons and Baumgartner 1994), outlines the general considerations for engineering a vault and presents a detailed conceptual design for a reference disposal facility.

It is emphasized that the brief introductory sections here on vault engineering (i.e., Sections 4.2.2 to 4.4) are presented to establish a context for the subsequent descriptions of vault sealing technology. For a detailed description of vault engineering, the reader is referred to Simmons and Baumgartner (1994).

4.2 FACTORS AFFECTING VAULT DESIGN

4.2.1 Waste-Form and Container Characteristics

Both the characteristics of the waste form and the container can significantly affect vault design. The characteristics of used-fuel bundles and vitrified reprocessing wastes are discussed in Chapter 2. Of particular note is the cooling time of the fuel prior to disposal, which, in conjunction with the spacing of containers, can be used to control the maximum temperature reached in a disposal vault.

The size and shape of the disposal container and the choice of material for its construction would influence handling procedures, the size and shape of container emplacement rooms or boreholes, and the choice of sealing materials and their design and emplacement procedures.

For example, thick-walled containers might provide sufficient shielding to make contact handling feasible (NAGRA 1985). Thinner-walled containers would require the provision of shielding to protect personnel during container transport and emplacement operations. The disposal of used-fuel waste in massive steel containers, such as those proposed by NAGRA (1985), or concrete containers, such as the dry storage cask (Section 3.5.4.3), would not permit the deposition of the containers in boreholes in the floors of rooms as proposed in the reference vault design. Thus, emplacement of the containers in rooms was proposed by NAGRA (1985). Practical aspects of sealing technologies differ between the two disposal concepts. The use of carbon steel for construction of waste containers would introduce the additional issue of the production of H_2 as a result of corrosion, and the use of concrete containers could significantly change the geochemical conditions in the vault. These factors could affect both the choice of sealing materials and the facility design.

4.2.2 Site Conditions

The following site-specific, geological and hydrogeological factors at a disposal site would influence the vault design: the heat transfer properties of the rock; the in situ stresses and the related strength and deformational characteristics of the rock; the geothermal gradient; the degree of fracturing within the rock; and the potential occurrence of transient events, such as glaciation and seismic disturbances. These factors would affect the choice of depth for the vault, the size and geometry of excavations, and the spatial distribution of waste containers to meet any thermal constraints.

Three rock quality domains have been observed for the plutonic rocks of the Canadian Shield:

- fracture zones (faults), where intense fracturing is present;
- moderately fractured rock, in which widely spaced discrete fractures exist; and
- sparsely fractured rock, which contains microcracks and very sparsely distributed fractures that are not generally interconnected.

Such domains have been identified at the URL site and can be identified during site characterization in exploration boreholes and excavations (Davison et al. 1994a).

Sparsely fractured rock tends to have the lowest hydraulic conductivity, and volumes of such rock of suitable size would be favoured for waste emplacement. A possible sectional plan for a vault, presented in Figure 4-1 (after Simmons and Baumgartner 1994), shows that a vault might be segmented, with the waste containers deposited in emplacement areas in the sparsely fractured rock inside bounding fracture zones. A suitable minimum distance between the waste emplacement areas and the nearest highly fractured rock domain, termed the waste exclusion distance, would be determined from the results of disposal-system performance assessment calculations. It is likely that faults and fracture zones would be crossed by shafts and tunnels, and the intersection of these zones by excavations might require special attention during both excavation and final decommissioning and sealing of the vault.

The creation of the excavations to form the vault would disturb the natural stress fields and water flow paths in the host rock. Thus, it is likely that the hydraulic and radionuclide transport properties of the rock that immediately envelopes the excavations would differ from those of the undisturbed host media. Vault and seal designs would be required to accommodate these disturbances and their possible effects on system performance.

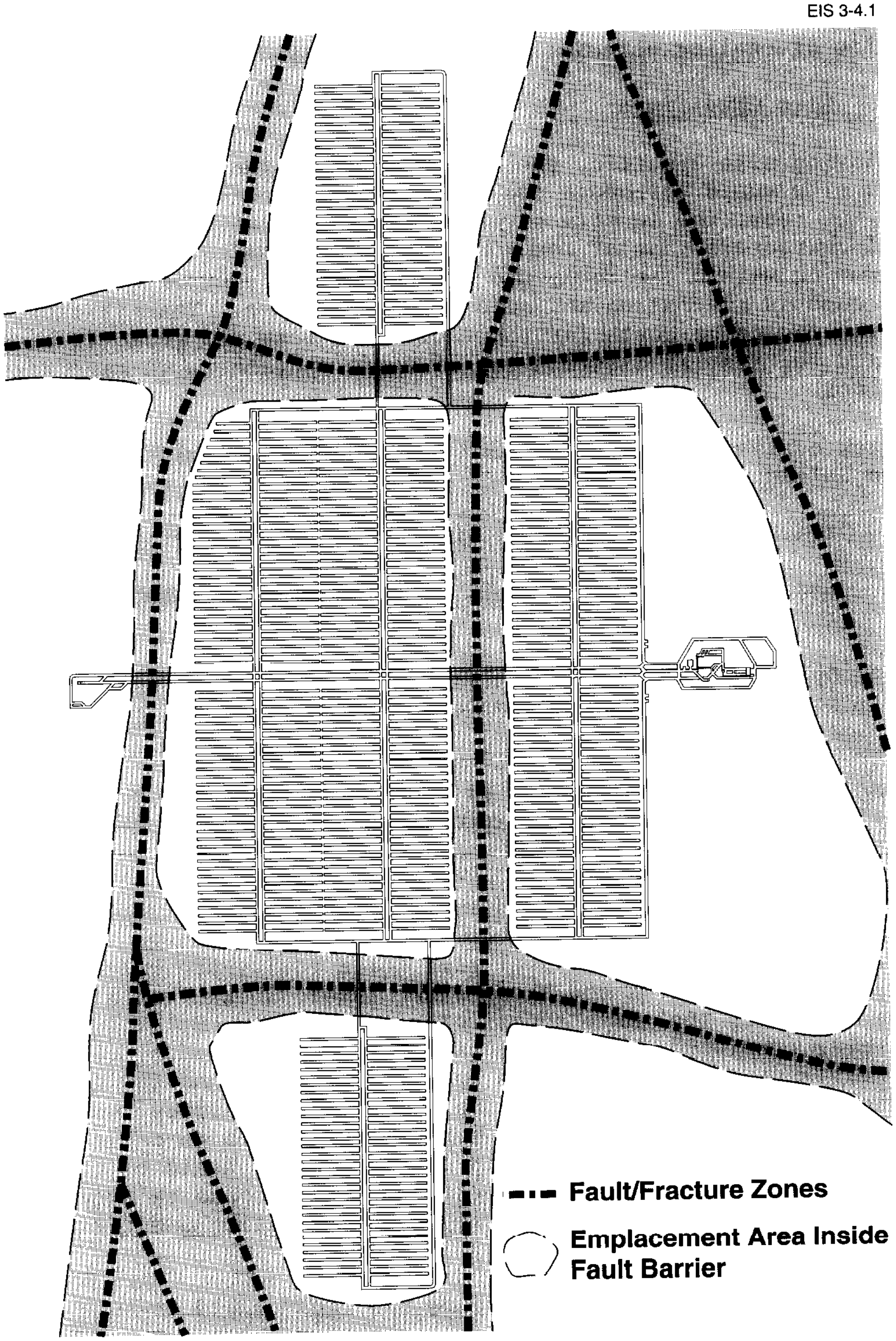

FIGURE 4-1: Disposal Vault Plan Partitioned to Suit Geological Conditions

Particularly, the possibility that the excavation-disturbed zones might short-circuit the hydraulic flow paths from the waste containers, through the sparsely fractured rock and to the fracture zones, would have to be considered in the design of sealing systems. Moreover, with time, temperature changes in the vault, arising from the dissipation of radiogenic heat from the waste through the seals and the host rocks, would alter the stress conditions in both the seals and the excavation-disturbed zones. The mass transport and hydromechanical properties of the sealing materials might be changed by thermal effects, and the consequent changes on the performance of sealing systems would need to be ascertained and incorporated in the design of the vault.

In this context, although the conceptual designs for the sealing systems described in this chapter use the most recently available data on the properties of the excavation-disturbed zones—data obtained through experiments carried out underground at the OECD/NEA[37] International Stripa Project (Börgesson et al. 1992, Gray 1993) and at AECL's Underground Research Laboratory (Martin et al. 1992)—it is likely that the specific properties of the excavation-disturbed zones in a vault would require refinement of the essentially preliminary designs for seals described in this report. To reach these initial designs, performance assessment calculations (Chan and Stanchell 1990) have been completed to evaluate the likely influence of the excavation-disturbed zones on radionuclide release from a vault, and sealing materials have been preferentially selected for their demonstrated ability to effectively function under the evolving geochemical conditions expected in a vault.

Seismic activity and glaciation may influence the stress conditions and degree of fracturing of a rock mass. The long-term seismic hazards at a potential disposal site would require evaluation to determine the seismic loads to which the rock would be exposed. Design issues include minimizing the number of fault intersections with shafts and tunnels and the selection of an appropriate waste exclusion distance between disposal rooms and adjacent faults. Although seismic and glacial loads may affect the hydraulic conductivity of the fracture network, they are not expected to affect the integrity of sealed disposal rooms that would be located in the intrablock regions of sparsely fractured rock (Davison et al. 1994a).

4.3 VAULT DESIGN ALTERNATIVES

A variety of vault design concepts have been studied both in Canada and internationally. These include the WP-Cave concept (SKB 1989b), the deep borehole emplacement concept (SKB 1989c), and the room-and-pillar concept that has been used for the reference vault design described by Simmons and Baumgartner (1994). The WP-Cave design concept consists of a multilevel array of disposal channels and shafts entirely surrounded by a 5-m-thick bentonite-sand barrier. This barrier is, in turn, surrounded by an array of tunnels and boreholes that would control the groundwater pressures around the vault. Groundwater flow would be deflected around the volume of

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[37] Organization for Economic Cooperation and Development/Nuclear Energy Agency

rock in which the waste was emplaced. The design is considered technically feasible, but has a greater need for technology development than does the room-and-pillar arrangement and does not appear to offer safety advantages.

The deep borehole emplacement concept involves emplacement of waste at depths of 4 to 5 km in stable foundation rocks. In this approach, deep large-diameter (375 to 800 mm) boreholes would be drilled from the surface; containers would be emplaced in the lower regions of the boreholes, and the upper 2 km would be filled with sealing materials. An assembly of waste containers surrounded by precompacted clay blocks would be fabricated and lowered into place in the boreholes. An assessment of the concept (SKB 1989c) concluded that it would require a substantial research and development program, because of the technical difficulty of emplacement, and that it would be significantly more expensive than alternative designs.

The majority of studies in Canada and internationally have focused on the room-and-pillar method of vault construction. Regularly spaced rooms and tunnels would be excavated in the rock. Pillars of rock left between adjacent rooms and tunnels would carry the load of the overlying rock. The waste containers could be emplaced in the rooms or in boreholes drilled into the host rock from the rooms.

A number of design studies have been performed in Canada. These have focused on borehole emplacement and have examined multiple-level vaults with emplacement at each level (Acres and RE/SPEC 1985); a multiple-level long-hole configuration, where waste would be emplaced in boreholes between two levels (Acres 1993); and a single-level configuration involving borehole emplacement in the floors of disposal rooms (AECL CANDU et al. 1992).

These studies were performed to identify and study important engineering issues, to provide a focal point or common basis for research on materials properties and engineering, and to define a methodology for the development of design concepts. They do not reflect a final selection of a design concept. Specifically, the option to dispose of waste containers in-room (as well as in boreholes) has been considered in the selection of sealing materials, engineering and seal design.

4.4 THE REFERENCE DISPOSAL VAULT DESIGN

A specification was developed in 1984 as the basis for a study of a used-fuel disposal centre. The completion of this study led to the reference disposal vault design described by Simmons and Baumgartner (1994), which includes various designs for vault seals. The reference disposal vault is a single-level, room-and-pillar design excavated at a depth of 1000 m. Waste containers are deposited in an array of large-diameter boreholes drilled in the floors of emplacement rooms. Specifications for the design included the following:

1. The maximum temperature of the container outer skin and the surrounding buffer material should not exceed 100°C, in order to limit crevice corrosion of the Grade-2 titanium container and thermal alteration of a bentonite-clay buffer.

2. The reference used fuel for thermal calculations was assumed to have a burnup of 685 $GJ \cdot kg^{-1}$ U and to have cooled for 10 a prior to disposal.

3. Irreversible far-field rock mass displacement should not extend more than 100 m below the ground surface. Such displacements could occur when the stresses in the rock mass change with temperature, as a result of the heat from the waste being dissipated through the host media.

4. The integrated average strength-to-stress ratio for the rock webs around emplacement boreholes would be 2 or greater. In addition, the extraction ratio on the emplacement horizon should be approximately 0.25.

The reference vault is essentially square, has an area of 4 km^2 (Figure 4-2), and is designed to receive about 140 000 containers, each holding 72 used-fuel bundles. The total mass of fuel for disposal is about 191 000 Mg (U). The reference container is shown in Figure 3-11. Each disposal room is 8 m wide, 5 m high and 230 m long and contains 282 vertical emplacement boreholes drilled in the floor. The boreholes are 1.24 m in diameter and 5 m deep. Prior to the emplacement of a container in the reference vault, a bentonite-clay-based buffer material, consisting of 50% by dry mass bentonite and 50% by dry mass graded silica sand, is compacted into the borehole and a central hole is augered into the buffer to accept the container. After emplacement of a container, the radial gap of about 50 mm between the container and buffer is filled with silica sand and additional buffer material is compacted above the container. When all the boreholes in a room are filled, the room is backfilled by placing and compacting a mixture of 25% by dry mass glacial-lake clay and 75% by dry mass crushed granite to fill the lower 3.5 m of the room. The upper portion of the room is filled by spraying in an upper backfill material that is similar in composition to the buffer material. A concrete bulkhead is constructed at, and grouted into, the room entrance to seal the room.

When the reference vault has been filled with waste, monitoring data are assessed to show compliance with regulatory and design criteria. After the decommissioning and closure plan for the vault is approved, the access tunnels and shafts are backfilled and sealed, the surface facilities decommissioned and disassembled, and the site is permanently marked and returned to a state suitable to allow public access to, and use of, the surface.

4.5 SEALING

Following closure of the vault, it is assumed that the rock and the vault system would eventually become water-saturated and the regional groundwater conditions would recover. It is anticipated that, eventually, the containers would fail by corrosion processes, and the used fuel would slowly dissolve and release radionuclides into the groundwater. In these circumstances, working in harmony with the natural barrier, the main purpose of engineered seals would be to control and minimize water flux in and around the vault and to retard contaminant release into the surrounding rock.

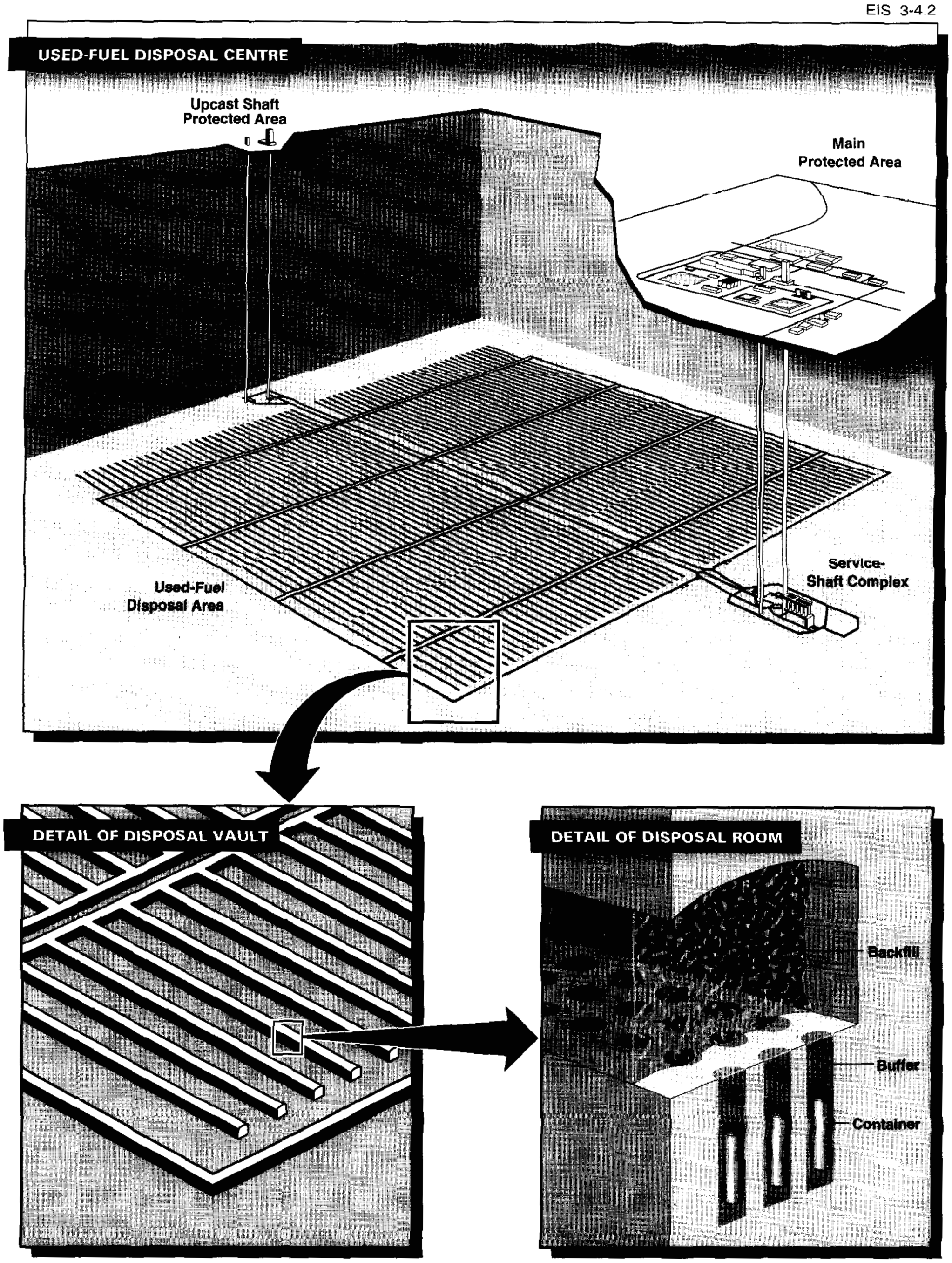

FIGURE 4-2: Schematic Representation of a Nuclear Fuel Waste Disposal Facility

In common with other granitic rock masses, plutons in the Canadian Shield contain discrete fractures, fracture sets and faults in which water circulates (Davison et al. 1994b). In the vicinity of vault excavations, the degree of fracturing and the flow paths would change both as vault excavations proceeded and with time after a vault was sealed.

During excavation, the integrity of the rock immediately adjacent to the vault would experience some degree of damage due to the excavation processes. Moreover, the natural stress field in the rock would be changed. These changes would cause changes in the hydraulic properties of natural fractures in the rock. The natural stresses might be sufficiently concentrated to cause local failures on the surfaces of excavations. Longer-term, time-dependent changes in both natural and induced water flow paths would occur as a result of thermal expansion and contraction of the rock mass, mineralogical transformation of fracture infilling materials, and dissolution and precipitation reactions involving the rock, any engineered materials and the groundwater. In contrast with excavations in media such as salt or clay, which can be expected to close as the surrounding rocks creep into the openings, excavations in granite would be stable and would need to be appropriately filled and sealed. The ability to design, emplace and predict the performance of seals in these conditions could ultimately significantly influence the final vault configuration and the selection of an appropriate container design.

As discussed in Section 4.3, a variety of layouts for vaults in granite have been considered in studies performed in Canada, Sweden and Switzerland. Constraints on and expectations of seal engineering and performance vary depending on the vault design concept. However, with the exception of the WP-Cave vault concept (SKB 1989b), which relies on the performance of engineered materials and structures to divert water flow around the entire region of waste emplacement, engineered seals are used in concert with the features of the natural barriers as local controls on water flow. Of all the vault layouts considered, the opportunities to work with the natural features of the rock are probably greatest with the room-and-pillar construction being considered in the reference vault concepts proposed in Sweden, Switzerland and Canada.

For all the vault configurations, the following four basic sealing strategies are employed to limit radionuclide release from the vault:

1. Minimize water flow around the container to limit container corrosion and, subsequently, the rate of dissolution of used fuel.

2. Decrease the hydraulic conductivity of the vault system by using low-hydraulic-conductivity materials so that water in contact with the container is virtually stagnant; thus, the slow processes of diffusion would dominate radionuclide transport in the engineered and natural barriers near the containers.

3. Provide enhanced seals at hydraulically critical points in the vault, such as intersections between excavations (tunnels and shafts) and faults and regions of intense natural fracturing.

4. Retard radionuclide release and migration by incorporating materials that inhibit water movement and have the potential to entrap radionuclides and/or chemically condition the groundwater.

The environmental conditions under which seals are expected to function would vary across the vault. The layout of the vault, the location and design of the seals, and the materials from which seals are built would be determined by the observed geological conditions and the anticipated changes in environmental factors, such as temperature, groundwater pressure and hydrogeochemistry. The strategies apply to seals near the waste in and around rooms and tunnels, and to those farther away from the waste in and around access shafts, ramps and exploration boreholes.

The models used to describe total vault system performance are, necessarily, simplified representations of our understanding of the various factors that control the performance of a vault. However, to ensure the validity of the modelling results, the seals must be engineered so that their performance complies with the performance criteria assumed in the model. Conversely, the models must accommodate the practical limitations of available seal-engineering technology. The total system performance model used to carry out the performance-assessment case study divides the disposal system into three major subsystems—the vault, the geosphere, and the biosphere—and links these subsystems to assess total system performance. For the reference vault, the buffer and backfill materials are incorporated into the vault model (Johnson et al. 1994). The geosphere model (Davison et al. 1994b) indirectly incorporates the performance of sealed shafts and boreholes in assuming that they do not act as preferred pathways for radionuclide migration. Sensitivity analyses using modified geosphere models have been carried out to test the implications of this assumption (Davison et al. 1994b, Johnson et al. 1994). Similarly, simple diffusion models for the vault have been used to assess the effects of changing the sizes of the buffer and backfill barriers (Cheung and Chan 1988). In all these assessments the numerical values of the parameters that define the hydraulic properties and contaminant transport characteristics of the sealing materials have been selected to accommodate the uncertainties inherent in engineering works. Moreover, ranges in the values of the material parameters (phenomenological coefficients) have been defined to include the possible changes that would occur in the properties of the sealing materials as the vault system evolved (e.g., the ranges of radionuclide diffusion coefficients used include the measured effects of salinity and temperature changes).

The CNFWMP has been directed to evaluate a concept for disposal of nuclear fuel waste in plutonic rock of the Canadian Shield. The conceptual designs are not site-specific and, thus, a wide variety of hydrogeological conditions can be envisaged. Moreover, various options exist for the design and handling requirements of the waste package. Thus, to accommodate uncertainties in design, it has been necessary to carry out a broad-based evaluation of possible sealing technologies. In part, these evaluations have been directed to provide the data used as input for total system performance assessment and, conversely, to define the practical limits within which the vault and geosphere models can be reliably applied. To limit the scope of these studies to practical achievable objectives, the reference vault design described by Simmons and Baumgartner (1994) has been used to determine the relative effectiveness of different sealing materials, methods and strategies. With possible sealing systems established for reference conditions, variations can then be considered and appropriate seal designs for these alternatives attempted.

In keeping with the sealing strategies, the studies into sealing the reference vault have attempted to define materials and methods for the following purposes:

- infilling vertical excavations such as shafts and exploration boreholes;
- infilling tunnels, ramps, rooms and horizontal exploration boreholes;
- creating special seals around the waste container;
- creating special seals where excavations intersect major water-bearing features in the rock; and
- decreasing the hydraulic conductivity of the excavation-disturbed zones (EDZ).

This chapter describes the major considerations and sealing methods that have led to the seal designs incorporated in the reference vault design. Where appropriate, the application of the technologies to alternative vault designs is discussed. Possible measures for quality control of the materials and the performance of the seals are described. The requirement for and possible methods of seal performance assessment and monitoring are reviewed.

In general, materials with low hydraulic conductivity and porosity have been studied as sealants. The materials need to be in adequate supply—millions of cubic metres of excavation will need to be filled—and need to be workable[38] using available technology. Moreover, the performance of the materials over very long time periods needs to be reasonably predictable. A number of screening studies (Cameron 1982, Coons 1987, Mott et al. 1984) have identified clay-based, cement-based and bitumen-based materials as having the highest likelihood of meeting the vault sealing requirements. Although the possible advantages of using bituminous materials to seal vaults in granite are being increasingly recognized (Allison et al. 1989), studies in Canada and abroad have focused on clay- and cement-based materials. These materials are extensively used in civil engineering practice, and a wealth of information on their properties, performance and use is available. Moreover, bituminous materials would introduce relatively large quantities of organic matter into the vault. While analyses have shown that organic matter of the type present in clays proposed for seal materials would not contribute significantly to radionuclide transport (Johnson et al. 1994), the potential effects of larger amounts of organics have not

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[38] Workable - capable of being placed to the design specifications.

been studied. For these reasons, discussion is limited to pertinent engineering properties and possible uses of clay- and cement-based materials.

4.6 SEALING MATERIALS

4.6.1 Clay-Based Sealing Materials

Clays can be broadly defined as particulate materials with particle sizes less than 2 μm. Within this definition there exists a class of minerals, the clay minerals, that imparts the well-known properties of low hydraulic conductivity and plasticity to materials such as clay soils. Crystal structures of three common clay mineral groups, kaolinite, illite and montmorillonite, are shown in Figure 4-3. The figure illustrates that clay minerals are, generally, characterized by a platey structure formed from sheets of silica and alumina. The sheets can be stacked in different orders to generate different crystal structures and, hence, to form materials with ranges of physical, chemical and engineering properties. Imperfections in the crystal lattices can impart surface electrical charges to the minerals. The small particle size (high specific surface area) and the surface charge make the clay minerals highly surface-active.

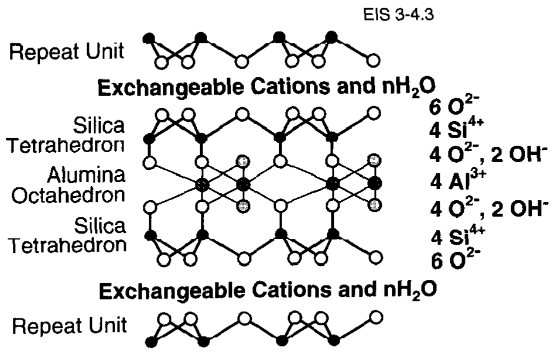
The high surface activity of clay minerals is reflected in their ability to sorb cations. The cation exchange capacity (CEC) of the three clay minerals represented in Figure 4-3 is shown in Table 4-1. The table also presents values for K_d, the distribution coefficient, for selected radionuclides. The distribution coefficient is the ratio of the amount of a species associated with the clay to the concentration of the species in

TABLE 4-1

SUMMARY OF CEC AND K_d VALUES FOR SELECTED RADIONUCLIDES ON CLAY MINERALS
(after IAEA 1990)

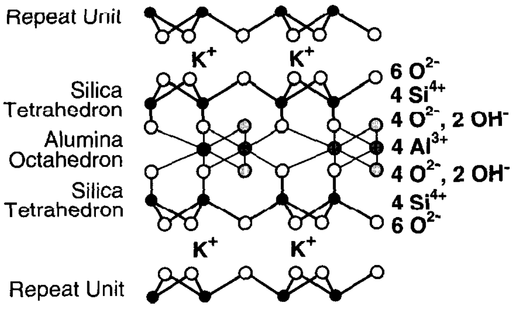
Material	CEC	K_d ($mL \cdot g^{-1}$)				
	(meq/100 g)	Cs	Tc	Am	Pu	Sr
Kaolinite	5-10	1-20*	0-3	1-10*		1-10
Illite	15-40	40-1000	0-10		100*	5-20
Smectite	70-100	20-700	0.1-10	10-1000	100-1000	1-500

* For these cases there are no available measured values.
The numbers quoted are expected values based on expert opinion.



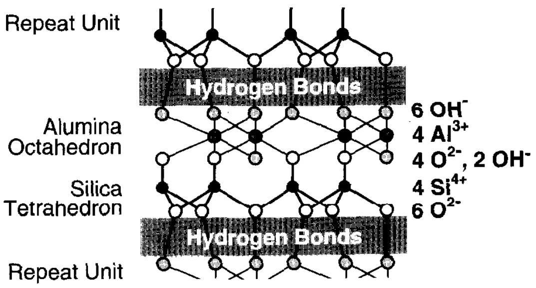
Montmorillonite Crystal Structure

Isomorphous substitutions and imperfections in the crystal lattice give high negative charge. (Cation exchange capacity = 80 meq/100 g, specific surface area = 600 m^2/g.)



Illite Crystal Structure

Structure is similar to montmorillonite; potassium ions bond the silica-alumina layers. Crystal size is greater and surface activity is less than that of montmorillonite. (Cation exchange capacity = 20 meq/100 g, specific surface area = 80 m^2/g.)



Kaolinite Crystal Structure

Kaolinite has the lowest surface activity and largest crystal size.

(Cation exchange capacity = 5 meq/100 g, specific surface area = 20 m^2/g.)

FIGURE 4-3: Crystal Structures of Some Common Clay Minerals (after Lambe and Whitman 1969) solution at equilibrium. Montmorillonite, a member of a group of clay minerals termed smectites and the predominant clay mineral in bentonite clay, is one of the more highly surface-active clay minerals. In addition to its ability to sorb and retain cations, montmorillonite (and thus bentonite clays, because of their high surface activity) has a number of special properties that make bentonite clays particularly attractive as sealing materials. Discussed in some detail below, these properties can include a very low hydraulic conductivity and an ability to absorb water and swell, thus sealing any unfilled voids in the vault.

Figure 4-4 shows that the measured hydraulic conductivity,[39] k, of water-saturated clays decreases with increasing density,[40] ρ_c (decreasing porosity).[41] At the same density, k of smectite is several orders of magnitude lower than that of illite or kaolinite. While Darcy's law is generally considered to be valid for groundwater flow in porous media like sands and silts, there is no clear consensus of scientific opinion on its validity for clays, such as bentonite. Deviations from the law, such as possible variations in k with hydraulic gradient, i, and evidence for a threshold value of hydraulic gradient before flow is initiated, have been observed (Yong and Warkentin 1975, Olsen 1985). Clay-water interaction forces and complexities in the clay fabric (i.e., the arrangement of clay particles and, thus, the size distribution and connectivity of pores) have been used to qualitatively explain these deviations, which tend to increase with the activity and density of the clay (Yong and Warkentin 1975). Irrespective of the existence of a threshold gradient, increasing the density of a clay will decrease its k. Compacting the material to a known specified minimum density will define, within limits, the hydraulic properties of a clay seal.

In addition to Darcian flow, water can also move in saturated clays under spatial variations in temperature (thermal osmosis), electrical potential (electro-osmosis) and solute concentrations (normal osmosis). The effects of thermal osmosis on water flow are generally considered to be insignificant when compared with those of hydraulic conduction, electro-osmosis and

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[39] Darcy's law states that the mean velocity of water flow, q, through saturated porous media is directly proportional to the hydraulic gradient, i, with the hydraulic conductivity, k, as the constant of proportionality. $i = \Delta h/\Delta L$, where Δh is the loss in water head over the distance ΔL.

[40] For clays and clay-sand mixtures, effective clay dry density (ρ_c) can be used. This is defined as the ratio of the dry mass of clay to the sum of the volumes of the dry clay and the voids. The mass and volume of the sand are not included in the calculation of ρ_c. In clay technology and soil mechanics, the term dry density, ρ_d is more commonly used. This is defined as the mass of solids (dried at 105°C) per total volume (solids + voids).

[41] Porosity, n, is the volume of voids per total volume (solids + voids). n and ρ_d are related by the equation $n = 1 - \rho_d/G_c$ where G_c is the specific density of the solids.

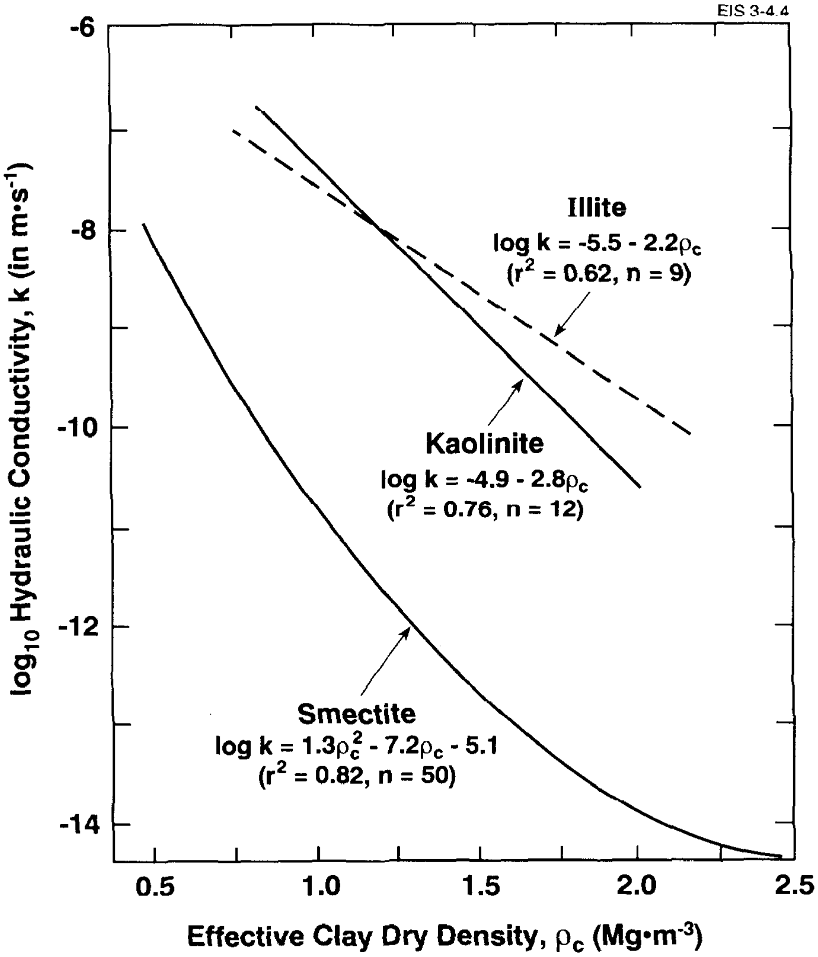

FIGURE 4-4: Relationship Between Hydraulic Conductivity and Effective Clay Dry Density for Selected Clay Minerals (after Dixon et al. 1987); r^2 is the Correlation Coefficient and n is the Number of Samples Tested

normal osmosis (Mitchell 1976, 1991). Osmotic effects become more pronounced with increasing clay density and clay surface activity. As no significant electrical potential gradients can be reasonably envisaged in or around a vault, the conditions for electro-osmosis are unlikely and only normal osmosis needs to be considered.

Although mechanical factors play a role, the processes of normal osmosis have been shown to largely explain the swelling properties of montmorillonite-rich bentonite clay (Yong and Warkentin 1975, Mitchell 1976, Pusch 1980, Gray et al. 1985). In contact with free water, such as the groundwater in the rock, osmotic potential differences between the free water and the water in the pores of the clay tend to drive water into the clay. If the clay is unconstrained, water will flow into the clay, which will expand to fill available space or until the solute concentration in the pore water, which is derived from residual salts, is sufficiently diluted to equilibrate with the free water. When the clay is totally confined, the solute concentration in the clay pore water will remain virtually unchanged, and the material will exert an expansion or swelling pressure on its confinement that is equivalent in magnitude to the difference between the mean osmotic potential of the pore water and that of the water with which the clay is in contact. In Figure 4-5, the swelling pressures developed by compacted bentonite clays are shown to increase with ρ_c. The data presented in Figure 4-5 show that the swelling properties of bentonite clay products made in Canada are very similar to those of the industrial standard produced in Wyoming, U.S.A. The latter have been proposed for sealing disposal facilities for nuclear waste in Sweden (SKBF/SKB 1983). In common with any normal osmotic pressure, the clay swelling pressures increase with temperature and decrease with increasing ionic concentrations in the free water. Osmotic swelling is most pronounced with surface-active clays such as bentonite. In a vault in granite, the effects of osmotic potentials on the volumetric stability and other mechanical properties of the less active clay types present in materials such as the reference lower backfill would not be significant and have been ignored in the design and selection of these materials.

To obtain the lowest possible hydraulic conductivity, clays should be used at the highest achievable density. For non-swelling clays this also maximizes their strength and minimizes deformation under load (Schofield and Wroth 1969). Similar tendencies are seen in the strength-deformation behaviour of swelling clays (Graham et al. 1989). The highest achievable density in a disposal vault would depend on the location in the vault where the clay was used as a sealant and on the methods used for its placement. For example, to be workable as a grout, clays would need to behave as liquids during injection into the rock; alternatively, when used to fill

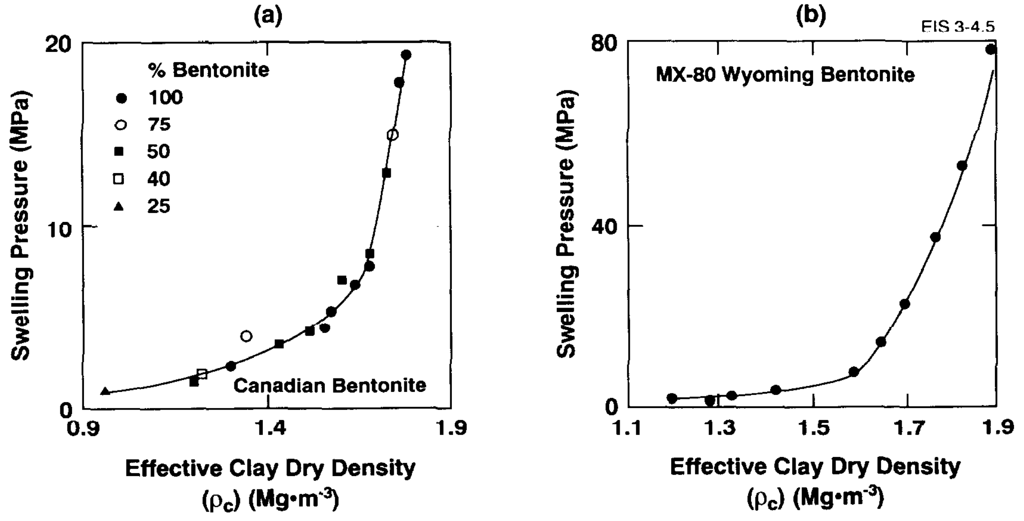

FIGURE 4-5: Influence of Effective Clay Dry Density on Swelling Pressures Developed by (a) Compacted Sand-Bentonite Mixtures (after Gray et al. 1985), and (b) Compacted Bentonite (after Pusch 1980)

excavations, the clays could be placed as precompacted blocks or compacted in situ to solids of the required high density.

Figure 4-6 shows that the required material consistency can be obtained by varying the water content of the clay. The consistency limits shown in the figure are material characteristics that vary with the clay mineralogy and the clay content. In conjunction with other measurable parameters, they can be used to provide quality control for clay materials. In general, clays can be compacted in situ or preformed at water contents at and below the shrinkage limit. At water contents at and above the liquid limit they can be injected as grouts. Because of the higher water contents, clay grouts have lower densities and, hence, higher hydraulic conductivity than otherwise similar compacted clays.

Particulate aggregates may be mixed with clays to produce materials possessing improved characteristics for particular vault sealing applications, as outlined below:

1. The density to which clay aggregate materials can be compacted in situ tends to increase with increasing aggregate content (Yong et al. 1986, Dixon et al. 1985).
2. The thermal conductivities of clays are less than those of granite rock. In hotter sections of a vault, where upper temperature criteria must not be exceeded, aggregates could be mixed with the clays to increase their thermal conductivity and heat capacity (Radhakrishna 1984).

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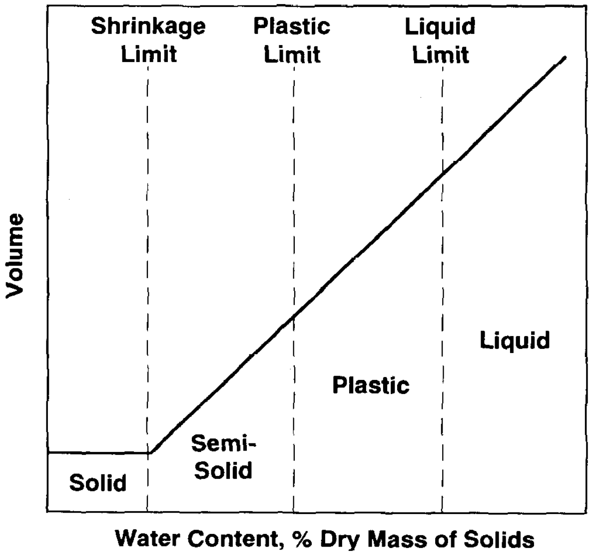

FIGURE 4-6: Consistency Limits for Clay Classification and Quality Control

3. It has been suggested that minerals could be added to the clay to retard the migration of specific radionuclides. In this context, Cu, Bi, Fe, Hg and hydrotalcite minerals have been studied to attempt to retard ^{129}I migration. Oscarson et al. (1986a,b) showed that there is no significant retarding effect, and these minerals have not been included as admixtures in the clay seals for the reference vault.

Ideally, since the prime function of clay seals is to limit the rate of water flow, the hydraulic properties of the clays should not be adversely affected by the inclusion of aggregates. Very high densities are attainable (Pusch and Gray 1989), because the densities of materials prepared as compacted blocks are limited only by the capacity of the press used to form the blocks. Provided the aggregate content does not exceed about 80% (by total dry mass), the densities achievable through in situ compaction are sufficiently high that the hydraulic conductivities of clay-aggregate mixtures are virtually the same as those of the clay alone (Yong et al. 1986, Dixon et al. 1987). For less active clays, such as kaolinite or illite, the hydraulic conductivity of material compacted in situ should be in the order of 10^{-10} $m \cdot s^{-1}$; for bentonite (dry density, ρ_d, of 1.75 $Mg \cdot m^{-}3$, see Section 4.7.1), k is in the order of 10^{-12} $m \cdot s^{-1}$. These values are in the same range as those expected for granite rock masses.

