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**PNL-6329**

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## **Spent Nuclear Fuel as a Waste Form for Geologic Disposal: Assessment and Recommendations on Data and Modeling Needs**

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**September 1987**

**Prepared for the U.S. Department of Energy  
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory  
Operated for the U.S. Department of Energy  
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*operated by*  
BATTELLE MEMORIAL INSTITUTE  
*for the*  
UNITED STATES DEPARTMENT OF ENERGY  
*under Contract DE-AC06-76RLO 1830*

Printed in the United States of America  
Available from  
National Technical Information Service  
United States Department of Commerce  
5285 Port Royal Road  
Springfield, Virginia 22161

NTIS Price Codes  
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
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SPENT NUCLEAR FUEL AS A WASTE FORM  
FOR GEOLOGIC DISPOSAL: ASSESSMENT  
AND RECOMMENDATIONS ON DATA AND  
MODELING NEEDS

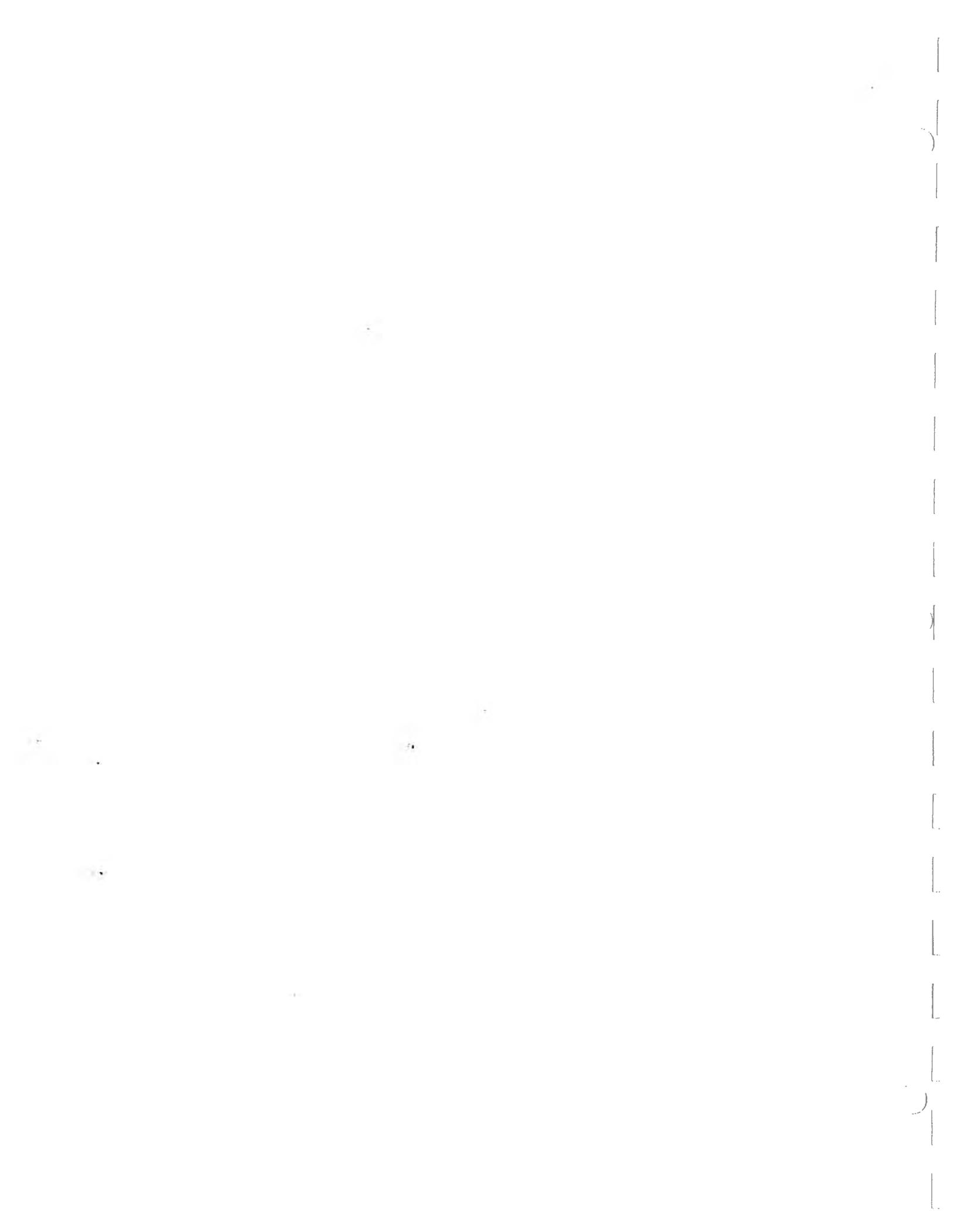
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## EXECUTIVE SUMMARY

The objective of this study was to assess the status of knowledge pertinent to evaluating the behavior of spent nuclear fuel as a waste form in geologic disposal systems. This assessment is to be supportive of the U.S. Department of Energy's (DOE) mined geologic repository program by providing background information that can be used by the DOE to address the information needs that pertain to compliance with applicable standards and regulations.

To achieve this objective, applicable federal regulations were reviewed, expected disposal environments were described, the status of spent-fuel modeling was summarized, and information regarding the characteristics and behavior of spent fuel was compiled. This compiled information was then evaluated from a performance modeling perspective to identify further information needs. A number of recommendations were made concerning information still needed to enhance understanding of spent-fuel behavior as a waste form in geologic repositories. These recommendations are summarized as follows.

### Cladding

- quantification of the number of failed rods coming out of the reactors
- gas contents and release rates
- heat generation and radioactivity
- creep rupture behavior during storage
- corrosion under expected repository environment conditions for both stainless steel and Zircaloy claddings
- stress corrosion cracking propensity under expected storage and disposal conditions; fuelside and waterside corrosion
- annealing data under higher temperature storage conditions
- hydride distribution and migration potential
- radionuclide content, chemical form, location, and potential release mechanisms

- physicochemical properties (sorptive and redox-buffer capacities) of intact and altered cladding materials
- role of physical presence of material in governing ground-water access to radionuclide release from the  $UO_2$  fuel
- modeling of the above processes and characteristics that may be important in determining the contaminant failure time and/or radionuclide release rates.

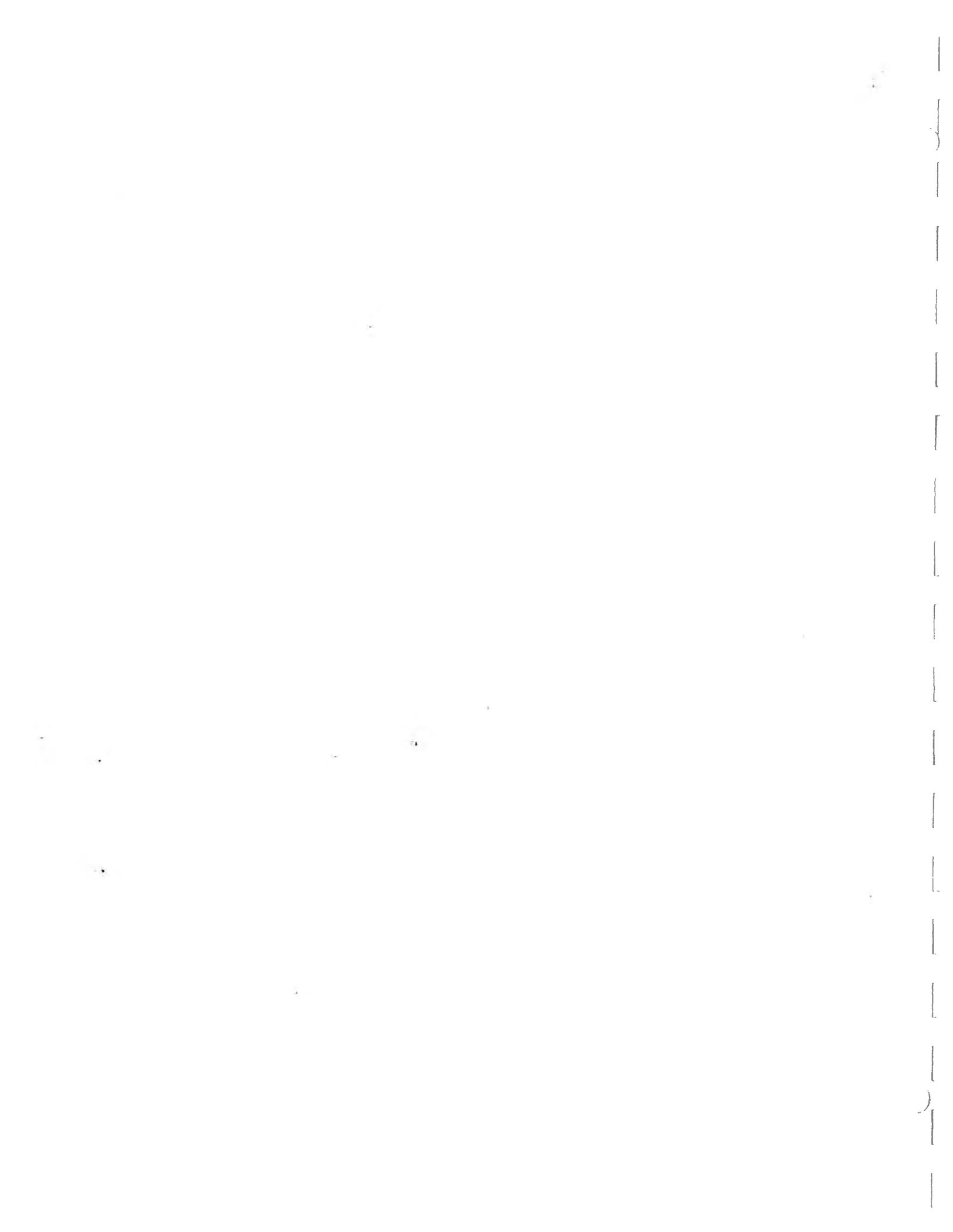
#### Irradiated $UO_2$ Fuel

- elemental and compound composition and radionuclide-specific distributions in terms of grain, grain boundary, and gap inventories
- oxidation rates in moist air, steam, and other potential storage and disposal environment conditions
- mechanism of radionuclide release as related to fuel oxidation
- accurate characterization of spent fuel expected at the repository