Using advanced grouting techniques, it has been shown (Pusch et al. 1988) that clay-based grouts can be injected into discrete fissures in granite rock at water contents of about 1.2 times the liquid limit (see Figure 4-6) of the material. With this consistency, k for bentonite-based grouts can be as low as 10^{-9} $m \cdot s^{-1}$. For other clay types k is higher. To attain the best hydraulic seal, bentonite clays would be the preferred clay grouting materials.

The less active clay minerals are found in significant proportions in many natural clay soils deposited and formed on the Canadian Shield, and it is reasonable to assume that exploitable resources should be available within economic distance of a disposal centre. In contrast, bentonite deposits in Canada are found throughout the Prairie regions and are currently being commercially exploited in Manitoba, Saskatchewan and Alberta. The principal bentonite beds lie in Alberta and western Saskatchewan. Proven reserves in Saskatchewan are sufficient to supply the requirements for the reference disposal vault design and larger unproven deposits are thought to exist there. Moreover, much larger reserves exist in Wyoming (Dixon et al. 1992).

Studies of Canadian deposits have shown that the montmorillonite-rich swelling bentonite is present in 0.3- to 1.0-m-thick layers that are sandwiched between layers of less pure material. Typically, the layers are close enough to the surface to be quarried and processed to provide products of different quality. The purer materials (with liquid limits of 350% or higher) obtained by processing only the montmorillonite-rich layers are used for special applications, as in the production of drilling muds and foundry sands. Civil engineering grade materials used in diaphragm walling, for grouting and for sealing hazardous waste ponds are mixtures of higher- and lower-grade materials. Typical properties of the civil engineering grade bentonite clay materials are shown in Table 4-2. The ranges shown were derived from measurements made on different batches of material supplied to AECL Research over a period of eight years and have been used to establish specifications for bentonite products for use in the reference vault. Different quality bentonite products may be used for different purposes when sealing a vault. From Table 4-2 it can be seen that, in contrast with the wide ranges in liquid limit, plasticity index and swelling capacity, the measured hydraulic conductivities of compacted bentonite materials lie in the limited range $10^{-13} < k < 5 \times 10^{-11}$ $m \cdot s^{-1}$ and, as required, are far less than the critical value of 10^{-9} $m \cdot s^{-1}$ below which advective transport in clay is considered to be negligible.

Clays would need to be processed prior to use in vault sealing. Processing, which would be similar for both swelling and non-swelling clays, would include the following three activities: excavation, drying, and milling. Typically, excavation is carried out using scrapers in open-pit quarrying operations; the quarried materials are air-dried prior to kiln-drying in rotary furnaces, and the dried product is broken down in ball or rod mills to form the final, dry powdered product. Some of the equipment for performing these operations is shown in Figure 4-7. To ensure the quality of vault seals, the processing operations would require careful control. The properties of bentonite clay products can be particularly sensitive to the processing procedures.

Clay products to be used for vault sealing would be delivered either as powders or precompacted blocks to the vault site. In the case of powders, they would be further processed on site before being placed as sealants. This latter processing step, which could include mixing with aggregates and water, would require further careful quality control.

4.6.2 Cement-Based Sealing Materials

Cements are commonly used in civil engineering practice as the principal component of concretes (mixtures of cement, water and coarse and fine aggregate), mortars (mixtures of cement, water and fine aggregate), and grouts (mixtures of cement and water). While a wide variety of cement types are available, each being tailored to particular applications, the most commonly used materials are termed portland cements. These are anhydrous, powdered calcium silicates and aluminates produced by grinding the clinkers formed when mixtures of clay and limestone or chalk are fired at temperatures of approximately 1450°C. Mixed with water, the cements hydrate to form hardened masses that, when intact, possess very low hydraulic conductivities and significant strength. These properties render the material suitable for the construction of a wide variety of civil engineering structures, including water-retaining and control structures such as dams, weirs, tanks, culverts and pressure tunnels.

The desirable properties of both unset and hardened cementitious materials can be enhanced by adjusting a number of mix design variables. Possible variables include cement type; water-to-cement ratio; aggregate type, size

TABLE 4-2

VARIABILITY IN CIVIL ENGINEERING GRADE BENTONITE PRODUCT FROM A SINGLE MANUFACTURER IN CANADA. TESTS CARRIED OUT ON MATERIALS DELIVERED TO AECL FROM 1982 TO 1990

Property	Maximum	Minimum	Proposed Specification
Liquid limit, %	370	200	>250
Plasticity index (Ip)	320	150	>200
Cation exchange capacity (meq/100 g)	85	50	>60
Specific surface area ($m^2 \cdot g^{-1}$)	630	500	>550
Maximum dry density (ρ_d) (50:50 silica sand) ($Mg \cdot m^{-3}$)	1.78	1.67	>95% of maximum measured in ASTM-D-1557-78 (ASTM 1982)
Swelling pressure (kPa) at ρ_d = 1.67 $Mg \cdot m^{-3}$ in DDW:*			
At Ip = 150	1000	500	
At Ip = 200	1800	1200	
Hydraulic conductivity ($m \cdot s^{-1}$)	5×10^{-11}	10^{-13}	$<10^{-11}$

* DDW - distilled deionized water

and content; and the nature and quantity of additives, such as pozzolans,[42] accelerators, expansive agents, air-entraining agents, plasticizers and water-reducing agents.

Portland cements are available in a number of standard forms conforming to specifications set by the Canadian Standards Association (CSA). Screening studies (Hooton and Mukherjee 1982, Hooton 1983, Ballivy et al. 1988) indicate that sulphate-resisting cement (CSA Type 50) is probably the most suitable for use in vault sealing. Some groundwaters in granitic rock contain sufficient quantities of sulphates to be considered aggressive to

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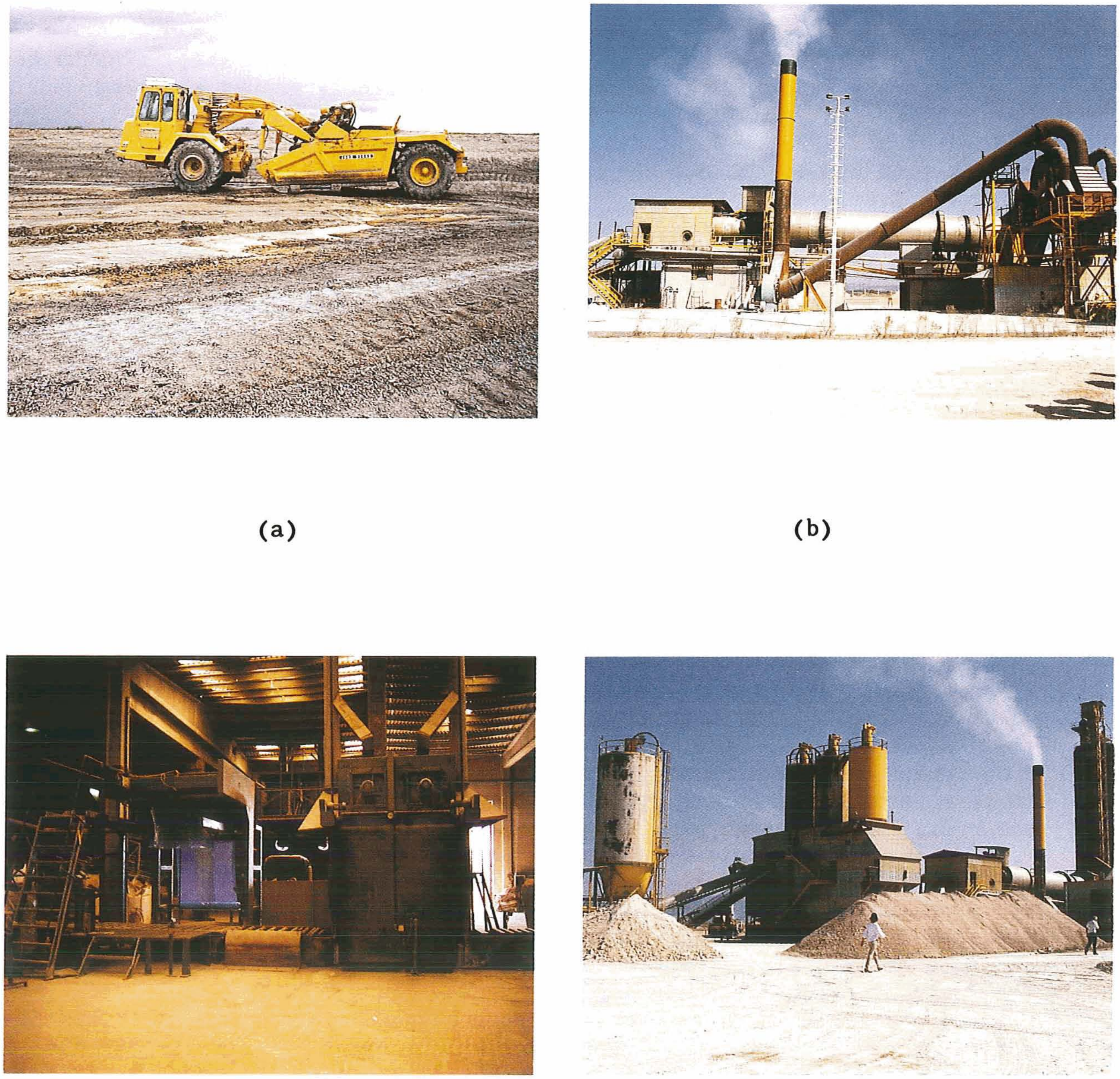
[42] Pozzolans are finely divided siliceous or aluminous materials that, in themselves, possess little or no cementitious value yet in the presence of water will react with calcium hydroxide to form compounds with cementitious properties.



(a)

(b)

(c)

(d)

FIGURE 4-7: Typical (a) Excavation, (b) Drying and (c) Bagging Equipment Used for Bentonite Clay Processing; (d) Shows Stockpiles of Air-Dried Bentonite Clay Ready for Processing cementitious materials (Gray 1993). Type 50 cement is also the major cementitious constituent of concrete designed for the fabrication of the Ontario Hydro dry storage container (see Section 3.5.4.3). This container design is being considered for the storage, transportation and, possibly, disposal of used CANDU fuel. Other cement types, such as sulphate-resisting oil-well cements (American Petroleum Institute - API), expansive Type K cements, and special sulphate-resisting finely ground grouting products may also find use and have been studied (Gray and Keil 1989, Onofrei et al. 1989). Regrinding to a Blaine fineness[43] of 600 $m^2 \cdot kg^{-1}$ has been carried out to enhance the penetrability of cementitious grouts into very fine fractures.

Unhydrated cement is composed of the following six major compounds: tricalcium silicate (C_3S),[44] dicalcium silicate (C_2S), tricalcium aluminate (C_3A), tetracalcium ferroaluminate (C_4AF), gypsum, and alkali sulphates. When hydrated and exposed to sulphate-bearing water, the aluminate can react to form ettringite (calcium sulpho-aluminate hydrate). The solid-volume increases accompanying this reaction can generate expansive stresses in the cement and cause the cement to crack. The CSA specifications for Type 50 cement limit the proportion of C_3A and thereby restrict the formation of ettringite. Thus, with improved mineralogical stability, the durability properties of cements and concretes are enhanced.

The hydration reactions of the cement, which are exothermic, liberate lime ($Ca(OH)_2$), which has the lowest strength and is the most water soluble of the reaction products. Admixing pozzolans limits the presence of lime in the hardened material. In the long term, the pozzolans tend to decrease porosity and increase strength (Neville 1981). While some natural materials are pozzolanic, fly ash and pulverized fuel ash (PFA) from coal-burning power stations are the most commonly used materials.

When included in significant proportions (i.e., >20% by mass of cement), these materials can be used to limit the rate of evolution of heat during the hydration reactions and, hence, to control the maximum temperatures reached in mass concrete structures. The composition of PFA varies within and between sources. Variations arise from natural variations in the fuel and from the burning processes. The ASTM recognizes these variations and provides specifications to which the material can be controlled for use in concrete (ASTM-C 618). Chemically, the classes of PFA are separated by their sesqui-oxide, sulphate and carbon contents. Some physical test criteria must also be met. Pozzolanic, condensed silica fume, produced as a by-product of the ferro-silicon industry, is becoming increasingly used as an additive to cements to improve their properties. Silica fume is amorphous silica, generally containing less than 5% by mass of impurities. This can be contrasted with PFA, in which, for the most reactive PFA, the sum of the masses of silica, alumina and ferrite must be at least 70% of

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[43] Blaine fineness is a parameter used to describe the fineness and surface area of cement particles, expressed in $m^2 \cdot kg^{-1}$.

[44] In cement chemistry the following notations are used: $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $H = H_2O$.

its total mass. Moreover, silica fume has an average particle size of less than 1 μm and a specific surface area that is approximately 10 times greater than that of cement or PFA. Adding 20% by mass of silica fume to cement has been shown to virtually eliminate the presence of lime in the hydrated product (FIP 1988). As a result, it is possible to greatly reduce the amount of OH^- that might be released from a cementitious material upon leaching by groundwater; thus concretes, mortars and grouts of this type that do not significantly affect the pH of the groundwater can be considered for use.

The effects of adding 10% by mass of silica fume on the unconfined compressive strength of Type 50 portland cement at different water-to-cementitious materials ratios (W/CM) are shown in Figure 4-8. The data show that the compressive strength is increased by the addition of silica fume and that, as with most cement-based materials, strength increases with decreasing W/CM. Stoichiometrically, portland cement can be fully hydrated at W/CM $\simeq$ 0.3. In practice, most cement materials are placed at water contents that are higher than 0.4. The extra water is needed to provide workability to the mix and it increases the porosity of the cement paste. The high specific surface area of silica fume increases the need for "workability" water. This can be offset by the use of additives called plasticizers. A subset of these materials, called superplasticizers, has been studied for use in cementitious materials for vault sealing purposes.

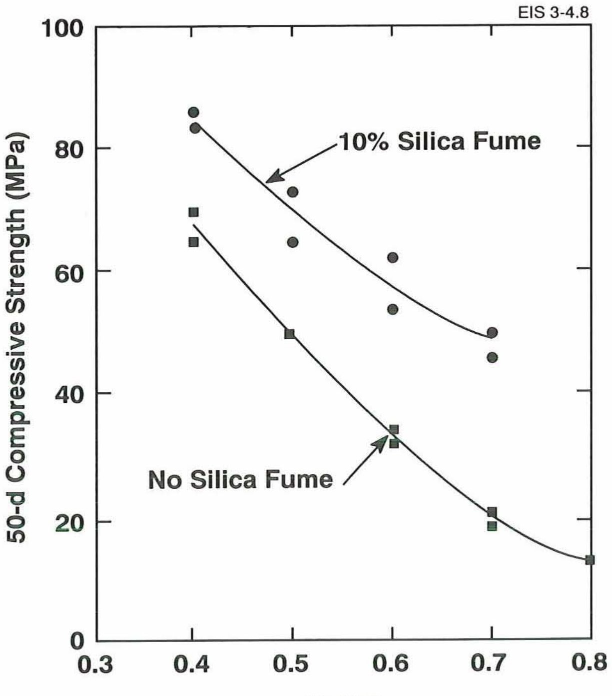
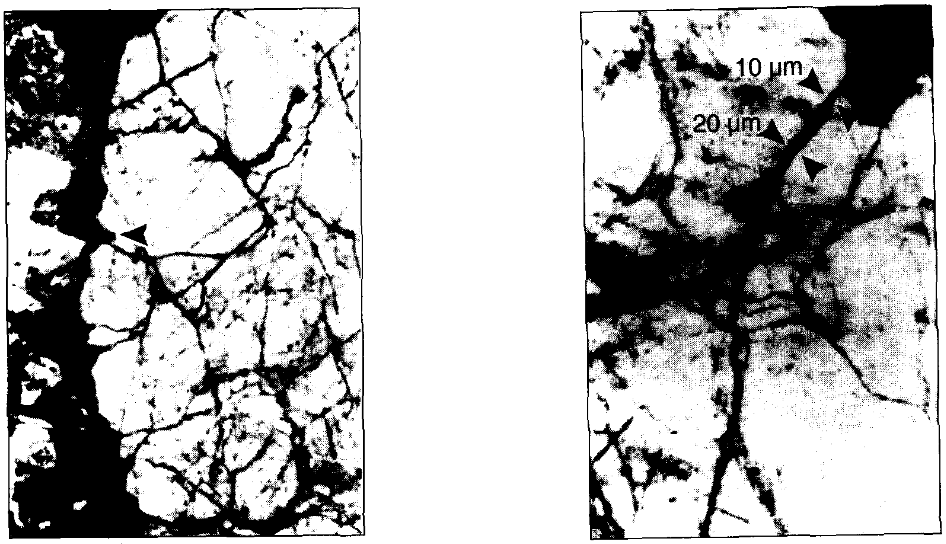


FIGURE 4-8: Effects of Silica Fume and W/CM on the 50-d Unconfined Compressive Strength of Cement Paste (Type 50 cement, Blaine fineness 600 $m^2 \cdot kg^{-1}$) (after Al-Manaseer and Keil 1990)

The most commonly used superplasticizers are sulphonated salts of melamine or naphthalene formaldehyde. The effects of a naphthalene-based superplasticizer on the flow properties of Type 50 portland cement with 10% silica fume are shown in Figure 4-9. As little as 0.75 wt.% (in the order of grams per cubic metre of concrete) of the superplasticizer is sufficient to turn the mixture with W/CM = 0.4 from a stiff, viscous paste to a flowing, pumpable fluid. Experiments at AECL's URL (Onofrei et al. 1989, Gray and Keil 1989) have shown that this material can be used to grout fissures in granite rock with apertures as narrow as 20 μm (Figure 4-10). Figure 4-10a shows that the grout conforms totally to the irregular fracture morphology on the rock surface; Figure 4-10b shows that the grout penetrated fissures in the rock with apertures as small as 20 μm. Moreover, the superplasticizer is chemically bound in the hardened mortar and should not detrimentally influence the long-term properties of the grout (Onofrei and Gray 1989).

Through their fluidifying action, superplasticizers permit grouts and concretes to be workable at low W/CM. In combination with silica fume the superplasticizers have led to the development of high-performance cements and concretes that are becoming increasingly used in civil engineering practice. High-performance cementitious materials have higher strengths,

FIGURE 4-9: Mixture of 90% Type 50 Portland Cement, 10% Silica Fume at a Water-to-Solids Ratio of 0.4 Without Superplasticizer (left), and with 0.75% Superplasticizer (right)



(a) (b)

FIGURE 4-10: Photomicrograph of a Thin Section of Cement-Grouted Rock Recovered from Fracture Zone 2 at AECL's Underground Research Laboratory (after Onofrei et al. 1989). The area marked by the arrow in (a) is enlarged in (b).

better durability characteristics and lower hydraulic conductivity than ordinary cement-based products. Knowledge of and experience with these materials is rapidly growing. For example, high-performance concretes have been used for the construction of the Condeep Oil Platform (Ronneberg 1989), for dry docks (Collepardi et al. 1989) and major multistorey buildings (Randall and Foot 1989, Ryell and Bickley 1987), and are now virtually the only concrete materials used for major construction in Norway (Ronneberg 1989). High-performance cements and concretes are expected to become increasingly used and are the cement-based materials on which the vault sealing studies for the CNFWMP have focused.

The hydraulic conduction properties and the porosity of cementitious materials are of general concern in engineering practice. These properties control the rate of fluid flow through the materials and govern their durability. The hydraulic conductivity is largely controlled by connected capillary porosity (Powers 1958), which, for freshly hardened cements and concretes, decreases with decreasing W/CM (Coons and Alcorn 1989) and is decreased further by the use of pozzolans (Hooton 1986a,b; Thomas et al. 1989). For normal cements and concretes, hydraulic conductivity has been shown (Coons and Alcorn 1989) to increase virtually linearly with increasing W/CM, from approximately 10^{-12} $m \cdot s^{-1}$ at W/CM = 0.4 to approximately 10^{-6} $m \cdot s^{-1}$ at W/CM = 1. High-performance concretes can be virtually impermeable with $k < 10^{-15}$ $m \cdot s^{-1}$ (Hooton 1986a, Al-Manaseer and Keil 1990). With these very low k values, water flow is only measurable under very high hydraulic gradients, and the normal direct and linear relationship between flow rate and hydraulic gradient i suggested by Darcy's law does not apply. Even under very high hydraulic gradients (i = 28 000), hardened high-performance grouts have been shown to totally resist the measurable throughflow of water (Onofrei et al. 1989, 1992).

The porosity, pore-size distributions and hydraulic conductivities of cements and concretes can be expected to change with time. These changes arise from crystallization of amorphous phases, changes in habit (atomic structure and form) of crystalline phases, reaction of the products of cement hydration with ions from internal and external sources diffusing through the material, dissolution of soluble compounds such as $Ca(OH)_2$, and progressive hydration of the cement. In this latter regard, microscopic examination of samples of historic concretes has nearly always revealed the presence of unhydrated material even when these materials were known to be placed at relatively high W/CM (Mallinson and Davies 1987). The structure of the hydration products formed on the surfaces of cement grains appears to control the rate of hydration of the grains' inner cores. Moreover, calcium carbonate, resulting from the carbonation of lime, is invariably found both in concretes used by ancient civilizations and in more recent, historic, portland-cement-based concretes that have been used since the middle of the nineteenth century.

The presence of unhydrated cement, the processes of carbonation, and the effects of dissolution and reprecipitation generally explain the observed ability of some fractured cement-based materials to self-seal (Lauer and Slate 1956). Figure 4-11 (after Pusch et al. 1988) shows how the hydraulic conductivity of a fractured thin film of grout composed of Type 50 portland cement and 10% silica fume decreased with time after being fractured. The elevation in temperature is thought to have accelerated the reactions (Onofrei et al. 1991). The decreases in the porosity and the changes in the pore-size distribution of the same grout caused by flowing water through hardened material are shown in Figure 4-12. The decrease in the average pore size and in the total porosity after exposure to water are thought to result from the formation of hydration products within pores as water moves through the grout.

Available data on longevity aspects of high-performance cementitious materials indicate that, with the use of appropriate quality control procedures and in rock masses where hydraulic gradients are small and groundwater flow is slow, cement-based sealants with low hydraulic conductivity and porosity can persist for hundreds of thousands of years. Figure 4-13 presents the results of predictions of the periods through which high-performance cement-based grouts can be expected to maintain very low hydraulic conductivity. These predictions were made by Alcorn et al. (1992) for the International Stripa Project (Fairhurst et al. 1993). The predictions are based on numerical (Alcorn et al. 1992), experimental (Onofrei et al. 1992) and theoretical (Alcorn et al. 1991) evaluations of the thermodynamic processes

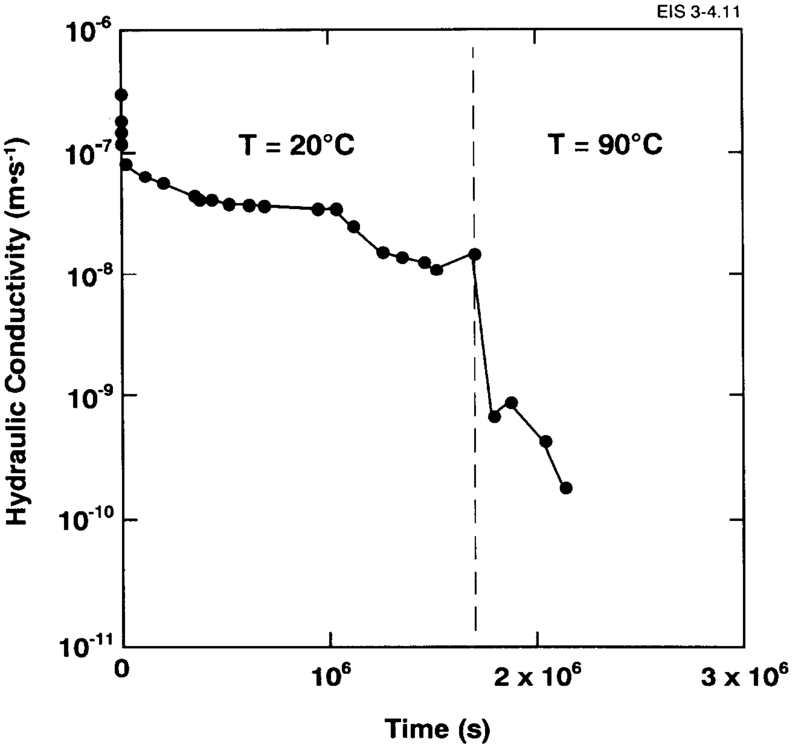


FIGURE 4-11: Change in Hydraulic Conductivity of a Thin Film of High-Performance Cement-Based Grout with Time and Temperature (Pusch et al. 1988)

occurring with time in cement-based materials in contact with granite rock and groundwaters typically encountered in the Canadian Shield (Pusch 1992, Gray 1993). The predictions suggest that hydraulic conductivities of grouts will remain constant for 10^4 to 10^5 a. For the open systems referred to in Figure 4-13, water was assumed to flow through the pores of the cement and to remove dissolved solids. For the equilibrium system, 75% of the products of reaction between the pore water and the cement solids were assumed to precipitate in the pores of the cement.

Used in structures on the earth's surface, cements and concretes degrade because of cyclic effects such as freezing and thawing and wetting and drying. In an underground vault the materials would not be exposed to these cycles. Cracking and fracturing of cement-based vault seals could arise only from stresses generated by excessive physical forces, shrinkage and expansion, occurring autogenously or as a result of temperature variations, and from degradation reactions such as dissolution of the cement or ettringite formation.

Hsu et al. (1963) have shown that, under normal air curing conditions, microcracks in conventional concrete begin to propagate when loads exceed 30% of the ultimate strength, and continuous patterns of cracks exist through cement pastes at stresses of 70% or more of the ultimate strength.

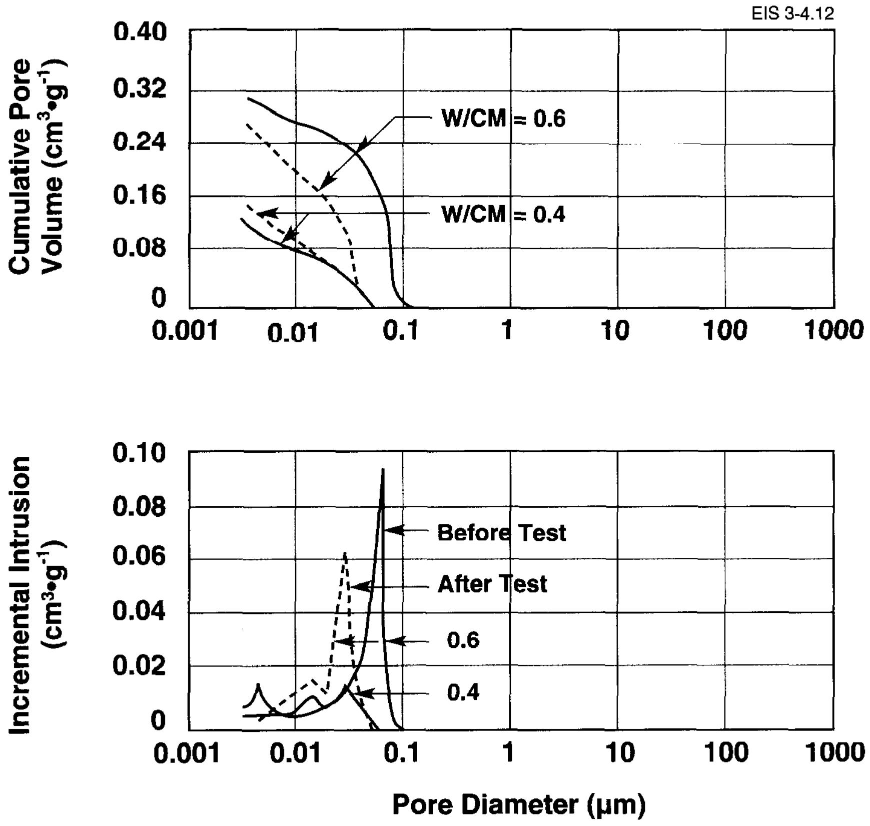


FIGURE 4-12: The Changes in Porosity and Pore Size Distribution Caused by Flowing Water Through a Cement Grout at Different W/CM (after Onofrei et al. 1992)

Thus, it can be suggested that restricting imposed loads to values such that internal stresses do not exceed 30% of the ultimate strength could ensure watertight, durable concrete sealing structures. The tendency for concretes to microcrack can be further minimized by the careful selection of aggregates, the shape, size and type of which all influence the onset of microcracking (Neville 1981). Moreover, in the event that the cement-based seals crack in moist conditions, such as in a vault, it is likely that the autogenous healing properties of concrete would cause the cracks to be filled with precipitates and reaction products. Thus, the effects of cracking on the hydraulic performance of the barrier would be minimized.

The most common cause of shrinkage in cements and concretes and of the associated cracking and increased hydraulic conductivity is loss of water. Strategies that minimize the free-water content of the cement paste, prevent water loss or otherwise improve the volumetric stability of the seal material (such as maximizing aggregate content) can be used to minimize the detrimental effects of shrinkage. Experience shows that

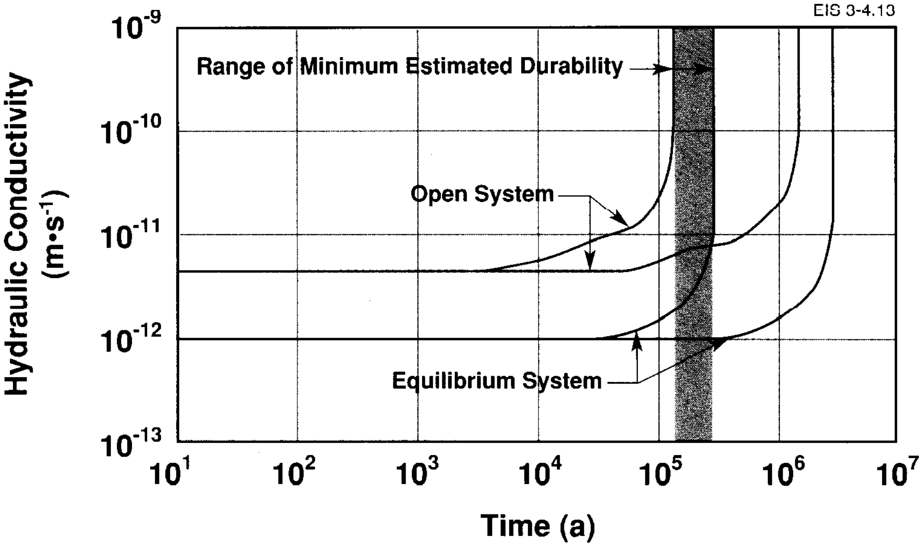


FIGURE 4-13: Calculated Changes in the Hydraulic Conductivity with Time of a Cement Grout in the Presence of Granitic Groundwater (after Alcorn et al. 1992)

conventional concretes tend to expand if cured in water; much of the drying shrinkage that occurs if the same material is cured in air can be reversed if the material is subsequently placed in water. Data (Figure 4-14) show that high-performance cements and concretes exhibit similar behaviour (Al-Manaseer and Keil 1990, Onofrei et al. 1992). In a vault that would eventually become water-saturated, the effects of shrinkage due to water loss on the hydraulic performance of cement and concrete seal material should be minimal.

Differential thermal expansion and contraction between a cement-based seal and the host rock resulting in crack formation is a possible mechanism through which the hydraulic efficiency of the seal material might be impaired. Thermal movement would occur locally as mass concrete structures hydrated and as the temperature of the vault changed under the influence of the radiogenic heat given off by the waste. Numerical models are being developed that will allow the stress-strain response of concrete to changing temperatures to be estimated (Storer et al. 1986). Currently, available models are limited in the geometries that can be studied: generally, the models only allow for two-dimensional treatment of three-dimensional problems. Furthermore, detailed knowledge of the properties of the cement-based materials that would be used to seal a vault is not yet available. With these limitations, and assuming that conventional concrete materials were employed, scoping calculations indicate that the main concern for mass concrete structures is tensile cracking of the concrete as it cools after liberation of the heat of hydration. Large mass concrete structures are proposed in the reference vault design to plug emplacement rooms and access tunnels, ramps and shafts (see Figure 4-17). Established concrete placement techniques (use of cooled water, crushed ice and cooled aggregates during concrete production and placement) and appropriate materials choice ("low heat" cements and the use of pozzolans) could be

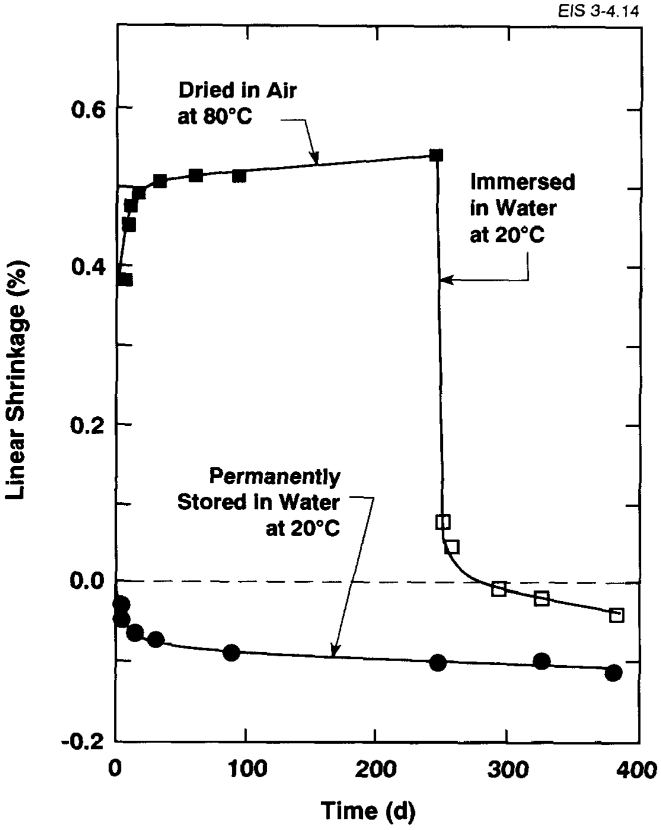


FIGURE 4-14: Shrinkage and Expansion of High-Performance Cement-Grout Material (after Al-Manaseer and Keil 1990)

used to reduce stresses in the concrete arising from heat of hydration effects. The thin films of cement grouts should not suffer from the heat of hydration effects possible in mass concrete plugs. Movement along grouted joints arising from stress changes in the rock mass associated with the dissipation of heat from the waste might disrupt the grout or the bond between the grout and the rock. It has been shown, however, that high-performance cement grouts can self-seal when disrupted. The processes giving rise to self-sealing could minimize the effects of disruption on the hydraulic properties of a grouted rock mass and might also ameliorate the effects of thermally induced cracking in mass concrete structures.

Cements are commonly used construction materials and are available in adequate supply and to high manufacturing standards in Canada. Through studies at AECL's URL (Gray and Keil 1989) it has been shown that the special finely ground materials needed for rock grouting can easily be prepared from the standard materials. Silica fume, fly ash and superplasticizer additives are available in adequate supply and as well-controlled commercial products in Canada.

Aggregates for use in concretes, and for the preparation of clay-aggregate backfilling materials, would likely be manufactured from the rock spoil generated during vault excavation. The appropriate rock handling, crushing, sizing plant, storage and mixing facilities are included in the reference vault design (Simmons and Baumgartner 1994). Standard test procedures would be used to control the quality of the crushed rock products. Current research suggests that special natural aggregates (uncrushed, river-run sands and gravels) may be needed to produce very high-performance concretes (Sarkar et al. 1990). These materials would be imported to the site and controlled by methods similar to those employed for crushed materials.

Accepted, statistically based methods are available to measure and control the quality of cement grouts and concretes both on delivery from the mixing plant and during use. These include tests for composition, particle-size distribution, setting times, consistency, viscosity, shrinkage and strength. For cement grouts, viscosity, setting time and strength tests would likely be the most commonly used field tests for quality control. For concretes, strength and consistency tests along with analyses of mix composition would likely be used.

Despite objective tests on material quality, the most important factor in ensuring the high "as-placed" quality of cement and concrete products is properly trained and supervised personnel. Some of the high-performance cementitious materials that might be used in a disposal vault, and some of the possible procedures for material placement (such as preplaced aggregate concretes, dry compacted concrete, shotcreting, and deep injection grouting) are likely to require special knowledge. To provide the necessary personnel and to maintain contemporary understanding of materials properties and performance, there would be a need to establish appropriate technical educational and support facilities.

4.6.3 Summary

For clay-based sealing materials, the hydraulic properties depend on the predominant clay mineral and the quantity of clay-sized material in the mixtures. Coarse and fine aggregates can be mixed with the clay to provide desirable engineering properties. The materials should be placed at the highest practically achievable density to achieve the lowest hydraulic conductivity and the tightest seal. The water content of the materials can be varied so that they could be made workable for different sealing purposes and with different placement techniques. Montmorillonite is a highly surface-active clay mineral that imparts the special properties of swelling and very low hydraulic conductivity to bentonite clay. Canada appears to have sufficient supplies of clays to seal the reference vault. In particular, bentonites could be quarried from formations in western Canada and processed to meet a range of possible specifications needed for different vault sealing applications.

Recent years have seen significant advances in cement and concrete technology. These have arisen through the invention and use of special additives, such as superplasticizers and silica fume, in concrete mixtures. These advances are likely to continue at a rapid pace into the next century, and conventional contemporary concretes are unlikely to be used for vault sealing. Available information suggests that high-performance cements and concretes developed from these materials would have negligible hydraulic conductivities associated with very low porosity. Microcracks generated in this material from overstressing, shrinkage or thermal loads would likely tend to self-seal. The self-sealing properties of high-performance materials are largely explained by processes causing autogenous healing in contemporary concretes. Existing practice and standards provide considerable guidance for the methodologies that would be used for the construction and the quality assurance of cement-based vault seals. The constituent materials for the construction of cement-based seals are in abundant supply in Canada. The performance of concrete seals would very largely depend on high-quality workmanship. The need for a highly qualified work force would demand special consideration when establishing the vault operating infrastructure.

4.7 NEAR- AND FAR-FIELD SEALS

The sealing properties of clays, clay-aggregate mixtures, cements, grouts, mortars and concretes have been presented in Section 4.6. In Section 4.7, possible applications of these materials in a vault are considered. We examine how factors such as the hydrogeological conditions, the chemical compatibility between the container and the sealants, the thermal conductivity of the sealants, the location of specific seals and the methodologies for seal placement and construction would affect the selection of seal materials and the design of seals. In the absence of a site-specific design for a vault, the discussions are, by necessity, generalized. However, through examination of the choices made for the reference vault design described by Simmons and Baumgartner (1994), the seal material selection and seal design processes that could be used for a vault are outlined. Specifically, in Section 4.7.1 we describe the rationales for the selection of the clay-based buffer and backfill materials and the design of the concrete bulkheads that form the near-field seals used in the reference vault design to fill and seal emplacement rooms containing the waste containers. In Section 4.7.2 we examine the rationales for the selection of the materials and methods used for the far-field seals, which include plugs for investigation boreholes used for hydrogeological characterization of the vault site, and plugs and seals for the shafts and tunnels needed for vault access and operation.

4.7.1 Near-Field Seals

Section 4.2.2 has summarized the likely ground conditions to be expected at the site of a disposal vault in plutonic rock of the Canadian Shield. These conditions, and subsequent changes in these conditions caused by the presence of the vault, generally define the possible range of environments in which the sealing materials would be expected to function. Figure 4-1 suggests that waste disposal would be confined to "intrablock regions"—i.e., volumes of rock that did not contain hydraulically active features such as major faults and crushed-rock zones. In this context, near-field seals are defined here as those materials used to separate the containers from the rock and to fill the excavations in the "intrablock" regions. In addition, specially designed plugs and associated treatment such as grouting of the EDZ would be needed to isolate the waste containers and the backfills from the major hydraulically conductive pathways through which water could flow in the rock. For the vault described by Simmons and Baumgartner (1994), the near-field seals include the clay-based buffer, the clay-based room and tunnel backfills, the cement-based plugs for rooms and tunnels, and grouts used at plug/rock interfaces and within the rock mass. In addition, it is likely that investigation boreholes drilled at the emplacement horizon would be plugged and grouted to ensure the integrity of the near field. Special plugs and seals would be located where excavations intersected the hydraulically active features, and would be required to maintain very low hydraulic gradients and water flows in the zones of rock where waste was deposited. The dimensions of the special plugs and seals and the volumes of rock from which waste emplacement was excluded would depend on the site-specific conditions encountered during vault excavation and on associated total system performance assessment. Numerical analysis of the performance of the reference disposal system, including bentonite-based buffer material, backfilling of excavations with materials with hydraulic conductivities of $<10^{-10}$ $m \cdot s^{-1}$, and a vault located in sparsely fractured rock with at least a 50-m distance between waste containers and the nearest major fracture zone, indicates that regulatory criteria can be met (Goodwin et al. 1994).

Both in general and more specifically for the reference vault, clay-based and cement-based sealing materials are proposed for sealing the near field. Studies for the CNFWMP have examined appropriate methodologies for applying the seals, and aspects of seal performance in the near-field environments have been investigated. In this latter context, in addition to the demands of compatibility with and performance of the geosphere, particular attention has been given to the interactions that may occur between sealing materials, the waste and the container. The effects of elevated temperature, temperature changes and groundwater chemistry on these interactions have been explored.

Conventional concretes and cement-based materials elevate the pH of waters with which they are in contact. pH values in excess of 12.5, the value for saturated lime solution, have been measured when silicate minerals and their alteration products are suspended with hydrated cement in groundwater. The corrosion performance of candidate container metals may be less predictable in these highly alkaline solutions than at more neutral pH in the range from 7 to 10. For example, corrosion-resistant metals such as titanium and titanium alloys may become more prone to localized crevice corrosion at high pH (Schutz and Thomas 1987). Moreover, the groundwaters may contain high Cl^- contents. At high pH, the surface of copper would be passivated (de Zoubov et al. 1966), and with the high Cl^- content in the groundwater, passive copper surfaces would be more likely to degrade by pitting than by uniform corrosion. Hence, clay-based sealing materials that would maintain, or chemically buffer, the pH of groundwaters to neutral or slightly alkaline values ($7 < pH < 9$) are preferred as the buffer and backfill materials near titanium or copper containers. Although high pH (up to pH 12) is unlikely to increase the dissolution rate of used fuel, it could enhance the dissolution rate of vitrified reprocessing waste, although radionuclide solubilities are generally very low under alkaline conditions.

In general, in addition to an ability to chemically buffer the groundwaters that may contact the container, buffer material could be used to limit the rate of release of radionuclides from breached containers to the rock. In Section 4.6.1 we indicate that bentonites have the highest capacity of common clay minerals to sorb radionuclides from solution and that, when placed at high densities, bentonites would have very low radionuclide diffusion coefficients and hydraulic conductivities. Coupling these properties with the high swelling capacity of compacted bentonites explains why bentonite is preferred over other clays as buffer material. Table 4-3, which lists the reference clay-based buffer materials being examined in various national programs for the construction of geological disposal facilities in granitic formations for heat-generating radioactive wastes, shows that, almost exclusively, bentonite-based materials have been selected as clay-based buffers.

Located nearest to the container, the buffer would experience the highest temperatures of any of the vault seals. Under these conditions the buffer would be required to mechanically support the container without significant deformation either under the weight of the container and other imposed loads or from its own propensity to swell. Excessive deformation could

TABLE 4-3

COMMONLY PROPOSED BUFFER MATERIALS FOR GEOLOGICAL DISPOSAL FACILITIES

Country	Emplacement Geometry	Reference Buffer Material	Dry Density (ρ_d) ($Mg \cdot m^3$)	Compaction Method
Canada	Borehole	50:50 sand: Na-Ca-bentonite	>~1.67	In situ
Finland	Borehole	Na-bentonite	1.4-1.8	Precompacted blocks
France	Long borehole	Ca-bentonite	1.4-1.8	Precompacted blocks
Spain	Borehole	Na-bentonite	1.4-1.8	Precompacted blocks
Sweden	Borehole	Na-bentonite	1.4-1.8	Precompacted blocks
Switzerland	In-room	Na-bentonite	1.4-1.8	Precompacted blocks
Japan	In-room	25:75 sand: bentonite		Precompacted blocks/in situ

conceivably crack or decrease the density of the buffer and cause its hydraulic conductivity and radionuclide diffusion coefficients to increase, thereby decreasing the sealing efficiency of the buffer. To function effectively and predictably as a buffer, compacted bentonite-based materials need to be confined (i.e., the space into which it is allowed to swell needs to be defined and controlled). Under these conditions, the tendency for bentonite to swell imparts an ability for the material to self-seal any deformation-induced cracks, construction joints and natural fractures in the rock into which it can intrude. The swelling properties of a bentonite-based buffer material would impart a self-sealing ability to the material that needs to be maintained over long periods of time in a vault environment. Two mechanisms have been identified through which a bentonite-based buffer might lose its swelling capacity. These are illitization, in which the swelling smectitic mineral (montmorillonite) in bentonite clay can be chemically converted into a non-swelling clay (such as illite); and silicification, in which silica in the groundwater, which is either dissolved from the minerals in the rock or from the clay itself, is precipitated in and cements the clay buffer mass. Loss of swelling capacity and the ability to self-seal any cracks in the buffer might result. Both illitization and silicification have been studied extensively in the Canadian program (see Johnson et al. 1994) and internationally (Gray 1993, Pusch et al. 1991a). It has been shown that, provided temperatures do not exceed about 120°C, silicification is not a concern. Similarly, in compacted bentonite buffer materials at temperatures below 120°C, the illitization reaction is controlled by the concentration of K^+ in the groundwater and the rate of diffusion of K^+ in the clay. The reference vault is designed so that temperatures do not exceed 100°C, and K^+ concentrations in the groundwaters of the Canadian Shield are sufficiently low as to render the illitization process insignificant.

The swelling pressures developed by confined bentonite buffer material would act as imposed loads on the container. Moreover, hydraulic pressures of up to approximately 10 MPa (the static hydraulic pressure 1000 m below the groundwater table) could also act on the container, which must be designed to resist these forces. In a fully water-saturated vault, a container surrounded by a bentonite-based buffer would experience a pressure that is equal to the sum of the hydraulic pressure and the swelling pressure (Graham et al. 1992). The relationship between swelling pressure and density is well understood (Gray et al. 1985, Yong and Warkentin 1975), and, within limits defined by the mass transport properties of the compacted clay, the buffer material could be selected so that its swelling properties accommodated the constraints of the container design.

To reduce the hydraulic conductivity and radionuclide diffusion coefficients of bentonite clays to values at which the materials could be used as buffers, the clay should be compacted to a minimum effective clay dry density of approximately 1.2 $Mg \cdot m^{-3}$ (Cheung et al. 1987, Cheung and Gray 1989). Densities in excess of this value can be achieved when the buffer is placed as precompacted blocks (SKBF/SKB 1983) and when the clay is compacted in situ (Dixon et al. 1985). Similarly, effective clay dry densities (ρ_c) of 1.2 $Mg \cdot m^{-3}$ or higher can be achieved in bentonite-sand mixtures provided the clay content exceeds approximately 40% by dry mass of the mixture (Dixon et al. 1985). A bentonite-sand mixture with a clay density of 1.2 $Mg \cdot m^{-3}$ would have similar mass transport properties to a bentonite clay compacted to the same clay density. Totally confined, at the same clay density both materials would exert similar pressures on the confinement. Allowed to swell freely, the bentonite-sand mixture would expand less than the clay alone. The bentonite-sand mixture would undergo less drying shrinkage than the clay. Moreover, the clay would deform more under load and, when water-saturated, would have lower thermal conductivity and heat capacity than the bentonite-sand mixture. With this knowledge, a bentonite-based buffer material could be selected for different vault configurations, geometries and engineering practices. The reference vault design provides an example of this selection process, which is described below.

For operational reasons, including worker safety and the need to handle large quantities of material, for the reference vault it was decided to investigate the possibility of placing and compacting the buffer in situ (Simmons and Baumgartner 1994). Because of limitations on the quantities of energy that can be used, in situ compaction imposes a practical limit on the achievable maximum ρ_c. Using bentonite with a liquid limit of ~300% and a plasticity index of ~250, Dixon et al. (1985) showed that the maximum ρ_c attained through in situ compaction is $\simeq$1.3 $Mg \cdot m^{-3}$; for bentonite-sand mixtures with sand contents ranging from 0 to 50% the maximum ρ_c that can be achieved by in situ compaction does not vary significantly with sand content. For a bentonite-sand mixture using graded silica sand and clay in equal dry mass proportions, ρ_c is $\simeq$1.3 $Mg \cdot m^{-3}$, which corresponds to a dry density, ρ_d, of 1.75 $Mg \cdot m^{-3}$. These values were obtained in laboratory tests carried out in accordance with procedures detailed in ASTM D-1557-78 (ASTM 1982). In common engineering practice, 95% of the maximum value from the laboratory test (i.e., 1.66 $Mg \cdot m^{-3}$) would be specified as a density that could be achieved in situ. At this ρ_d, ρ_c = 1.21 $Mg \cdot m^{-3}$. This density would give a maximum swelling pressure of about 2000 kPa, which is compatible with the design loads for the reference used-fuel disposal container. The lower drying shrinkage, higher bearing capacity and higher thermal conductivity of the bentonite-sand material indicate that, in some respects, the performance of the mixed material as a buffer may exceed that of 100% clay at the same ρ_c. Thus, a bentonite-sand mixture consisting of bentonite and graded silica sand in equal proportions by dry mass was selected as the reference buffer material (RBM) for the reference vault design. The important properties of the RBM are summarized in Table 4-4. The reference buffer thickness of 0.25 m was based on several factors, including consideration of reasonably achievable borehole excavation diameters, materials handling issues, and scoping calculations of mass transport through buffers of various thicknesses (Gray and Cheung 1986, Cheung et al. 1987).

Through tests carried out in situ at AECL's URL, it has been shown that the RBM can be compacted in situ to the specified minimum density in large-diameter (1.25-m diameter, 5 m deep) emplacement boreholes (Kjartanson et al. 1992). The methods used were too labour-intensive for use in a vault and would require further refinement and improvement if the borehole-emplacement option for deposition of the waste container, as described for the reference vault by Simmons and Baumgartner (1994), was eventually

TABLE 4-4

COMPOSITION AND SELECTED PHYSICAL PROPERTIES OF THE REFERENCE BUFFER AND BACKFILL MATERIALS SELECTED FOR THE USED-FUEL DISPOSAL CENTRE CONCEPTUAL DESIGN STUDY

Property	Reference Material		
	Buffer	Lower Backfill	Upper Backfill
Composition			
Clay type	bentonite	lake clay	bentonite
Clay content	50% dry weight	25% dry weight	50% dry weight
Aggregate type	silica sand	crushed rock spoil	silica sand
Aggregate content	50% dry weight	75% dry weight	50% dry weight
Selected Physical Properties			
Dry density (ρ_d) ($Mg \cdot m^{-3}$)	>~1.67	>~2.10	>~1.40
Swelling pressure* (kPa)	800-2000	>50	250-800
Free swell* (%)	80-175	<~10	20-50
Hydraulic conductivity ($m \cdot s^{-1}$)	$<1 \times 10^{-11}$	$<1 \times 10^{-10}$	$<1 \times 10^{-10}$
Drying shrinkage (%)	<5%	<2%	<5%
Effective angle of internal friction (degrees)	~14-16	~28-30	~14-16

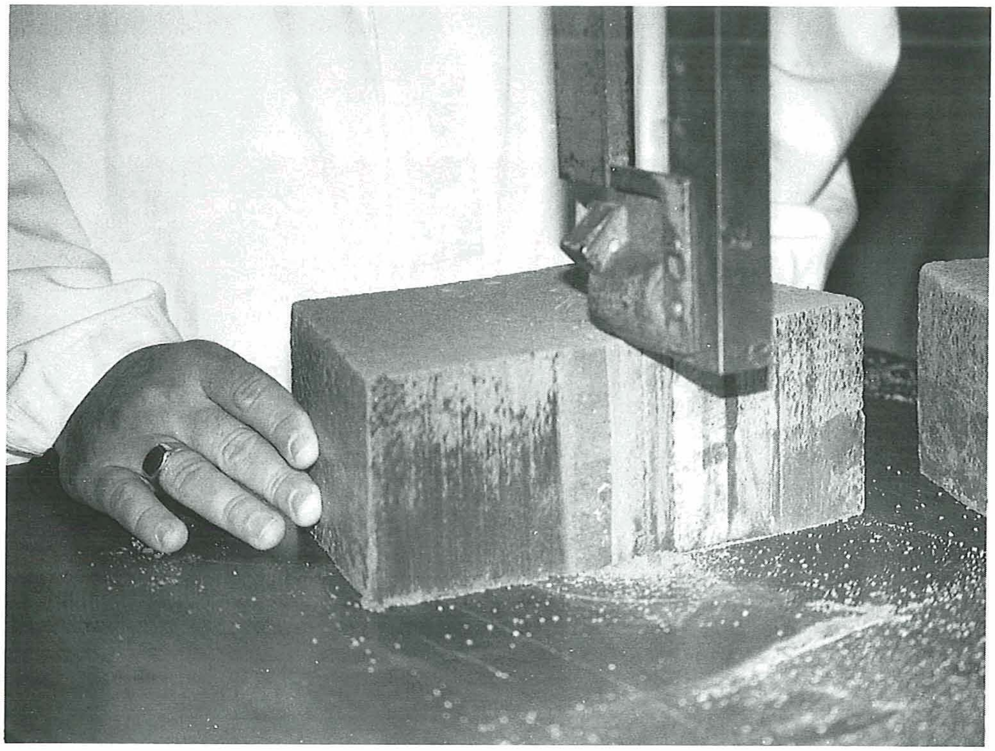
* The range results from assumed variations in groundwater chemistry. Higher salinities tend to decrease swelling pressures.

selected for implementation. In the event that the waste containers were to be placed in-room, general civil engineering experience in earth moving, soil compaction and the construction of clay barriers for hazardous waste disposal is sufficient to convincingly state that equipment and procedures exist to compact the RBM in situ, in-room, to the minimum specified dry and clay densities.

After compaction, the RBM has the consistency of a stiff, unfired clay brick. Figure 4-15 shows that the materials can be readily sculptured with machine tools. This indicates that boreholes large enough to accept the fuel-waste containers could be drilled into the RBM following its compaction in a disposal borehole. Gaps left between the buffer and the used-fuel container, arising from the need to provide working clearances during container emplacement, would need to be filled. The infilling materials would be needed to provide a continuous heat flow path from the container through the RBM to the rock, and to minimize the free swelling of the RBM. A free-flowing granular material such as sand or the glass beads used to fill the packed-particulate container would be appropriate for this purpose. An ability to place this material has been partly demonstrated through our Buffer/Container Experiment in the URL. Figure 4-16 shows sand filling a 50-mm annular gap between a simulated heat-emitting waste container (heater) and encapsulating buffer material. These tests were carried out under non-radioactive conditions. Remotely placing the granular media in the presence of a radioactive fuel-waste container would require refinement. Once the container and the enveloping sand layer were placed in the borehole, the remaining open section of the borehole would be plugged with compacted buffer. For the reference vault this would be compacted in place over the container, which must accommodate the loads imposed by the compaction process.

The rock would act as a virtually rigid restraint to lateral expansion of the RBM. For both in-room and borehole-emplacement options the upper surface of the RBM would need to be restrained to minimize vertical expansion and associated density decreases in the buffer. For the reference vault design, a low-permeability clay-based material has been designed and characterized to act as the major component of the seals in the rooms above the emplaced waste and RBM. The mix design and some of the important properties of this reference backfilling material are given in Table 4-4. As discussed by Johnson et al. (1994) this material, which is a mixture of 25% by dry mass lake clay with 75% by dry mass graded, crushed granitic aggregates compacted to a dry density (ρ_d) of not less than 2.1 $Mg \cdot m^{-3}$, should adequately restrain the RBM from expanding vertically. The density specification for the reference backfill was derived using testing procedures and reasoning similar to that used to define the specification for the RBM. Such density specifications are achievable with available compaction technology. In fact, using the same procedures developed for in situ buffer compaction, it was shown at the URL that the reference backfill materials could be compacted to meet the dry density specification outlined in Table 4-4 (Kjartanson et al. 1992). The cap of RBM over the used-fuel container can be made sufficiently thick to effectively shield the room backfilling operations from direct radiation from the container. Thus, none of the room backfilling operations described for the reference vault need to be performed using remote handling.

The compaction machinery for the room backfill requires headroom to operate. Thus, the depth to which the room can be filled with the reference backfill (lower backfill, Table 4-4) is limited, and a space estimated to be approximately 2 m high would exist between the top of the backfill and the back (ceiling) of the emplacement room. Experiments for the International Stripa Project have demonstrated that this space can be filled



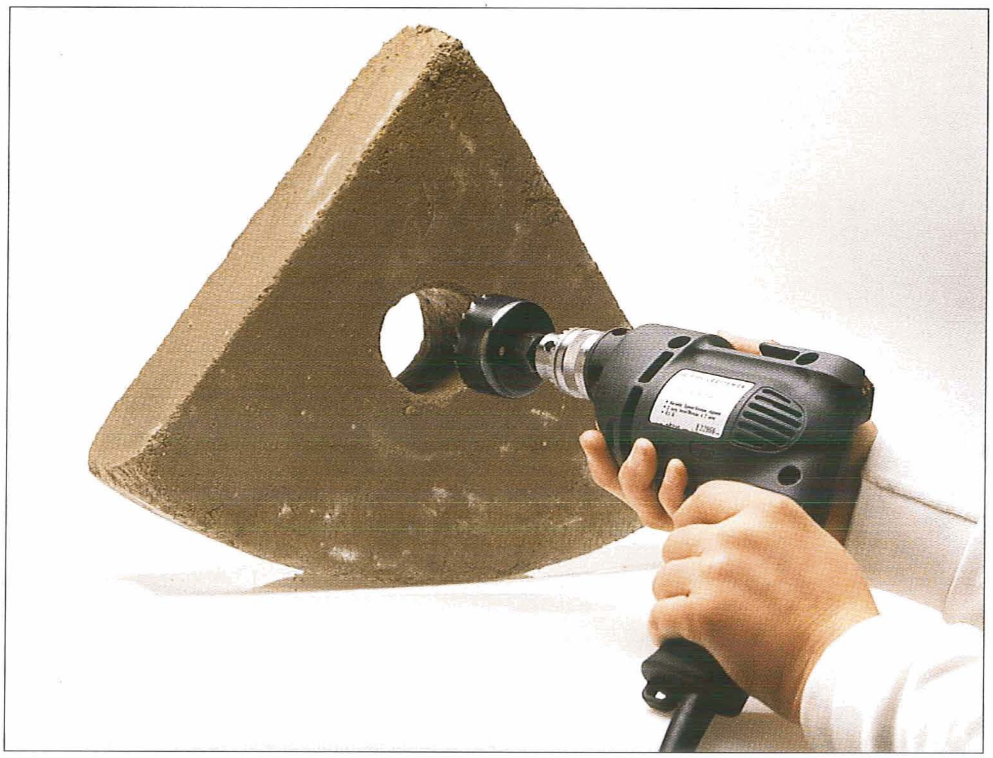


FIGURE 4-15: Large Precompacted Blocks of the Reference Buffer Material Being Sawn in a Band Saw (top) and Being Augered (bottom)

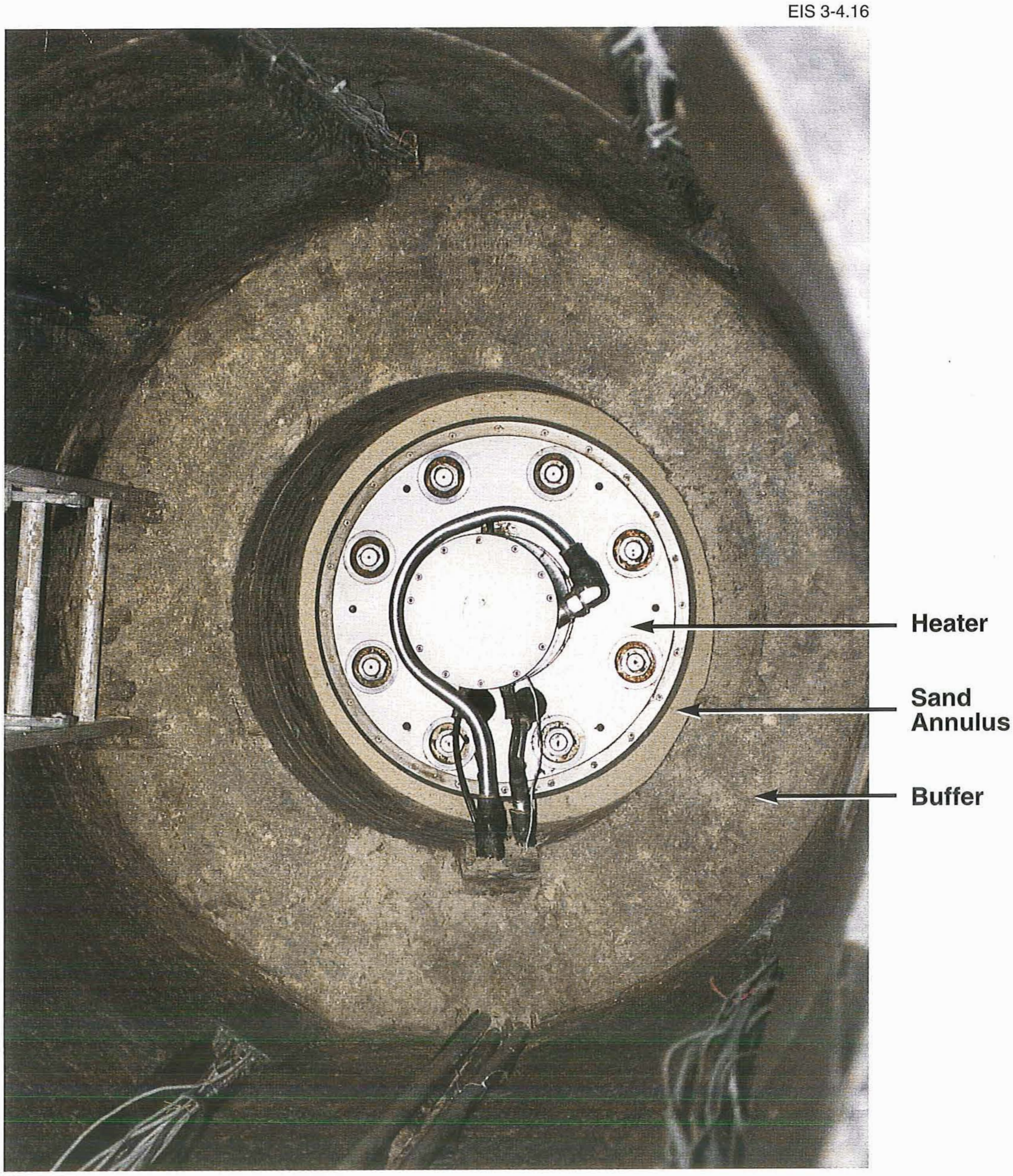


FIGURE 4-16: The Sand Infill Between the Buffer and the Heater in the URL Buffer/Container Experiment

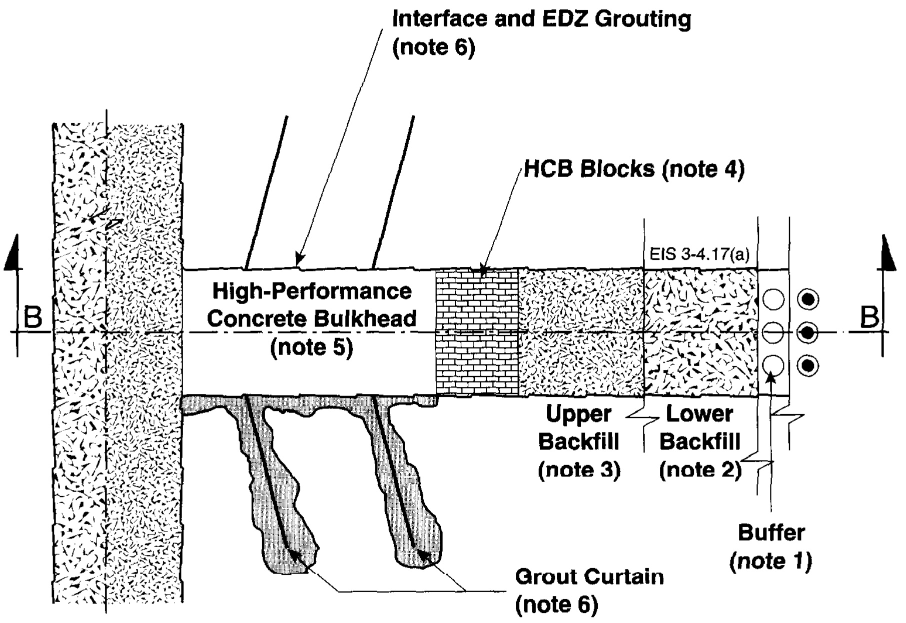
with sand-clay mixtures using remotely operated shotcreting (pneumatic) technology (Pusch et al. 1985). Swelling bentonite-sand mixtures can be placed to densities estimated to be at least 75% of those attained in tests to ASTM D-1557-78. At this density a shotcreted bentonite-sand backfill (upper backfill) would have the properties shown in Table 4-4. The swelling properties of this upper backfill material would ensure complete closure of the room cavity with material with a hydraulic conductivity of $<10^{-10}$ $m \cdot s^{-1}$.

After the excavations were backfilled, water would flow principally in the fractures in the rock and at the interfaces between the backfill and the rock. These flows would be restricted as far as possible by the construction of concrete bulkheads at the ends of emplacement rooms. In addition to plugging the rooms, these bulkheads would provide a restraint for any pressure grouting operations that might be required to seal the interfaces between the rock and the concrete plug or, where possible, to reduce the hydraulic conductivity of the EDZ. The concrete plugs would resist swelling and movement of the room backfills as well as any hydraulic pressures that might develop as the backfills saturated with groundwater.

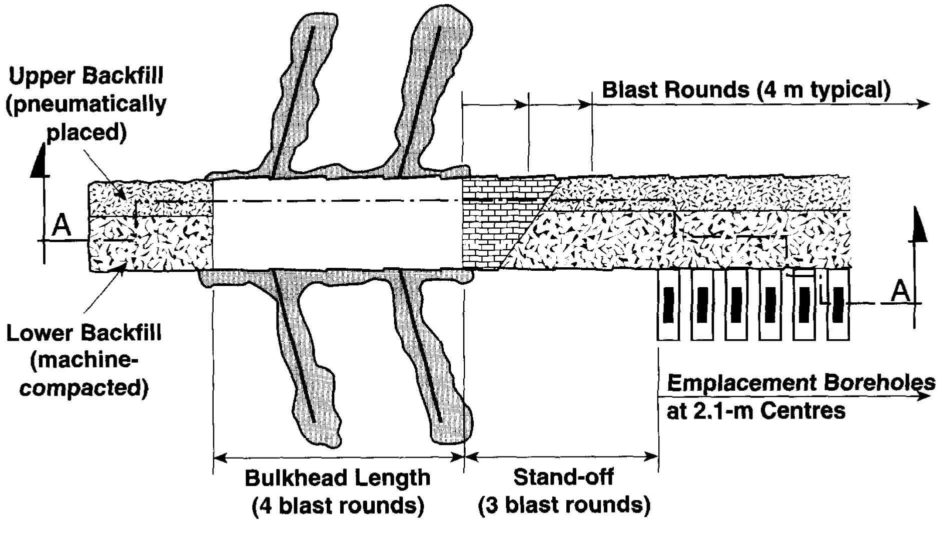
One approach for proposed near-field seals is shown schematically in Figure 4-17a. The clay-based buffer, and the lower and upper backfill materials, the compositions and important properties of which are given in Table 4-4, would be used next to the containers and to fill the rooms above the waste packages. High-performance concrete bulkheads would be used to plug and seal the entrances to emplacement rooms. Similar structures would plug and seal access tunnels that passed through hydraulically active fracture zones. The bulkheads would confine the backfill and allow for the full swelling pressure of the upper backfill to develop. The backfills would therefore be firmly pressed against the rock, and flow along the backfill-rock interface would be restricted. Tests undertaken in the Stripa Mine have shown that gaskets of highly compacted bentonite (HCB) placed next to concrete bulkheads can be used to virtually eliminate groundwater flow along the plug-rock interface (Pusch et al. 1987a). Thus, the possible near-field seal designs shown in Figure 4-17a include an HCB gasket on the innermost surface of the bulkhead, although these were not specified for the reference vault design of Simmons and Baumgartner (1994).

At ρ_c greater than 1.75 $Mg \cdot m^{-3}$ HCB would need to be placed as prefabricated precompacted blocks and would generate swelling pressures in excess of 10 MPa. This pressure would act on the rock and bulkhead surfaces and enhance the interface seals over and above those effected by the backfills, which would exert a pressure of only 200 to 300 kPa. To ensure stability and maintain function, the bulkheads would need to be structurally designed to accommodate the combined pressures (thrusts) from the backfill, bentonite gaskets and any water pressure differences that could develop across the plug. Unless grouted, the excavation-damaged and disturbed zones in the rock around the bulkhead and the backfills might, while the vault was open, act as drains and prevent excess water pressure buildup behind the plug. This might limit the maximum hydraulic pressure across the bulkhead.

The high pressures acting on the rock surfaces from the bentonite gaskets might alter the flow characteristics of the EDZ. Under the high swelling



Plan View, Section A-A



Section B-B

FIGURE 4-17a: Near-Field Seals - Emplacement Room
(see page 227 for notes)

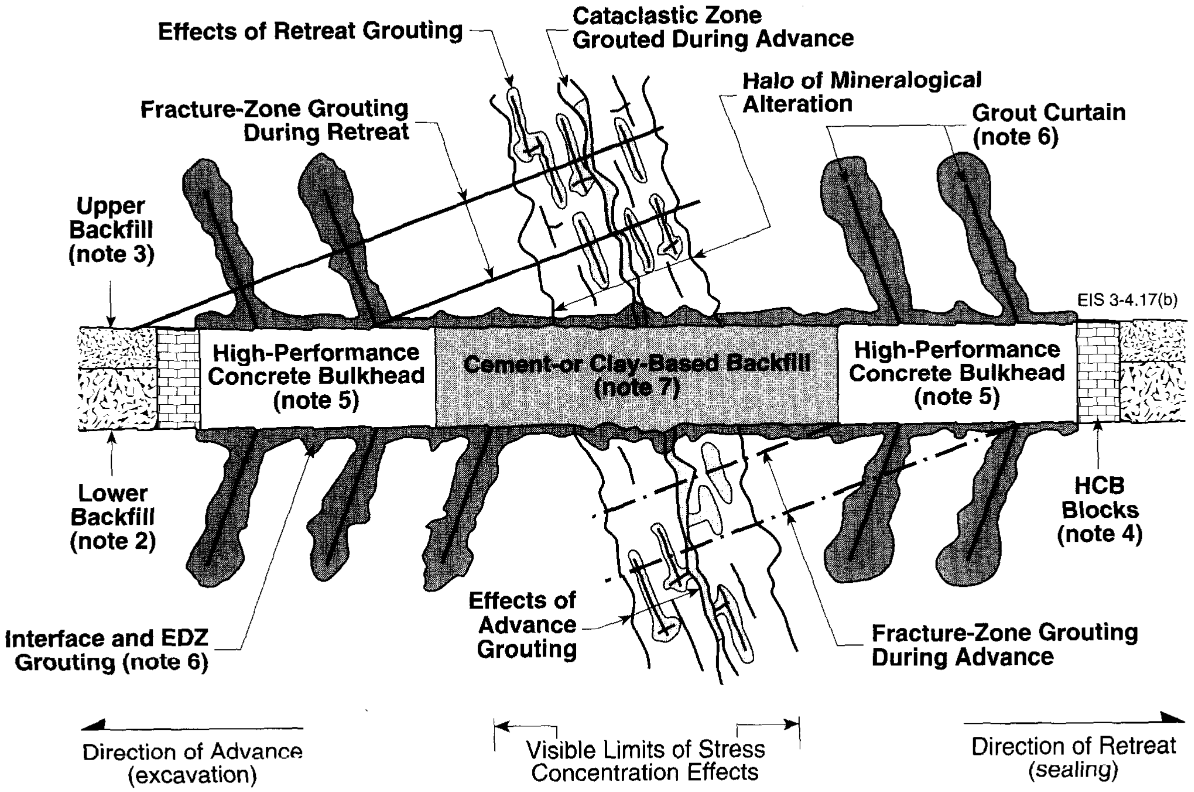


FIGURE 4-17b: Near-Field Seals - Fracture-Zone Isolation Elements

1. Reference buffer material defined in Table 4-4 compacted in situ.

2. Lower backfill material defined in Table 4-4 compacted in situ.

3. Upper backfill material (Table 4-4) stowed pneumatically as described by SKBF/SKB (1983).

4. HCB similar to materials proposed for buffer material by SKBF/SKB (1983) and described in Table 4-3: MX-80 Wyoming bentonite, or similar, isostatically compacted in an air-dry condition to very high dry densities ($> 1.7\ \mathrm{Mg \cdot m^{-3}}$) and placed as a brickwork to act as a gasket against the bulkhead. Voids would be filled with bentonite powder or small offcut pieces of HCB.

5. Low W/CM, high-performance concrete necessitating the use of superplasticizer. Cement would conform to specifications for Canadian Type 50 cement and would be mixed with a pozzolan. A current specification would include silica fume (10% by mass of cementitious materials) and high cementitious materials contents (i.e., in excess of $350\ \mathrm{kg \cdot m^{-3}}$). Possible methods of forming the bulkhead include continuous pour, pneumatic stowing and preplaced aggregate concrete. Aggregates would likely be derived from crushed granite spoil. Construction joints would need particular attention and nominal reinforcement would likely be included to limit the effects of shrinkage and expansion.

6. A microfine cement grout, preferably based on Canadian Type 50 cement, and similar to that described by Gray and Keil (1989) is currently proposed.

7. Cement-based backfill could be dry-compacted, high-performance concrete placed as in Note 2, pneumatically stowed concrete (dry or wet), or high-performance concrete similar to that used for bulkhead construction. Clay-based backfills would be identical to the upper and lower backfill materials described in Notes 2 and 3.

pressures, the HCB would tend to intrude and seal fractures in the rock that were exposed or generated by the excavations and would also tend to close circumferential fractures by increasing the normal stress across them. In rock where the hydraulic conductivity of the EDZ was less than approximately 10^{-8} m·s^{-1}, the effects of the swelling pressure from the HCB on the rock surfaces and the intrusion of the bentonite into the fractures on the rock surfaces might be the only mechanisms through which the hydraulic conductivity of the EDZ around the bulkhead could be modified. Experiments at the Stripa Mine (Pusch 1992, Gray 1993) and at the URL (Gray and Keil 1989) have shown that rock with hydraulic conductivities greater than about 10^{-8} m·s^{-1} can be grouted using either clay-based or cement-based grouts. The effects of such grouting on the hydraulic conductivity of the rock mass remain uncertain, although hydraulic conductivities of 10^{-9} m·s^{-1} or less have been measured in grouted rock masses (Pusch et al. 1991b, Gray and Keil 1989). It has not yet been shown that EDZ with hydraulic conductivity lower than 10^{-8} m·s^{-1} can be effectively grouted with either cement- or clay-based grouts (Gray 1993). Thus alternative geometries and construction details for bulkheads have been considered. Some conceptual designs include a cutoff wall that extends from the bulkhead through the EDZ. It is not yet clear whether this wall would perform its desired function. The effectiveness of the cutoff would depend on the rock conditions surrounding the excavations. Excavating the rock to accommodate the wall would generate further disturbance in the stress field around the excavation, which might increase the hydraulic conductivity of the rock near the new excavation and thus water might bypass the cutoff. The Mine-by Experiment in the URL (Martin and Simmons 1992) is designed, in part, to examine this hypothesis. At present, it appears that the decision to use a cutoff wall and/or grouting to seal the EDZ around a tunnel bulkhead could be made only when the desired location of the bulkhead and the near-field rock conditions were known through field observations and measurements at a specific site.

Technical opinions vary, but it is likely that changes in the natural stress field caused by excavating an opening in the rock would have less impact on the hydraulic conductivity of the rock than the damage caused by the excavation process. At the Stripa Mine, where conventional drilling and blasting techniques were used for excavation, measurements and analyses indicated that the hydraulic conductivity of the rock was significantly increased to distances of 0.5 to 1 m into the rock from the excavation surfaces (Börgesson et al. 1992, Gray 1993). The average hydraulic conductivity of this zone was calculated to be in the order of 10^{-8} m·s^{-1}.

Similar observations have been made in the floors of rooms at the 240 Level at AECL's URL (Martin et al. 1992). Moreover, the tests at the URL showed that the measured hydraulic properties of the EDZ can depend on the scale of the test and the degree of preparation of the rock surfaces prior to the installation of plugs and seals. In general, rooms and tunnels at the URL have been excavated using careful drilling and blasting techniques. Each drill-and-blast cycle advances the excavation by about 4 m, after which the broken rock is removed (mucked) and another cycle (round) is initiated. The tests at the 240 Level included the construction of two concrete dams in a tunnel, ponding water to known depths between the dams and measuring the outflow through the EDZ in the floor of the room. A concrete slab on the floor of the room was first built inside the dam to cover a distance along the room that was less than one blast round. After completing flow tests with this configuration, the concrete slabs were extended to cover more than one blast round and the flow tests were repeated. The results showed that at this specific test site the hydraulic connection of blast-induced fractures was not continuous (Martin et al. 1992). The careful blasting techniques employed for excavation at the URL and preparation of the rock surfaces prior to the construction of the dams may have led to this result. However, the fact that the natural fracture frequency in the Stripa granite is significantly higher than that in the sparsely fractured rock mass of the URL, combined with the fact that the stress and hydraulic characteristics of the rock masses at the two sites differ significantly, may have been more responsible for the different results than the technologies employed to excavate the two facilities.

These observations confirm that the final design for a bulkhead, including materials selection, construction methodology and the geometry and arrangement of bulkheads and associated seals for the EDZ, could not be made until the vault site conditions were known. Using the URL results as an example, an effective mechanism for sealing rooms and tunnels would be to dimension bulkheads to span two or more blast rounds. This would ensure minimum water flow in the EDZ around the plug.

Massive high-performance concrete plugs, associated grouting and bentonite gaskets are also suggested as the means for sealing tunnels where they pass through hydraulically active shear zones (Figure 4-17b). The remainder of the access tunnels in the reference vault would be backfilled and sealed using the clay-based backfills and associated technologies described for emplacement rooms. Hydraulically active faults act as discontinuities in the stress field of the geosphere (Martin et al. 1990). The general stress field in a rock mass is disturbed for tens of metres beyond the visible limits of the faults, and, when penetrated by excavations, the near-field stress patterns become extremely complex. In these circumstances, to facilitate modelling of plug performance and plug-rock interactions, it would be necessary to extend the plugging concrete structure into zones of rock where the stress field was not significantly influenced by the fracture zone. This might require the construction of concrete plugs that filled the excavations to distances of 25 or 30 m on either side of the discontinuity. Moreover, as noted by Martin et al. (1992), concrete plugs extending over several blast rounds may effectively reduce interconnected permeability effects created by the blasting. Detailed observations of the stress and hydraulic characteristics of the rock mass during vault excavation would help define the final dimensions of the plug. These observations would be coupled with predictions of the hydromechanical response of the fracture zone to the thermally induced stresses arising from the presence of the heat-generating waste and imposed on the natural stress domains. Because of the local variations in the stress field, it would not be possible to precisely predict the response of the fracture zone to the imposed stresses, and therefore the hydraulic response can be described only in general and stochastic terms.

As in the case of grouting the EDZ, the ability to grout fracture zones would depend on their hydraulic properties. Observations at the URL have shown that the equivalent hydraulic conductivity of fracture zones ranges from 10^{-7} to 10^{-12} $m \cdot s^{-1}$. Experiments at the URL have demonstrated that high-performance cement-based grouts can be used to seal fracture zones with hydraulic conductivities as low as 10^{-8} $m \cdot s^{-1}$ (Gray and Keil 1989). Figure 4-10 shows that cement-based grouts can be successfully injected into and seal rock fissures as narrow as 20 μm. However, even in conditions where the zones can be grouted, the effects on hydraulic conductivity remain uncertain and are difficult to quantify. The grouts would only penetrate and seal those channels that were open at the time of grout injection. Subsequent changes in stresses across grouted fractures, arising from temperature changes in the rock mass as heat dissipated from the waste, would have the potential to open new flow paths in the grouted rock mass.

Consequently, at present, the long-term effects of grout injection into the fracture zones cannot be quantified. Despite this long-term uncertainty, it is likely that grouting operations would improve system performance and would be needed as a construction expedient. Thus, grouting operations would be performed in accessible sections of faults and fracture zones. Because of the uncertainties in the long-term performance of grouted fracture zones, and because it is conservative in performance assessment calculations to take no credit for the potential for grouting to reduce groundwater transport, the effects of grouting on the hydraulic properties of fracture zones have not been included in the vault and geosphere models used to predict the performance of the reference vault.

4.7.2 Summary of Near-Field Seals

Near-field seals for a disposal vault facility are considered to be those materials used to separate the containers from the rock and to fill the remaining excavations in the intrablock regions (i.e., the zones of sparsely fractured rock in which containers would be deposited). These seals would be supplemented by plugs and grouts that would isolate the intrablock regions from hydraulically active fracture zones and minimize water flow in the EDZ around tunnels. The near-field seals, plugs and grouts would be made of both cement- and clay-based materials. The materials choice would be based on considerations of the hydraulic function and engineering practicability, and also on the chemical and physical interactions between different components of the waste disposal system.

Clay-based materials would be used next to the containers and to fill the rooms above the waste packages. Studies have led to the selection of a reference buffer material that would surround the container. The RBM is composed of bentonite and silica sand mixed in equal proportions by dry mass and would be compacted in situ to a minimum effective clay dry density (ρ_c) of 1.21 $Mg \cdot m^{-3}$. Compared with highly compacted 100% bentonite at the same density, the RBM has a higher thermal conductivity, similar hydraulic properties and would exert a significantly lower swelling pressure.

A reference backfill material, composed of crushed granite and lake clay mixed at a ratio of 3:1 in dry mass proportions has also been developed. The backfill material would also be compacted in situ and would have a hydraulic conductivity of $<10^{-10}$ $m \cdot s^{-1}$. A swelling clay-based material similar to the buffer would be pneumatically placed to complete the filling of the rooms above the lower backfill (Figure 4-17a). The compositions and important properties of the buffer and the two backfill materials are given in Table 4-4.

The entrances of rooms in which waste containers were emplaced would be plugged with bulkheads built with high-performance concrete. Similar materials would be used to plug access tunnels where these tunnels passed through hydraulically active fracture zones. The concrete bulkheads and plugs would be enhanced with highly compacted bentonite gaskets. The swelling properties of the bentonite would give gaskets an ability to virtually eliminate flow at the interface between the plug and the rock. The remainder of the access tunnels would be backfilled like the emplacement rooms.

The EDZ around the concrete bulkheads and plugs would, where possible, be grouted with cement-based grout or sealed with cutoff walls extending from the plugs into the rock. The EDZ around the backfilled excavations would remain ungrouted. Grouts would also be used to seal the hydraulically active fracture zones where they were intersected by the excavations.