- factors that control release of highly soluble and/or nonsorbing radionuclides
- release rate tests under conditions relevant to that expected for waste packages in a given repository
- models that can be used to predict the lifetime characteristics of out of reactor fuel through storage, handling, and disposal.

The ranking of these recommendations may need to be site specific because the potential failure modes/processes depend on the environment of the waste package. It is conceptually possible to engineer a waste package such that some concerns regarding the containment behavior of clad spent fuel are no longer important. For example, it may be desirable to not take into account the existence of the cladding in a waste package performance assessment. The strategy is then to allocate all containment and release performance to the engineered container and the  $UO_2$  waste form in its packing-material/host rock environment.

## ACKNOWLEDGMENTS

This report is a product of the Performance Assessment Scientific Support (PASS) Program of the Pacific Northwest Laboratory (PNL). The PASS Program assists the Office of Civilian Radioactive Waste Management, U.S. Department of Energy. Several PNL staff members contributed to this report. Sections 1 and 2 were written by A. E. Van Luik. The principal author for Section 3 was R. E. Guenther; he was assisted by W. J. Bailey, E. R. Gilbert, J. H. Haberman, and R. E. Williford. The principal author for Section 4 was M. J. Apted, and he was assisted by R. Peters, R. J. Serne, and J. Shade. M. J. Apted, R. E. Guenther, and A. E. Van Luik all contributed to Section 5. This work was funded by the Office of Civilian Radioactive Waste Management's Office of Geologic Repositories under the U.S. Department of Energy Contract DE-AC06-76RLO 1830.



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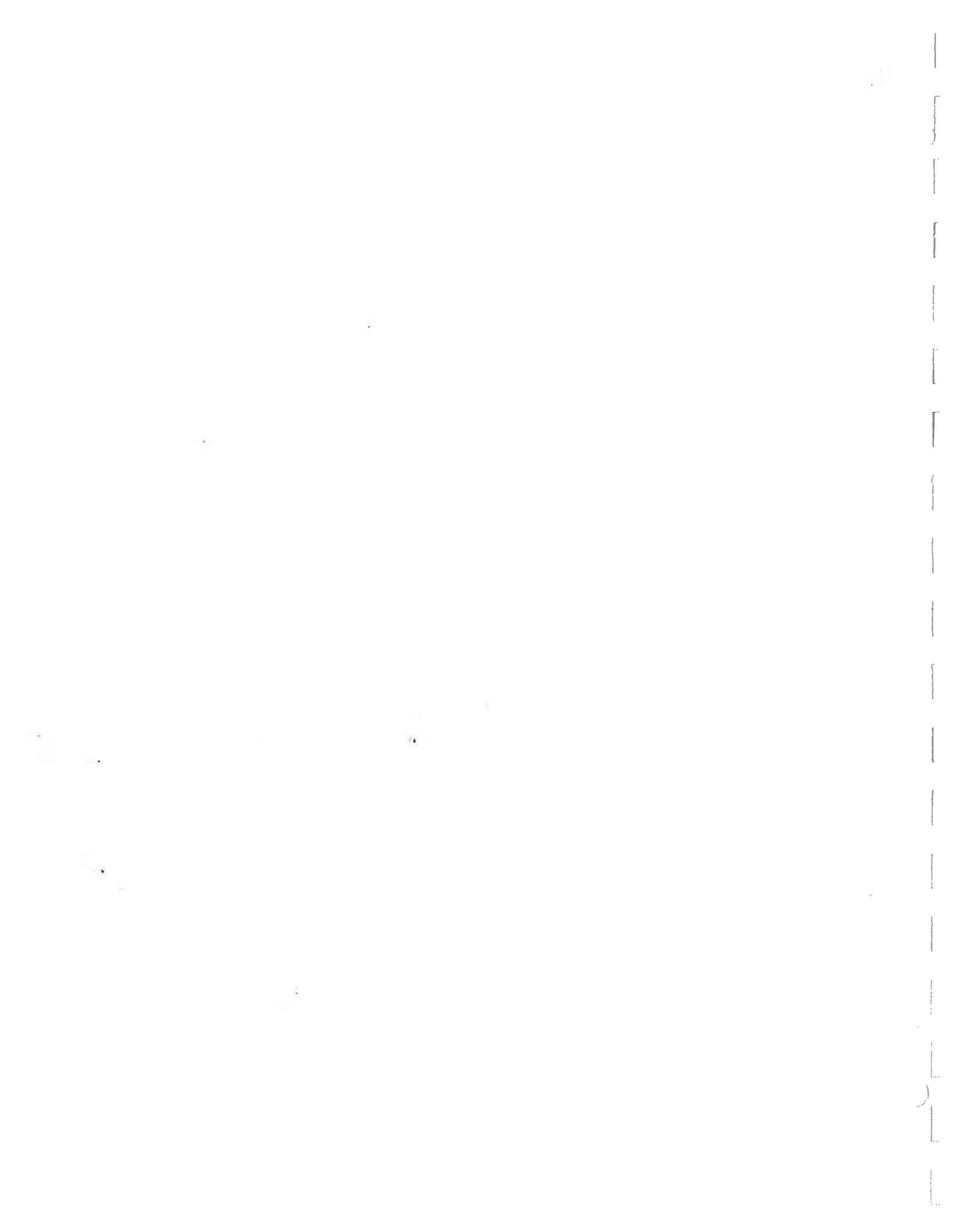
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## 1.0 BACKGROUND AND INTRODUCTION

The purpose of the Nuclear Waste Policy Act (NWPA) of 1982, Public Law 97-425, was in part "to provide for the development of repositories for the disposal of high-level radioactive waste and spent nuclear fuel" and "to establish a program of research, development, and demonstration regarding the disposal of high-level radioactive waste and spent nuclear fuel." The U.S. Department of Energy's (DOE's) Office of Civilian Radioactive Waste Management's Office of Geologic Repositories requested that the Pacific Northwest Laboratory's (PNL's) Performance Assessment Scientific Support (PASS) Program evaluate the suitability of spent nuclear fuel as a waste form. This report is to be the first of a series addressing this topic. The purpose of this study is to assess the status of current knowledge regarding the isolation performance of spent nuclear fuel as a waste form in repositories.

### 1.1 BACKGROUND

The NWPA of 1982 requires that high-level nuclear waste and nonreprocessed spent nuclear fuel be disposed of in a repository: a mined, geologic disposal system. In the NWPA, certain attributes and performance requirements are specified for this disposal system and for some of its subsystems. Research on spent nuclear fuel must, in part, address the role this waste form plays in determining the performance of the mined geologic disposal system and its subsystems.

#### 1.1.1 Impact of the Nuclear Waste Policy Act of 1982

The NWPA specifically mandates that the DOE, the U.S. Nuclear Regulatory Commission (NRC), and the U.S. Environmental Protection Agency (EPA) produce certain planning and regulatory documents. These documents provide part of the background for the present study. The DOE is to produce a Mission Plan (USDOE 1985) and general guidelines for site selection (USDOE 1984 [10 CFR 960]). Features of the Mission Plan that are salient to this work are its commitments to the permanent disposal of spent nuclear fuel and to the consolidation of

spent-fuel rods before placement in a disposal container. Consolidation means the removal of individual spent-fuel rods from assemblies, and the close-packing of these rods in containers.

The general siting guidelines have been published as Chapter 10 of the Code of Federal Regulations, Part 960 (10 CFR 960). Similarly, the EPA (USEPA 1985 [40 CFR 191]) has produced standards applicable to a mined geologic disposal system for high-level nuclear waste and spent nuclear fuel. The standards are part of Chapter 40 of the Code of Federal Regulations, Part 191 (40 CFR 191). The NRC's applicable regulations (USNRC 1983 [10 CFR 60]), consisting of technical requirements and criteria, are contained in the Code of Federal Regulations, Chapter 10, Part 60 (10 CFR 60).

The NWPA specifies that NRC is to exercise license control over DOE's repository. The licensing procedure outlined in the NWPA requires DOE to submit a license application to NRC to allow DOE to build, operate, and close a mined geologic disposal system for high-level nuclear waste and spent nuclear fuel. This license application will constitute the record by which NRC will judge whether or not applicable regulatory standards, requirements, and criteria can be met with reasonable assurance.