The properties and engineering performance of the backfills and buffer are sufficiently well understood and certain to allow for their effects to be included in the vault model used for numerical analyses of the safety of the vault system. In this context, radionuclide transport through buffer and backfill materials and the long-term performance of these materials is discussed by Johnson et al. (1994).

The site-specific conditions encountered during excavation of a vault would ultimately determine the layout of the vault and, thus, the locations and dimensions of concrete plugs and bulkheads as well as the extent of grouting activities. Grouting would be used as a construction expediency and to increase confidence in the long-term performance of seals. The effects of these grouting activities are not included in the vault and geosphere models used in the postclosure assessment case study.

4.7.3 Far-Field Seals

The sealed intrablock regions in which the waste containers would be deposited would be connected to the ground surface by shafts, ramps and tunnels that provided access and ventilation for the working vault operations. Moreover, the vault levels would be penetrated by exploratory boreholes used to investigate the site and define the geotechnical, geochemical and hydrogeological conditions. Unsealed, these openings might present preferential pathways for water flow and radionuclide migration. Materials and methods used to plug or otherwise seal these potential pathways constitute the far-field seals.

The systems described in Section 4.7.1 for sealing emplacement rooms and access tunnels in the near field could also be used in the far field for tunnels and ramps. Similar materials could be used for shafts. However, the shaft geometry would limit the working space and necessitate alternative methodologies for placing the sealing materials. For the reference vault, the access tunnels, ramps and shafts are projected to be open for a minimum period of about 40 a, during which waste containers are deposited and the performance of the vault system is monitored (Simmons and Baumgartner 1994). Over this period, the normal contaminants arising from vault operations (grease, oils, vehicle fumes, dust particles, etc.) would accumulate on the rock surfaces and some weathering and possible degradation of the rock surfaces of the tunnels, ramps and shafts would occur. Depending on observed conditions, the rock surfaces might require cleaning and scaling before seals were installed.

It is likely that to limit rock spalling, and thus ensure worker safety, rock bolts would be installed, where required, in tunnels and ramps. Similarly, wire mesh might also be used. Where possible, before seals were constructed, the bolts and mesh would be removed and the rock scaled and cleaned. At present, it is envisaged that concrete roadways would be broken out to reveal the rock floors of the tunnels and ramps, which, like the walls and backs of the excavations, would be scaled and cleaned before the installation of seals. These measures would be carried out to increase the probability of effectively closing the rock-backfill interface and to limit possible effects of increased hydraulic conductivity in the EDZ.

In addition to rock bolts and wire mesh, concrete liners might be installed in some of the shafts. Observations at the URL, at many mines in the Canadian Shield and at the Stripa Mine indicate that this is not always necessary for worker safety. However, engineering studies (Golder Associates 1993) concluded that in the unlikely and inadvertent event of the release of radioactive materials in a shaft, a concrete shaft liner would facilitate clean-up operations. Moreover, the smoother surface provided by lining a shaft with concrete, as opposed to leaving the rock surfaces rough and bare, assists the flow of ventilating air. Liners also limit the need for rock bolts and meshing by providing long-term ground support.

To enhance the effectiveness of shaft seals, Golder Associates (1993) suggest that, as with roadways in tunnels, shaft liners should be removed prior to backfill emplacement and plug construction. Shafts are likely to be excavated using drilling and blasting techniques similar to those employed to excavate the URL. Golder Associates (1993) note that reaming machines exist that should allow for both the liner and the blast-damaged rock to be removed before shafts are backfilled and sealed. Essentially raise boring machines, the reamers would leave a regularly shaped and clean rock surface in the shaft. Figure 4-18, which presents views of the finished surfaces of the URL blasted main shaft and the raise-bored ventilation shaft, shows the benefits of reaming the shafts prior to seal installation. Alternatively, rather than reaming the entire shaft, the rock behind the liner could be grouted and sealed as the liner was installed. The liner would then be removed only locally where a concrete/HCB composite seal, similar to the room and tunnel bulkheads, was to be installed.

In appropriate geological conditions, where there were no proven adverse influences on the near field, the reamed shafts could be completely backfilled with high-performance concrete. Studies suggest that this material

FIGURE 4-18: Surface Appearance of Shafts in Intact Granite Excavated by Blasting (top), and by Raise Boring (bottom)

could maintain hydraulic conductivities as low or lower than those of the intact rock for hundreds of thousands of years (Alcorn et al. 1992). Alternatively, the backfilling and sealing technologies used in the near field could be adopted for the shafts. The major fraction of the shafts could be filled with earthen backfilling materials, and special plugs would be built where the shafts intersected hydraulically active discontinuities in the rock mass. Headroom constraints encountered during the backfilling of rooms and tunnels would not exist in shafts, and a nominally swelling backfill, such as the reference lower backfill material specified in Table 4-4, would be appropriate for use. A 6-m-diameter, 100-m-deep shaft would occupy a volume of approximately 28 000 m^3.

There are five shafts included in the reference vault design (Simmons and Baumgartner 1994). The diameters of the shafts reflect their different uses: two of the three ventilation and safety shafts are 4.9 m in diameter, and the other is 3.95 m in diameter; the service shaft is 7.9 m in diameter and the waste delivery shaft is 4.6 m in diameter. To fill these shafts would require approximately half a million tonnes of compacted reference backfill material. Conventional civil engineering and mining practice does not require placement of dense earthen backfill material; special equipment would need to be developed for this large-scale shaft-backfilling operation. This equipment would need to allow for the delivery of unsegregated backfilling material from a surface mixing plant to the elevation in the shaft where the material would be spread and compacted in horizontal layers. Some preliminary concepts for machinery for shaft-backfilling operations, based on existing earth-moving, compaction and mining equipment, have been suggested by Golder Associates (1993).

It is likely that the performance of composite seals, consisting of earthen backfills and special concrete plugs, would exceed that of shafts completely filled with earthen backfill (Golder Associates 1993). The concrete plugs would control water flow at strategic locations in the shaft and provide support for the backfill. As in the case of the EDZ around seals in the near field, the EDZ around the shafts would present the greatest level of uncertainty in determining sealing system performance. Comments made in Section 4.7.1 with regard to near-field seals, relating to the ability to minimize flow in this disturbed zone through grouting or the use of cutoff walls, are also valid for the EDZ in shafts. In brief, it may not be possible to grout the EDZ, and, as yet, the long-term performance of grouted rock masses as their properties change under the influence of stress changes arising from temperature transients and surficial glacial loading cannot be predicted. The hydrogeological conditions at the vault site, and the hydraulic characteristics of the EDZ would ultimately control the locations and final designs of the special seals intended to plug the shafts and intersect flow paths in the EDZ.

Experience from general mining and civil engineering activities in granitic rock bodies, measurements made in the Stripa and URL granite rock masses, and the preliminary design of shaft seals for the reference disposal vault have provided information to define a possible range of hydraulic and geotechnical circumstances in which shaft seals may be required to function. Materials appropriate for sealing have been defined and conceptual designs for the seals have been developed. Detailed designs would be developed as vault excavations proceeded and as associated observations on groundwater flow and excavation disturbance to the flow and stress fields were made. The limits to which contemporary technology can be used to decrease flows in the EDZ are known. These limits are likely to change as knowledge of and confidence in grouting and sealing technologies are increased through experiments that are either planned or in progress at the URL. It is likely that the findings of the URL tests would need to be confirmed through tests and measurements at the selected disposal site during the excavation, development and operation of a vault.

Typically, investigation boreholes used to characterize a site for vault development would have diameters of 100 mm or less. It is not obvious that, for purely technical reasons, penetrations of this size would need to be sealed. Results from performance assessment studies indicate that to control radionuclide release it might only be necessary to seal boreholes where they penetrated the intrablock regions where waste was deposited. The real need to seal boreholes is likely to be site-specific and, in fact, location-specific within a site. However, the borehole seals have been categorized as important barriers satisfying the concept of "defence-in-depth" (Klingsberg and Duguid 1980), and it is likely that all the investigation boreholes would be plugged and sealed along their entire length. In this context it has been shown (Chan and Stanchell 1990) that an unsealed or open borehole that penetrates a water-bearing fracture zone and intersects the vault within a pillar between two waste disposal rooms may create a significant pathway for radionuclide transport from the vault to the biosphere. Similarly, the penetration of a hydraulically active fracture zone by a well from which water is being regularly drawn could cause increased radionuclide transport to an open borehole that penetrates the vault horizon (Goodwin et al. 1994).

Lingle et al. (1982) report that the EDZ around a borehole is probably only one or two grain sizes deep, which in granitic rock at the URL corresponds to an average dimension of about 5 mm. The EDZ around investigation boreholes, which is about 5% of the dimension of the opening, is likely to be less significant to hydraulic flow than the EDZ around shafts, tunnels and ramps, where the blast-damaged zone alone can have a thickness of 1 m, which is about 15% of the average cross-sectional dimension of the opening. The core logs and any hydraulic or hydrogeochemical test results obtained from the borehole would define the conditions in which the seals would be required to perform.

In addition to choosing the plugging material, the shape and length of the plug, and the method of material placement for exploration borehole seals, it may be necessary to remove any casings or instrumentation in the hole prior to sealing, and to grout or otherwise pretreat the rock penetrated by the borehole prior to the insertion of the plug.

As in the case of shafts, casings for exploration boreholes would not generally be required for stability reasons in the rock mass. Shallow casings might be required where boreholes passed through relatively unstable overburden materials and to collar the boreholes. Special deep casings for instrument strings used to assess and monitor the site would be used in selected boreholes. It is not certain that casing removal would benefit borehole seal performance. Hydrogeological factors and the possible effects of corrosion of the casings on total system performance would need to be considered for the selected vault site. If these studies showed that removal of the casing was necessary, the technology exists for so doing. Shallow casings can be pulled; deep casings can be overcored or reamed. These practices could also be used to extract otherwise irrecoverable instruments and any shallow casing materials that could not be pulled.

Boreholes disturb the hydrogeological conditions only insofar as they interconnect fracture zones and other water-bearing features in the rock. Successfully sealing the boreholes where they passed through the sparsely fractured rock mass between the fracture zones might be enough to meet vault performance requirements. The boreholes could be plugged over their entire length or only at locations selected for maximum hydraulic effect. However, because of the small diameter of the boreholes, it is likely they would be completely filled with sealing materials. Benefits can potentially be gained by using composite seals rather than a single material to plug boreholes, as is the case when sealing larger openings such as shafts and tunnels. A schematic view of the different orientations of the boreholes that might have to be sealed is shown in Figure 4-19; these include horizontal, vertical, and both upwardly and downwardly inclined boreholes. The configurations of the seals and the materials and methods used would vary with the hydrogeological conditions and the inclination of the boreholes.

Methods for plugging both horizontal and vertical boreholes up to 100 m long with HCB (Pusch et al. 1987b) have been demonstrated in the OECD/NEA International Stripa Project (Gray 1993). Blocks of HCB encased in an exoskeleton of perforated copper tube were used to fill and seal boreholes. The copper tube provides the rigidity required to push the sealing system into the borehole. The perforations give groundwater access to the HCB, which extrudes into and seals the annular gap between the copper tube and the borehole wall. The effectiveness of sealing short vertical boreholes by gravity-feeding HCB pellets into the boreholes has also been measured (Daemen et al. 1983). To effectively function, HCB plugs, like the buffer material, need to be restrained. Cement-filled sections of the borehole would confine the bentonite and allow for full development of its swelling properties and sealing potential.

High-performance, cement-based plugs and grouts can be used to fill and seal boreholes at any inclination. The methods used to place the material would vary with the borehole inclination. Cement-based materials can be applied using methods established for standard grouting practices to completely fill a borehole. These include retreat pressure grout injection through specially designed, moveable, mechanical, hydraulic or pneumatic borehole packers. Used in combination with clay seals, the "balance method", used to place grouts and mortars for sealing oil and gas wells (Smith 1976), has been suggested (Seymour et al. 1987) for placing long sections of cement seals in vertical exploration boreholes. The method allows for controlled placement of long sections of cement-based sealants and for subsequent pressurization of the sealing material to limit the presence of voids and vugs in the plug. Pressurizing cement grouting and sealing materials in the borehole can also result in the penetration and

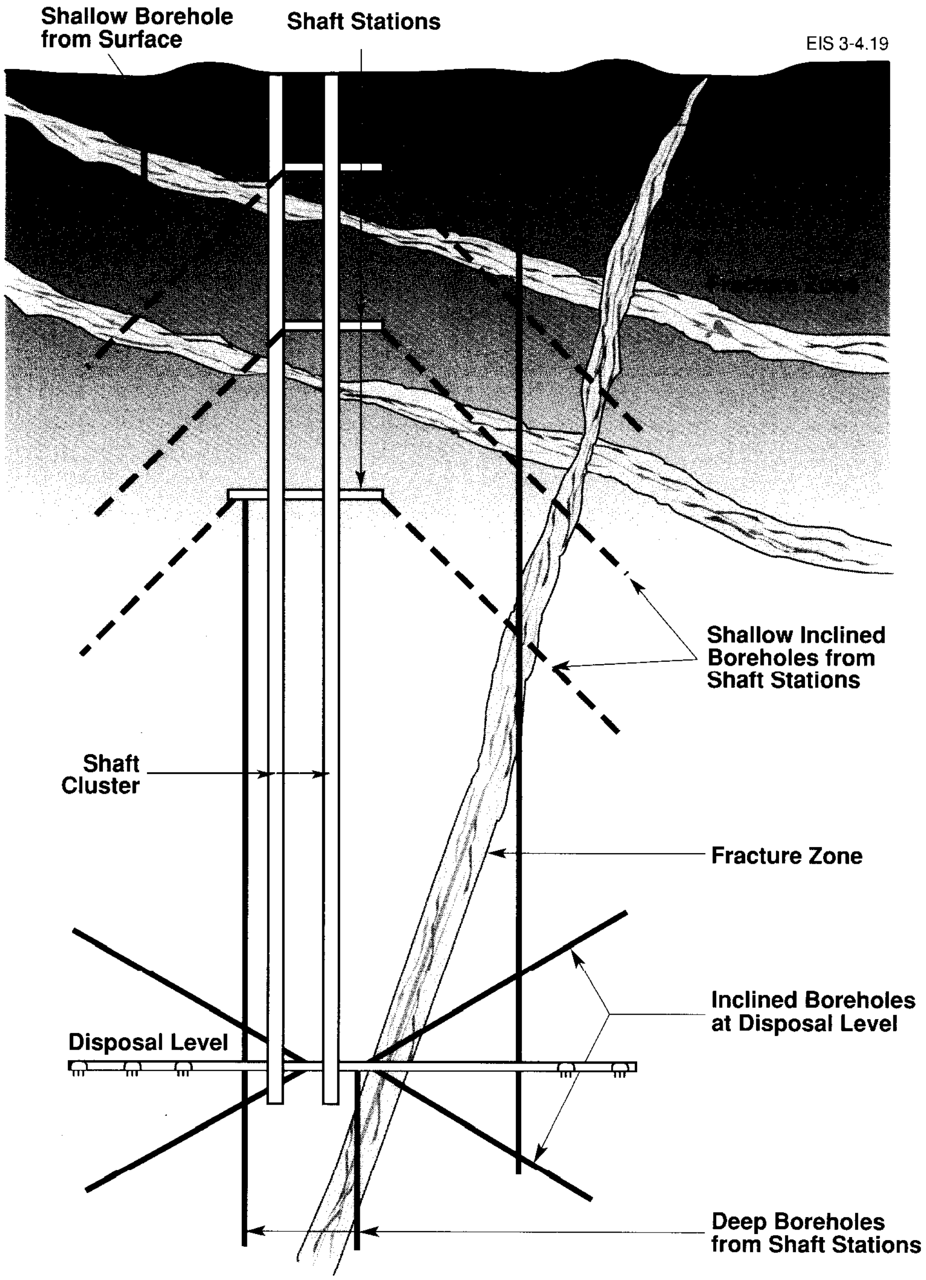


FIGURE 4-19: Schematic View of Possible Orientations of Boreholes to be Sealed

sealing of open fractures in the rock that are intersected by the boreholes.

Borehole sealing differs from shaft and tunnel sealing in that it is a remote process. Direct inspection of the as-placed sealing materials is impossible and remedial works may be neither possible nor desirable. Because of scale effects, differences between field and laboratory practice, and sampling disturbance, the performance of different seal configurations cannot be determined through laboratory testing of borehole seals. Investigations during the development and operation of the disposal vault, or in other in situ conditions, are needed to develop the method specifications that would ultimately be needed for borehole seal construction.

4.7.4 Summary of Far-Field Seals

The far-field seals for a disposal facility are defined as materials and methods used to plug or otherwise seal shafts, tunnels, ramps and exploration boreholes that connect the near field to the ground surface. The systems and materials defined in Section 4.7.1 for sealing the near field could also be employed to seal shafts, tunnels and ramps in the far field. Before the seals were constructed, where possible, roadways would be broken out, walls and backs of tunnels would be scaled, and rock bolts, wire-mesh screens and shaft liners would be removed to minimize the effects of vault operations on seal function. Composite seals consisting of bulkheads supporting clay-based backfills and sealed with HCB gaskets and grout appear to offer the best possibility of minimizing flow in the excavations and the EDZ. It is not obvious that investigation boreholes would need to be sealed. The need would depend on the hydrogeological conditions at the vault site and the location of boreholes relative to the waste and hydraulically active features. Nonetheless, it is anticipated that all investigation boreholes would be sealed with highly compacted bentonite and high-performance cement plugs and grouts. The inclination of the boreholes and the hydrogeological conditions would dictate the design of the seal. Methods exist for placing both clay and cement-based seals in the different borehole configurations and conditions. Unlike shaft and tunnel sealing, borehole sealing is a remote process and requires the use of method specifications, which would need to be developed, tested and verified in future experimental work and at an actual disposal site.

4.8 SEAL QUALITY ASSURANCE

Vault sealing operations would be carried out under an appropriate quality assurance program and would be subject to the general requirements for planning, reviewing, controlling and documenting work that this program prescribed.

The quality of clay- and cement-based materials used for various vault sealing functions would be verified and controlled at each step of the processing stream, starting with the raw materials and extending to the final emplacement of the engineered seal in the vault. Performance limits specified for the end-product seals would be translated backward through the processing stream to determine acceptable limits of variability at each step. Where end-product specifications were not practicable, appropriate method specifications would be applied.

Materials would be procured from suppliers who had effective, auditable quality assurance programs. These materials would undergo acceptance testing prior to their entry into the processing stream at the disposal centre. Tested, untested, and nonconforming materials would be clearly labelled and stored separately.

Acceptance criteria for clay-based materials and sand, and the buffer and backfill mixtures, would be based on standard physical tests that characterize their mechanical and hydraulic behaviour. These tests would include determinations of Atterburg limits, particle-size distributions and water contents. Additional physical, mineralogical and chemical tests might be specified or developed to screen bentonite, lake clays and aggregates for impurities that might be detrimental to hydraulic performance of the buffer and backfill. Cation exchange determinations might be required to ensure that bentonite clays were received and maintained in their specified form.

Cement-based materials would be handled in a similar fashion to clay-based materials, but would, of course, be subject to different tests and control limits. Standard testing would include gradation and mineralogical analysis of aggregate, shrinkage and slump testing of concrete mixes, and compressive strength testing of concrete samples. Screening and testing methods might need to be developed for high-performance concretes or grouts that had been designed for low viscosity, low hydraulic conductivity, minimum microcracking, or other special characteristics.

As part of the overall quality assurance program for a vault, records would be kept to track, in space and time from their point of manufacture through each step of the processing stream, the disposition of individual batches of clay, aggregate and cement materials. The records would include procurement papers, process route sheets, test results, as-built drawings, shift reports, control charts, logs, and other evidence of compliance with design specifications and program requirements. The records would form an auditable trail that would facilitate the backward determination of causes of nonconformances and the forward projection of potential deficiencies in derived materials or processes, which would ensure the use of materials and processes that conformed to the vault design specifications.

An important aspect of record keeping would be the co-ordination of vault characterization data with materials and process records, since sealing materials would be designed to perform specific functions under varying rock and hydrologic conditions in the vault. In this situation, careful tracking would be required to ensure that materials were not used in inappropriate locations or under the wrong circumstances.

The emplacement of seals, backfills, plugs, cutoffs, grout curtains and other similar hydraulic barriers is considered a "special process" that cannot be verified by direct inspection or testing. Because of this, emphasis would be placed on verifying conformance to method specification during the emplacement process.

For the near field, a test and inspection plan would be developed that would cover each step of buffer emplacement, compaction and boring. These tests would include standard methods for determining in situ density and water content. In addition, special tests and equipment might be required to measure and confirm the proper positioning of waste containers in the buffer. If nonconformances were detected during the emplacement processes, work would be stopped and corrective actions would be taken to immediately bring the process into specified limits. This might require actions such as the removal and replacement of defective buffer materials. For the reference vault design, in some circumstances it might be necessary to abandon boreholes before waste containers were sealed in, and to relocate the waste containers in alternative boreholes.

Irrespective of the details of the vault design, it would likely be necessary to monitor components of the engineered barrier system after emplacement and throughout the operational lifetime of the vault to ensure that performance requirements or criteria were met. A monitoring approach for a used-fuel disposal facility has been discussed by Simmons et al. (in preparation). In developing a monitoring plan, the important criteria relating to disposal system performance would be determined and parameters relevant to these criteria would be identified. A monitoring plan would indicate which parameters would be monitored, the measurement method, and acceptable ranges for parameters being measured.

In a vault it might not be possible to monitor some of the engineered barrier system components without compromising the integrity of disposal-room or near-field seals. In these circumstances, it might be necessary to construct a component test area to obtain the data needed to give confidence in vault performance. For the reference vault it is suggested by Simmons and Baumgartner (1994) that a test area be located near the service shaft complex and that testing begin during the underground evaluation of the site and continue during the construction and operating lifetime of the vault.

Examples of activities in the component test area relevant to engineered barriers might include the following:

- demonstration of the suitability of quality control procedures for buffer, backfill and seal emplacement;

- emplacement of retrievable waste containers to monitor their performance over the operating life of the vault;

- emplacement and testing of borehole seals in specially drilled boreholes to determine their performance; and

- monitoring various buffer, backfill and rock interactions, such as the development of swelling pressures and changes in the groundwater pressures and temperatures under prolonged heating periods.

The purpose of these tests would be to confirm the performance of the engineered barriers over a period of several decades and to support the application for approval to decommission and close the disposal vault.

5. SUMMARY

A disposal system for nuclear fuel waste would consist of a natural barrier, the rock in which the disposal vault would be located; and engineered barriers, including a low-solubility waste form, a corrosion-resistant container, and sealing materials to retard water movement and potential radionuclide transport.

A variety of alternative designs and materials exist for all components of the engineered system. Based on studies performed in Canada, a reference vault design and system of engineered barriers was selected in order to undertake conceptual engineering studies and to demonstrate performance-assessment methodologies for a hypothetical disposal facility. It is stressed that the reference vault design does not represent the final selection of a disposal system; rather, it provides a common basis for focused engineering and materials studies and safety assessments.

The reference vault design is based on a single-level disposal vault at a depth of 1000 m in plutonic rock of the Canadian Shield, and is discussed in detail by Simmons and Baumgartner (1994). The major components of the reference vault include

- a waste form consisting of intact CANDU used-fuel bundles;
- a thin-walled (6.35 mm) ASTM Grade-2 titanium container with internal support for the shell provided by a packed particulate of glass beads;
- emplacement of containers in boreholes in the floors of disposal rooms, with a borehole spacing designed to give a maximum container surface temperature of 100°C;
- a compacted buffer material made up of 50 wt.% bentonite clay and 50 wt.% sand surrounding the containers in the boreholes;
- a compacted mixture of 75 wt.% crushed granite and 25 wt.% glacial lake clay used to backfill most of the other parts of the excavations; and
- a combination of buffer, backfill and cement-based materials to provide seals in the shafts and other strategic locations in the vault.

Alternative designs and materials exist for all components of the engineered barrier system.

The properties of used fuel are well understood, and used-fuel bundles can be safely stored, transported and emplaced in final disposal containers. The long-term dissolution mechanism of used fuel has been extensively studied, and well-established models have been incorporated into system performance assessment models.

Although high-level radioactive wastes in Canada are currently in the form of CANDU used-fuel bundles, it is possible that at some time in the future this material will be reprocessed to recycle fissile material for the production of new reactor fuel. The approaches that can be used to treat and solidify the wastes arising from reprocessing used fuel to render them resistant to leaching by groundwater are generally well developed and are currently in use in France, the United Kingdom and Japan. Canadian studies have focused on sodium borosilicate and aluminosilicate glasses and glass-ceramics for solidification of reprocessing wastes. These waste forms are feasible to produce and are resistant to leaching by groundwater. A variety of special products for solidification of low- and intermediate-level wastes have been developed. The total volumes of solidified waste arising from reprocessing are comparable to the volume of used fuel from which they would be derived.

A 500-a minimum containment target has been established for nuclear fuel waste containers, based on the observation that the vast majority of the activity in used fuel will decay over a period of several hundred years. A variety of options exist for container materials and designs. Several design options for a thin-walled titanium container have been built and structurally tested at full and half scale and have met the primary structural requirements for disposal at a depth of 1000 m. Similar design approaches have been prepared for copper containers with a 25-mm wall thickness. Welding and inspection techniques have been evaluated and demonstrated for both titanium and copper.

The corrosion performance of copper and titanium is well understood and it has been shown that the minimum containment target can easily be achieved with containers constructed from either of these materials. A model for the lifetime of titanium containers has been developed. Lifetimes greater than 1000 a are expected, based on conservative (pessimistic) assumptions regarding corrosion performance and the evolution of redox conditions in a disposal vault. A more realistic model that takes into account the limited propagation of crevice corrosion as vault conditions become anoxic suggests that container lifetimes of tens to hundreds of thousands of years are more probable. For copper containers with a wall thickness of 25 mm, a conservative model has been developed that considers both pitting and uniform corrosion. It is based on the assumption that aerated conditions exist indefinitely in the vault and suggests container lifetimes of 30 000 to $>10^6$ a. A more realistic assessment based on vault conditions eventually becoming anoxic indicates that the combined penetration due to pitting and uniform corrosion would be <10 mm for periods up to 10^6 a.

Sealing systems and materials have been developed that would permit excavations to be effectively sealed to ensure that diffusion rather than advection would be the dominant mode of groundwater movement in a disposal vault in plutonic rock.

Clay-based materials are favoured for sealing in the vicinity of containers and in disposal rooms. Bentonite-sand mixtures can be tailored to a variety of applications. For example, a reference buffer material consisting of 50 wt.% bentonite and 50 wt.% sand has been designed and extensively tested and would be used to surround waste containers in the reference vault. This material can be compacted in situ, would have a hydraulic conductivity of less than 10^{-11} $m \cdot s^{-1}$ and a swelling pressure of 1 to 2 MPa. One hundred percent bentonite can be precompacted into blocks that could be used to construct shaft and tunnel seals. Very high (>10 MPa) swelling pressures are developed with these materials, which could further enhance sealing at the excavation boundary.

Cement-based materials have been developed that can be used in the form of grouts to seal fractures and as concretes to produce tunnel and shaft seals and disposal room bulkheads.

The sealing materials and design approaches that have been developed could be adapted to suit a variety of disposal vault configurations, including both in-room and borehole emplacement of waste containers. Detailed designs and final materials selections would be established on the basis of site-specific investigations, selection of a waste-container design and emplacement method, and feedback from system performance assessments.

The performance of and flexibility provided by the various materials and design options presented here support the view that engineered barriers can be designed to suit the range of disposal conditions expected at a disposal site in plutonic rock of the Canadian Shield and that safety requirements can be met.

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LIST OF ACRONYMS

AISI	American Iron and Steel Institute
API	American Petroleum Institute
ASM	American Society for Metals
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
AVM	Atelier de Vitrification de Marcoule
BEC-I	Borehole Emplacement Container, Mark I
BWR	boiling water reactor
CANDU	CANada Deuterium Uranium, registered trademark of AECL Research
CEC	Commission of the European Communities
CEC	cation exchange capacity
CNFWMP	Canadian Nuclear Fuel Waste Management Program
CRL	Chalk River Laboratories (of AECL Research)
CSA	Canadian Standards Association
DDW	distilled deionized water
DHC	delayed hydride cracking
DIW	deionized water
DSC	dry storage container
EB	electron beam (welding)
EDZ	excavation-disturbed zone
EIS	Environmental Impact Statement
ETP	electrolytic tough-pitch (copper)
FIP	Fédération Internationale de la Précontrainte
FRW	fuel-reprocessing waste
FUETAP	formed under elevated temperature and pressure (concrete)

GMA	gas-metal-arc (welding)
GTA	gas-tungsten-arc (welding)
HCB	highly compacted bentonite
HIC	hydrogen-induced cracking
HLW	high-level waste
HTF	Hydrostatic Test Facility
HTR	high-temperature reactor
IAEA	International Atomic Energy Agency
IBSS	iron-based stressed-shell (container design)
IGC	intergranular corrosion
IGSCC	intergranular stress corrosion cracking
ILW	intermediate-level waste
KBS	Kärnbränslesäkerhet (Swedish Nuclear Fuel Safety Project)
LLW	low-level waste
LWR	light-water reactor
MIC	microbially induced corrosion
MOX	mixed oxide (fuel cycle)
MPC	Multi-Purpose Canister (U.S.)
NAGRA	National Cooperative for the Storage of Radioactive Waste (Switzerland)
NGS	nuclear generating station
NPD	Nuclear Power Demonstration reactor (Rolphton, ON)
OECD/NEA	Organization for Economic Cooperation and Development/Nuclear Energy Agency
OFHC	oxygen-free high conductivity (copper)
OFE	oxygen-free electronic (copper)
PFA	pulverized fuel ash

P-GTA	pulsed-current gas-tungsten-arc (welding)
PWR	pressurized-water reactor
QA	quality assurance
RBM	reference buffer material
R/D	resistance-heated diffusion (bonding)
RDE	rotating disc electrode
RU	recovered uranium
SCC	stress corrosion cracking
SCSSS	standard Canadian Shield saline solution
SEU	slightly enriched uranium
SLC	sustained load cracking
SRB	sulphate-reducing bacteria
TEC-I	Trench Emplacement Container, Mark I
TGSCC	transgranular stress corrosion cracking
UI	ultrasonic inspection
UNS	unified numbering system (ASTM)
URL	Underground Research Laboratory
USDOE	United States Department of Energy
WIPP	Waste Isolation Pilot Plant (New Mexico)
Zr-4	Zircaloy-4

LIST OF SYMBOLS

ρ_c	effective clay dry density; ratio of the dry mass of clay to the sum of the volumes of the dry clay and voids
ρ_d	dry density; mass of solids per total volume (solids plus voids)
i	hydraulic gradient
I_p	plasticity index
k	hydraulic conductivity
K_d	distribution coefficient; ratio of the amount of a species associated with the clay to the concentration of the species in solution at equilibrium
n	number of voids per total volume
W/CM	water-to-cementitious materials ratio

APPENDIX A

SOLIDIFIED FUEL-REPROCESSING WASTES

CONTENTS

continued...

CONTENTS (continued)

continued...

CONTENTS (concluded)

A.1 INTRODUCTION

As an alternative to direct disposal of used fuel, AECL has investigated the solidification (immobilization) of wastes generated by reprocessing used fuel to remove fissile material (e.g., ^{239}Pu or ^{235}U) that could be recycled in the fabrication of new power reactor fuel. The reprocessing option is no longer being studied in Canada. However, since fuel reprocessing and recycling fissile material is the policy of a number of countries, such as France, Germany and the U.K., AECL addressed the possibility that reprocessing CANDU[1] fuel could be a future issue in Canada and that it should demonstrate the methodology and technical feasibility for solidifying these wastes in a suitable waste form, as well as the methodology for characterizing and disposing of these waste forms.

In 1978, a program was initiated within the Canadian Nuclear Fuel Waste Management Program (CNFWMP) to investigate the solidification (vitrification) of highly radioactive (high-level) wastes that might arise from future used-fuel reprocessing. This program focused on borosilicate glass, but also studied aluminosilicate glasses and titanosilicate glass-ceramics as potential alternative waste forms for deep geological disposal. An analysis of the economics of reprocessing, conducted by AECL and Ontario Hydro in 1985, showed that at the then current price of uranium, and with the low concentration of Pu and ^{235}U left in used CANDU fuel compared with the enriched fuels used in other countries, it was not economically feasible to consider reprocessing CANDU fuel. In 1987 it was decided that sufficient work had been carried out at the laboratory and small scale to demonstrate both the feasibility of engineering processes for vitrified waste-form production and the suitability of borosilicate glasses and alternative waste forms for high-level waste vitrification. Further research and development would only be required if a decision were made in the future to reprocess CANDU fuels, and, at that time, advantage could be taken of any advances in product and process technology.

The objectives of the waste immobilization (solidification) program in the CNFWMP were (a) to develop waste forms and process technologies for the production of glasses and alternative waste forms for the immobilization of high-level liquid reprocessing wastes, and (b) to characterize the physical and chemical properties of these waste forms under the conditions appropriate for disposal in a geological environment typical of the plutonic rock of the Canadian Shield. For the purposes of defining a typical reprocessing waste stream, the well-proven Purex (Plutonium Uranium Reduction Extraction) process technology (Bebbington 1976) used in France, Japan and the U.K. was chosen as a reference process. For the purposes of demonstrating vitrification technology, the AVM (Atelier de Vitrification de Marcoule) process, currently used in commercial fuel-reprocessing plants in France, was chosen as an example of existing technology for high-level waste (HLW) solidification in glass. The process technology demonstrated by AECL was based on the AVM process as well as on processes developed in other countries.

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[1] Canada Deuterium Uranium, registered trademark of AECL.

The remainder of this section gives a brief description of the Purex process and the HLW vitrification processes currently practised internationally, and provides some historical perspective on their development.

A.1.1 TECHNOLOGY FOR REPROCESSING USED NUCLEAR FUEL

An International Atomic Energy Agency (IAEA) publication (IAEA 1987) summarizes international strategies and options for the reprocessing and recycling of used fuel; for the transportation, conditioning, handling and storage of used fuel or fuel-reprocessing wastes; and for waste disposal. The technology for reprocessing power-reactor fuel has been developed over the last 40 to 50 a in a number of countries with nuclear power reactors. Reprocessing facilities for power-reactor fuels have been in operation in the U.K. since 1952 at the Sellafield (formerly Windscale) facilities. France has been reprocessing fuels since about 1958 at facilities in Marcoule and later at La Hague. Both the French facilities, operated on a commercial basis by COGEMA, and the U.K. facility, operated by British Nuclear Fuels PLC, accept fuels for reprocessing from other European countries. COGEMA is also contracted to reprocess fuels from Japan. France began immobilizing fuel-reprocessing wastes in borosilicate glass in about 1978 at their Marcoule facility, where these solidified wastes are also stored. Countries with contracts to reprocess fuels in France will eventually take possession of the resulting solidified waste and will be responsible for its disposal. Japan has also been reprocessing some of its own power-reactor fuel since about 1977 at a facility in Tokai-Mura. The U.S. has a number of facilities for reprocessing defence-reactor fuels for the recovery of fissile materials for their defence weapons program, and have reprocessed light-water reactor (LWR) (power reactor) fuels at West Valley, NY from 1966 to 1972 (Lutze 1988). At the present time, the liquid reprocessing wastes in the U.S. are stored in tanks at their reprocessing facilities.

Depending on the nature of the fuel and the economics of reprocessing fuel and recycling fissionable material, there are a number of alternative aqueous, non-aqueous and dry process technologies that could be employed to reprocess used fuel (Selvaduray et al. 1979). However, these technologies are not all mature. Only the Purex process has been proven on a commercial scale for oxide fuels, and it is currently used at facilities in France and the U.K.

The Purex process involves dissolving used fuel (after a cooling period of 5 to 10 a) in a nitric acid solution, and then extracting ~99.5% of the uranium and plutonium through an organic solvent extraction process. The plutonium and uranium are then chemically separated and purified. The plutonium can be recycled in new Pu/U enriched fuels, and the uranium can be sent to an enrichment facility for the fabrication of new UO_2 fuel. The nitric acid solution, which contains virtually all the stable and radioactive fission products and actinides from the fuel, constitutes the HLW stream that requires solidification.

During reprocessing, a number of other waste streams are generated that could also require solidification. The volatile off-gases arising from used-fuel dissolution contain ^{3}H, ^{85}Kr, ^{129}I and ^{14}C. During the vitrification process, other radioactive and stable isotopes of elements, such as Cs, Ru, Mo, Se, Sb and Tc, are also partially volatilized and are trapped on the off-gas filters. These filters are collected and treated as part of the HLW stream. The technologies available for off-gas abatement and potential waste forms for the immobilization of the gaseous nuclides are discussed in Section A.11. The intermediate- and low-level liquid or solid waste streams from reprocessing, including the undissolved Zircaloy fuel sheath (fuel hulls) and fuel dissolver residues would also require solidification before disposal. In France, for example, the solid wastes and fuel hulls are placed in drums or tanks or are immobilized in cement and placed in storage at their reprocessing facilities. The volumes of wastes arising from reprocessing are discussed in Sections A.12 and A.13.

Technologies have already been implemented internationally for the immobilization of some low- and intermediate-level wastes from reactor operation or from reprocessing facilities. Immobilization usually involves mixing the wastes with cement or bitumen in metal drums. Some countries have operational facilities for low- and intermediate-level waste disposal (Clelland et al. 1989); the technologies and disposal strategies are discussed in a recent IAEA (International Atomic Energy Agency) publication (IAEA 1989). Sweden, for example, has an operational repository below the seabed for the disposal of low- and intermediate-level reactor waste (Hedman et al. 1989), and Germany is disposing of low- and intermediate-level wastes in the abandoned Asse salt mine (Hubenthal 1989). Low- and intermediate-level waste forms for reprocessing wastes are discussed briefly in Section A.11.

A.1.2 PROCESS TECHNOLOGY FOR THE VITRIFICATION OF REPROCESSING WASTE

A number of waste forms for immobilizing reprocessing wastes have been researched and developed by the nuclear industry over the last 30 to 40 a. Borosilicate glasses are considered internationally to be the preferred waste form for the vitrification of reprocessing wastes, and the process technology for making glasses has reached a high degree of technical maturity. For example, in 1978 the U.S. Department of Energy (USDOE) commissioned a review panel to recommend the "best" waste form that should be pursued for the immobilization of the U.S. defence fuel-reprocessing wastes. The review panel (Alternative Waste Form Peer Review Panel 1979, 1980, 1981; Hench et al. 1984) recommended that borosilicate glass should be the preferred waste form, and the DOE subsequently developed a set of preliminary waste-form acceptance specifications for glass production and disposal (USDOE 1983, Oversby 1984). France, Japan and the U.K. have also chosen borosilicate glasses for the vitrification of their reprocessing HLW. A comprehensive international overview of the development history and current status of research on products and processes for the solidification of nuclear fuel reprocessing wastes can be found in a review entitled "Radioactive Waste Forms for the Future" edited by Lutze and Ewing (1988).

The immobilization of reprocessing wastes involves incorporating the radioactive wastes generated from the acid dissolution of used fuel in a stable host matrix such as borosilicate glass. There are a number of reasons why borosilicate glasses have been internationally accepted as a waste form.

They can be fabricated easily using conventional, commercial glass-making technology, and the development of remote processes to permit their fabrication in radiation-shielded facilities has reached a high degree of technical maturity. Borosilicate glass properties are relatively insensitive to variations in reprocessing waste-stream compositions. It is also felt that, even if major changes in the composition of the glass are required to immobilize reprocessing wastes from different reactor fuels (e.g., LWR, CANDU, mixed-oxide fuels), it would have little effect on the process technology for vitrification (Lutze 1988). Finally, borosilicate glass waste forms can be produced to be highly resistant to aqueous dissolution, and they are, therefore, suitable candidates for permanent geological disposal.

The French AVM process is an example of a commercial reprocessing and vitrification operation that uses borosilicate glasses for waste solidification. In this process, the acidic, radioactive reprocessing waste stream is fed to a rotary calciner (rotating heated drum), where the liquid is evaporated to leave a solid residue of waste nitrate salts. This solid is then heated to temperatures of 700-900°C to convert the nitrate salts to solid oxides (calcine). The vitrification process involves combining this calcined oxide waste with crushed borosilicate glass and heating the mixture in an induction-heated refractory (metal) pot to temperatures above 1000°C. At these temperatures, the glass melts and the radioactive waste oxides dissolve in the melt. This melt is then poured into a stainless steel container (about 50 cm in diameter and 1 m high, which can contain about 360 kg of glass) and allowed to cool to room temperature under controlled conditions. The majority of the waste oxides are homogeneously distributed at the atomic level throughout the solidified glass; however, some fission products, such as Pd, Rh and Mo, may be present as metallic particles or precipitates (<1 μm in diameter). The fission-product oxide content of the glass is about 11-13% by weight. These containers are then sealed and stored in concrete shielded areas. Before being permanently disposed of in a waste vault, the containers would be sealed inside a corrosion-resistant outer container. A conceptual design for a CANDU reprocessing waste container based on the AVM process and the AVM container is discussed in Chapter 3 of the main text (Section 3.5.3.5).

Germany has considered an alternative vitrification technology. A pilot-plant demonstration facility (PAMELA (Pilotanlage Mol zur Erzeugung Lagerfähiger Abfälle) project) was commissioned for active operation in 1985 in Mol, Belgium, and reprocessing wastes from the Eurochemic facility were vitrified. The PAMELA facility is not currently in use. It used a vitrification process involving mixing existing acidic HLW with borosilicate glass frit to form a slurry, which was then fed to a joule-heated ceramic melter (JCM). In the JCM, a pool of glass is kept molten by the resistance heating of a current passed between electrodes immersed in the glass melt. Evaporation of the water and calcination of the nitrate wastes to oxides occurs directly at the molten glass surface, and the resulting waste oxides are dissolved into the glass. The molten glass is then poured, in a batch or continuous process, into metal containers.