#### 1.1.2 The Engineered Barrier System and the Multiple Barrier System Requirement

The NWPA requires that NRC promulgate technical requirements and criteria that "shall provide for the use of a system of multiple barriers." The NRC, accordingly, has defined a geologic repository to include "the portion of the geologic setting that provides isolation of the radioactive waste," and an "engineering barrier system." In effect, the definitions given in 10 CFR 60.2 describe a mined geologic disposal system as being composed of a natural barrier system and an engineered barrier system.

In 40 CFR 191, EPA limits the horizontal extent of the natural barrier system to less than 5 km from the edge of the original location of the emplaced nuclear waste. The natural barrier system may be composed of one or a number of geologic structures, each of which may be described as a barrier in that each may prevent or substantially delay the movement of water or radionuclides

(10 CFR 60 and 40 CFR 191 definitions of barriers). Thus, the natural barrier system may be a multiple barrier system for some geologic settings and not for others.

The EPA and NRC emphasize that the engineered barrier system should be a multiple barrier system. In 40 CFR 191, it is suggested that a container, a waste form, and materials placed over or around a waste form may be barriers. The engineered barrier system is defined in 10 CFR 60 so that, from an isolation perspective, its main functional component is the waste package. The waste package, in turn, is the waste form, its container(s), shielding, and any absorbent or other materials packed around each individual container (packing materials). Some, but not necessarily all, of these possible waste package components may be the multiple barriers that functionally define the isolation capacity of an engineered barrier system. Current usage within the DOE defines a container as the primary barrier that ensures meeting the containment criteria of 10 CFR 60. A canister, on the other hand, is any other encapsulating metal barrier.

### 1.1.3 Potential Barriers in a Spent-Fuel Waste Package System

The spent-fuel waste package may consist of a stainless steel or low-carbon steel container containing spent-fuel rods. These rods will probably have been consolidated, or removed from the fuel assembly hardware that kept individual fuel rods separated for use in reactor cores. Each rod is clad with either Zircaloy, an alloy that is 98% zirconium, or stainless steel. A small, as yet undetermined percentage of the cladding may have small defects that could allow some ground-water contact with some of the spent fuel shortly after container failure. Thus, the irradiated  $UO_2$  waste form is an important component within the multiple barrier system, and the release behavior of radionuclides from  $UO_2$  under repository conditions must be known to predict the long-term performance of the entire engineered barrier system.

A significant fraction of the mass inside a typical spent-fuel waste package may be Zircaloy and/or stainless steel cladding. Hence, these materials and their corrosion products may also be a barrier within the engineered

barrier system. Whether credit can be taken for cladding as a barrier depends on the need and the ability to evaluate its behavior and the behavior of its corrosion products under repository conditions.

By design, the container is a barrier during the containment period. After a container has been breached, continued corrosion in entrance paths may produce corrosion products that may continue to constitute a sorption barrier to the migration of specific radionuclides.

Finally, packing materials are to be used in some repositories to control ground-water flux and to selectively delay the migration of some radionuclides by sorption. Packing materials may consist of clays alone or mixed with crushed host rock, or crushed host rock alone.

The NRC's release rate requirement applies to the engineered barrier system, and from a performance perspective, the waste package is the most important part of that system. Therefore, evaluation of spent-fuel performance in a repository needs to consider the entire waste package as a system consisting of a container, a fill gas inside the container, cladding, waste form, and, for some repository designs, packing materials and/or a canister.

## 1.2 STANDARDS, REQUIREMENTS, AND CRITERIA

According to 40 CFR 191, the engineered and natural barrier systems, constituting the postclosure mined geologic disposal system, may not release radionuclides to the accessible environment in excess of the amounts allowed by 40 CFR 191, which specifies radionuclide-specific cumulative release limits in curies for 10,000 years after permanent closure. These release limits are based on the results of environmental transport and population-dosimetry modeling. The EPA standard, therefore, incorporates limits on population dose commitments and resulting health effects.

To provide an increased degree of confidence that the 40 CFR 191 standard will be met, NRC has promulgated a number of technical requirements and criteria in 10 CFR 60 that are specific to the engineered barrier system. The requirements are that the waste packages provide substantially complete containment of radionuclides while fission-product decay-heat and radiation are

high, and that the engineered barrier system allow only small fractional radionuclide releases over long periods of time after substantially complete containment has been lost.

The NRC criteria that quantify these requirements specify a 300- to 1000-year range for the containment period that may be set for a given mined geologic disposal system. In addition, after the period of substantially complete containment, releases are not to exceed one part in 100,000 per year of the inventory of any radionuclide calculated to be present at 1000 years after permanent closure. An exception exists for radionuclides released at a yearly rate that is less than  $10^{-8}$  of the total 1000-year system curie inventory. For the latter radionuclides, the release-rate limit is the ratio of  $10^{-8}$  of the total 1000-year curie inventory of the system to that radionuclide's inventory at 1000 years. This somewhat complex exception allows slightly higher releases for lower inventory radionuclides. Since 10 CFR 60 complements the 40 CFR 191 standard, its requirements are also in force for 10,000 years. This time limit somewhat curtails the ambiguity of the release rate requirements with regard to in-growing daughter radionuclides, such as radium-226.

These NRC criteria specifically apply only in the case where no unanticipated processes or events are assumed (such as faulting or human intrusion). Determining the likelihoods of unanticipated processes and events and of resulting releases is a site-specific process. The discussion of engineered barrier system criteria needed to ensure compliance with 40 CFR 191 in the event of unanticipated process or event scenarios is beyond the scope of this work. Only the 10 CFR 60 criteria for anticipated processes and events (slow corrosion, radionuclide transport by diffusion or by migrating ground water, etc.) were considered in our evaluation of the status of research assessing spent fuel as a waste form for mined geologic disposal.

### 1.3 STUDY OVERVIEW

The regulatory requirements suggest that the engineered barrier system be a multiple barrier system and the waste form (i.e., spent fuel) be a barrier within that system. To be a barrier, spent fuel must substantially delay the movement of radionuclides under repository conditions. A multifaceted review

was conducted to assess the availability of data that may allow the characterization of spent fuel and its behavior over wide ranges of conditions.

The objective of this study was to assess the status of knowledge regarding the spent-fuel waste form in terms of its likely behavior in a mined geologic repository. Although these information needs may ultimately pertain to showing compliance with applicable standards and regulations, the needs described in this document are modeling needs: information needed to model spent-fuel behavior as a waste form.

We reviewed relevant literature that addressed or could be used to address the question of spent-fuel behavior in geologic disposal systems. Specifically, the barrier properties of clad spent fuel were of greatest interest. Barrier properties of spent fuel are those properties that delay the movement of radionuclides. Containment is a separate barrier function that is to be provided by the container, not the clad spent-fuel waste form.

Expected ranges of repository conditions are described, as were the expected properties of clad spent fuel before disposal, during the thermal period and for the postthermal period when containment is likely to be lost (i.e., after ground water enters the container and contacts spent fuel). Factors controlling releases from clad spent fuel in the postthermal period are examined in some detail, because it is in this period that the properties of spent fuel will be most important in contributing toward the overall performance of the mined, geologic disposal system.

The regulations require that predictions of system behavior, using performance assessment modeling, be carried out to 10,000 years for the purpose of showing regulatory compliance. In addition, 100,000-year cumulative release calculations are required by the general siting guidelines (10 CFR 960) for the specific purpose of comparing sites in the site selection process. These requirements emphasize the importance of both the experimental programs and the performance modeling efforts. The scope of this study, therefore, encompassed both data and modeling progress and needs.

Needs exist for showing where data gathering and modeling efforts are, what has and has not been adequately covered, and what general recommendations

could help focus future spent-fuel research and modeling efforts. Our approach, therefore, was to obtain and analyze the available literature and also to ascertain the scope and progress of ongoing work.

The report consists of the following sections:

- 1.0 Background and Introduction--a review of the regulatory performance requirements and a statement of the scope, objectives, and methodology of this study.
- 2.0 Expected Spent-Fuel Waste Package Environments and Performance--a description of what the current expectations are in terms of the environments that will be experienced in each host rock type and what the expected containment times will be. These expectations reflect DOE project thought and calculations, and do not necessarily reflect the judgments of the authors of this report in every respect.
- 3.0 Containment by Clad Spent Fuel--a collection of information judged to be relevant to determining the ability of clad spent fuel to contribute the containment of radionuclides. Both the cladding and the irradiated  $UO_2$  fuel are examined in detail in terms of characteristics and potential failure modes and processes.
- 4.0 Postcontainment Release from Spent Fuel--a discussion of the radionuclide release process with emphasis on the role of the cladding and of the physical and chemical makeup of the  $UO_2$  matrix. Highly soluble and/or nonsorbing radionuclides receive special attention in this section, as do the potential sorption characteristics of waste package metal barriers and their alteration products.
- 5.0 Summary and Recommendations--summarizes Sections 1.0, 2.0, 3.0, and 4.0 and recommends clad-spent-fuel research and modeling needs.

The analyses of available data and modeling results focus on evaluating whether or not certain basic questions regarding the characteristics and expected behavior of spent fuel have been addressed properly and the degree to which they have been answered. Perceived data and modeling needs are discussed, and summary data and modeling needs are presented in tabular form for the convenience of the reader.