There are a number of vitrification processes involving variations on both the way in which HLW is evaporated or calcined (fluidized bed calciner, spray calciner, rotary calciner) and the way glasses are melted (resistance furnace, induction furnace, microwave furnace). These technologies are currently being advanced internationally through the development of better furnace construction and heating methods, and through the development of more corrosion-resistant construction materials capable of operating at higher temperatures. Improvements in these areas would complement studies on the development of alternative waste forms that have the potential to improve on the chemical durability already offered by borosilicate glasses. Lutze (1988) has reviewed the current status of vitrification technologies.

A.1.3 INTERNATIONAL PERSPECTIVE ON REPROCESSING AND VITRIFICATION TECHNOLOGIES

Since the early 1950s, a number of countries have been involved in research to develop waste forms and processes for the immobilization of reprocessing wastes. In general, the research has focused on vitrification using silicate-based glasses, since it was recognized that these materials could incorporate a wide variety of waste elements into solid solution and could accommodate wide variations in the composition of the waste stream.

In the early 1950s, Canada was among several countries to begin research on glasses as a waste form for liquid radioactive wastes; the research focused on the production of silicate glasses. From about 1958 to 1962, a small-scale study demonstrated the vitrification process and produced a series of small (~2 kg) aluminosilicate glass blocks containing radioactive waste from fuel-reprocessing experiments. The waste-loaded glasses were melted in clay crucibles under remote conditions (radiation-shielded cells). Concurrent with laboratory testing of the durability of this glass, a "field burial" experiment was initiated to investigate their dissolution behaviour in a sandy soil aquifer on AECL property (Merritt 1976). The radionuclides released to the aquifer from these glasses have been monitored for over 30 a (Merritt 1976, Killey et al. 1990); the results are discussed briefly in Section A.5. The process and product development studies, conducted as part of the CNFWMP, are discussed in Sections A.2 and A.3. Although Canada does not reprocess CANDU reactor fuel, AECL has commercial radioisotope-production facilities at its Chalk River Laboratory (CRL) to generate specialized isotopes (such as ^{99}Mo) for medical, research and industrial uses, and hence has a small-scale isotope separations facility. Liquid wastes arising from isotope separation are stored in tanks at CRL.

France has a policy to reprocess its used fuels and has been doing so since about 1958. At about the same time, France began conducting research on glasses for the immobilization of reprocessing waste. A pilot-plant demonstration of a batch vitrification process to immobilize Purex wastes operated at Marcoule from 1969 to 1980. The commercial-scale AVM facility began active operation in 1978, and as of 1991 November, had produced 672 tonnes of radioactive glass from reprocessing LWR fuel (Moncouyoux and Sombret 1992). COGEMA's new "R7" and newer "T7" vitrification facilities at the UP3 reprocessing plant at La Hague have been operational since 1989 and 1992 respectively, and have produced ~1500 containers (~580 t) of HLW glass (Giraud and Kelly 1993). These vitrification facilities are based on scaled-up AVM technology.

Germany has no commercial reprocessing facilities; they do endorse the reprocessing of used fuel, but are also examining the direct disposal of used fuel where the reprocessing option is not economical (Bloser 1990). Germany stores its used fuel at reactor sites and at a central fuel storage facility at Gorleben. They currently have fuel-reprocessing contracts with COGEMA in France and British Nuclear Fuels PLC in the U.K. Research on waste forms and batch vitrification technology for uranium-bearing wastes began in the mid-1960s, and in 1977 construction commenced on the PAMELA process demonstration plant for the specific purpose of vitrifying wastes from the Belgian Eurochemic reprocessing facility that has since ceased operation. This demonstration facility commenced operation in 1985, and by 1991 February, 455 tonnes of radioactive borosilicate glass had been produced (LeRoy et al. 1992).

Japan has a policy to reprocess their used nuclear fuel. Since 1977, the Power Reactor and Nuclear Fuel Development Corporation (PNC) plant at Tokai-Mura has been reprocessing a portion of their fuels and storing the wastes, but the bulk of their fuel is reprocessed in France and the U.K. Their research on waste forms has centred on high-silica borosilicate glasses produced by either JCM or induction-heating technology (Torata et al. 1981). Full-scale, non-radioactive tests were completed on a liquid-fed JCM, and, on the basis of this experience, the technology will be incorporated into a new Tokai vitrification facility expected to be commissioned in 1994 (Yoshioka et al. 1991, PNC Review 1992). A new reprocessing, vitrification and waste management facility is under construction at Rokkasho-Mura to handle the reprocessing and vitrification of domestic fuels and the storage of vitrified wastes from fuels reprocessed under contracts with France and the U.K. (Nagano et al. 1993).

The U.K. has been reprocessing its used MAGNOX reactor fuels since 1952 and has stored these liquid wastes at Sellafield. Advanced gas-cooled reactor (AGR) fuels are currently stored and will be reprocessed in the new THORP (Thermal Oxide Reprocessing Plant) facility expected to be commissioned for active operation in early 1994 (Nuclear Issues 1993, Wilkinson et al. 1987). Research on waste forms began in the mid-1950s, and has focused on borosilicate glasses (Grover and Chidley 1960). A pilot-plant demonstration of a vitrification process produced glasses containing Sellafield reprocessing wastes, and a scaled-up process underwent inactive testing in the 1970s (Morris and Chidley 1976). In 1981, British Nuclear Fuels decided to adopt the French borosilicate AVM process for use in its new vitrification plant at Sellafield, which began active operation in 1990 (LeRoy et al. 1992).

In the U.S., two types of high-level reprocessing wastes are scheduled to be vitrified in borosilicate glass: defence high-level wastes arising from reprocessing defence-reactor fuels for the recovery of fissile materials for the U.S. weapons program; and high-level wastes arising from reprocessing commercial power-reactor fuels at West Valley, NY (no commercial-fuel reprocessing facilities are currently operating in the U.S.). A full-scale vitrification facility for immobilizing high-level defence waste in borosilicate glass is being constructed at the Savannah River Laboratories Defence Waste Processing Facility. The HLW will be vitrified using a JCM, and the molten glass will be poured into steel containers. These containers will be stored at the facility until a federal geological repository is selected (Hutson et al. 1992). A demonstration project was established at West Valley, NY, in 1980 to develop technology to vitrify the stored reprocessing wastes. This remedial action program will vitrify these wastes in borosilicate glass produced using JCM technology. The U.S. had a large program to develop a number of different waste forms for HLW immobilization, but their program is now focused on silicate glasses. An overview of the research and development of waste forms at various laboratories in the U.S. can be found in Lutze (1988).

Waste-form research and process development work on silicate glasses has also been conducted in Italy, India and the Soviet Union. A brief summary of these studies can be found in Lutze (1988).

Summary

The technology for reprocessing used power-reactor fuels is well established; industrial-scale facilities using the Purex process are operating in France, the U.K. and Japan. Facilities for reprocessing defence-reactor fuels are operating in the U.S. The industrial-scale technology for vitrification (solidification) of the radioactive fuel-reprocessing liquid wastes in glasses has reached a high degree of technical maturity in the international community. Vitrification facilities have been in operation in France since about 1978 at their Marcoule and La Hague reprocessing facilities, and more recently at Sellafield in the U.K. Other countries, such as Germany, the U.S. and Japan, have demonstration- or pilot-plant-scale vitrification facilities. Borosilicate glasses are internationally recognized as a waste form for the solidification of fuel-reprocessing wastes.

A.2 DEVELOPMENT OF WASTE IMMOBILIZATION PROCESSES FOR CANDU FUEL

In defining the scope of the waste immobilization program in the CNFWMP, criteria were established that specified the composition of the reprocessing waste stream, the container design and the design of the disposal vault. A reference CANDU fuel burnup of 685 $GJ \cdot kg^{-1}$ initial U was adopted for the conceptual vault design on the basis of predicted equilibrium burnups for CANDU reactors (Mylvaganam 1992) (Section 2.2.3 of the main text); a fuel cooling time of 10 a before reprocessing was chosen. The Purex process was selected as a representative and proven reprocessing technology, and it was assumed that 99.5% of the total inventory of U and Pu would be removed from the dissolved fuel; 0.5% (U + Pu) would remain with the high-level waste stream. (This is a conservative estimate, as the actual separation efficiency is >99.9% (Encyclopedia of Chemical Technology 1982)). The inventories and the decay heats of radionuclides in the reference fuel (685 $GJ \cdot kg^{-1}$ U burnup, 10-a cooled, 99.5% (U + Pu) removal) were calculated by Smith et al. (1987). A typical high-level waste stream composition is given in Table 2-3 of the main text. The composition of the waste is presented in wt.% of the element oxide, since the radioactive elements would mostly be in this state in the vitrified waste form (exceptions are noted in the table). The conceptual container design for vitrified wastes is described in Section 3.5.4.5 of the main text. It was also established that the temperature of the surface of a disposal container should be no greater than 100°C after emplacement and closure of the vault (Simmons and Baumgartner 1994). Using the above criteria, and the radionuclide decay heats, it was established from heat transfer calculations for the reference vault design that the fission-product oxide loading (concentration) in a waste form should not exceed 6 wt.% if the container surface was to remain below 100°C (Baumgartner et al. 1994). (Note that increasing the spacing between containers in the disposal vault would permit the waste form to have a higher waste loading.)

It was decided that, rather than trying to improve existing process technology to produce high-temperature waste forms, vitrification technology should first be demonstrated using current nuclear waste immobilization technology. In order to ensure that the waste form could be poured easily from a melter into a container, the melt should have a viscosity of about 100 poise[2] at the operating temperature of the melter. Commercial vitrification facilities normally operate at temperatures ranging from 1000 to 1150°C. Conventional glass-melting technology is available to melt glasses at temperatures of 1500°C or higher; however, operation of a melter at these high temperatures could cause excessive melter corrosion as well as off-gas problems resulting from radionuclide volatilization. The process technology work has therefore focused on waste forms that could be produced at temperatures in the range from 1000 to ~1300°C, where volatility and corrosion problems are likely to be of less concern.

A.2.1 PROCESS DEVELOPMENT STUDIES

Research on processes for high-level waste solidification concentrated on establishing and demonstrating the necessary engineering technology for the pretreatment and vitrification of liquid reprocessing wastes. A Waste Immobilization Process Engineering (WIPE) facility was designed and constructed to evaluate the performance of an integrated process. This involved the design, construction and operation of (a) a fluidized-bed calciner (Sridhar 1981) and a roto-spray calciner (Figure 2-13 in the main text) (Sridhar 1988) to convert the nitric acid reprocessing-waste solutions to a dry, calcined oxide/nitrate solid mixture; (b) a small-scale joule-heated ceramic melter (Figure 2-14 in the main text) capable of producing 10 kg of glass an hour at 1150°C, to incorporate the calcined waste into a borosilicate glass (Sridhar 1989) that could be poured into steel containers (875 mm high by 252 mm in diameter); and (c) off-gas technology to recover Kr and volatiles from the process stream (Ruthven et al. 1981, 1984; Sridhar 1989). Experiments were conducted on simulated (non-radioactive) waste solutions to fabricate borosilicate waste forms containing up to 15 wt.% equivalent fission-product oxide loading (Sridhar 1985). The experiments successfully demonstrated the continuous production of a simulated calcined waste, its subsequent incorporation into a borosilicate glass, casting into metal containers, and the abatement of NO_x off-gases from the melter and calciner.

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[2] 1 poise = 0.1 Pa·s

A laboratory-scale JCM was also designed and constructed to demonstrate the production of titanosilicate glass-ceramics, at temperatures up to 1350°C, containing up to 15 wt.% simulated waste (Section A.6) (Hayward 1988). A series of 5- and 8-L carbon-steel containers were filled with the glass-ceramic melt and cooled under controlled conditions to produce the glass-ceramic. These experiments indicated that a glass-ceramic waste form could be fabricated with physical properties comparable to those produced by melting in small crucibles in laboratory furnaces. Although the JCM process required higher operating temperatures than those used for the borosilicate glasses, results indicated that the release of volatiles (e.g., Mo, Cs) from the melt was comparable to releases from the lower-temperature borosilicate glass process (Hayward 1988).

In the late 1950s AECL initiated research on the development of processes for waste glass production and the abatement of volatile radionuclides (^{137}Cs, ^{106}Ru) (Watson et al. 1958a, 1958b; Erlebach 1960). The technology to produce aluminosilicate glasses using batch crucible melting techniques was studied. The aluminosilicate glass-making chemicals were mixed together with nitric acid reprocessing wastes to form a slurry. This slurry was then poured into small clay crucibles and heated at temperatures up to 1350°C. A series of fifty 2-kg glass blocks was produced by this technique; the blocks were subsequently used in the Chalk River in situ burial test (Section A.5).

Summary

Small-scale engineered facilities were constructed at AECL to demonstrate an integrated process for the immobilization of reprocessing wastes. Liquid-waste calcination technology and volatile off-gas recovery technology were demonstrated. Borosilicate glasses, containing up to 15 wt.% simulated (non-radioactive) reprocessing wastes, were produced at 1150°C using a joule-heated ceramic melter capable of continuous production at a rate of 10 kg of glass per hour. Small-scale facilities were used to successfully demonstrate the production of titanosilicate glass-ceramics at 1350°C (Hayward et al. 1988). The production of aluminosilicate glasses, containing radioactive reprocessing wastes, was demonstrated using a batch crucible melting technology.

If any of these processing technologies were to be applied to the immobilization of wastes from the reprocessing of used CANDU fuel in the future, the process would have to be matched to a selected waste form. If borosilicate glasses were selected, the technologies for their production are well established. If glasses with higher melting temperatures were selected, some redesign of the existing technology and the development of more corrosion-resistant melter construction materials would likely be required. In addition, considerable process optimization would be required, and the technology would need to be tested on a larger scale before a full-scale commercial facility could be constructed. Since the basic technologies for glass production are well established internationally, the experiences from facilities operating in other countries would be taken into consideration in any future plant design.

A.3 DEVELOPMENT OF WASTE FORMS FOR CANDU FUEL REPROCESSING WASTES

The only realistic process that could lead to the release of radionuclides from the waste form to the waste vault, and subsequently to the geosphere and biosphere, is dissolution of the waste form by groundwaters. In choosing waste-form materials for investigation, one of the most important considerations, therefore, is the potential durability (resistance to dissolution) of the material when contacted by aqueous solutions (groundwaters) in a disposal vault environment.

Although research in the CNFWMP has focused on the development of waste forms for the vitrification of the high-level liquid wastes, some attention was also given to developing materials or methods for the immobilization of specific radionuclides, such as ^{129}I, that are released during the fuel reprocessing and vitrification processes. A summary of these technologies is presented in Section A.11.

Three materials were chosen for development as high-level waste forms:

- borosilicate glasses based on compositions in the Na_2O-B_2O_3-SiO_2-X system (where X = reprocessing wastes, process additives and/or minor glass components);
- aluminosilicate glasses based on compositions in the Na_2O-CaO-Al_2O_3-SiO_2-X system; and
- titanosilicate glass-ceramics based on compositions in the Na_2O-Al_2O_3-CaO-TiO_2-SiO_2-X system.

Borosilicate glasses were chosen on the basis of their international acceptance as a waste form. The aluminosilicate glasses were chosen on the basis of early waste vitrification experience at AECL. The titanosilicate glass-ceramics are an AECL product, developed because they have the potential to offer higher durability towards aqueous dissolution than borosilicate glasses in the proposed granitic geological disposal environment, although they may be more technically complex to produce.

A fundamental reason for choosing to examine glass-ceramics in particular is that these materials contain crystalline phases that are potentially more durable towards aqueous dissolution than a glass phase of the equivalent composition. (For example, the equilibrium solubility of crystalline quartz (SiO_2) is less than its amorphous (glassy) form). A crystalline phase could establish a thermodynamic equilibrium with its dissolution products in solution, which would strongly inhibit further dissolution. A glass, on the other hand, is thermodynamically unstable with respect to crystalline phases of equivalent composition. The dissolution products of a glass in solution cannot establish an equilibrium with the solid glass phase, and can only establish an equilibrium with crystalline alteration products that precipitate from solution. Thus, the dissolution of a glass is kinetically controlled by the rate at which material can be dissolved into solution and the rate at which the dissolution products form either amorphous or crystalline alteration products.

The primary objectives of the waste-form development work were to identify compositions for the three selected materials that would be the most appropriate for use as a high-level waste form, and to establish the characterization methodology that could be applied if a product and process for waste immobilization were to be selected and optimized. The characterization work focused on the evaluation of waste-form durability under disposal conditions, the determination of waste-form dissolution mechanisms, the evaluation of the physical properties of importance to waste-form fabrication and disposal, and the determination of phase constitution of ceramic products. It was also decided that the waste-form composition should not be limited by the temperature constraints of conventional waste-glass melters, and that compositions with higher melting temperatures (that could potentially be chemically more durable than glasses melted at lower temperatures) should be investigated.

Various groundwaters, ranging from deionized water and low-ionic-strength surface groundwaters to the high ionic-strength groundwaters typical of those found at the 500- to 1000-m depth in granitic rock of the Canadian Shield (Gascoyne 1986), were used to investigate their effect on waste-form durability. Other factors that could potentially affect the dissolution behaviour of the waste form were also studied: e.g., the effects of various components of the disposal system (metal container, clay buffer, granite rock), and the effects of radiation-induced structural damage to the waste form and radiation-induced changes to the groundwater chemistry (radiolysis).

In addition to studies of the effects of waste-form composition on dissolution behaviour, some of the physical properties of particular importance to fabrication (e.g., melt viscosity, electrical conductivity) and disposal (e.g., thermal conductivity, thermal expansion, density, fracture toughness) were also investigated. Optimization studies to find the "best" glass or glass-ceramic composition were not, however, carried out in this research phase, since it was judged that this type of study should be undertaken only when fuel recycling was seen to be a viable option and when the most appropriate technologies for reprocessing CANDU fuel and solidifying the reprocessing wastes were chosen.

The following sections summarize the research results on each of the three waste-form materials.

A.4 BOROSILICATE GLASSES

There have been many international investigations over the last 30 a that have focused both on determining the relationship between borosilicate glass composition and dissolution in a variety of aqueous media, and on the characterization of physical properties of these glasses. As a result, there is a considerable database available on physical properties (e.g., viscosity, volatility, mechanical, electrical and thermal properties) for a wide variety of glass compositions. For most glasses in the borosilicate system that might be suitable for waste immobilization, the mechanical, electrical and thermal properties do not vary significantly with composition. A detailed review of these properties can be found in Lutze (1988).

There are a number of factors that influence the dissolution behaviour of borosilicate glasses. The international literature on borosilicate glass dissolution is extensive, and several reviews have been published, including those by Tymochowicz (1977), the IAEA (1979), Harvey (1984) and Lutze and Ewing (1988). A series of reports on joint studies of the Commission of the European Communities (Roggendorf et al. 1992) and reports from joint JSS (Japan, Switzerland, Sweden) studies on the dissolution of waste forms (JSS 1987, 1988) have also been published. The main body of the literature on waste-form dissolution and properties can be found in a series of publications entitled "Scientific Basis for Nuclear Waste Management" published by the Materials Research Society and in international conferences on nuclear waste management published by the American Ceramic Society.

Before discussing the results from durability studies on borosilicate glasses, there are a number of general observations regarding the most important factors that affect glass durability that can be drawn from the above-mentioned sources. These observations are summarized in the following section.

A.4.1 FACTORS INFLUENCING THE CHEMICAL DURABILITY OF SILICATE GLASSES

One of the most important parameters that will determine the acceptability of a waste form is durability towards aqueous dissolution. Recently, international investigations have been assessing the long-term dissolution behaviour of glasses; this involves determining the temperature dependence of glass dissolution and radionuclide release mechanisms, determining the composition of alteration products, and determining the effects of waste vault components on release. These studies have been conducted both on non-radioactive glasses using "simulated" reprocessing wastes and on "active" glasses containing radioactive reprocessing wastes. The factors that appear to most strongly affect aqueous dissolution are the glass composition, the solution pH, the groundwater composition, the solution temperature and flow rate, the sample surface area:solution volume ratio, the rate of formation of alteration layers on the glass, and radiation effects in the solid waste form and in solution.

A.4.1.1 Glass Composition

The formulation of a highly durable glass is a complex function of all the glass constituents and waste products, and no single glass can be identified as having the "highest" durability. In general, however, glasses that are high in silica (SiO_2) content (45 to 70 wt.%) usually demonstrate high aqueous durability. Glass durability is generally decreased by the addition of the alkali metal oxides (Na_2O, K_2O) and to some extent B_2O_3, whereas additions of Al_2O_3 or Fe_2O_3 generally increase durability (Lutze 1988). The addition of waste to a glass can also potentially affect durability. Comparisons of the leaching behaviour of a number of simulated nuclear waste glasses with their fully radioactive counterparts (JSS 1988) showed that there were no significant differences between the behaviour of the radioactive glasses compared with the non-radioactive glasses under similar experimental conditions.

A.4.1.2 Solution pH

The pH and groundwater composition can be strongly altered by glass dissolution under low-flow conditions. Generally the solution becomes more alkaline (higher pH) as alkali ions (e.g., Na, K) are released from the glass. The solubility of silica increases rapidly in solutions with pH > 9.5, but is relatively constant over the pH range from 3 to 9. The formation of alteration phases, particularly in groundwaters containing Mg^{2+}, appears to moderate (or buffer) changes in pH to the range from 6 to 8, where silica solubility is low. This pH buffering is generally attributed to the formation of clay minerals, such as sepiolite (Strachan 1982), or aluminosilicate or $BaSO_4$ alteration phases (Malow 1982). Many borosilicate glasses have been found to exhibit a relatively weak dependence on dissolution rate in waters with pH ranging from 4 to as high as 10, even after leaching times of 3 a or longer (Lutze 1988).

A.4.1.3 Solution Composition

High silicate ion concentrations in solution, present either naturally in the groundwater or as silicate dissolved from the bentonite clay or the glass, generally decrease the observed glass dissolution rate. However, dissolution of the glass does not appear to be totally inhibited, even in solutions saturated with SiO_2. High concentrations of silicate or aluminate ions and ions such as Fe^{3+}, Mg^{2+} or Ca^{2+} may, as noted below, promote the formation of alteration phases on the glass surface and may inhibit glass dissolution. Dissolution rates are generally higher in deionized water; however, as glass constituent ions dissolve in solution (particularly silica) the glass dissolution rate decreases markedly with time, and becomes limited by both the rate at which ions can diffuse through a hydrated surface layer on the glass and into solution, and by the dissolution rate of silica from the surface.

A.4.1.4 Solution Flow Rate

The dissolution rate of a glass is dependent on the flow rate of the solution, being greatest under high-flow conditions, when silica or other glass constituents cannot accumulate in solution and the formation of alteration layers is not promoted. At sufficiently high flow rates, the rate of glass dissolution becomes independent of flow rate and is limited by the rate at which the glass surface can dissolve into solution. At sufficiently low flow rates, the dissolution rate will also become independent of flow rate, and will behave as if the solution were static. In low-flow or static systems, the dissolution rate of the glass is initially high, but decreases to a lower rate as the solution becomes "saturated" with glass dissolution products (e.g., silica, alumina), which may promote the formation of alteration phases on the glass surface, which, in turn, may further decrease the dissolution rate. Mechanisms of release under low-flow conditions are the focus of many of the continuing investigations on borosilicate glasses, since they represent the most likely disposal conditions.

A.4.1.5 Temperature

The main effect of an increase in solution temperature is to increase both the glass dissolution rate and the solubility of glass components in solution. This effect is best understood in the temperature regime from 50 to 150°C, where the formation of alteration phases is easier to predict and understand. At temperatures below about 50°C, dissolution rates can be so low that experiments would have to be carried out for many years to get sufficient material in solution to establish dissolution rates with any certainty. The evolution of alteration products at low temperatures cannot necessarily be extrapolated from high-temperature (>150°C) results, because the rates of formation and stability of the new phases is highly temperature-dependent.

A.4.1.6 Alteration Layers

The formation of alteration layers on the surface of a borosilicate waste glass is a relatively common phenomenon, particularly at temperatures above about 60°C in solutions that are static or slowly flowing. Typically, after a glass has been in contact with water for some period of time (weeks to months), a hydrated layer is formed at the surface that is Si-rich, depleted in the highly soluble glass constituents (e.g., Na, Ca, B), and enriched in less soluble constituents (e.g., Zn, Fe, Al) (Mendel 1984). One example is the Savannah River Laboratory (SRL) TDS-161 glass (Wallace and Wicks 1983), which appears to form an altered surface layer that acts as a diffusion barrier for either water transport to the surface of the glass or the transport of reaction products away from the glass surface. These alteration layers may be only a few micrometres thick or may be several hundreds of micrometres thick. There may be other layers of crystalline or clay-like alteration products that precipitate from solution onto this layer. The hydrated layer and alteration layers are generally non-adherent (easily removed by mechanical disturbance). Once formed, however, these layers could potentially inhibit the transport of water to the underlying bulk glass, or they could provide a barrier to release of glass constituents to solution by diffusion (Lutze 1988). As previously mentioned, a glass is an amorphous, thermodynamically unstable solid that cannot establish a true thermodynamic equilibrium with its dissolution products in solution. Thus, unless the hydrated layer or alteration layer provides some diffusional barrier to release, soluble components of the glass may continue to be released to solution even though the solution becomes saturated with respect to silica or some other alteration mineral phase.

A.4.1.7 Redox Potential

The solution redox potential can affect the solubility and oxidation state of radionuclide ions released from the glass to solution. However, it should have no effect on the solubility of the major glass matrix ions (e.g., Si^{4+}, B^{3+}, Na^{+}, Ca^{2+}, Al^{3+}), since they cannot be oxidized or reduced in the pH-Eh regime expected in a disposal vault. Thus, it is very unlikely that glass dissolution would be affected by the redox potential of the solution (although Li and B have been found to be released slightly more slowly from a borosilicate glass under anoxic than oxic conditions (Jantzen and Bibler 1986)).

A.4.1.8 Radiation Effects on Glasses

The potential effects of radiation on glasses would be related mainly to the chemical durability of the waste form. Solid-state radiation damage effects in the glass are caused predominantly by α-particles or α-recoil nuclei displacing atomic nuclei in the glass. This could produce defects in the glass that could make it more susceptible to aqueous dissolution. Alpha-, β- and γ-radiation could also interact with the solution in contact with the waste form (radiolysis effects), after the disposal container was breached, to produce chemically reactive species that could enhance waste-form dissolution. Neutron dose rates are very low in comparison with β- and γ-dose rates, and their effect on structural damage can be considered to be insignificant. Radiation-induced solid-state damage effects and radiolysis effects on glass and glass-ceramic waste forms have been reviewed by Tait (1993).

Solid-State Damage in Borosilicate Glasses

The relative atomic displacement damage caused by α-, β-, and γ-decay events along with spontaneous fission and neutron events are shown in Table A-1 for a waste form loaded with 6 wt.% fission-product oxides (Tait 1993). It can be seen that α-decay accounts for the largest fraction of displacement damage in the glass over the first 1000 a, followed by β-damage and spontaneous fission fragment damage. About 90% of the atomic displacements are caused by α-recoil nuclei and the remaining 10% by α-particles. A secondary consequence of α-decay is the formation of helium gas that can build up in the waste form and introduce stresses in the glass structure. This could result in a loss of chemical durability. The table also illustrates that β-events result in far fewer displacements per event than α-events, since most of this energy results primarily in ionization of atoms (creation of charged species) within the waste form, which contributes little to structural damage. Gamma radiation results almost totally in ionization events. A number of international studies have investigated radiation damage effects in borosilicate glasses doped with high levels of short-lived α-emitting nuclides to simulate the structural damage that would accumulate in a waste form over about 10^6 a compressed into a laboratory time scale of several years. These studies have been summarized by Lutze (1988) and Tait (1993). The results of the studies show that although significant structural changes may occur as a result of self-irradiation, aqueous dissolution rates of the glasses increased only slightly, and by no more than a factor of three. Other studies, using high-energy ion bombardment of glass surfaces to simulate the structural damage induced by α-decay, have shown that the aqueous dissolution rates in these samples increased by a factor of up to 50. However, the validity of these tests has been questioned, since ion bombardment affects only the surface layer (~20 nm), and differential stresses between the surface and underlying bulk glass could have contributed to the observed increase in dissolution rate (Lutze 1988).

TABLE A-1

ATOMIC DISPLACEMENTS RESULTING FROM DIFFERENT RADIATIONS FOR A WASTE GLASS CONTAINING ~6 wt.% FISSION-PRODUCT OXIDE CONTENT (Tait 1993)*

Radiation	Energy (MeV)	Range	Number of Displaced Atoms/Event	No. of Atoms Displaced** (cm^{-3})	Energy Transfer Mechanism
α-particle	~5	~20 μm	~180	3×10^{20}	mostly ionization
α-recoil	~0.1	~30 nm	~1200	2×10^{21}	displacement/ ionization
β-particle	~1	~1 mm	~1	5×10^{19}	ionization
γ-photon	~2	cm-dm	<0.01	-	ionization
Spontaneous Fission Nuclei	65-95	~10 μm	10^3-10^5	10^{16}-10^{18}	ionization
Neutron	~1	~100 cm	1000	~10^{16}	ionization

* Table adapted from Burns et al. (1982) and Vance et al. (1981a).

** Conservatively calculated assuming that all energy is used for displacing atoms; total atoms displaced over first 100 a following solidification.

Experiments on borosilicate glasses, irradiated with high-energy electrons to simulate β-radiation damage (Burns et al. 1982) and subsequently placed in an aqueous solution, showed no appreciable loss of chemical durability. Gray (1982) demonstrated that nuclear transmutation (e.g., β-decay of ^{137}Cs to ^{137}Ba) results in only minor changes in microstructure, chemical durability and density. Gamma irradiation of glasses can affect physical properties, such as density, refractive index, thermal expansion and helium permeability. However, there is no convincing evidence that glasses subjected to high levels of γ-irradiation prior to dissolution tests suffer any subsequent loss of chemical durability (Kelley 1975). There has also been no evidence that He gas buildup in the glass leads to any significant loss in glass durability (Tait 1993). Radiation-induced structural damage would have a limited effect on the mechanical properties of the waste form and on waste-form durability (Lutze 1988).

Solution Radiolysis Effects on Glass Durability

Alpha-, β- and γ-radiation can potentially alter the chemistry of aqueous solutions in contact with the waste form or in the region of the container/buffer/host rock. The range over which these radiations are effective is shown in Table A-1; γ-radiation is the most penetrating and would extend beyond the container; α- and β-radiation would be confined within the waste form and would be of consequence to solution radiolysis only after containment was breached. The container would be designed to remain intact for a minimum of 500 a (Section 3.3.1 of the main text). The majority of the fission products (which are responsible for most of the β-and γ-radiation field from the waste form) would decay to stable, non-radioactive elements in the first 200 to 500 a. Thus, during the first 500 a, only γ-radiation effects on the water in the buffer would be of potential consequence.

The effects of radiation on the chemical durability of glass waste forms have been reviewed by a number of authors (Burns et al. 1982, Weber and Roberts 1983, Mendel 1984, IAEA 1985, Lutze 1988, Tait 1993). There have been few studies that have dealt specifically with the effects of α-radiolysis on glass durability. There is some evidence that α-radiolysis of air-saturated solutions can drive the solution pH acidic as a result of the radiolytic production of HNO_3 from N_2, which could lead to enhanced actinide solubility or enhanced glass dissolution rates. This pH decrease, however, only occurs at α-dose rates that are much higher than those anticipated from a typical waste form. Also, it is likely that groundwaters in a granitic rock environment would be oxygen-depleted and would not support oxidation of N_2 in the groundwater to NO_2.

Most research has addressed the effects of γ-radiolysis of solutions (Tait, 1993). Gamma-radiolysis at dose rates of 10^5 $Gy{\cdot}h^{-1}$ (10^7 $rad{\cdot}h^{-1}$) has been found to drive the pH of aerated solutions acidic, as a result of the production of HNO_3 from N_2; this resulted in enhanced glass dissolution. At lower dose rates (100 $Gy{\cdot}h^{-1}$), even in aerated solutions, no decrease in pH was observed. The presence of bicarbonate in solution ($\sim 10^{-3}$ $mol{\cdot}L^{-1}$) in the high-dose-rate experiments mitigated the drop in pH by buffering the solution pH near neutral. When air was excluded from the experiments, there was no observable decrease in pH, and only minor increases in dissolution rates (less than a factor of five) were observed. The formation of carboxylic acids (from CO_2), which could act as complexing agents, or reaction of the glass with hydroxyl (•OH) radicals in solution have been suggested as possible explanations for this somewhat enhanced dissolution rate.

These studies have demonstrated that, at solution γ-dose rates up to 10^4 $Gy{\cdot}h^{-1}$, which is approximately the same dose rate anticipated for a waste form containing 6 wt.% fission-product oxides when placed in a disposal environment (Tait 1993), dissolution rates of glasses do not increase more than a factor of five. Also, the dissolution rates of glasses containing radioactive reprocessing waste have been found to be similar to glasses containing simulated (non-radioactive) wastes, suggesting that radiation effects on dissolution are small. Since the γ-and β-dose rates would decrease by several orders of magnitude to <0.1 $Gy{\cdot}h^{-1}$ during the first 500 a, the minimum design lifetime for the container, the impact of solution radiolysis on waste glass dissolution would be minimal. Also, γ-irradiation of glasses at high dose rates, followed by aqueous dissolution tests, produced no change in the chemical durability of the glass. However, since radiolysis effects are dependent on solution (groundwater) composition, any assessment of the importance of this effect on waste-form behaviour should be considered for a specific optimized waste-form composition and the specific disposal-vault groundwater conditions.

A.4.2 DURABILITY STUDIES IN THE CNFWMP ON BOROSILICATE GLASS

Canadian studies on borosilicate glasses have focused both on understanding how variations in glass composition affect glass durability and on understanding the dissolution mechanism of relatively simple borosilicate glasses containing few additives. Borosilicate glasses in the compositional range from 5 to 30 mol% Na_2O, 5 to 30 mol% B_2O_3 and 40 to 80 mol% SiO_2 have been investigated.

In general, as the Si content of these borosilicate glasses increased, the durability increased. A marked increase in durability was observed when the silica content was increased above 70 mol%. Also, durability increased as the Na/B molar ratio approached a value of one (Harvey and Jensen 1982). Figure 2-15 in the main text shows the cumulative dissolution rate for glasses with the composition $Na_2O \cdot B_2O_3 \cdot xSiO_2$, where x = 2 to 12 mol, corroded for 30 d at 100°C in deionized water (DIW). The figure shows that the dissolution rate for $x > \sim 5$ is about 10^{-9} $kg \cdot m^{-2} \cdot s^{-1}$ and is relatively independent of silica content. Conclusions from this study were that the apparent dissolution rate of the glasses decreased with time (likely because of the formation of a gel layer that inhibits release by a diffusion control mechanism), and that dissolution of some high Na glasses could increase the solution pH above 9.5, thereby increasing the glass dissolution rate. The observed rise in solution pH is a result of the displacement of Na^+ ions in the glass by H^+ ions from solution; this results in an increase in OH^- ions in solution, and thus an increase in pH. For glasses with $x > 5$, the solution pH did not increase above about 9 because of the low Na content of the glass and because of the higher glass durability arising from the high SiO_2 content.

Harvey (1983) also demonstrated that these borosilicate glasses dissolved, at least in the initial stages, by a first-order dissolution mechanism (i.e., the concentration of dissolved species increased linearly with time), and that, upon saturation of the solution with "glass dissolution products," the glass continued to dissolve at a constant rate. Conclusions from later studies (Harvey et al. 1986, Harvey and Boase 1987, Harvey and Larocque 1989) corroborated these results. These dissolution studies also formed a database for the development of models to describe the dissolution behaviour of simple borosilicate glasses (see Section A.9.2) and a framework from which models could be developed to describe the dissolution of more complex glass systems.

In a literature survey of the aqueous dissolution rates of a wide range of silicate-based glasses, Harvey (1984) concluded that the dissolution rate of silicate-based waste glasses decreased as the ratio of SiO_2 to trivalent metal oxides (M_2O_3) increased. It was concluded that the dissolution rate of silicate glasses decreased as the proportion of Al_2O_3 and/or Fe_2O_3 increased in the glass, and increased as the proportion of monovalent oxide (M_2O) increased.

Studies have indicated that the dissolution of a glass surface is strongly affected either by ions initially present in the leachant or by ions released from the glass into solution (Tait and Jensen 1982). The dissolution rate of a sodium borosilicate glass was found to be about one order of magnitude higher than that of the comparable borosilicate glass containing 8.5 wt.% ZnO. The dissolution rate of the zinc-free borosilicate glass could be decreased by an order of magnitude by adding Zn^{2+} ions to the leachant solution. This increased durability was attributed to the incorporation or sorption of zinc ions on the surface of the glass, which inhibited glass dissolution.

The results from borosilicate glass dissolution studies in the CNFWMP are consistent with a simple dissolution mechanism:

$$Na_2O\text{-}B_2O_3\text{-}SiO_{2(glass)} + H_2O \rightarrow Na^+ + B(OH_4)^- + H_4SiO_4$$

Initially, dissolution of the glass is incongruent, and involves preferential release of Na^+ and B^{3+} ions by exchange with H^+ from solution. As a result, the solution gradually increases in pH because of the consumption of H^+ and the increase in concentration of OH^- in solution. The rise in pH may be limited in glasses with a high SiO_2 content and by the formation of alteration layers on the glass surface. Eventually, a steady state may be achieved where ions diffuse out of the glass through the surface layer(s) and are released to solution in proportion to their content in the glass (congruent or stoichiometric dissolution). High silica content and the formation of alteration layers appear to play key roles in increasing the durability of these glasses.

A.4.3 CHARACTERIZATION OF PHYSICAL AND MECHANICAL PROPERTIES OF GLASSES

A.4.3.1 Physical Properties

The published literature on the physical properties of a wide variety of silicate glasses is extensive. A good theoretical basis for predicting many physical properties has been developed and can be found in publications by Morey (1954), Doremus (1973), and Kingery et al. (1976). The physical properties that are of most interest for waste-form characterization include crystallization and phase separation in the solid glass and the viscosity of the glass melt.

Crystallization in Glasses

Solid glasses are amorphous (non-crystalline) materials and are thermodynamically unstable with respect to the crystalline state. There will always be a driving force for a glass to crystallize (devitrify); however, the rate of crystallization of a glass at temperatures below about 400°C is extremely slow, and complete crystallization would take millions of years at ambient temperatures. The rate at which crystallization can occur is limited by the mobility of ions in the glass structure. Crystallization in glass waste forms is thus likely to be of concern only if it occurs during the fabrication of the waste form.

As a waste glass cooled from the liquid to the solid state during fabrication, it would pass through a temperature region where crystalline sites might nucleate and crystal growth might be initiated. The extent of crystallization would depend strongly on the glass composition, the viscosity of the glass in the nucleation and crystal growth region, the rate of cooling and the concentration of certain impurities in the glass (e.g., some components of reprocessing wastes). Crystallization could cause microcracking of the glass, as a result of a mismatch in thermal expansion between the crystalline and glass phases, and could thus degrade the mechanical integrity of the final product. If crystalline phases formed, they might be chemically less durable than the bulk glass, or their formation could significantly alter the composition of the remaining glass phase, making it less durable. In addition, crystallization of a waste glass could result in waste products concentrating at a glass/crystal interface, which could potentially make them more accessible to dissolution in aqueous solution.

The reprocessing-waste stream contains metallic elements, such as Pd and Rh that remain as finely dispersed metallic particles in the glass. These phases are known to be capable of providing nucleation sites for crystalline phases in a glass. Other waste components, such as Mo, occur in sufficient concentrations in the waste (~3 wt.%) to form alkali and alkaline-earth molybdate crystalline phases during fabrication of the waste form. These phases develop because of the low solubility of MoO_3 in borosilicate glasses (Lutze 1988). This potential problem can be addressed by adding a reducing agent, such as carbon or iron, to the melt to reduce Mo to the Mo^{3+} state, where its solubility in the glass is substantially increased.

It is generally recognized that, although it may not be possible to completely suppress crystallization in a borosilicate glass, there are several approaches that could be followed to minimize the effects of crystallization (Lutze 1988). These approaches include altering the initial glass composition to reduce the tendency to crystallize and investigating the time-temperature dependency of the rate of crystallization. By choosing an appropriate rate of cooling from the melt, the tendency towards crystallization can be minimized.

Phase Separation

During prolonged heating at temperatures above about 600 to 700°C, glasses may undergo glass-in-glass or liquid-in-liquid phase separation. These phases may occur on a macroscopic or microscopic scale and may persist in the cooled glass. This can potentially affect glass durability. Phase separation typically results in the formation of two immiscible phases (in borosilicate glasses, one is usually SiO_2-rich and the other B_2O_3-rich), either or both of which may be less durable than the original non-phase-separated glass. One phase is usually continuous in nature while the other phase exists as discrete droplets within the continuous phase. Temperature and glass composition are the major factors that govern the tendency of a glass to undergo phase separation. Phase separation is not initiated in most silicate glasses at temperatures below about 500 to 700°C, because of the low ion diffusion rates in the solid. A comprehensive review on both the science and applications of phase separation can be found in a monograph edited by Mazurin and Porai-Koshits (1984).

If a glass undergoes phase separation into two or more distinct phases, minor constituents of the glass, or, in the case of nuclear waste glasses, reprocessing-waste components, may have different solubilities in each phase. Concentration of radionuclides in the phase that is more soluble in aqueous solution could result in preferential dissolution and enhanced radionuclide release. For example, certain borosilicate glass compositions undergo phase separation to produce a borate-rich phase and a silicate-rich phase; and during phase separation, metal oxides (most fission-product oxides) tend to partition into the boron-rich phase (Taylor 1990a). By the appropriate choice of glass composition, it is possible to avoid the phenomenon of phase separation. Phase separation in borosilicate glass compositions has been reviewed by Taylor (1990a) (Section A.4.3.3).

Viscosity

The viscosity of a glass melt would be important only to the fabrication of the waste form, since it would determine the ability of a glass melt to homogenize as a liquid and to be poured easily into a container.

The theory of glass viscosity is well understood and numerous studies have discussed the change in viscosity of a glass as a result of limited additions or substitutions of various glass modifiers (e.g., Al_2O_3 and SiO_2 additions tend to increase viscosity, whereas Na_2O, B_2O_3 and CaO tend to decrease viscosity) (Chick et al. 1981). As in the case of the properties discussed above, any glass composition can be altered, within limits, to produce a glass with the desired processing temperature and viscosity; however, the potential effects on glass durability must also be considered.

A.4.3.2 Mechanical Properties

Mechanical properties are important in the fabrication of glass waste forms. A glass waste form cooled too rapidly from the melt would contain residual thermal stresses that could cause spontaneous fracturing, and lead to a higher glass surface area in the container. Fracturing would be unavoidable in fabricating a large waste form, and excessive fracturing could lead to a higher initial radionuclide release to the waste vault because of the higher surface area available for dissolution. A number of studies that examined fracturing in a full-scale container of glass (Lutze 1988) found that the glass surface area was 5 to 15 times greater than the geometric surface area of an unfractured glass. The highest degree of fracturing was produced in containers that were rapidly cooled. It is not yet possible to theoretically predict the observed increase in surface area from a knowledge of the various mechanical and thermal properties.

In general, the performance of a waste form in a disposal system would not likely be limited by the mechanical properties of the waste form. The mechanical properties would need to be characterized to ensure that the integrity of the waste form was not compromised by fabrication or handling during disposal. Residual thermal stresses and fracturing during fabrication could be minimized by choosing suitable cooling rates for the waste form. Measurements of some mechanical properties could be used to ensure the quality and consistency of the waste form during fabrication. The theory and data available on the mechanical properties of nuclear waste glasses has been briefly reviewed by Lutze (1988).

A.4.3.3 Physical and Mechanical Property Characterization in the CNFWMP

The characterization of physical and mechanical properties of glasses in the CNFWMP has focused on establishing the methodologies for determining the extent of phase separation in borosilicate glasses and determining temperature-viscosity relationships in a simple sodium-borosilicate glass system. Since mechanical properties do not vary widely for borosilicate glasses in general, and since there is a broad range of data existing in the literature for a wide range of borosilicate glass compositions, a detailed examination of these properties would assume a greater importance if and when a waste form and process were selected for immobilizing CANDU fuel reprocessing wastes. The crystallization and phase separation behaviour of glass-ceramics, however, have been investigated in more detail than borosilicate glasses, since these properties are more fundamental to the understanding of the fabrication of glass-ceramic waste forms (Section A.6).

Simple sodium borosilicate glasses are known to have a wide compositional region within which they will undergo phase separation. Phase separation studies were initiated to establish the techniques for detecting phase separation in borosilicate glasses, to gain a basic understanding of the mechanisms of phase separation and to study the effects of a variety of both glass-modifying oxides and representative fission-product oxides on phase separation. The results of these studies are documented in a comprehensive review by Taylor (1990a) and are complemented by studies of Engell and Roed (1982) on the net effect of a simulated waste oxide mixture on phase separation in two multicomponent glass compositions developed in the Swedish waste management program.

Taylor (1990a) concluded that, in sodium borosilicate glass systems, phase separation can usually be suppressed, so long as glass compositions very low in Na_2O are avoided. Addition or substitution of ZnO, alkaline-earth oxides and rare-earth oxides can either suppress or enhance phase separation, depending on the starting composition of the glass. These conclusions are supported by the results of Engell and Roed (1982). There is a possibility that other phase-separation fields, distinct from the general type found in borosilicate systems, could be encountered in the fabrication of specific glass waste forms, and these systems would require specific characterization. Although the influence of various oxides on phase separation of sodium borosilicate glasses is complex, few oxides have been found to actually increase the tendency towards phase separation. Phase separation in waste-loaded borosilicate glasses (<20 wt.% waste oxides) is not expected to be a major problem as long as the glass composition lies outside well-established regions for phase separation and the concentration of components such as phosphate, sulphate and molybdate (Mo(VI)) is minimized. It is technically feasible to avoid phase separation in waste glasses by carefully choosing the glass composition.

The melt viscosities of a range of compositions within the $Na_2O-B_2O_3-SiO_2$ glass system have been determined as a function of temperature. The compositions studied covered the range that would be most likely to be of interest as a waste form (Tait et al. 1984). An empirical formula was derived to predict the relationship between temperature, viscosity and composition. If glass was chosen as a waste form for reprocessing wastes, any optimization of glass composition would also include a detailed study of the viscosity behaviour of the base glass and a study of the effect of the addition of reprocessing wastes.

A.4.4 SUMMARY OF BOROSILICATE GLASS CHARACTERIZATION

The fundamentals of the dissolution behaviour of borosilicate glasses are well understood and a large database of published dissolution results exists to support this understanding. Although only a relatively narrow range of glass compositions have been investigated in the CNFWMP, the general effects of glass composition, temperature, solution composition and pH, flow rate, and the potential effects of alteration layers on durability are understood. It is clear that should Canada decide to reprocess its used CANDU fuel, a waste form would have to be chosen that would offer a high durability. This would require a detailed comparison of dissolution rates of several candidate materials, such as those already studied in this program or from other studies, under the anticipated conditions of a selected disposal site. There is no evidence to suggest that radiation would cause structural changes to a glass waste form that would result in a reduction in chemical durability by a factor of more than three. Gamma-irradiation of solutions in contact with glasses increases the dissolution rate of glasses by a factor of about five. This is unlikely to have practical significance, because container lifetimes would exceed the time frame in which γ-fields would be significant.

In a waste-form optimization phase, the physical properties important to waste-form fabrication would need to be examined in detail. These include crystallization, phase separation and viscosity (which have already been examined for general borosilicate compositions). The mechanisms responsible for crystallization and phase separation would need to be determined, since they could potentially affect the chemical durability of the waste form. The viscosity would need to be determined as a function of waste loading and glass composition, as it affects fabricability. Other properties, such as fracture toughness, thermal and electrical conductivity, although varying little with borosilicate glass composition, would also need to be determined.

A.5 ALUMINOSILICATE GLASSES

Aluminosilicate glass compositions were investigated by AECL in the late 1950s as a potential waste form for immobilizing small volumes of liquid waste from fuel-reprocessing experiments. The glasses selected for small-scale tests were based on a mixture of CaO with the aluminosilicate mineral nepheline syenite. In 1958, 25 2-kg blocks of glass containing 1.11×10^{13} Bq of mixed fission products were fabricated using a crucible melting technique to produce hemispherical blocks. In 1960, a second set of 25 blocks, containing 4.07 x 10^{13} Bq, were fabricated. The first set was buried in 1958 about 3.5 m deep in a sandy soil aquifer on the CRL site. After 1 a there was no detectable radioactive release to the groundwater 3 m downstream from the blocks. A second test was therefore initiated in 1960, using the set of 25 2-kg blocks containing 4.07 x 10^{13} Bq of fission products. Laboratory leaching tests showed that the second set of blocks had a dissolution rate about 10 times greater than the first set. The second set of blocks, buried in a separate location at the same depth as the first set, had a measurable release to the aquifer after 1 a.

After 15 a, samples of the groundwater and soils about 3 m downstream from the first set of blocks indicated that there was still no measurable ^{90}Sr release (Merritt 1976). In contrast, the ^{90}Sr plume from the second set had migrated about 33 m from the glass blocks by 1971. The ^{90}Sr release rates to the aquifer from the second set of blocks indicated that the dissolution rate had decreased from 5 x 10^{-12} $kg{\cdot}m^{-2}{\cdot}s^{-1}$ in 1960 to about 6 x 10^{-15} $kg{\cdot}m^{-2}{\cdot}s^{-1}$ in 1974 (Melnyk et al. 1984). The latter dissolution rate is orders of magnitude lower than that measured for many radioactive glasses being considered for radioactive waste disposal. Although a wide variety of fission products and actinides were present in the glass blocks (Merritt 1977), only ^{137}Cs, ^{90}Sr, ^{154}Eu, ^{155}Eu and ^{241}Am were detected in the aquifer release plume (Merritt and Parsons 1964, Killey et al. 1990). If this field release rate of ^{90}Sr is representative of the bulk glass dissolution rate, it would take about 10 million years to completely dissolve each block.

The field dissolution rates can be compared with 100-d (25°C) laboratory leaching measurements, on samples of the same glass, of about 10^{-11} $kg{\cdot}m^{-2}{\cdot}s^{-1}$ (Melnyk et al. 1983). The relatively low dissolution rate measured in laboratory tests can be attributed in part to the high alumina and silica content of the glass. The much lower field dissolution rates have been attributed, in part, to the low ambient temperature of the aquifer (6 to 9°C) and to the possible formation of a mineralized surface layer, rich in alumina and silica (Walton and Merritt 1980, Tait et al. 1986). It was suggested that this layer inhibits diffusion of water to the underlying bulk glass, thereby inhibiting further glass dissolution and radionuclide release. However, analysis of the surface of a glass block retrieved in 1979 from the second burial test showed no evidence of an altered surface layer (Tait et al. 1986).

The time dependence of the ^{90}Sr release and migration in the aquifer from the second set of blocks was modelled in detail using an equilibrium sorption model (Melnyk et al. 1983, Killey et al. 1990). The results suggested that the glass was not dissolving by either a congruent or diffusion-controlled mechanism. The results were consistent, however, with release inhibited by a "protective layer" on the glass surface. Other laboratory dissolution experiments (Arneson et al. 1986) conducted at 100°C on samples of a glass block from the second burial experiment, retrieved in 1979, demonstrated that the release of ^{137}Cs from this glass effectively ceases when the solution becomes saturated with respect to major glass constituents (Figure 2-16 of the main text). This suggests that solution saturation effects or the formation of alteration products on the glass surface may inhibit dissolution.

A number of dissolution studies have been conducted to determine which regions in the Na_2O-CaO-Al_2O_3-SiO_2 system exhibit the highest durability. Harvey and Litke (1984) identified compositional regions in which glasses had durabilities that were similar to or better than the Chalk River glasses discussed above. Increasing Al_2O_3 content increased the durability of the glass. To investigate solution saturation effects, dissolution tests were conducted in which glass samples were placed in a solution that had been previously saturated with dissolution products from a finely crushed glass of the same composition. After about 100 d, the samples ceased to lose weight, suggesting that solution saturation was inhibiting dissolution either by the formation of an alteration layer that inhibited diffusion of glass constituents through a hydrated layer on the surface, or by the formation of crystalline alteration products that achieved a thermodynamic equilibrium with dissolution products.

Tait and Mandolesi (1983) investigated the dissolution of glasses in the Na_2O-Al_2O_3-SiO_2 system; dissolution rates of $\sim 7 \times 10^{-10}$ $kg \cdot m^{-2} \cdot s^{-1}$ at 100°C were obtained, which are about the same as those observed for high-silica borosilicate glasses (Harvey and Jensen 1982). Addition of up to 2 wt.% simulated waste had no effect on dissolution rates. The leaching results suggested that the predominant dissolution mechanism involved preferential release of alkali or alkaline-earth elements from the surface of the glass, leaving a surface enriched in silica and alumina.

The aluminosilicate glasses discussed here can be fabricated easily on the laboratory scale. However, temperatures of 1400 to 1600°C are typically required to produce a homogeneous glass. To fabricate full-scale aluminosilicate glass waste forms, considerable process development work would be required, since conventional joule melting technology may not be appropriate at these temperatures. Refractory materials would need to be carefully chosen and tested for their compatibility; dissolution properties at higher melt temperatures and the effect of temperature on the production of volatile off-gases would need to be investigated. Low-temperature fabrication methods, such as sintering or sol-gel techniques, or alternative melting technologies, such as the induction-heating process used in the AVM facility, could be considered.

The crystallization and phase separation behaviour of aluminosilicate glasses were not extensively investigated. There are a large number of potentially stable aluminosilicate minerals that could form during cooling of an aluminosilicate glass melt. The minerals formed would depend primarily on the glass composition. Similarly, phase separation behaviour would be dependent on glass composition, although, in general, additions of alumina tend to suppress phase separation (Taylor 1990a). Both phase separation and crystallization behaviour would have to be investigated in detail for any chosen waste-form composition. With judicious choice of base glass constituents, the tendency of a glass to crystallize or phase-separate could be minimized. The mechanical properties and radiation damage effects on aluminosilicate glasses are expected to be similar to those observed in borosilicate glasses. However, these properties would have to be characterized and assessed if aluminosilicate glasses were to be developed as an alternative waste form to borosilicate glasses.

A.5.1 SUMMARY OF ALUMINOSILICATE GLASS CHARACTERIZATION

Aluminosilicate glasses appear to have strong potential as a waste form. Certain compositions, such as those used in the active glass block burial experiment, exhibit durabilities, both in the laboratory and in field burial experiments, that are about an order of magnitude greater than the high-silica borosilicate glasses studied in the CNFWMP. In solutions that have become saturated with glass dissolution products, it appears that further dissolution of the aluminosilicate glass, and thus the release of radionuclides, is strongly inhibited. This behaviour may result from the formation of an alteration layer on the surface of the glass that controls dissolution. This can be contrasted with the behaviour of simple borosilicate glasses, which do not appear to cease dissolution in solutions saturated with glass dissolution products. More complex borosilicate glasses (such as SRL TDS-131 (Wallace and Wicks 1983)), however, also appear to form an alteration layer that can inhibit dissolution.

A.6 TITANOSILICATE GLASS-CERAMICS

A glass-ceramic is a partly crystalline/partly amorphous material that is prepared by either slowly reheating a solid glass or slowly cooling a glass melt to a temperature region where the growth of crystalline phases within the glass can occur. If the composition of the original (precursor) glass is appropriately chosen, a glass-ceramic can be prepared that consists typically of discrete, fine-grained (~1 μm) crystalline phases of the desired composition homogeneously dispersed within a continuous glass matrix.

Typically, a glass-ceramic is formed by mixing the appropriate glass constituents with the waste oxides and heating the mixture to form a fluid glass melt. This melt is rapidly cooled and then slowly reheated to a temperature between about 600 and 1000°C, where crystallization occurs throughout the glass. During this process, the constituents that are used to form the crystalline phase(s) are removed from the glass phase and the glass phase thus becomes enriched in those constituents that are not taken up by the crystalline phase. With a good understanding of the kinetics of crystal nucleation and growth, as well as the effects of changes in the initial composition of the glass precursor, the composition of the final glass and crystalline phases can be "tailored" to produce the desired glass-ceramic product.

There are a number of properties of glass-ceramics that, in certain cases, have the potential to make them a more durable waste form for nuclear waste immobilization than glasses. The crystalline phases of a glass-ceramic are more thermodynamically stable than a glass of the equivalent composition and are thus likely to be more durable. Unlike a glass, crystalline phases may establish a thermodynamic equilibrium with the leachant, which could inhibit dissolution. Glass-ceramics in general have higher impact and mechanical strengths than their parent glasses; this property would make them less susceptible to cracking on cooling, and thereby minimize the surface area available for leaching (Hayward 1988).

In tailoring the composition of glass-ceramic waste forms, it would be desirable to ensure that the major crystalline phases formed would be thermodynamically stable in the anticipated geochemical environment of a disposal vault, that the residual glass phase itself would be highly durable, and that the crystalline phases were capable of incorporating a majority of the radionuclide waste ions into the crystalline structure. Those radionuclides that could not be incorporated should be readily incorporated in the residual glass phase of the glass-ceramic.

Comprehensive reviews of candidate ceramics developed internationally for high-level waste immobilization (Hayward 1982, 1987, 1988) indicated that a glass-ceramic in the Na_2O-Al_2O_3-CaO-TiO_2-SiO_2 system would be most appropriate for the Canadian waste disposal concept. Other ceramics, such as Synroc (synthetic rock) (Section A.8), tailored ceramics, TiO_2, monazite and FUETAP (Formed Under Elevated Temperature and Pressure) concretes, have been studied in other international programs and the research on these materials has been reviewed in Lutze and Ewing (1988).

A number of naturally occurring anhydrous minerals are abundant in crystalline rock formations, and, from their observed durability in common geochemical environments, they appear to be thermodynamically stable and to have very low rates of alteration or dissolution (Hayward 1988). The mineral sphene (titanite), $CaTiSiO_5$, was selected from a variety of possible mineral phases as a potential host for reprocessing wastes in the CNFWMP. This decision was based on a number of factors (Hayward 1988):

- Sphene is a mineral commonly associated with granitic rock formations typical of the Canadian Shield and is often found to have withstood alteration and weathering processes in igneous and metamorphic rocks for millions of years.

- Thermodynamic calculations indicate that sphene should be stable towards aqueous dissolution in the Ca-Na-Cl groundwaters of the Canadian Shield.

- Analyses of naturally occurring specimens of sphene show that they have incorporated a wide range of impurities, including Th, U^{4+} and rare-earth elements, into their crystal structure.

- Some naturally occurring specimens of sphene appear to have become partially amorphous over millions of years as a result of radiation-induced structural damage from α-emitting radionuclides, such as U and Th, that were incorporated during mineral formation. In spite of this, studies have shown that these sphene crystals retained their chemical durability.

The research conducted in the CNFWMP on sphene-based glass-ceramics was primarily focused on investigating the mechanism of crystallization, determining the thermodynamic stability of the sphene phase in Canadian Shield groundwaters, and studying the mechanism of dissolution of radionuclides from the glass and sphene phases. In addition, the effect of waste ions on crystallization, the extent of waste ion partitioning between the glass and crystalline phases, the effects of radiation damage (metamictization) on dissolution, and the physical and mechanical properties of the glass-ceramics were investigated.

On the basis of scoping experiments on a wide range of compositions, a "base" composition (6.6 Na_2O, 5.1 Al_2O_3, 16.5 CaO, 14.8 TiO_2, 57.0 SiO_2 (mol%)) near the centre of the sphene crystallization region was chosen for characterization (Hayward 1988).

A.6.1 FORMATION OF THE SPHENE-BASED GLASS CERAMIC

Figure A-1 shows the compositional regions in the CaO-TiO_2-SiO_2 system where glasses or crystalline phases form (Hayward 1988). Crystalline sphene forms within a narrow range in this system. With appropriate additions of Na_2O, Al_2O_3 and further SiO_2, a sphene-based glass-ceramic can be produced. The "base" glass constituents were melted at about 1400°C. On cooling this melt to below about 700°C, the glass undergoes rapid unmixing (phase-separation) to form a solid glass with two distinct glass phases (see Figure 2-17 in the main text). One glass phase (the dark phase in Figure 2-17a) is a Ti-Ca-rich silicate phase, while the other (light) phase is a Na-Al-rich silicate phase. On reheating this phase-separated glass to about 950°C, nucleation and crystallization of sphene is initiated in the Ti-Ca-rich phase, and the sphene crystalline phase rapidly grows to form discrete cylindrical crystals (~1 to 5 μm in length; ~0.1 to 0.2 μm in diameter) surrounded by a continuous aluminosilicate glass phase (Figure 2-17b). When waste ions are added to the base composition, most of these ions are incorporated in the sphene phase, and the aluminosilicate glass phase accommodates the remaining waste ions. Since the aluminosilicate glass phase is formed by a phase-separation process, the temperature required to produce this component phase is far lower than would be required to produce the aluminosilicate glass alone.

A.6.2 CHEMICAL DURABILITY OF SPHENE GLASS-CERAMICS

The dissolution behaviour of a sphene glass-ceramic is a complex function of the dissolution of the two component phases (aluminosilicate glass and crystalline sphene). To understand the dissolution properties of the component phases, a sphene ceramic ($CaTiSiO_5$) and an aluminosilicate glass whose composition was equivalent to that in the glass-ceramic were prepared.

A.6.2.1 Dissolution of Crystalline Sphene

The dominant cations present in deep groundwaters in the Canadian Shield are Ca^{2+} and Na^+ (Frape et al. 1984). Groundwater pH values typically range from 5 to 6.8; dissolved silica concentrations are virtually independent of depth and lie between the saturation values for quartz and amorphous silica (1×10^{-4} and 2×10^{-3} $mol \cdot L^{-1}$ at 25°C). A synthetic standard Canadian Shield saline solution (SCSSS) groundwater based on average

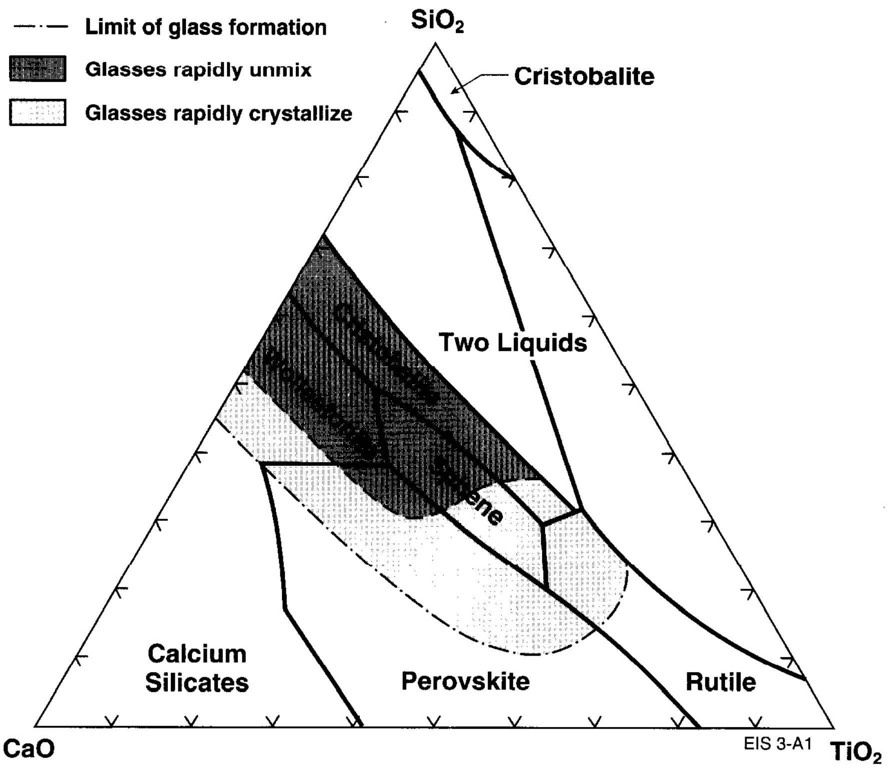

FIGURE A-1: Areas of Glass Formation and Major Phase Fields in the $CaO-TiO_2-SiO_2$ System

groundwater compositions at the 500-m depth (Gascoyne 1986) was used in the dissolution experiments.

The main aqueous dissolution reaction of the sphene component of the glass-ceramic produces solid rutile (TiO_2) (or anatase, a TiO_2 polymorph) and orthosilicic acid in solution:

$$CaTiSiO_5 + 2H^+ + H_2O = Ca^{2+} + TiO_2 + H_4SiO_4$$

where the equilibrium constant, K, for the reaction is described by

$$K = [Ca^{2+}][H_4SiO_4]/[H^+]^2 \quad (\log K = \log([Ca^{2+}]/[H^+]^2) + \log[H_4SiO_4]) \ .$$

At the mean postclosure temperature anticipated in a disposal vault after 500 a (about 60°C), and at the groundwater compositions and silica concentrations found at depths of 400 to 1000 m, the activity diagram for sphene (Figure A-2) indicates that sphene stability, relative to rutile, is strongly promoted by high $[Ca^{2+}]$ and low $[H^+]$ (alkaline pH).

The above reaction has been confirmed by dissolution studies, which showed that, in acid and neutral pH, the dissolution mechanism was dominated by $H^+:Ca^{2+}$ ion exchange and silica dissolution. Anatase (TiO_2) was observed

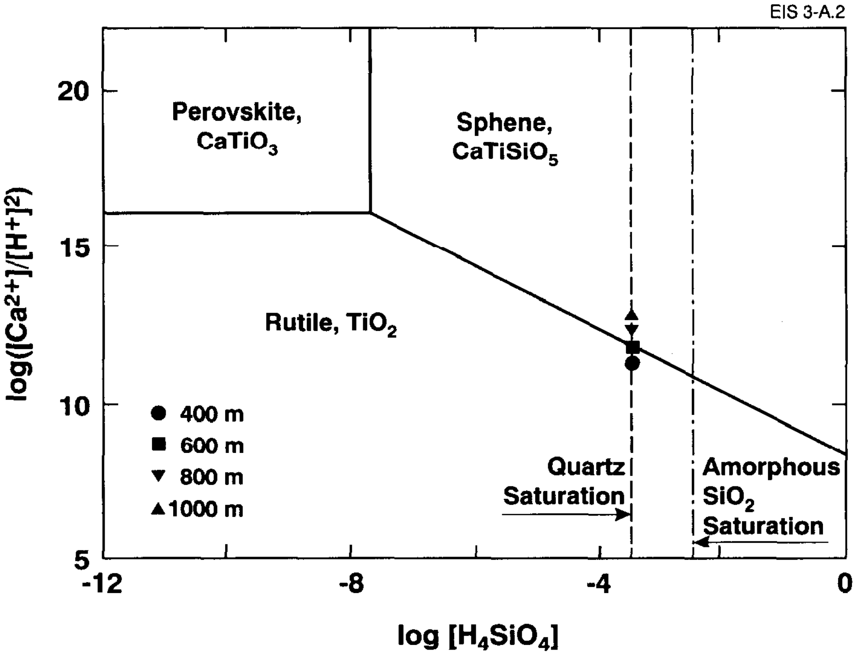

FIGURE A-2: Activity Diagram for H^+-H_2O-CaO-TiO_2-SiO_2 at 60°C

to form on the dissolving surfaces and partially passivated the surface towards further dissolution. In alkaline solution, markedly lower dissolution rates were observed because of the low concentration of H^+. Equilibrium calculations showed that, even in the presence of gypsum ($CaSO_4$) and calcite ($CaCO_3$), which are typically found in groundwaters, sphene would be the stable phase at pH ≥ 6.5 and temperatures in the range from 25 to 150°C.

Dissolution experiments on a glass of the sphene composition in SCSSS groundwater showed that the glass was sparingly soluble and precipitated crystalline sphene on the glass surface, as predicted from the stability diagram (Figure A-2). Similar dissolution experiments on natural sphene crystals and synthetic sphene ceramic (crystalline) showed no dissolution after 30 d at 100°C (Hayward 1988). Synthetic sphene ceramic containing simulated waste was corroded in both DIW and SCSSS groundwater for 10 d at 100°C. Scanning electron microscopy (SEM) and secondary ion mass spectrometry (SIMS) surface examination indicated little evidence of dissolution. After 360 d in SCSSS the samples showed no change in weight. Similar dissolution experiments at 25, 60 and 100°C indicated that little or no dissolution occurred below 60°C, and that the dissolution rate was insensitive to Na^+, Ca^{2+} or Cl^- concentrations. These observations are thus consistent with the thermodynamic prediction that sphene is stable towards dissolution.

A.6.2.2 Dissolution of the Aluminosilicate Glass Phase

Dissolution experiments at 100°C on an aluminosilicate glass with a composition similar to that of the aluminosilicate glass phase in the base glass-ceramic (including 10% simulated HLW) indicated that the dissolution rate was less than 5×10^{-10} $kg \cdot m^{-2} \cdot s^{-1}$. The elemental release rates and bulk dissolution rates are presented in Table A-2 for temperatures of 100, 60 and 25°C. For these temperatures, all elements appear to attain a constant concentration in solution after about 60 d, possibly because of the formation of alteration products such as Ca, Sr and Ba carbonates. The results imply that, although the release rate from the aluminosilicate glass phase may be initially higher than from the sphene phase, the glass phase may eventually "passivate" and exhibit dissolution rates approaching those of sphene. The residual aluminosilicate glass phase formed thus possesses the high chemical durability found in other aluminosilicate glass compositions (Tait and Mandolesi (1983); Harvey and Litke (1984); Arneson et al. (1986); Section A.5)

A.6.3 DISSOLUTION OF SPHENE GLASS-CERAMICS CONTAINING SIMULATED HLW

Dissolution rates of a sphene-based glass-ceramic doped with 5 wt.% simulated HLW in DIW at 100°C are given in Table A-3. The higher releases of Na, Al and Si, compared with Ca and Ti, indicate that the aluminosilicate glass phase is, at least initially, preferentially dissolved. The low dissolution rates observed for Ti, U and La are almost certainly due to the formation of low-solubility alteration products on the surface of the glass-ceramic. Surface analysis showed that the dissolution of the sphene phase was greatly reduced when SCSSS was used as the leachant rather than DIW (as

TABLE A-2

NORMALIZED RELEASE RATES ($kg \cdot m^{-2} \cdot s^{-1}$) FOR

ALUMINOSILICATE GLASS PHASE IN SPHENE GLASS-CERAMIC*

Element	100°C	60°C	25°C
Na	20.5×10^{-10}	4.5×10^{-10}	3.1×10^{-10}
Ca	8.5×10^{-10}	$<0.02 \times 10^{-10}$	$<0.02 \times 10^{-10}$
Si	7.8×10^{-10}	0.8×10^{-10}	0.2×10^{-10}
Sr	6.6×10^{-10}	0.5×10^{-10}	$<0.02 \times 10^{-10}$
Ba	2.9×10^{-10}	0.6×10^{-10}	$<0.4 \times 10^{-10}$
Mo	7.3×10^{-10}	$<0.3 \times 10^{-10}$	$<0.3 \times 10^{-10}$
Glass**	7.6×10^{-10}	0.7×10^{-10}	0.2×10^{-10}

* After 91 d in deionized water (surface area:volume ratio of 10:1 (Hayward 1987). Normalized to ion concentration in the glass.

** Based on glass sample weight-loss measurements.

TABLE A-3

NORMALIZED LEACH RATE ($kg \cdot m^2 \cdot s^{-1}$) FOR SPHENE GLASS-CERAMIC*

Element	30 d	60 d	100 d
Na	14.6×10^{-10}	13.8×10^{-10}	10.9×10^{-10}
Ca	0.9×10^{-10}	0.9×10^{-10}	0.8×10^{-10}
Si	4.8×10^{-10}	8.7×10^{-10}	8.7×10^{-10}
Sr	6.9×10^{-10}	5.2×10^{-10}	5.3×10^{-10}
Al	6.1×10^{-10}	3.6×10^{-10}	4.7×10^{-10}
Ti	$<0.7 \times 10^{-10}$	$<0.2 \times 10^{-10}$	$<0.1 \times 10^{-10}$
U	$<0.4 \times 10^{-10}$	$<0.2 \times 10^{-10}$	$<1.5 \times 10^{-10}$
La	$<4.5 \times 10^{-10}$	$<2.3 \times 10^{-10}$	$<0.7 \times 10^{-10}$

* In deionized water at 100°C (Hayward 1987).
Normalized to ion concentration in the glass-ceramic.

expected from the stability diagram). Dissolution rates were deduced to be less than 3.8×10^{-10} $kg \cdot m^{-2} \cdot s^{-1}$ in SCSSS.

Dissolution experiments were conducted at 100°C in SCSSS for periods of up to 569 d. In these experiments, samples of the aluminosilicate glass phase, the sphene phase and the glass-ceramic were doped with the radioisotopes ^{22}Na and ^{45}Ca to allow their concentration to be followed in the Na-Ca-Cl brine leachants. The observed releases were consistent with the occurrence of both surface ion exchange and bulk dissolution of the glass phase and with surface ion exchange of the sphene phase. The results support the contention that the component phases of the glass-ceramic dissolve independently and that radionuclide release from each phase would be proportional to the relative ion concentration in each phase.

A.6.4 PRECURSOR GLASS CRYSTALLIZATION

After melting the base glass at about 1400°C and cooling it rapidly to below about 700°C, the glass undergoes glass-in-glass phase separation into two distinct phases (see Figure 2-17a in the main text). Studies were conducted to investigate how waste ions partition between the glass and sphene crystalline phases of the glass-ceramic (Hayward 1988). The rare-earth ions (simulants for the actinides) preferentially partitioned into the crystalline phase, whereas Cs was preferentially incorporated into the glass phase. Uranium was preferentially incorporated into the glass phase as U(VI), with a minor component residing in the sphene phase as U(IV). The metallic phases, such as Pd, Rh and Ru, were dispersed as microscopic aggregates throughout the glass phases and may serve as nucleating agents for sphene crystallization. Other waste ions did not appear to affect sphene crystallization and were not present in sufficient concentrations in the waste to exert any significant effect. At waste loadings higher than

15 wt.%, rare-earth and U-containing phases were formed; however, because of disposal vault temperature restrictions, loadings this high would not be used for producing a waste form for disposal.

Crystallization studies demonstrated that to form a sphene-based glass ceramic, the melt should be rapidly cooled and then reheated to 1050°C to achieve a single crystalline phase (sphene) glass-ceramic. Melting under neutral or oxidizing atmospheres had little or no influence on the phase constitution of the final product (Hayward 1988). Waste loadings of less than 15 wt.% had little or no effect on the crystallization properties of the glass-ceramic.

A.6.5 RADIATION EFFECTS

The potential effects of radiolysis and radiation damage on waste forms were briefly discussed for glasses in Section A.4.1. Unlike the situation for glasses, α-radiation could potentially be more damaging to a crystalline phase, since it could result in the conversion of the crystalline phase to an amorphous (glass) phase (a process known as metamictization) whose dissolution properties may be significantly different.

Radiation damage effects were investigated by bombarding samples of powdered sphene ceramic or glass-ceramic with 3-MeV Ar^+ ions to simulate the effect of α-decay. Samples were irradiated with ion fluences sufficient to approximate the equivalent dose that a glass-ceramic matrix containing ~10 wt.% HLW would receive over a 10^6-a storage period. Following irradiation, samples were corroded in DIW and SCSSS; their dissolution rate increased by less than a factor of five. The dissolution rate of a partially metamict natural sphene, which had received about 20% of the dose required to produce complete metamictization, was about three times greater than an identical natural sample that had been heat-treated to anneal α-damage structural effects (Hayward 1988).

The effects of β-radiation have been simulated by using 200-keV electrons to irradiate natural sphenes to a dose considerably higher than that which would be accumulated by a waste form over 10^6 a. No structural defects were detected and it was concluded that β-radiation effects can be ignored in assessing solid-state radiation damage effects in sphene (Hayward 1988).

The effects of γ-radiolysis (gamma irradiation of samples in aqueous solution) on the dissolution of a glass-ceramic doped with simulated waste were also investigated. The samples were corroded at 100°C in DIW and SCSSS groundwater for 485 d at a γ-dose rate of 4 $Gy \cdot h^{-1}$ (similar to the dose rate from a fuel bundle after cooling for 50 to 100 a) (Tait 1986). In most cases, the dissolution rates for the irradiated samples were no more than a factor of three higher than for the unirradiated samples; in some cases the dissolution rates of irradiated samples were lower. These results imply that γ-radiolysis has no significant detrimental effect on the dissolution rate of the glass-ceramic. No differences were observed between surface alteration products on samples corroded in the presence or absence of a γ-radiation field.

A.6.6 PHYSICAL PROPERTY MEASUREMENTS

The bulk physical and mechanical properties important to assessing the feasibility of waste-form fabrication and to assessing transportation and manufacturing risks have been characterized for the glass-ceramic, with and without simulated HLW (Hayward 1988). These properties are roughly similar to those of typical borosilicate waste glasses, suggesting that the current fabrication techniques for glasses could be applied to the glass-ceramics as well, and that their mechanical performance under disposal conditions would be similar.

A.6.7 SUMMARY OF TITANOSILICATE GLASS-CERAMIC CHARACTERIZATION

A glass-ceramic based on the mineral sphene has been developed that provides a highly durable host for the immobilization of nuclear fuel reprocessing waste. The sphene crystalline phase has been shown to be thermodynamically stable towards dissolution under the saline groundwater conditions anticipated for a vault constructed in the Canadian Shield. Its dissolution rates are typically one to two orders of magnitude lower than for most borosilicate waste glasses. The aluminosilicate glass phase in the glass-ceramic has also been shown to be highly durable. Dissolution of constituents from the glass phase is kinetically controlled, whereas dissolution from the sphene crystalline phase is thermodynamically controlled. Solid-state radiation damage in the sphene phase was found to increase the dissolution rate by about a factor of five and solution radiolysis was found, in some cases, to increase the dissolution rate by about a factor of three. It would appear that the sphene glass-ceramic is a viable alternative candidate to borosilicate glasses for waste loadings up to at least 15 wt.%. If a sphene-based glass-ceramic were chosen as a waste form for HLW, considerable product and process development research would still be required to optimize the fabrication technology and tailor the composition to specific waste types.

A.7 PERFORMANCE UNDER DISPOSAL CONDITIONS

The performance of the three candidate waste forms have also been investigated under the conditions anticipated in an engineered vault in granite rock. Dissolution tests were conducted in the presence of clay buffer materials, container materials, and granite rock (Tait 1986). The results indicated that the engineered barrier materials and the rock had no major detrimental effects on the dissolution behaviour of the waste forms. This may in part be due to the buffering of the pH at ~8.5 and the silica-saturated conditions in the leachant, which may be beneficial to the long-term performance of these waste-form materials.

In situ burial tests of simulated waste forms are the subject of both an international program to test HLW waste forms under repository conditions (clay, granite, salt) (CEC 1989, Roggendorf et al. 1992), and a European program to test HLW waste forms (Hall 1987). The European program indicates that waste-form mass losses increase in the presence of clay, compared with dissolution in DIW; the increase has been attributed to cation adsorption by the clay (Hall 1987). Experiments on other glasses (Werme 1989) have indicated that, although small amounts of bentonite clay in the leachant may enhance dissolution, increasing the bentonite clay fraction decreases the extent of dissolution, and that the long-term dissolution rate was not affected by the presence of bentonite.

The effect of engineered barriers appears to be complex, and in any future assessment studies, the effect of specific engineered barriers on any chosen waste form would need a complete investigation.

A.8 ALTERNATIVE WASTE FORMS FOR HLW IMMOBILIZATION

Considerable international effort has also been directed over the last 10 to 15 a to studies on a wide range of products, in addition to borosilicate glasses, suitable for the immobilization of high-level reprocessing wastes. These include high-silica glasses, aluminosilicate glasses, sintered glasses, glass-ceramics, tailored ceramics such as Synroc and "supercalcine" ceramics, titanite ceramics, clay-based ceramics, coated ceramics, cermets, and cement-based products. Some of these products were investigated because they could offer a simpler processing technology than borosilicate glasses. Others have the potential to offer higher chemical durability than borosilicate glasses, but would require more complex processing technology or higher processing temperatures. A detailed description of the product development work on these waste forms can be found in a series of review papers (Lutze and Ewing 1988).

It should be noted that from 1979 to 1981, the USDOE Alternative Waste Form Peer Review Panel (1979, 1980, 1981) conducted an assessment of the various waste forms available at that time and concluded (Hench et al. 1984) that the differences in the performance of the waste forms would not result in significant differences in the final "dose to man" upon dissolution and release of radionuclides to the waste vault. On the recommendations of this panel, most research on alternative waste forms in the U.S. (and to some extent in international programs) was curtailed and research concentrated on borosilicate glasses. However, this assessment also concluded that Synroc, a multiphase crystalline material developed in the Australian program, should be considered to be the "official alternative" waste form to borosilicate glass.

Although Australia has no nuclear power program, considerable product and process development research has been conducted on Synroc since the late 1970s, and this material has generated considerable international interest (Ringwood et al. 1988). Synroc is a synthetic, multiphase crystalline (ceramic) material composed of four titanite (TiO_2)-based mineral phases. These mineral phases (zirconolite, hollandite, perovskite and titanium oxide) are found in many geological environments and have been shown to incorporate many of the elements that would occur in HLW. These minerals have survived for millions of years in hydrothermal geochemical environments where temperatures exceed 100°C. A number of Synroc formulations have been developed and tailored to immobilize a variety of both commercial and defence fuel-reprocessing wastes from the U.S. program. Synroc has been extensively characterized as a waste form and a summary of the research can be found in Ringwood et al. (1988).

Dissolution tests comparing Synroc with a well-characterized reference borosilicate glass, PNL-76-68 (Reeve et al. 1982), demonstrate that Synroc is intrinsically more stable than glasses, particularly at high temperatures in a hydrothermal environment, and that radionuclide release rates, unlike most borosilicate glasses, decrease rapidly with time (Ringwood et al. 1988). The dissolution rate of Synroc in deionized water at 100°C decreased rapidly with time to 10^{-11}-10^{-12} $kg{\cdot}m^{-2}{\cdot}s^{-1}$. The solubility of the principal component of Synroc (TiO_2) is three to four orders of magnitude lower than that of SiO_2. The long-term release of HLW species is likely governed by the rate at which the TiO_2 and ZrO_2 matrix is dissolved. The higher stability of Synroc also results, in part, from the stability of the main component mineral phases. The dissolution mechanisms of Synroc are complex and are the subject of ongoing studies (Smith et al. 1992). Comparisons of the dissolution rate of Synroc with borosilicate glasses are strongly dependent on leachant flow rates and alteration rates of the borosilicate glass. A quantitative comparison of Synroc versus a variety of borosilicate glasses remains to be done and the details of the Synroc leaching mechanism need to be more firmly established, particularly over long time periods (Lutze and Ewing 1988), to make any comparison meaningful.

A non-radioactive pilot plant has been constructed at the Australian Nuclear Science and Technology Organization (ANSTO) to demonstrate the fabrication of Synroc on a scale equivalent to a commercial-scale vitrification plant for borosilicate glass (Ringwood et al. 1988). Various techniques have been developed to produce Synroc, involving the preparation of oxide or hydroxide precursors to the mineral phases, or the production of Synroc precursors using sol-gel technology. The precursors and waste oxides are slurried or mixed together and then exposed to a high temperature and hot-pressed in a metal bellows container to form a monolithic multiphase ceramic. Specific Synroc formulations have been developed to accommodate variations in composition between various reprocessing wastes (e.g., U.S. defence wastes, high-uranium wastes, high-alumina wastes).

There is currently little information that permits the comparison of the durabilities of alternative waste forms with borosilicate glasses or, for that matter, the intercomparison of the various alternative waste forms. To compare the dissolution properties of these waste forms, tests would have to be conducted under the specific anticipated conditions of a waste vault to address long-term dissolution behaviour and provide a fundamental knowledge of the mechanism of dissolution and radionuclide release. Consideration would also need to be given to results of a safety assessment on a specific disposal site. The broader issues of the risks involved in the production of these various waste forms are beyond the scope of current programs on waste-form development.