#### 1.4 REFERENCES

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## 2.0 EXPECTED SPENT-FUEL WASTE PACKAGE ENVIRONMENTS AND PERFORMANCE

Waste package environments are expected to vary with time. For example, before waste emplacement, the temperature of portions of the host rock can be below ambient because of ventilation. The temperature will rise as soon as waste packages are emplaced; will peak sometime before or after repository closure, depending on host rock type and waste package and emplacement assumptions; and will decrease slowly thereafter. Of particular interest from a performance-modeling perspective is the environment of the waste package in the period after spent fuel has become accessible by ground water when radionuclide migration may begin. Part of the emphasis of this section is on the lifetime of the waste package's primary containment barrier. Until this primary barrier is breached, the spent-fuel waste form is assumed to be essentially in dry storage and not materially changed from its emplacement condition (see Section 3.0).

Three time ranges were chosen to facilitate the discussion of waste package environments in this section: 1) preclosure--before waste package emplacement and after emplacement, as the thermal period begins but before repository sealing; 2) postclosure--the thermal period after repository sealing, and 3) postthermal--the period after the thermal output of the emplaced spent fuel has dropped to near negligible levels. For convenience, we chose 1000 years after permanent closure as the beginning of the postthermal period. After 1000 years, the thermal power of a fuel assembly is expected to be about 25 watts (USDOE 1980), and repository heating is expected to be negligible (USNRC 1983).

Potential repository environments are discussed in the following section, in alphabetical order: basalt and crystalline (i.e., granitic or gneissic rocks), salt, and tuff. Some priority was given basalt, salt, and tuff, however, because these are the host rock types considered for the first repository and have the most detailed site information available.

The terms "far field," "near field," and "very near field," are used in this report to qualitatively denote approximate location within the mined, geologic repository system. Far field indicates the area where hydrologic and

radionuclide migration modeling is treated as if it were the geologic setting. Thus, the far field may contain parts of the engineered systems, such as the shaft-seals, if they are modeled as part of the geosphere rather than as part of the engineered barrier system. The near field is the engineered barrier system. From a modeling perspective, the near field provides the source term for the far field hydrologic/migration model. The very near field is not a term of importance in modeling, but a convenience term for the space including the waste form and perhaps its first containment structure. This containment structure may or may not be the container if a waste package design includes a canister.

Expected performance of the spent-fuel waste package [as shown in the tuff, basalt, and one of the salt site Environmental Assessments (EAs) (USDOE 1986a,b,c) and its supporting documents] are summarized in this section. This summary emphasizes the major conceptual assumptions and results of these preliminary repository performance assessments.

## 2.1 PRECLOSURE ENVIRONMENTS

Spent-fuel emplacement in any repository may take in excess of 25 years (28 years are scheduled for emplacement in USDOE 1985). A period of similar length may be required to provide assurance of performance before permanent closure (a 50- to 90-year total preclosure period is mentioned in USDOE 1985). At closure, therefore, spent fuel may have been in place for 25 to 50 years.

The two major preclosure environments are pre- and postemplacement. The preemplacement environments will be defined during site characterization. In situ testing, part of ongoing site characterization work, will help to predict expected postemplacement preclosure conditions. It must be emphasized, therefore, that the following postemplacement environment descriptions consist of expert opinion guided by limited, available site-specific field data and, where appropriate, a limited amount of field experience from comparable locations. Information is given in this section on the environmental conditions during preclosure and includes the topics of radiation, temperature, redox potential, ground-water flow, ground-water composition, and stress. This type of information is given for basalt and crystalline rock, salt, and tuff geologies following introductory comments on the general importance of the

particular environmental parameter. Some aspects of the possible preclosure environmental effects of waste emplacement are not addressed for lack of significance in terms of adverse consequences. One of these possible environmental effects may include the reduction of gaseous nitrogen on hot metal surfaces to form  $\text{NH}_3$ , which may dissolve to form  $\text{NH}_4\text{OH}$  in ground water.

### 2.1.1 Radiation

The preemplacement radiation environment is generally an engineering concern in terms of mine safety: radon gas and dust-borne daughter products of radon must be controlled. Of concern in this study is the postemplacement, preclosure radiation environment and its possible effects on the packing materials, backfill, and/or host rocks. Although packing materials and backfill may consist of the same materials, they serve different functions. Packing materials physically separate the container from the host rock, help control dose rates into the drift, control water movement very near the container, and may retard transport of some radionuclides from the container surface to the host rock. Backfill, similarly, serves to control water movement, but at a larger scale in the postclosure repository. (Repository closure consists of completing the drift backfilling process and sealing shafts and boreholes.)