In a recent independent assessment of waste forms, based on published work to about 1987, Lutze and Ewing (1988) concluded that, although there can be no simple comparison of various waste forms, borosilicate glasses and Synroc were the two waste forms that have the advantage of being the most highly characterized and whose dissolution performance has been studied under repository conditions. The dissolution mechanisms of borosilicate glasses and Synroc are reasonably well understood and the technologies for their production are well advanced. They also concluded that

> there is no demonstrated alternative available to produce any of the (alternative) waste forms . . . other than borosilicate glass . . . on a large scale. This fact alone justifies further world-wide support of alternative waste-form development programs. . . . One must be able to choose the waste form that best suits the type of waste . . . and the geology of the repository.

A.9 MODELLING WASTE-FORM DISSOLUTION

To be able to predict the dissolution behaviour of a waste form for periods beyond the time frame of normal laboratory experiments, it is necessary to understand the dissolution mechanism under disposal conditions and to develop mathematical models to describe radionuclide release. Such models should be based on a secure theoretical foundation, be verifiable against the observed dissolution behaviour of a waste form, and be applicable to dissolution under repository conditions.

A.9.1 INTERNATIONAL PERSPECTIVE

The early studies on waste-form dissolution conducted in international programs were not directed towards understanding the dissolution mechanisms to develop predictive dissolution models; they were focused on explaining the initial dissolution process over times of minutes to days. Dissolution experiments were aimed at comparing the performance of different waste-form compositions and were conducted at a variety of temperatures, solution flow rates and compositions, pH conditions, and glass surface area to leachant volume ratios. In spite of the disparity in experimental conditions, the results from a large number of experiments suggested that releases from a diversity of waste forms may be controlled by a small number of common factors. It is now generally accepted (Lutze 1988) that the dissolution mechanism of a silicate glass is predominantly determined by the factors discussed in section A.4.1.

Early glass dissolution models were based on a dissolution mechanism that involved an initial dissolution period during which ions diffused out of the glass by exchange with protons from water diffusing into the glass surface. At longer times, the dissolution mechanism was dominated by steady-state diffusion though a "corrosion layer" established during the initial dissolution period (Zagar and Schillmöller 1960, Boksay et al. 1967, Doremus 1983). More complex models were later developed; these involved expressions to account for solid-state diffusion, solubility, dissolution and diffusion rate constants, and mass transfer coefficients. These models were successfully applied to data from dissolution tests under flowing water conditions (Machiels and Pescatore 1981, 1982). Kuhn and

Peters (1983) developed a model that accounted for the accumulation of species in solution and readsorption of species on the glass surface, but neglected precipitation reactions in solution. Wallace and Wicks (1983) developed a diffusion-based, steady-state dissolution model, which took into account the concentration of silica in solution and its rate of diffusion through a precipitated layer of variable thickness on the glass surface. This model predicted that dissolution would cease when the solution became saturated with silica, which is not in accordance with more recently observed results.

Grambow (1984, 1985, 1987) developed a more comprehensive model that accounted for the influence of solution pH, temperature, flow rate, alteration layer formation and solution saturation effects. The data from dissolution experiments on a Japanese-Swedish-Swiss (JSS) inactive borosilicate glass and a radioactive glass have been used to validate this model (JSS 1987). The model fitted the dissolution data for a variety of dissolution conditions, with deviations of less than ~30% between predicted and measured solution concentrations; however, factors of two or more difference were found for solution concentrations of precipitated phases, since precipitation kinetics were neglected in the model and the model could not distinguish which solid phases were most likely to actually precipitate from solution.

A.9.2 GLASS DISSOLUTION MODELS IN THE CNFWMP

In the CNFWMP, glass dissolution models that are based on an approximate solution to the linear diffusion equation have been developed and applied to experimental conditions ranging from static (non-replenished) to flowing leachant conditions and infinite or finite leachant volumes. The models also account for saturation effects in solution. The models have been validated against experimental data on glasses corroded for periods up to several years, and, where possible, have been validated against exact solutions to the linear diffusion equations. Harvey (in preparation (a)) has reviewed the models developed in the Canadian program as well as those developed internationally.

The glass dissolution models developed in the CNFWMP are based on a generally accepted mechanism of dissolution for glasses. This mechanism involves both diffusion of a specific ion through a hydrated layer on the glass, across the glass/water interface and into the bulk solution, and release of molecular constituents (glass or waste) of the glass matrix to solution. This basic model is broadly similar to the solubility-limited model used to describe dissolution of used fuel (Johnson et al. 1994). The glasses investigated to validate the models can be divided into two classes: glasses that do not develop an alteration layer ("simple" glasses), and glasses that form an alteration layer during the dissolution process that may, or may not, inhibit the dissolution process.

A.9.2.1 Borosilicate Glass Dissolution Models

For simple glasses (non-layer-forming glasses) the early stages of dissolution follow a $t^{0.5}$ time dependence in agreement with a diffusion-controlled mechanism. Applying Fick's law of diffusion, it can be shown that the release of a quantity of glass, Q_g, to solution at time t can be described by

$$t = A[e^{-MQ_g} + MQ_g - 1]$$

where $A = D/2\phi^2$, $M = 2\phi/(D\rho)$ and where ϕ is the velocity that the hydration front at the glass surface is moving into the bulk glass, ρ is the density of the glass and D is the diffusion coefficient of water in the glass. This equation was used to fit data from the dissolution of a VYCOR™ (high silica) glass, a sodium borosilicate glass (64 wt.% SiO_2), and a soda-lime glass into an infinite volume of deionized water at 100°C. The fit to the data for the borosilicate glass is shown in Figure A-3 (Harvey et al. 1986).

This basic model was extended to describe dissolution into a finite solution, and it was able to account for the buildup of glass dissolution products in solution and precipitation from solution back onto the glass, but did not include the saturation of glass dissolution components in solution. The model was successfully fitted to the dissolution of soda-lime and VYCOR glasses; however, the model diverged from the VYCOR data at glass surface area/solution volume (SA/V) ratios less than 1:10 at longer times, and this was attributed to saturation of the leachant by silica (Harvey and Boase 1987).

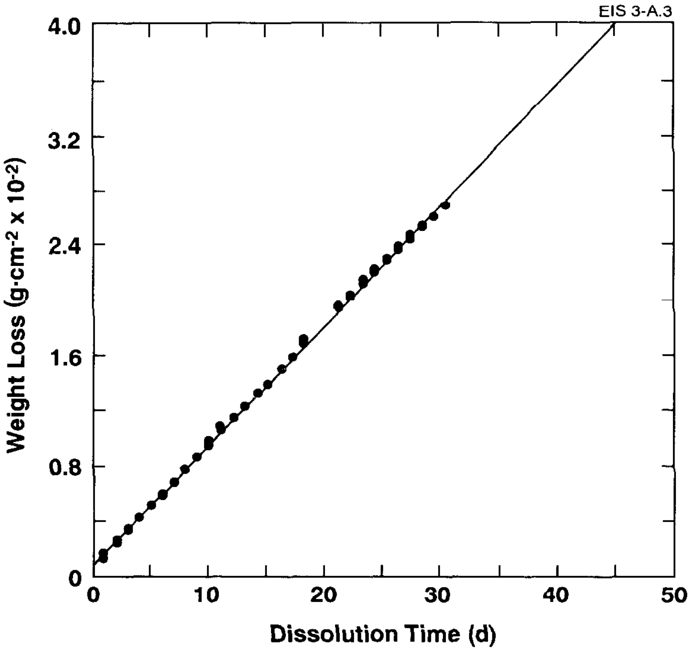

FIGURE A-3: Weight Loss at 100°C in Deionized Water as a Function of Time for Borosilicate Glass 1003 with Best-Fit Line (Harvey et al. 1986).

Harvey and Larocque (1989) presented a model describing dissolution in a finite volume of water that is replenished or through which there is a small flow. To account for the occurrence of saturation and supersaturation of silica in solution, the model was further extended, and the cases of static and low-flow solutions were addressed, as were the possibilities of silicate species precipitating from solution and continued glass dissolution in a silica-saturated solution. These cases were validated by following the dissolution of VYCOR glass in DIW at 100°C at pH 10, with various replenishment rates, and the dissolution of a borosilicate glass in static DIW solution at 100°C that had been buffered to pH 10. Figures A-4a and A-4b show the fit of the model to the observed VYCOR leaching data (Harvey and Larocque 1989).

Having derived and validated models to describe the dissolution of simple glasses, models were developed to account for dissolution of a glass that forms an adherent surface layer of constant thickness. The adherent-surface model was applied to the data published by Macedo et al. (1986) for an SRL TDS-131 glass that was reported to form an adherent surface layer during dissolution. Satisfactory agreement with their data was observed when a mass balance equation was added to the adherent-surface model to account for quantities of the glass matrix that are dissolved and either reincorporated in, or precipitated on, the surface layer (Harvey and Larocque 1990a).

A borosilicate glass, with a composition similar to the French AVH waste glass (which is known to form an adherent surface layer) was corroded at 100°C in DIW buffered to pH 9 under either static or replenished leachant conditions (Harvey and Larocque 1990b). The results indicated that, following an initial dissolution period, the dissolution rate of the glass decreased by at least two orders of magnitude. This decrease is attributed to an adherent surface layer that strongly inhibits further dissolution. No optimization experiments were performed on this composition to investigate methods of further reducing dissolution rates. The model was able to completely describe the dissolution behaviour of the glass including the behaviour after a surface film had formed.

A.9.2.2 Aluminosilicate Glass Dissolution Models

A number of models have been developed to describe the observed radionuclide release from the Chalk River aluminosilicate glass block burial experiment (Section A.5). Harvey and Litke (1984) developed a dissolution model that was based on dissolution into an infinite water source with the glass covered by a precipitated layer that inhibits diffusion of ions through the layer to solution. The model was a good fit to the observed ^{90}Sr field release to groundwater over the time period from 10 d to 20 a. The model suggests that the leach rate may be tending towards a $t^{-0.5}$ (diffusion limited) time dependency at longer times; however, much longer-term release data (>100 a) would be required to verify this prediction. Melnyk et al. (1984) demonstrated that there was good agreement between the leach rate time dependence derived from 17 a of ^{90}Sr concentrations in groundwater downstream of the blocks and those obtained from laboratory leaching results on a glass block. These results indicated a $t^{-0.8}$ to $t^{-1.3}$ time dependence of the leach rate. The field results suggest the

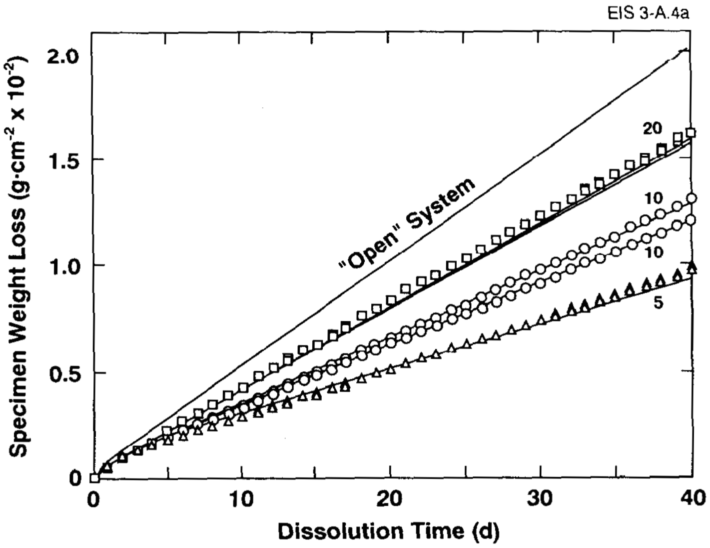

FIGURE A-4a: Experimental Weight-Loss/Time Data for Three Replenishment Rates (5, 10, 20 mL·d^{-1}), Together with Calculated Best-Fit Curves Derived from the Model. The experiment was performed at 100°C in deionized water buffered (Hydrion) at pH 10 at a surface area:volume ratio of 1:10. The entire volume was replenished for the "open system."

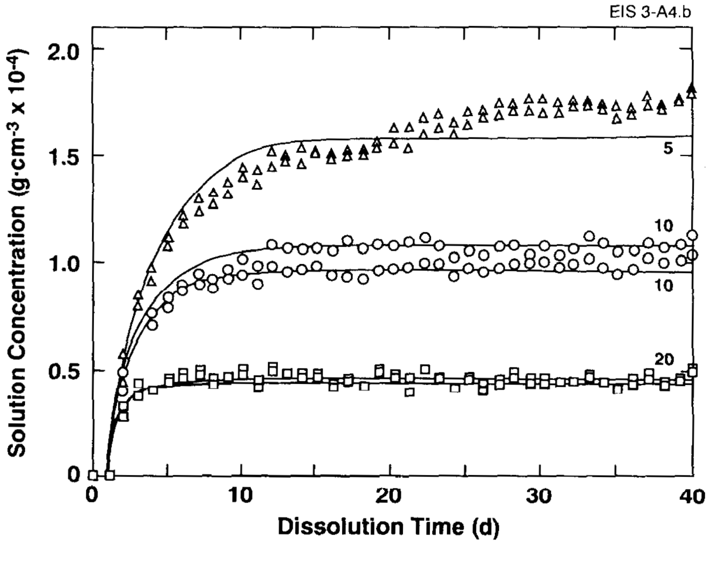

FIGURE A-4b: Solution Concentration/Time Data, Calculated from Experimental Weight Loss, Together with Best-Fit Curves Derived from the Model. The experiment was performed as in Figure A-4a. Replenishment rates were 5, 10 and 20 mL·d^{-1}.

formation of a protective layer on the glass surface that inhibits glass dissolution; however, the presence of such a layer has not been demonstrated by direct observation. Geochemical kinetic models have also been successful in describing the observed field migration behaviour of the released ^{90}Sr (Walton and Merritt 1980, Melnyk et al. 1984) in the soil. Since dissolution is extremely slow at the ambient temperature of the field experiment (~6 to 10°C), and dissolution rates are continuing to decline, the predictions of these models are difficult to verify (it would take several hundreds of years to verify them at these low dissolution rates). Model development for aluminosilicate glasses under conditions expected in a nuclear waste disposal vault would be similar to the development of models for borosilicate glass; however, validation would be necessary and this would need to be carried out at higher dissolution temperatures than those used in the field in situ burial tests to gain any confidence in their long-term behaviour.

A.9.2.3 Sphene Glass-Ceramic Dissolution Model

No modelling work has been carried out on the sphene-based glass ceramics, although a conceptual model has been proposed that is consistent with the observed independent dissolution behaviour of the component glass and sphene phases (Section A.6, Hayward 1988). The conceptual model would involve two independent models: one to describe the dissolution behaviour of the aluminosilicate glass phase, which could be developed from current models on borosilicate glass dissolution; and a second to describe the dissolution of the sphene crystalline phase, based on an understanding of the kinetics and thermodynamic stability of sphene in groundwaters typical of a granite disposal vault. These two models could be combined to provide a model suitable for the assessment of this waste form as a host for the disposal of reprocessing wastes.

A.9.3 SUMMARY OF MODELLING OF GLASS DISSOLUTION

International programs have been successful in developing glass dissolution models based on diffusion and precipitation kinetics, solution saturation and layer formation. These models can describe the observed release behaviour from borosilicate glasses over periods of several years at temperatures up to about 100°C. The work carried out in the CNFWMP has also developed and validated a series of silicate-glass dissolution models that have been validated for both simple glasses and more complex glasses that develop surface layers that may inhibit dissolution. These models also address conditions anticipated in a disposal vault, including static or slowly flowing groundwater, and conditions of saturation and precipitation of species from solution.

Although no formal safety assessment has been carried out by AECL on releases from glass or glass-ceramic waste forms, the principles of how a model can be adapted to provide a source term for safety assessment purposes can be illustrated by taking a simple, conservative scenario. It could be assumed that the waste form would contain radionuclides dispersed homogeneously throughout the matrix, that release to the groundwater would be by congruent dissolution of the matrix at a constant dissolution rate, and that no secondary mineralization, layer formation or retardation through a "leached" layer occurred. It might also be assumed that the concentration of radionuclides in solution would be limited by their solubility and the flow rate of water through the waste vault. Simple models such as this, which have been experimentally verified in this research program, can be cast into a suitable form for generating a source term for performance assessment purposes. The more complex models, and the methodology of using them, do not differ in principle from those currently in use to assess the dissolution of used UO_2 fuel.

Although the models developed internationally and in the CNFWMP have had success with modelling releases over periods of several years, the long-term kinetics and temperature dependence of the dissolution of glasses are not yet well understood and will require continuing experimental studies (Lutze 1988).

A.10 NATURAL ANALOGUES

The models developed to describe glass dissolution have been applied only to laboratory situations for data accumulated over periods of months to a few years. It is necessary, when evaluating waste forms for disposal, to be able to extrapolate, with some degree of confidence, the results of short-term experiments to periods spanning thousands to tens of thousands of years. A number of comprehensive studies have been conducted on naturally occurring volcanic glasses, such as basaltic glasses and rhyolitic glasses, and meteoric glasses and tektite glasses that, depending on their age, have survived thousands to hundreds of millions of years of weathering in the environment. There are certain similarities between the conditions that natural glasses have experienced over geological time periods and the anticipated conditions of a waste glass in a disposal vault that can confirm the kinetic and thermodynamic equations used to describe glass dissolution in laboratory-scale experiments. If the dissolution process in natural glasses is dominated by the dissolution of silica, this can provide a basis for suggesting how nuclear waste glasses might behave over the long term. A summary of these types of comparisons has been reviewed by Lutze (1988), and a more detailed discussion can be found in Ewing and Jercinovic (1987).

Laboratory measurements on dissolution rates of many naturally occurring glasses are generally consistent with the extent of dissolution measured on natural glasses that have corroded in the environment over geological time periods (e.g., Barkatt et al. 1986). In addition, alteration products present on the surface of these naturally weathered glasses show important similarities to altered products observed on the surface of experimental borosilicate glasses, and they can provide important information on the stability of these phases. For example, dissolution studies on natural analogues have identified metastable alteration phases that form over short time periods (Crovisier et al. 1986). Combining this information with the identification of the phases present under natural weathering conditions can provide evidence for the genesis of these metastable phases to more stable phases.

There have been several cases where the long-term dissolution behaviour of naturally occurring glasses has been modelled. One case used a thermodynamic approach (Jantzen and Plodinec 1984, Jantzen 1986) to determine the relationship between the glass dissolution rate (based on silica release) and the extent of hydration and the calculated free energy of hydration. This approach has been reasonably successful in ranking observed durabilities of naturally occurring volcanic glasses and nuclear waste glasses. Chemical speciation and mass transfer codes such as PHREEQE have also been applied (Grambow et al. 1986) to predict the sequences of alteration products resulting from natural glass dissolution, and have had some success in correctly predicting the observed alteration products. International studies continuing on naturally weathered glasses will provide a valuable source of information to test the validity of the kinetic and thermodynamic models used to predict the long-term dissolution rates of waste glasses.

Provided it can be shown that the properties of silicate glasses or crystalline waste forms are similar to naturally occurring glasses or minerals, there may be justification for using these similarities to infer dissolution mechanisms, rate and time dependency and the sequence of alteration product formation, as well as to decide what factors are the most important in determining long-term dissolution behaviour. Natural analogues in themselves may not provide direct proof of waste-form behaviour, but they may provide a basis and rationale for extrapolation of waste-form dissolution behaviour over long time periods.

A.11 LOW- AND INTERMEDIATE-LEVEL WASTE FORMS

In addition to the high-level waste stream from a reprocessing facility, several other low- and intermediate-level waste (LLW and ILW) streams would be generated. These waste streams include fuel hulls and undissolved residues, ion-exchange resins, incinerator ash, various liquid and solid low-level wastes, and off-gases containing ^{3}H, ^{14}C, ^{85}Kr and ^{129}I. The Canadian HLW research program has addressed only some aspects of the capture of ^{85}Kr and the development of potential waste forms for ^{129}I and ^{14}C immobilization. Internationally, solid wastes, such as fuel hulls, are cemented and stored at the reprocessing facility. Ion-exchange resins, used to treat liquid waste streams, and filters, used to remove iodine and other off-gas isotopes, are either stored without treatment or immobilized in cement or bitumen before storage. Considerable work has been done internationally on technologies for the capture and immobilization of off-gas streams and the conditioning and immobilization of dissolver residues. Summaries of these waste stream conditioning and immobilization studies can be found in a series of reviews by Taylor (1990b, 1990c, 1990d, 1991).

Many countries are either planning, constructing or have licensed facilities for the disposal of LLW or ILW arising from either reprocessing facilities or from reactor operation. These strategies involve either deep underground or shallow land burial or a combination of the two (Clelland et al. 1989). Sweden, for example, has completed and licensed an under-sea disposal site for low- and intermediate-level reactor operational wastes

(Hedman et al. 1989, Norrby et al. 1989, Clelland et al. 1989). International strategies for the treatment, conditioning, waste-form characterization and disposal of LLW and ILW have been discussed in a recent symposium (IAEA 1989).

Canada has a LLW management program that addresses waste conditioning, modelling, safety studies and prototype engineering and containment studies for wastes generated by the Canadian nuclear industry. Overviews of the AECL LLW and ILW management program and research on engineered barriers for waste disposal have been presented by Charlesworth and Howieson (1989) and Buckley et al. (1989). Characterization studies on a wide range of low- and intermediate-level waste forms, such as cements and bitumens proposed by the European Communities, have also been described by Brodersen and Nilsson (1989) and are beyond the scope of this document.

A.11.1 HULLS AND DISSOLVER RESIDUES

In general, undissolved fuel hulls, containing activation products and traces of fission products and actinides, would likely need immobilization or containment before storage or disposal. The fuel hulls contain ^{60}Co, ^{55}Fe and ^{125}Sb as major short-lived radionuclide impurities. Beyond 1000 a, the majority of the activity comes from the long-lived isotopes ^{14}C, ^{93}Zr and ^{93m}Nb, with small contributions from actinide residues. A number of methods have been considered internationally for conditioning the hulls, including compaction followed by immobilization in metallic alloys, glass, ceramics, cements, metals or graphite compounds, or melting the hulls to form a dense mass. The most promising matrix materials for immobilization appear to be either a lead alloy or a low-porosity, low-water concrete (Taylor 1990b); however, more advanced materials may well be proven to be superior in the future if the need arises to immobilize fuel hulls in Canada. At present, the hulls arising from international reprocessing facilities are stored either compacted or uncompacted, in stainless steel drums, or they are immobilized in cement before storing. The most promising technique being investigated for the immobilization of the dissolver residues is incorporation in a glass or glass-ceramic waste form (De Regge et al. 1986).

A.11.2 ^{3}H RECOVERY AND WASTE FORMS

Tritium (^{3}H, $t_{1/2} = 12.3$ a) arises mainly from ternary fission in nuclear fuel; minor components arise from nuclear activation of H-containing impurities in the fuel and Zircaloy sheath. The majority of the tritium inventory in a reactor arises from activation of the coolant and moderator and is removed at the reactor site. Up to 60% of the ^{3}H generated in the UO_2 of light-water reactor fuels has been found to migrate into the Zircaloy sheath (Bleier et al. 1984), where it reacts to form hydrides. Measurements on CANDU fuels indicate similar partitioning to the Zircaloy sheath (Tait et al., in preparation). During reprocessing, the tritium remaining in the fuel is retained by the acid solution. Tritium is not currently recovered in commercial reprocessing facilities.

A number of technologies have been developed on a laboratory scale to separate and concentrate ^{3}H from the aqueous reprocessing waste stream;

these include water distillation, hydrogen distillation, electrolysis and H_2/H_2O exchange (Taylor 1991). A pilot-scale removal facility based on electrolysis and isotopic exchange columns has been demonstrated at the Mol demonstration reprocessing facility in Belgium (Hebel et al. 1986). A plant to recover ^3H from the CANDU heavy water moderator has been built at the Chalk River Laboratories and is based on a combination of liquid-phase exchange using a wetproofed catalyst and distillation of hydrogen (Holtslander et al. 1988). A vapour phase catalytic exchange process followed by cryogenic distillation of hydrogen is operated by Ontario Hydro at the Darlington reactor site in Ontario as a commercial recovery system. Although there is limited experience with ^3H extraction processes designed for fuel-reprocessing plants, there is a wide body of knowledge for ^3H removal from aqueous systems in reactors that could potentially be applied to fuel-reprocessing requirements.

Since ^3H has a short half-life, it need only be isolated from the environment for periods of hundreds of years. Thus ^3H could be immobilized in cement and retained in an impervious and durable container until it decayed, or it could be incorporated in a form that is resistant to dissolution by aqueous solutions, such as a hydride of titanium or zirconium. Inorganic solids such as hydrated calcium phosphates may also be worthy of further research. Taylor (1991) has reviewed the current international status of tritium abatement and immobilization.

A.11.3 CARBON-14 RECOVERY AND WASTE FORMS

Nuclear activation reactions of ^{14}N and ^{17}O are the primary production paths for ^{14}C ($t_{1/2}$ = 5730 a) in nuclear power fuels. ^{14}N is present as an impurity, and ^{17}O is the naturally abundant isotope of oxygen present in the UO_2. The ^{14}C generated is contained within the fuel or in the gap region of the fuel and is released mainly as $^{14}CO_2$ or ^{14}CO in fuel dissolver off-gases during reprocessing. (A second source of ^{14}C in the reactor is from activation reactions in the D_2O moderator that produces much larger quantities of ^{14}C than in the fuel. This ^{14}C is removed from the D_2O moderator using on-line ion exchange columns.)

During reprocessing, the CO_2 in the off-gas stream can be removed either by scrubbing with a strongly basic solution (NaOH) followed by precipitation as $CaCO_3$ by addition of $Ca(OH)_2$, or by direct reaction with $Ca(OH)_2$ or $Ba(OH)_2 \cdot 8H_2O$ slurries or solids (Taylor 1991). Traces of CO can be removed by catalytic oxidation at ~500°C to produce CO_2.

The need to limit ^{14}C releases to the environment has been recognized, and a number of waste forms are favoured for ^{14}C immobilization. The most widely favoured are $BaCO_3$ and $CaCO_3$, because of their low solubility. Scheele and Burger (1982) conducted a review of the candidate waste forms for ^{14}C; Taylor (1987, 1991) reported on a wide variety of solid inorganic carbonates and compared solubilities and stabilities at 25°C. Reduced carbon waste forms, such as graphite, metal carbides or organic materials, were not considered in these studies.

Most of the alkali metals, alkaline earths, main group elements, transition metals, and lanthanides and actinides will form carbonates. Taylor (1987) applied two criteria, solubility and thermal stability, based on solid metal carbonate and metal carbonate/oxide or carbonate/hydroxide thermodynamic equilibria, to determine which solids showed the greatest promise as a waste form for ^{14}C. This review dismissed a number of classes of compounds from consideration, including the alkali carbonates (high solubility), beryllium carbonates (toxicity) and Mg carbonates (marginal stability). Most second and third row transition elements were either toxic, unstable or too soluble.

The carbonates of Ca, Sr and Ba are quite insoluble ($K_{sp} \sim 10^{-8}$ $mol^2 \cdot dm^{-6}$, where K_{sp} is the solubility product) and are thermally stable. Their performance as a waste form is limited only by their increasing solubility as the pH decreases below ~11. The abundance of Ca in groundwaters and minerals would tend to favour a $CaCO_3$ waste form, even though Sr and Ba carbonates have lower solubilities. Disposal of such a waste form in a calcite-saturated groundwater environment may be an acceptable approach, although the importance of isotope exchange equilibria with ^{13}C, solid speciation and possible alteration product formation needs to be assessed.

Other systems that were identified as potential candidates are lead carbonate (hydrocerussite), bismuth carbonate (bismutite), manganese carbonate (rhodochrosite), and the lanthanide series carbonates (all naturally occurring phases in mineral deposits).

Taylor (1987) concluded that the calcium and barium carbonates, either alone or incorporated in a concrete, are favoured as waste forms for ^{14}C immobilization and disposal, although care must be taken in selecting the appropriate environment to ensure their stability and low solubility. Bismutite, hydrocerussite and rhodochrosite would be sufficiently stable and are lower in solubility than $CaCO_3$, and would warrant further consideration under near-neutral disposal conditions. Areas needing further investigation include radiation stability, the possible loss of ^{14}C by isotopic exchange with natural aqueous carbonate, and mechanisms of retardation of groundwater transport by exchange with natural carbonate minerals.

A.11.4 IODINE-129 RECOVERY AND WASTE FORMS

Iodine-129 ($t_{1/2} = 1.6 \times 10^7$ a) is one of the more abundant of the long-lived fission products in used fuel (~0.045 g/kg initial U). The most stable form of iodine is I^-, which is highly soluble, does not sorb significantly on most mineral surfaces, and is not significantly incorporated into glass or ceramic waste forms because it is volatilized in the immobilization process. For effective control of ^{129}I, it must be removed as an off-gas in the dissolver stage, or it may become dispersed in the numerous separations waste streams. This can be accomplished by volatilizing the iodine as I_2, followed by precipitation or sorption. Current technology involves removal from off-gas streams by caustic scrubbers or by sorption on silver-impregnated porous silica type filters ("AC-6120") (Hebel et al. 1986). The collected ^{129}I could then be concentrated and chemically converted to iodic acid or a metal iodate before immobilization; however, the choice of an appropriate waste form is still unresolved in international programs.

Taylor (1990d) reviewed methods for ^{129}I immobilization and focused on three classes of solids: metal iodides (Taylor et al. 1989), metal iodates and silicates. The release of ^{129}I from iodides and iodates is likely to be solubility-controlled, whereas release from silicates is likely to be kinetically controlled.

A.11.4.1 Metal Iodides and Iodates

Simple iodides or iodates are quite soluble in water ($>10^{-3}$ $mol \cdot L^{-1}$) or are susceptible to hydrolysis in near-neutral solutions. As a consequence, very few natural minerals contain iodine as a component. However, iodide minerals of Cu, Pb, Hg and Ag, and iodate salts of Ca, Sr, Ba and Bi (Bi_5O_7I, bismuth oxyiodide) have been identified as potential waste-form candidates (Taylor et al. 1989).

Taylor (1990d) developed a general approach to assessing the thermodynamic stability of iodine waste forms that included studies of solubility, hydrolytic and thermal stability, redox chemistry of both iodine and the cationic component, anion displacement reactions and metal complexation reactions. This assessment concluded that AgI and ($Bi_5O_7I + Bi_2O_3$) would be the most promising inorganic iodides for ^{129}I immobilization and disposal. Silver iodide showed greater resistance to anion displacement than bismuth oxyiodide in common groundwaters as demonstrated by the coexistence of AgI and BiOCl in some natural mineral assemblages. The stability of AgI is more limited than Bi_5O_7I under reducing conditions. The most suitable environment for disposal of either waste form would be cool (<60°C), non-reducing groundwaters that are low in dissolved salts.

Iodates, as a class, are unstable in reducing environments where reductive dissolution as iodide occurs, and would be far inferior to AgI as a waste form. However, iodates should not be completely dismissed as a waste form under oxidizing disposal conditions, since they are compatible with some iodine-collection methods that convert iodide to iodic acid or other iodates in the process, and since iodates (unlike iodide) are more significantly sorbed on some mineral surfaces (e.g. iron oxides), which may mitigate releases from iodate waste forms.

A.11.4.2 Silicate-Based Waste Forms for Iodine

Discussion of silicate-based waste forms can be divided into two main areas: the production of an iodide-sodalite silicate-based waste form, and the direct disposal of iodine trapped on solid sorbents.

Iodide-Sodalite

Sodalite is an aluminosilicate mineral capable of incorporating a variety of anions, such as chloride or iodide, in its structure (Barrer and Cole 1970). Although natural sodalites contain only trace quantities of iodide (Brehler and Fuge 1978), synthetic materials can be prepared that approach the theoretical stoichiometry, $Na_4Al_3Si_3O_{12}I$, which would contain 22 wt.% of iodine.

The synthesis of iodide-sodalite has been discussed by Taylor (1990d); it involves preparation from a mineral and chemical precursors using a variety of high-temperature synthetic techniques. Preliminary measurements of the dissolution behaviour of iodide-sodalite indicate that it is comparable to AgI (when each material was incorporated in portland cement-based concrete (Burger et al. 1981)). After an initial rapid release of I^-, attributed to either residual NaI or surface depletion, Dunn et al. (1985) observed an I^- release at 50°C in deionized water of 6.5×10^{-11} $kg \cdot m^{-2} \cdot s^{-1}$, which is similar to the release observed from glass waste forms for HLW solidification.

Thermodynamic data are not available for iodide-sodalite, but the iodide is likely to exchange with groundwater chloride. This would be hindered, however, by the very low mobility of the large iodide ion between "cage" sites in the sodalite network structure (Barrer and Cole 1970). Vance et al. (1981b) also point out that sodalite is unstable at high-silica solution concentrations and in acidic solutions; thus, its effectiveness as a waste form may well be limited by the kinetics of alteration reactions under such conditions.

In conclusion, since an iodide-sodalite waste form would be kinetically rather than thermodynamically stable, it is difficult to compare it directly with other candidate materials. It appears to be competitive with AgI as a candidate waste form, and, hence, the most appropriate choice for detailed dissolution experiments in future. However, dissolution data in different representative groundwaters are required before iodide-sodalite could be selected or rejected as a waste form. Although it cannot be prepared by low-temperature chemical methods, the conditions for its synthesis do not appear to be unduly demanding.

Solid Sorbents

It has been suggested that solid sorbents, such as silver zeolites or AC 6120, which have been developed for removal of iodine from reprocessing-plant process streams, may be appropriate waste forms for final disposal of ^{129}I, either alone or in combination with cement (Taylor 1990d). A modification of this approach is to recover iodine from the silver-containing matrix and retrap it on a lead zeolite, thereby minimizing silver consumption.

Most experimental work on solid sorbents has, understandably, dealt with their performance under process conditions and with their thermal stability (McKay et al. 1981). Burger et al. (1981) compared the performance of silver mordenite, lead zeolite and several inorganic iodides and iodates, all combined with portland cement. Silver-impregnated silicate sorbents did not perform as well as AgI in cement or iodide sodalite waste forms, but should not be ruled out as a candidate waste form without further dissolution tests under conditions relevant to the Canadian waste disposal environment.

A.11.5 ^{85}Kr RECOVERY AND WASTE FORMS

Taylor (1990c) has reviewed the literature on methods to separate and immobilize ^{85}Kr arising from fuel dissolution or prior treatment of nuclear fuel during reprocessing. Krypton-85 ($t_{½}$ = 10.7 a) is a fission product residing in the fuel matrix, present at grain boundaries in the fuel and in the fuel-sheath gap region. Part of the ^{85}Kr inventory is released during desheathing of the fuel, and the remainder is released during fuel dissolution. Recovery of ^{85}Kr from the off-gas stream relies on physical methods, and cryogenic distillation techniques, used by the air-products industry, have been widely studied for ^{85}Kr removal. This technology is being demonstrated in most countries investigating reprocessing. Fluorocarbon absorption techniques, adsorption on mordenite (a molecular sieve) and adsorption on charcoal have also been investigated for ^{85}Kr abatement; but cryogenic processes appear to be the most advanced (Taylor 1990c).

After recovery, ^{85}Kr would need storage or immobilization for periods of at least 100 and perhaps several hundred years before it decays to insignificant levels. Simple approaches to immobilization include storage as a compressed gas in impermeable containers, or sorption of the gas on zeolites or activated carbon at atmospheric pressure followed by containment in a metal vessel. More sophisticated methods include implantation in a metal matrix by the ion bombardment of a metal that is being built up as a layer by sputtering. Stable products can be produced that contain a high concentration of krypton. Another approach involves incorporation by absorption in zeolite or other silicate minerals at high temperature and pressure to increase the concentration of krypton in the mineral, followed by encapsulation of the material in metal containers. (Taylor 1990c)

A.11.6 MODELLING OF DISSOLUTION OF LOW- AND INTERMEDIATE-LEVEL WASTE FORMS

The development of models to describe release from waste forms has been concentrated almost entirely on high-level waste forms. Although considerable data are available on the durability of waste forms for the immobilization of ^{129}I or ^{14}C, no models have been developed to describe their dissolution. In general, a dissolution model for a crystalline or "pure" material waste form, such as $CaCO_3$ or AgI, would likely be based on the thermodynamic stability and solubility. A model for low- and intermediate-level wastes immobilized in cements or glasses would likely be similar to models for glass or glass-ceramic dissolution. Models for release from a waste form for fuel hulls would again be based largely on a model to describe the dissolution of the host matrix, and radionuclide release would be limited by the dissolution behaviour of the fuel hulls themselves. Since ^{3}H and ^{85}Kr would likely be stored for extended periods, it may not be necessary to develop detailed release models for their dissolution behaviour.

A.11.7 SUMMARY OF LOW- AND INTERMEDIATE-LEVEL WASTE FORMS

There have been numerous international studies on technologies for the capture, conditioning and solidification of dissolver residues, fuel hulls and off-gas streams from a reprocessing facility. Canadian studies have addressed some aspects of immobilization of ^{14}C, ^{129}I and ^{85}Kr wastes and have suggested a number of potential waste-form candidate materials that would require detailed examination should reprocessing technology be implemented in Canada. The performance of the waste form under anticipated disposal conditions, its ease of handling, and cost are all important factors to consider in evaluating the feasibility of any particular process.

A.12 VOLUMES OF WASTE ARISING FROM VITRIFICATION OF REPROCESSING WASTES

In addition to recovery of fissile material, the reprocessing of used fuel could be viewed as a method to potentially reduce the volumes of radioactive wastes that would require disposal, relative to the volumes involved in the direct disposal of used fuel. To make such comparisons, it is necessary to assume a reprocessing and vitrification technology for CANDU fuel. The French AVM facility uses the Purex process and produces radioactive borosilicate waste glass in containers, and can be used as a reference process to illustrate the expected volumes of wastes arising were CANDU fuel to be processed in a similar manner. In addition to the HLW stream, low-level and intermediate-level liquid and solid wastes, as well as gaseous wastes, are generated that could require immobilization. The predicted arisings from these waste streams for the reference CANDU fuel using AVM process technology have been compared with available data on wastes arising from U.S., U.K. and French reprocessing facilities (Harvey, in preparation (b)).

Assuming that an annual inventory of 1200 Mg U (63 400 used CANDU fuel bundles per year) would be handled for direct disposal, one can estimate the total volumes of LLW, ILW and HLW generated in reprocessing the equivalent amount of reference fuel (685 $GJ \cdot kg^{-1}$ U burnup, 10-a cooled) for a 6 wt.% HLW fission-product oxide loading in glass (Harvey, in preparation (b)). A summary of these waste volumes is given in Table A-4. If the separated uranium product stream is considered to be a waste (the uranium contains ~0.2 wt.% ^{235}U) and if the separated plutonium stream is recycled into new fuel, the total volume of the containers of all solidified wastes (LLW, ILW and HLW) arising each year for potential disposal is predicted to be ~1038 m^3 (assuming the AVM type of container discussed in Section 3.5.4.5 of the main text). This could be reduced to ~854 $m^3 \cdot a^{-1}$ if the U waste stream is considered to be a resource and is enriched and recycled as new fuel. On the basis of the used fuel reference container design described in Section 3.5.2.2 of the main text, direct disposal of the same amount of fuel would generate ~880 containers per year with a total volume of ~622 $m^3 \cdot a^{-1}$ (72 bundles per container, 0.707 m^3 per container) plus about 26 $m^3 \cdot a^{-1}$ of solidified ion exchange resin from fuel handling and decontamination processes (Harvey, in preparation (b)). This comparison indicates that there would be no reduction in the total volume of wastes requiring disposal as a result of reprocessing and recycling CANDU fuel. Further developments in solidification technology could reduce the volume of some low- and intermediate-level solidified reprocessing wastes. For example, compaction of Zircaloy hulls and vitrification of some LLW could reduce the

TABLE A-4

VOLUMES OF WASTE ARISING FROM REPROCESSING 1200 Mg U (63 400 BUNDLES) OF USED CANDU FUEL PER YEAR*

Waste	Volume (m^3)	
LLW (Incinerated and Bituminized)	44.5	
LLW (Bituminized Solids)	288.3	
Volatiles: ^{14}C	2.25	
^{129}I	1.31	
^{85}Kr	0.75	
ILW: (Bituminized)		
Ion-exchange resins	20.0	
Liquids	82.5	
Solids	6.4	
Zircaloy Hulls (Cemented)	300.0	(subtotal 746)
HLW (Glass)	107.5	(subtotal 853.5)
Dried Uranium Waste Stream	185.0	
Total =	1038.5	

* Assuming Purex reprocessing, HLW vitrification in glass (6 wt.% fission-product oxide loading) (Harvey, in preparation (b)).

volume of the low- and intermediate-level wastes from ~746 $m^3 \cdot a^{-1}$ to ~135 $m^3 \cdot a^{-1}$ (Harvey, in preparation (b)).

To provide some evidence that these projections are comparable to waste arisings from operating reprocessing facilities, the results were compared with published information from facilities in the U.S., U.K. and French programs (Harvey, in preparation (b)). The foreign solidified waste volumes were based on reprocessing LWR fuel, which has a burnup 4 to 6 times that of CANDU fuel and thus has proportionally higher fission-product inventories. A comparison with CANDU fuel can be made by normalizing the data for pressurized-water reactor (PWR) fuel to an equivalent CANDU fuel burnup (685 $GJ \cdot kg^{-1}$ U), by assuming that the waste solidification processes are the same, and by using the same waste loading (6 wt.%). The waste arisings for the disposal of CANDU fuel reprocessing wastes and PWR fuel reprocessing wastes derived by Harvey (in preparation (b)) using this methodology are shown in Table A-5; they are based on a reprocessing-plant throughput of 1200 Mg U per year. (Note that uranium and LLW volumes in Table A-5 are based on uncompacted volumes and are thus higher that those in Table A-4.) Table A-5 shows that the projected waste arisings for reprocessed CANDU fuel are within the variations in volumes known to arise from operating reprocessing facilities.

The volume of vitrified high-level waste from reprocessing 63 400 CANDU fuel bundles per year would be about 107 $m^3 \cdot a^{-1}$ (206 containers, 0.522 m^3 per container), which is a factor of about 6 lower than the volume for direct disposal containers (622 $m^3 \cdot a^{-1}$, 880 containers). However, since the total amount of radioactive, heat-producing fission products in the vitrified waste is the same as in the original UO_2 fuel, the total heat generated by all the vitrified-waste containers is equivalent to that generated by all the used-fuel containers. Since there are about four times as many used-fuel containers as vitrified-waste containers, the heat load per vitrified-waste container would be about a factor of four higher than that of a used-fuel disposal container. To maintain a container skin temperature of ~100°C, and an average vault temperature equivalent to the used-fuel disposal vault design (Simmons and Baumgartner 1994), the vitrified-waste containers would either require a larger spacing, or the waste loading per container would need to be decreased, which would result in a larger number of containers. If the vitrified-waste containers were cooled for a longer time period before disposal (50-100 a), to allow the

TABLE A-5

COMPARISON OF PROJECTED WASTE ARISINGS FROM REPROCESSING CANDU FUEL WITH ACTUAL ESTIMATES OF WASTES ARISING FROM EXISTING REPROCESSING PROGRAMS* (m^3/a)

	CANDU	U.S.	U.K.	French
HLW (glass)	107	144-156	76.8	60-80.4
U + LLW (solids)**	5868	2136-4476	21360-41280	4680-53760
Fuel Hulls (cemented)	300	386-492	708	432-480
^{14}C ($CaCO_3$)	2.25	0.324	0.432	-
^{129}I	1.31	1.08-2.38	1.44	0.8
^{85}Kr	0.75	1.02-1.15	0.6	-

* Harvey (1990). Waste volumes from U.S., U.K. and French processes have been corrected to a burnup of 685 $GJ \cdot kg^{-1}$ U, a waste loading of 6 wt.% fission-product oxide, and a reprocessing-plant throughput of 1200 Mg U per year.

** Uncompacted and non-incinerated basis.

short-lived heat-generating fission products ^{90}Sr and ^{137}Cs ($t_{½}$ ~ 30 a) to decay, the vault volume required for disposal could be decreased; however, this would be true for either vitrified wastes or used-fuel waste. The vault volume required for disposal is thus directly related to the radioactive fission-product content of the waste containers. Thus, a disposal vault for used CANDU fuel would be approximately the same size as for vitrified waste if the same maximum container surface temperature constraint was applied.

The decay characteristics of a 10-a-cooled Bruce A CANDU fuel bundle can be seen from the activity and decay heats as a function of disposal time (see Figures 2-5 and 2-7 in the main text). In general, the decay characteristics for fuel-reprocessing wastes would be very similar to used-fuel decay characteristics except that, because almost all the Pu is removed during reprocessing, the activity and decay heats at times longer than 500 a decrease more rapidly for reprocessing wastes than for used fuel. Fuels with higher burnup would produce similar curves, but the activity and heat generated would be proportionately higher.

A.13 ADVANCED FUEL STRATEGIES AND EFFECTS ON VOLUMES OF WASTES ARISING FROM FUEL REPROCESSING

A.13.1 ADVANCED FUEL CYCLES

In the preceding discussion it was assumed that the Purex reprocessing technology would be used with CANDU fuel. The CANDU reactor was developed to allow the economical use of natural uranium fuel. This results in a fuel that is considerably lower in burnup (~700 GJ·kg^{-1} U), at discharge from the reactor, than fuels currently used in other power reactor designs (e.g., ^{235}U-enriched LWR fuel is typically a factor of 4 to 5 higher in burnup). Advanced CANDU fuel cycles that operate at a higher burnup and that could have significantly enhanced economics over the natural U fuel cycle have been considered (Moeck et al. 1989).

Advanced fuel cycles are being considered that range from slightly enriched uranium (SEU) or recovered uranium (RU) to mixed oxide Pu/U (MOX and TANDEM) and thorium cycles. The SEU and RU fuel cycles are currently the only cycles of economic interest for CANDU reactors (Moeck et al. 1989). The SEU cycle would use uranium oxide fuel enriched to about 1.2 wt.% in ^{235}U (natural UO_2 fuel has 0.7 wt.% ^{235}U). The RU fuel cycle would use either the recovered uranium from reprocessed LWR fuel or make direct use of the discharged LWR fuel, which has a ^{235}U content of about 1 wt.% still left in the fuel. The SEU fuel could achieve a burnup about three times higher, and the RU fuel about two times higher, than the average burnup achieved with natural U CANDU fuel.

The Pu/U fuel cycle is based on using both the U and Pu recovered from reprocessing either natural CANDU fuel or fuel discharged from LWR reactors (or adding the recovered Pu to natural U), to produce a new fuel whose burnup would be equivalent to SEU fuel. Another alternative is the thorium cycle, which would use a $(Th,Pu)O_2$ fuel in a CANDU reactor. This fuel produces ^{233}U, which would then be recovered by reprocessing and the ^{233}U and Pu fractions would be recycled back into the thorium fuel. This cycle offers the opportunity for a near-breeder reactor, or uranium self-sufficiency (Moeck et al. 1989). Burnups in the thorium cycle would be two to four times that of natural UO_2.

The implementation of these fuel cycles could have a potential effect on the volumes of waste generated that would require disposal. Increasing the fissile enrichment of the fuel would allow higher fuel burnups (and longer fuel residence times), which would proportionately increase the fission product and actinide concentration in the fuel, but would reduce the quantity of fuel discharged per kilowatt of electrical energy produced. The higher fission-product concentration in these fuels would thus result in higher heat generation per discharged bundle. Disposal of these fuels without reprocessing would thus result in a higher heat generation per container, and in order to maintain a container surface temperature below 100°C, the fuel would require extended cooling. The decay heat generated by the reference CANDU fuel is about 0.24 $W \cdot kg^{-1}$ U after 10-a cooling, dropping to 0.06 $W \cdot kg^{-1}$ U after 100 a (a factor of 4 reduction (Tait et al. 1989)). If the burnup were increased by a factor of 4, for example, the heat would increase proportionally and the fuel would thus need to be cooled for about 100 a to reduce the heat to that produced by natural CANDU fuel after 10-a cooling. Alternatively, the fuel disposal containers could be spaced farther apart in the disposal vault to achieve the desired heat loading. A full economic analysis of the implications of implementing advanced fuel cycles would be required to determine whether disposal costs would decrease. An analysis of the impact of these fuel cycles on the volume of waste generated per kilowatt hour of electrical energy produced would also be needed. The impact of introducing advanced fuel strategies on the total wastes generated in the entire fuel cycle (mining, fabrication, reprocessing, U/Pu recycle) is beyond the scope of the CNFWMP but would need to be considered.

The thorium cycle relies on reprocessing to separate the ^{233}U and Pu fractions for recycle into fresh thorium reactor fuel. This would require the development of reprocessing technologies other than the Purex process. Although these technologies have been investigated on a small scale at AECL, considerable development would be required to bring this technology to a full scale if this fuel cycle were to be adopted in CANDU reactors. These reprocessing technologies would likely produce a waste stream whose composition would be significantly different from a Purex waste stream and would likely contain different process chemicals. As a result, a waste form that was specifically tailored to accommodate the reprocessing wastes from this fuel cycle might be required.

Although the advanced fuel cycle waste streams are likely to have different compositions, the HLW components (fission products and actinides) would differ little from the natural U cycle except that their total inventories in the fuel would be proportional to the burnup of the fuel. Thus, the concentration of wastes in the reprocessing streams would be higher using these fuels. The actual volume of solidified waste, however, would continue to be governed by such constraints as the waste loading in the waste form and the cooling time before disposal, in order to maintain temperature limits in the waste vault. As a result, for an equivalent amount of electricity generated, the size of a vault for the disposal of CANDU fuel would be similar to that required for disposal of enriched fuel, although the number of containers required would be greater for CANDU fuel.

A.13.2 TRANSMUTATION OF ACTINIDE WASTES

Another technology that has been discussed internationally as a waste management strategy is the partitioning and transmutation of primarily long-lived actinides and some fission products. This technology has been discussed in detail with respect to the U.S. waste management program (Ramspott et al. 1992). The technology requires that the long-lived actinide radionuclides first be partitioned (separated) by reprocessing the fuel. This is followed by the use of fast-neutron reactors or proton accelerators (Venneri et al. 1993) to activate (transmute) these radionuclides to other shorter-half-life nuclides or stable nuclides for disposal. This technology, although theoretically possible, is currently in the research stage. Ramspott et al. (1992) concluded that transmutation is not an alternative to the geological disposal program in the U.S., and that there are no cost or safety incentives to introduce transmutation into the high-level waste management strategy. The conclusions of Ramspott et al. were based on their judgement that the risk from radioactivity from a disposal vault is very low and that removal and transmutation of the actinide products would not significantly reduce this risk. Transmutation would likely result in an increase in the volumes of low- and intermediate-level wastes that would require disposal. Ramspott also concluded that, although the actinide inventory that would go to a repository would be greatly reduced by transmutation, the total number of reprocessed-waste containers destined for the waste vault would not be much different from the number of used-fuel containers. Transmutation strategies are also discussed in the Environmental Impact Statement (EIS) (AECL 1994).

A.13.3 ADVANCED REPROCESSING TECHNOLOGIES

New developments in the area of chemical reprocessing could potentially reduce the total volume of wastes requiring disposal. These improvements involve "dry" or pyroreprocessing UO_2 fuels and are in the research and development stage (Selvaduray et al. 1979, Hoyt and Rhee 1979, Ramspott et al. 1992). These processes could reduce or eliminate the wet chemical separation steps and reduce the volumes of processing chemicals required; they could, thus, lead to significant reductions in volumes of low- and intermediate-level waste streams. There would be no reduction, however, in the volume of separated uranium waste that would be contaminated with fission-product wastes and would require disposal in an underground vault.

A.14 SUMMARY OF THE IMMOBILIZATION OF FUEL-REPROCESSING WASTE

The technology for reprocessing UO_2 reactor fuels to remove fissile material for recycling in new reactor fuel is well established internationally, as is the process for producing borosilicate glass waste forms for the vitrification of the liquid high-level wastes that arise from reprocessing. These processes have advanced to industrial-scale application. For example, France has been reprocessing fuels since about 1958 and has been producing containers of high-level borosilicate waste glass since about 1969; the U.K. has been reprocessing fuels since about 1952 and has constructed new reprocessing and vitrification facilities at Sellafield.

The application of roto-spray and fluid-bed calciners has been demonstrated in the CNFWMP for denitrating the simulated liquid reprocessing wastes to produce a solid calcined waste. The continuous production of both borosilicate glasses and titanosilicate glass-ceramics containing simulated (non-radioactive) reprocessing wastes has been demonstrated using a continuously fed joule-heated ceramic melter, as has the batch crucible production of aluminosilicate glass blocks containing radioactive reprocessing wastes. Off-gas technology has been demonstrated for the abatement of NO_x.

Borosilicate glasses are accepted internationally as the preferred waste form for the immobilization of high-level reprocessing wastes and there is a wide body of published data to support the understanding of the behaviour of the chemical and physical properties of the glasses as a function of their composition. The aqueous dissolution behaviour and mechanism of dissolution of borosilicate glasses are well understood, as are the factors most likely to affect the durability of the waste form. The parameters affecting the fabrication of these waste forms have been identified but they would need to be specifically measured for any chosen waste form.

Dissolution experiments on borosilicate glasses studied in the CNFWMP indicate that their dissolution performance is comparable to borosilicate glasses developed internationally, and that such glasses would be a suitable waste form for the disposal of Purex-type wastes that might arise from future reprocessing of CANDU fuel. High-silica borosilicate glasses have been developed that offer increased resistance to aqueous dissolution; however, these high-silica glasses would require higher fabrication temperatures and would require more complex fabrication technology.

Aluminosilicate glasses have been developed that offer a higher dissolution resistance than most borosilicate glasses, again at the expense of higher fabrication temperatures. A 30-a burial experiment on one aluminosilicate glass composition has confirmed the exceptional durability of this glass under flowing surface-aquifer conditions. Both laboratory dissolution tests and field burial tests have indicated that this class of glasses may form an altered surface layer that strongly inhibits dissolution. The field burial experiment is the only demonstration under natural groundwater conditions that has monitored the long-term release of radionuclides from a glass waste form.

Sphene-based glass-ceramics have also been developed that have a higher durability than most borosilicate glasses, and they have the additional benefit of incorporating virtually all of the actinide species and a majority of the long-lived fission products in a thermodynamically stable sphene crystalline phase. The remainder of the waste ions have been shown to be incorporated in the highly durable aluminosilicate glass phase in these glass-ceramics. The glass-ceramics also offer the potential of using fabrication processes similar to conventional borosilicate glass production technology with only a moderate increase in fabrication temperature and technical complexity.

The dissolution behaviour of glasses and glass-ceramics has been examined in the presence of γ-radiation fields comparable to those that would be present outside a waste container during the period from 20 to 500 a after disposal. In no case was an increase in dissolution rate observed that was more than a factor of five above that of waste forms corroded in the absence of a gamma field. In general, the effects of radiation damage and radiolysis are not expected to significantly increase the dissolution rate of the waste forms.

The development of models to describe borosilicate glass dissolution is internationally well advanced; in the CNFWMP, there has been considerable success with the development of variations on these models to describe silicate-glass dissolution. These models have been able to describe dissolution under both flowing and static dissolution conditions and the dissolution of both simple glasses and more complex glasses that develop alteration layers on their surface. These models could, in principle, be extended to describe the dissolution of aluminosilicate glasses, and, if combined with a thermodynamic model to describe the dissolution of crystalline phases, could be extended to glass-ceramics.

Other waste forms, such as Synroc, ceramics, glass-ceramics, or cement-based products have also been developed in international programs. The fabrication of most of these alternative waste forms has not been demonstrated on a large scale or a fully radioactive industrial scale; they would require substantial process development work to bring them to the current status of borosilicate glasses. Synroc is one of the more advanced alternative waste forms and has been found to be more durable than conventional borosilicate glasses, particularly under hydrothermal dissolution conditions. Synroc is well characterized and inactive products have been successfully produced on a large scale. Testing of a fully active process would be required to evaluate the industrial application of this fabrication technology, and further tests would be required to assess the applicability of this waste form to any specific geochemical disposal environment.

A direct comparison of the dissolution resistance of borosilicate glass waste forms and alternative waste forms has not been performed. In choosing the most appropriate waste form for any future reprocessing of CANDU fuel, it would likely be necessary to compare several of the most promising materials under the actual geochemical conditions of the site selected for a disposal vault. Detailed studies would also be required to optimize the waste form to the disposal environment and the technology and fuel type chosen for reprocessing. The long-term kinetics of the dissolution behaviour would need to be addressed to ensure a detailed knowledge of the dissolution mechanism of the waste form, as would studies on the effect of temperature and the thermodynamics and kinetics of the formation of alteration phases on the surface of glasses. Studies on natural analogues of glasses and mineral phases would provide valuable corroboration for the models and understanding of the genesis of alteration phase formation. In addition, a full safety assessment, similar to the assessment performed in the EIS for used-fuel disposal, would have to be performed using models developed to describe the dissolution behaviour of the selected waste form. Broader issues, involving a risk assessment of reprocessing and vitrification facilities would also need to be addressed to determine if reprocessing is a desirable option.

Although not addressed in detail in the CNFWMP, the development of waste forms for low- and intermediate-level wastes would also have to be addressed in any future reprocessing program. The development of waste forms for these classes of waste is well advanced internationally and several countries have implemented programs for their immobilization and disposal in a licensed facility. Research on specific waste forms suitable for the immobilization of specific radionuclides, such as ^{3}H, ^{14}C, ^{85}Kr and ^{129}I, are ongoing in most international programs, and no specific candidate materials have been chosen as being most appropriate for these wastes. Several candidate materials have been defined or studied in the CNFWMP for the immobilization of ^{14}C and ^{129}I waste forms under the anticipated geological conditions of the conceptual disposal vault. Further research in this area would be required to optimize a preferred waste form; detailed characterization under specific disposal conditions would be necessary, and models to describe the dissolution performance of the waste form would have to be developed.

A study of the volumes of waste likely to arise from a facility to reprocess CANDU fuel has shown that the total volume of solidified waste produced at a reprocessing facility would not be significantly different from the volume of used fuel that would be disposed of in the direct disposal strategy. Although the actual volume of vitrified high-level waste from reprocessing would be about a factor of six lower than the volume of used-fuel containers, the vault volume required for disposal of either waste form would be the same because of the heat constraints in a waste vault. There are a number of possible scenarios that might be considered to reduce the volume of both used fuel discharged from a reactor and the volume of waste that would be generated if these fuels were reprocessed. The introduction of advanced fuel cycles, with enriched fuels that would achieve a higher burnup and thus a lower volume of fuel discharged from the reactor, would not result in any reduction in the required volume of the disposal vault, because of their higher heat generations. Alternative technologies, such as actinide transmutation and improved fuel-reprocessing technologies are unlikely to significantly reduce the volumes of waste requiring disposal, or to reduce the long-term risks from a disposal vault. It is unlikely that any decision to reprocess used fuel would be made exclusively on the basis of potential reductions in the volume of solidified high-level waste. In addition to any economic considerations, any decision in the future to reprocess CANDU fuels could only be based on the safety of the entire fuel cycle (reprocessing, vitrification and disposal) for the reprocessing option compared with the safety of the option for the direct disposal of used fuel.

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APPENDIX B

ALLOWABLE THROUGH-WALL STRAIN IN TITANIUM-SHELL CONTAINERS

(after Teper 1988)

CONTENTS

B.1 RELEVANT BASIC PRINCIPLES

B.1.1 PLASTIC DEFORMATION OF MATERIALS UNDER LOAD

Consider a small cube of metal of unit dimensions on each side. If the cube is made to deform plastically by the application of a load that causes the material to be stressed above its yield stress (or "yield strength"), its shape will change; however, to a good approximation, its volume, V, will remain constant (Dieter 1986).

Consider first the case where the cube is loaded in tension to deform plastically along one axis only, e.g., along the y axis, by the application of a load, P_y (Figure B-1). The cube is loaded sufficiently to deform the material by an amount, D_y, or simply, D. In maintaining the condition of constant volume, the cube will shorten (compress) by an amount d_x along the x direction, and by d_z in the z direction. Mathematically,

$$\begin{aligned} V = 1 &= (1 + D)(1 - d_x)(1 - d_z) \\ &= 1 - d_x - d_z + d_x d_z \\ &\quad + D - Dd_x - Dd_z + Dd_x d_z \quad . \end{aligned} \tag{B.1}$$

Assume, for now, that the second- and third-order terms can be neglected.[1] Then,

$$1 = 1 - d_x - d_z + D$$

or

$$D = d_x + d_z \quad .$$

Assuming the material behaves isotropically and $d_x = d_z = d$, we obtain

$$d = D/2 \quad . \tag{B.2}$$

Consider next the case in which the material is subjected to biaxial loads, P_x and P_y, both of which cause the material to be stressed above its yield stress in the direction of each load, i.e., along the x and y axes (Figure B-2). The plastic deformation along these axes will be D_x and D_y respectively. To maintain constant volume, the cube will deform (compress) in the z direction by an amount d_z (or simply, d). Again, mathematically,

$$\begin{aligned} V = 1 &= (1 + D_x)(1 + D_y)(1 - d) \\ &= 1 - d + D_x - D_x d \\ &\quad + D_y - D_y d + D_x D_y - D_x D_y d \quad . \end{aligned} \tag{B.3}$$

Again, neglecting the second- and third-order terms,

$$1 = 1 - d + D_x + D_y$$

or

$$d = D_x + D_y \quad .$$

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[1] The resultant error will be shown to be small, see Section B.2.2.

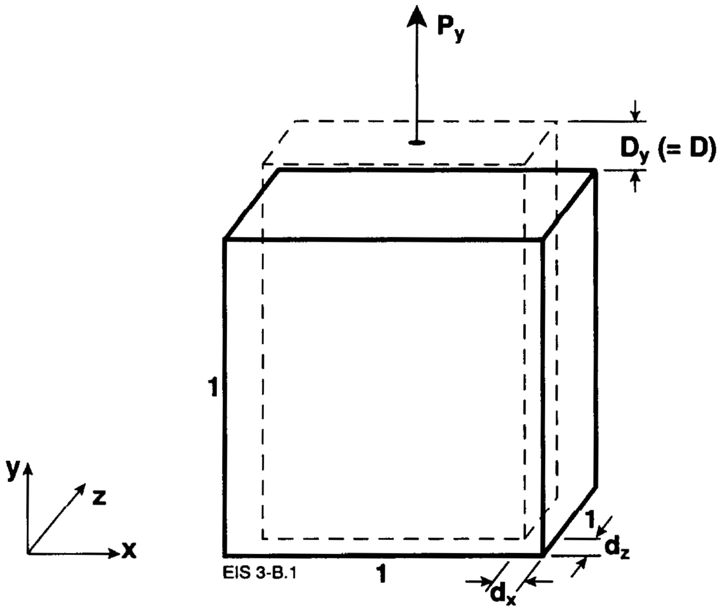

FIGURE B-1: Uniaxial Loading of a Small Cube of Metal, Causing Plastic Deformation

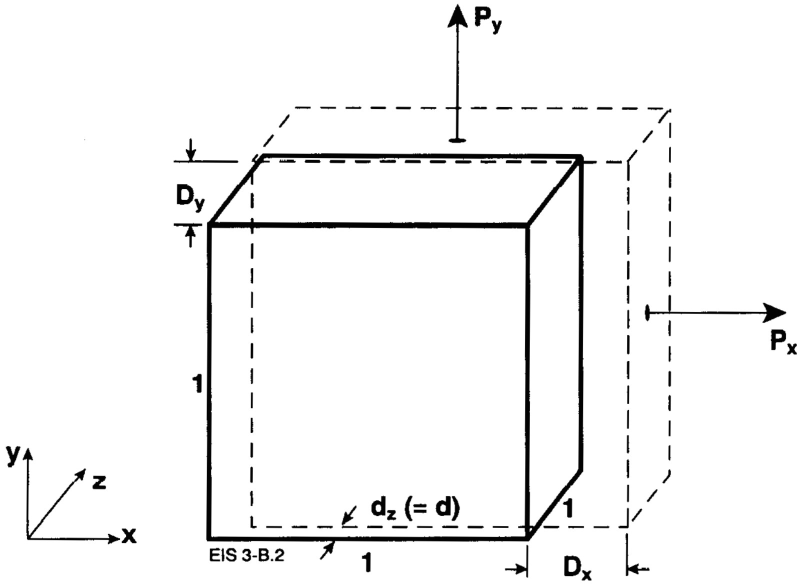

FIGURE B-2: Biaxial Loading of a Small Cube of Metal, Causing Plastic Deformation

If the strains in the x and y directions are equal, i.e., $D_x = D_y = D$, then

$$d = 2D \quad . \tag{B.4}$$

Comparing Equations (B.2) and (B.4) indicates that, if the cube forms part of a plate in which the z direction is the through-wall direction, and if the plate were to be loaded biaxially (in both the x and y directions) to a stress level causing plastic deformation, the through-wall thickness (the z direction) would strain (i.e. thin down) four times more than if the plate were loaded to plastic deformation uniaxially.

B.1.2 ENGINEERING AND TRUE STRESS-STRAIN PROPERTIES OF MATERIALS

If the stress in a material is below or near the material's yield stress, it is usually sufficient to describe the material's stress-strain characteristics in terms of "engineering" units. In an engineering stress-strain curve, the locus of points is derived by calculating the strain at each point based on the original gauge length of the specimen, and the stress based on the original area of the specimen. In the elastic region, the changes in the original gauge length and area are usually sufficiently small that the error in calculating stress and strain is also small for most design purposes.

At stress levels appreciably above the material's yield stress, where plastic deformation prevails, the length of the specimen can increase significantly, with an attendant significant reduction in specimen area. In this region, it is more appropriate to calculate the stress and strain, at each point on the stress-strain curve, on the basis of the instantaneous dimensions of the specimen. A stress-strain curve based on the instantaneous specimen dimensions is called a "true" stress-strain curve. It can be shown (Dieter 1986) that

$$\text{true strain, } \epsilon, = \ln(e + 1) \text{ and} \tag{B.5}$$
$$\text{true stress, } \sigma, = s(e + 1) \tag{B.6}$$

where e and s are the engineering values of strain and stress respectively. Therefore, an engineering stress-strain curve can be mathematically converted to a true stress-strain curve.

In an engineering stress-strain curve, the ultimate tensile strength of a test specimen, s_u, is defined as

$$s_u = P_{max}/A_o \tag{B.7}$$

where P_{max} is the maximum load applied to a specimen during a tensile test and A_o is the original specimen area. In a true stress-strain curve, the true stress at the maximum load on the specimen is the material's true tensile strength. If the cross-sectional area of the specimen at the maximum load on the specimen is A_u, it can be shown (Dieter 1986) that the true strain at the maximum load, ϵ_u, is

$$\epsilon_u = \ln(A_o/A_u) \tag{B.8}$$

and the true tensile strength, σ_u, is

$$\sigma_u = s_u e^{\epsilon_u} \quad . \tag{B.9}$$

Note that in Equation (B.9) only, e means the base of the natural logarithm, the irrational number 2.71828... .

B.2 ANALYSIS OF TITANIUM PLATE MATERIAL

B.2.1 MATERIAL FAILURE CRITERION

ASTM Grade-2 titanium is a ductile material with a 20% required minimum elongation in a tensile-test specimen with a 2-in. gauge length (ASTM 1993). As a specimen elongates (deforms plastically) under tensile loading, its diameter decreases, i.e., the specimen thins. Eventually, as loading is increased further, the specimen thins sufficiently in a local region such that only very small additional stress is needed to cause very rapid further thinning. For a titanium-shell container, the shell would be assumed to fail by mechanical rupture, under loading, at a condition of through-wall strain (thinning) for which only a very small increase in stress would result in further rapid thinning of the wall. An analysis was conducted to define, for titanium plate material, the through-wall strain above which such rapid thinning under a small stress increase might occur. This would then be specified, for current container-design purposes, as the through-wall strain above which container-shell rupture could occur.

A section of ASTM Grade-2 titanium shell material was modelled for deformation behaviour, under both uniaxial and biaxial loading conditions, using finite-element analytical techniques (Figure B-3). The short-term stress-strain properties of the material used in the analysis were obtained from a true stress-strain curve derived from a typical engineering stress-strain curve for this material. Figure B-4 shows the two curves. The true stress-strain curve was then linearized (Figure B-5) for input into the finite-element program. The results of the analysis are plotted in Figures B-6 and B-7.

Figure B-6 (uniaxial load applied to the plate) shows that as the stress in the material approaches 100% of the material's ultimate tensile strength, the resulting compressive strain (i.e., thinning) along each of the axes perpendicular to the direction of the applied load is about 8%. That is, at the point where the material has been stressed to near its ultimate tensile strength, the reduction in thickness of the material along the axes perpendicular to the direction of the applied load would be about 8%. At this point, any increase in loading would exceed the material's ultimate tensile strength and failure by fracture or tearing could occur.

Figure B-7 (biaxial load applied to the plate, and, for conservatism, equal in each direction) shows that as the stress in the material approaches 90% of the material's ultimate tensile strength, the strain along the direction of each of the applied loads is 4%, whereas the resulting compressive strain (thinning) along the axis perpendicular to the applied loads is 8%.

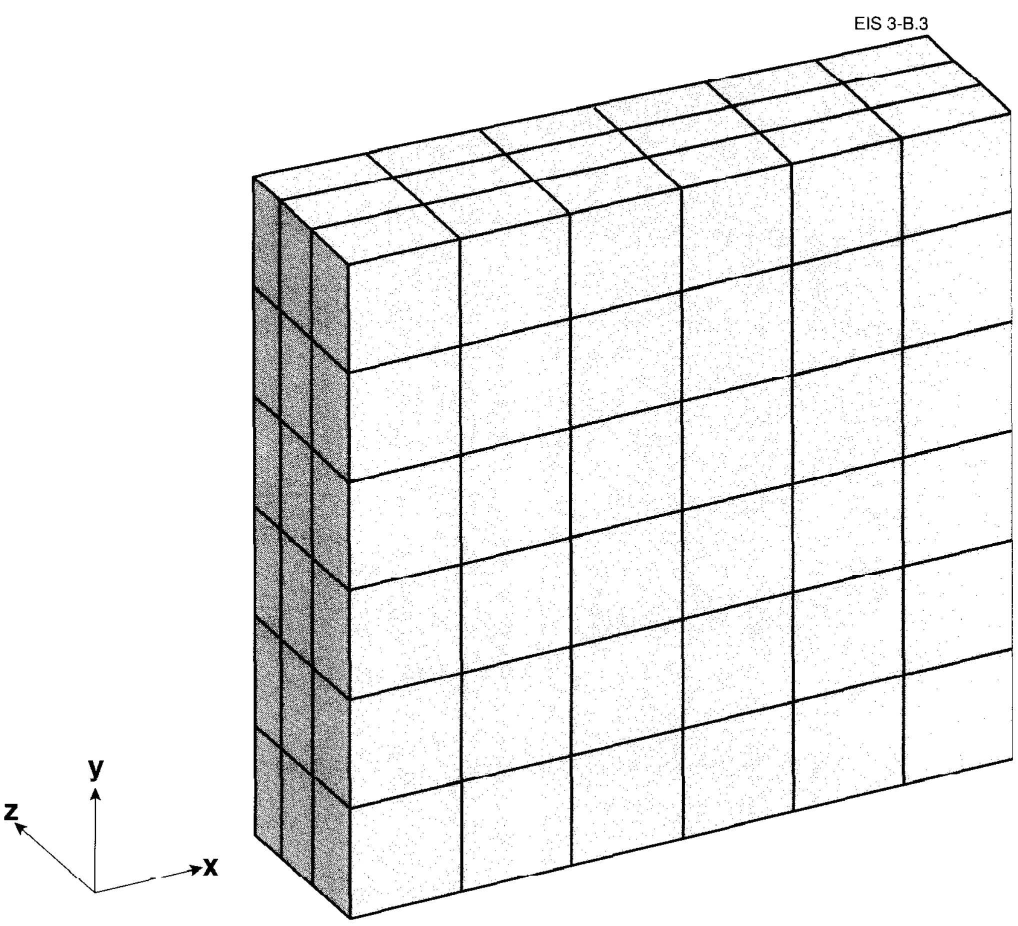

FIGURE B-3: Finite-Element Model of a Section of Titanium Plate, Used in Plate-Deformation Analysis

This shows that if the plate is under biaxial stress, the thinning in the unstressed direction will be much greater than if the plate is under uniaxial stress. If the stress due to the applied loading reaches more than 90% of the material's ultimate tensile strength, the strain in the unstressed direction will, according to the analysis, increase very rapidly. Thus, for titanium plate, when a through-wall thinning of 8% is reached as a result of biaxial loading in the other two perpendicular directions, this would appear to be the point at which further through-wall thinning could cause plate failure.

In a container subjected to external pressure loading, the resultant stress condition in the shell will be biaxial, along the longitudinal and circumferential directions of the shell. The direction perpendicular to the applied-stress directions will be the through-wall direction. In locations where any plastic deformation might occur, a through-wall thinning of 8% at that location represents a strain where material failure may be imminent.

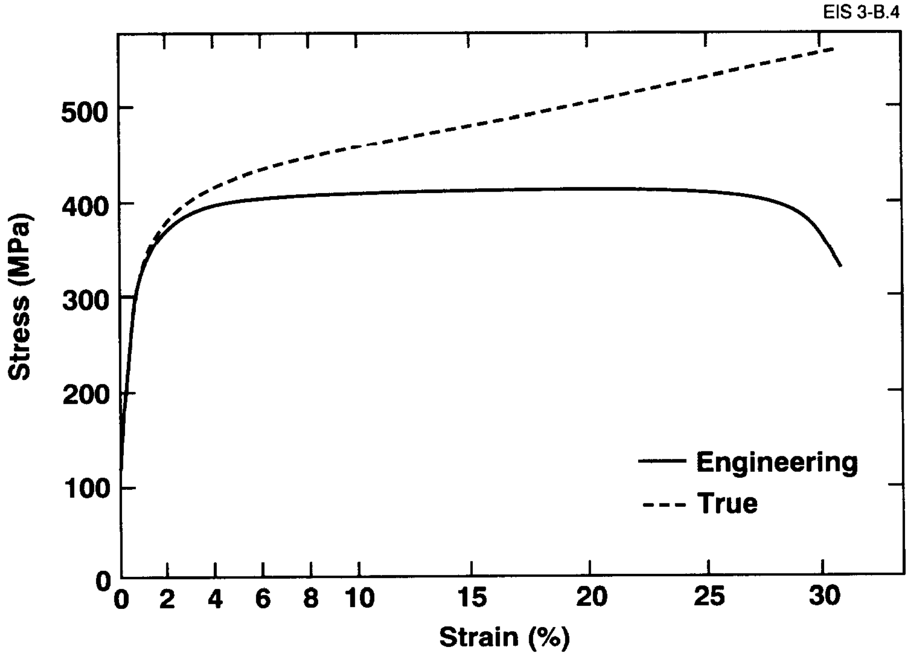

FIGURE B-4: Engineering and True Stress-Strain Curves for Titanium

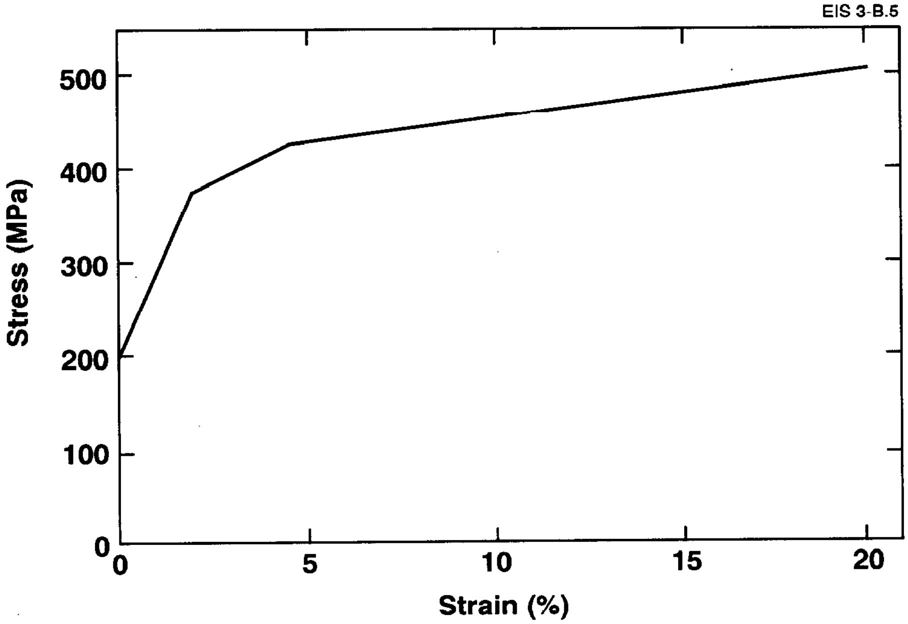

FIGURE B-5: Linearization of True Stress-Strain Curve Used in Finite-Element Analysis

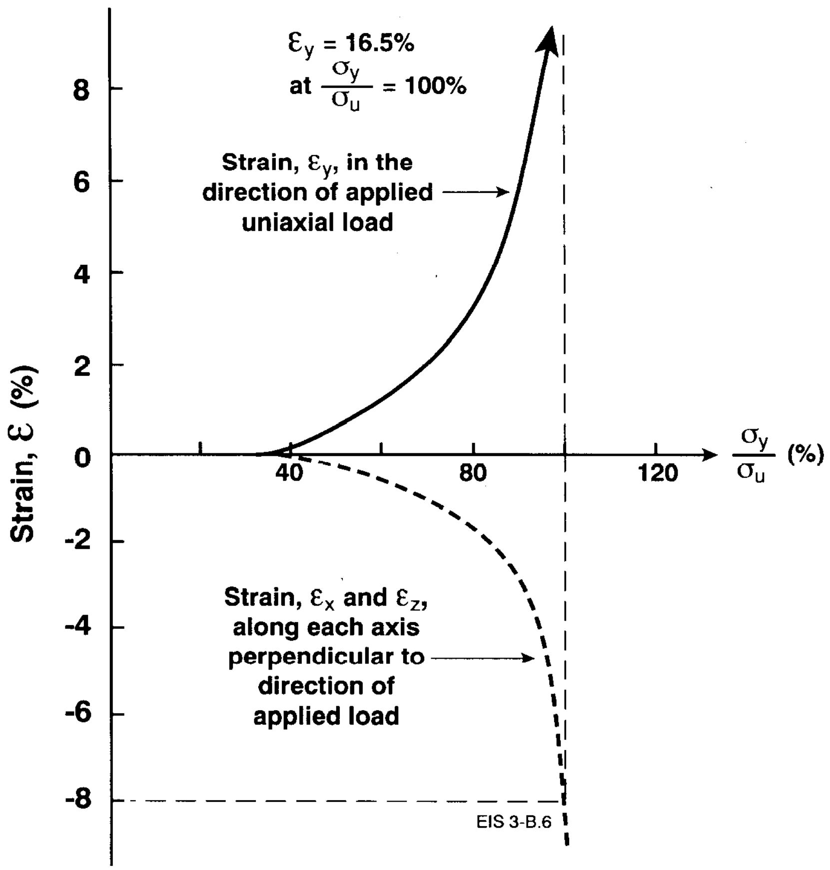

FIGURE B-6: Results of Finite-Element Analysis for Plate Under Uniaxial Loading, Showing Plate Strains as a Function of Stress. Stress is expressed as a percent of ultimate tensile strength.

As noted in Section 3.4.3.6 of the main text, the ASME Boiler and Pressure Vessel Code has been used as a guide for container design in the container-development program. As a design criterion for adequate strength of a structure, the Code frequently limits the allowable stresses in the material of construction to 2/3 of the ultimate tensile strength of the material (e.g., paragraph NB-3228.3 of Section III of the Code (ASME 1986)). By analogy with this limiting-stress criterion and for design conservatism, it was decided to apply a similar factor to the 8% through-wall strain, for which the previously described analysis determined that titanium plate failure might be imminent. Thus, the limiting through-wall strain criterion for titanium plate was set at 2/3 x 8% = 5.3%.

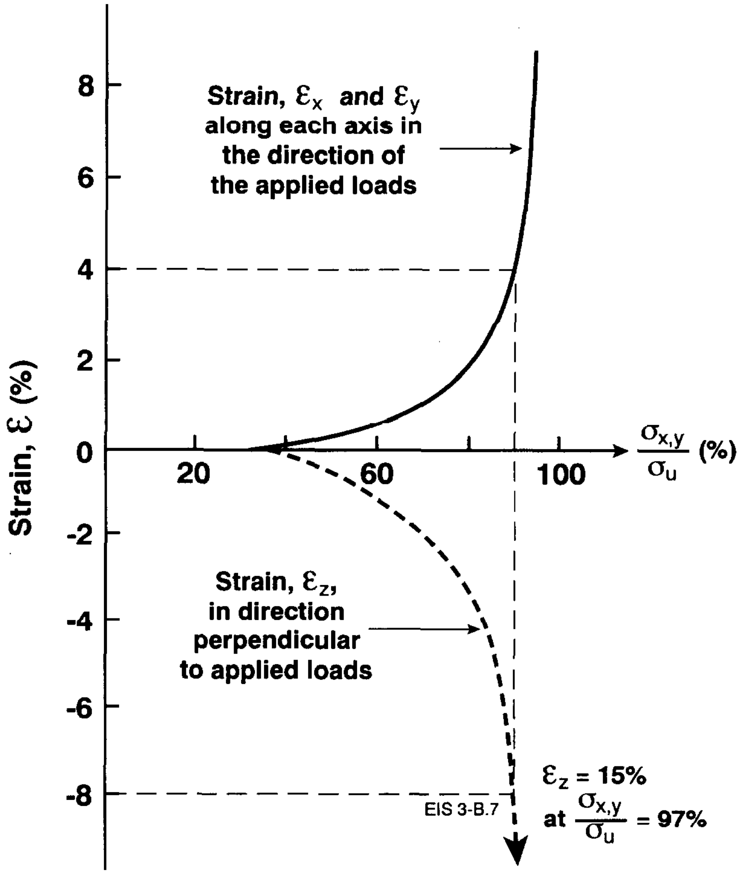

FIGURE B-7: Results of Finite-Element Analysis for Plate Under Biaxial Loading, Showing Plate Strain as a Function of Stress. Stress is expressed as a percent of ultimate tensile strength.

B.2.2 ERROR DUE TO NEGLECTING HIGHER-ORDER TERMS

B.2.2.1 Uniaxial Tensile Stress

The second-order terms neglected in Equation (B.1) were, for $d_x = d_z = d$,

$$-2dD + d^2 + Dd^2$$

which for D = 2d equals

$$-3d^2 + 2d^3 \quad . \tag{B.10}$$

For a strain, D, of 16.5% (in the direction of the applied load), d = 8%. Substituting this value into Equation (B.10) gives

$$-3(0.08)^2 + 2(0.08)^3$$

$$= -0.018 \text{ or } -1.8\% \quad .$$

B.2.2.2 Biaxial Tensile Stress

The second-order terms neglected in Equation (B.3) were, for $D_x = D_y = D$,

$$-2Dd + D^2 - D^2 d$$

which for d = 2D equals

$$-4D^2 + D^2 - 2D^3$$

or

$$-2D^3 - 3D^2 \quad . \qquad \text{(B.11)}$$

Substituting into Equation (B.11) for strains $D_x = D_y = D = 4\%$ in the directions of the applied loads (at which d = 8%) gives

$$-2(0.04)^3 - 3(0.04)^2$$

$$= -0.0049 \text{ or } -0.49\% \quad .$$

B.2.2.3 Summary

For both uniaxial and biaxial tensile loadings that result in a strain specified as the limit for the mechanical failure of titanium, neglect of the second-order terms introduces a small error. In the case of a plate under biaxial tension, which is similar to the stress condition in a thin-shell, fuel-waste disposal container under external hydrostatic loading, neglect of these terms introduces an error of about -0.5% strain.

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