Neutron and gamma flux rates during the preclosure period would be important if they could damage either the engineered materials or the host rocks in such a way as to diminish their properties as barriers to the movement of radionuclides or water. According to the U.S. DOE (1979), radiation dose rates on the order of  $10^4$  rad/h may be experienced adjacent to 5- to 10-year-old, 33,000 MWd/MTU burnup spent fuel. These dose rates reduce as fission product decay proceeds, approaching  $10^3$  rad/h after about 100 years. How these dose rates affect metal barriers, ground water, and host rock is specific to the engineered barrier design and host rock type. The age, burnup, and amount of spent fuel in a waste package, as well as engineered barrier thicknesses and compositions, determine the actual doses received in the near field.

#### 2.1.1.1 Basalt and Crystalline

The preclosure, postemplacement radiological environment very near the waste packages should be similar for a repository located below the water table

in either basalt or granitic host rocks for comparable waste package designs. Information compiled and presented by Smith et al. (1980) suggested that  $\gamma$ -radiation effects in basalt during this period will primarily consist of ground-water radiolysis. Conditions for the net radiolytic production of oxidizing products caused by preferential escape of radiolytically produced  $H_2$  gas may be enhanced at this time because the waste package system will be separated from the atmosphere by packing material and backfill only (Smith et al. 1980). On the other hand, the waste package system may remain essentially dry during this elevated temperature period, meaning that no ground-water radiolysis will take place.

During the preclosure period, the amount of water near the waste package will be limited by the high temperature within and near the waste package, the atmospheric pressure of the system, ventilation, and the mechanical pumping that will control water ingress. While water remains distant from the hot waste package, however, atmospheric nitrogen may radiolytically oxidize and diffuse away to dissolve in ground water to form nitric or nitrous acids. As underground excavations are backfilled, pumping would cease and liquid water could approach the waste packages. It may be decades before resaturation is complete, meaning that peak dose rates have been reduced to a fraction of their initial levels. According to the Reference Repository Conditions Interface Working Group (RRC-IWG), perhaps as much as one half of the cumulative 10,000-year gamma dose may already have been received by the host rock adjacent to the waste package before repository resaturation (RRC-IWG 1986).

Engineered materials may include a smectite clay and crushed host rock packing material and metal barriers. Experiments on kaolinite by Corbett, Burson and Young (1963) suggested that high gamma dose rates cause only minor damage to this nonexpanding silicate. Kaolinite is not smectite clay, however, and although these results are encouraging, they are not definitive. Near field gamma radiation effects on bentonite, a rock type composed predominantly of smectite clays, are currently being investigated in United States and Canadian programs. Until final results are available, gamma radiolysis effects on clays may be assumed negligible at the cumulative doses and dose rates that are likely during the preclosure period in a repository.

Based on realistic estimates considering expected waste form and waste package characteristics for a basalt repository, Reed, Bonar and Weiner (1985) calculated expected dose rates and cumulative doses to the packing material. Their calculations showed expected dose rates and doses to be much less than those needed in the laboratory to induce changes in the properties of clays. Reed, Bonar and Weiner concluded that the expected doses were sufficiently low so that radiation effects on the packing material would be insignificant.

#### 2.1.1.2 Salt

The possible near-100-year duration of the preclosure period means that the highest  $\gamma$ -dose rates and a possible 40% to 65% of the 10,000-year cumulative  $\gamma$ -doses will have been received by the host rock before permanent closure (Claiborne, Rickerston and Graham 1980). This condition holds for repositories in other host rock types as well (RRC-IWG 1986) but is particularly important for salt because of salt's apparent susceptibility to radiation damage (Panno and Czyscinski 1984). This apparent susceptibility to host rock/ground-water radiation effects may be alleviated by a conceptual waste package design for a salt repository that may include a 12-cm-thick steel container that would attenuate  $\gamma$ -dose rates by more than an order of magnitude, according to preliminary estimates (Clark and Bradley 1984), or as much as two orders of magnitude, according to later, more definitive calculations (USDOE 1986c).

Panno and Czyscinski (1984) reviewed experiments conducted on brine migration, thermal and radiation effects, and synergistic effects of elevated temperature and irradiation on salt/brine mixtures. Their review focuses on studies that have shown that both acidic and alkaline conditions have been observed as a result of exposing salt and brine to elevated temperature and  $\gamma$ -radiation fields. Generally, radiolysis of brine produces  $H_2$ ,  $O_2$ ,  $H_2O_2$ , and  $Cl_2$ , resulting in an oxic condition. Radiation may also affect the brine's pH by causing  $H_2$  and  $Cl_2$  in solution to combine to form  $HCl$ , which lowers the pH, or by oxidizing atmospheric nitrogen that may be present, which forms nitric or nitrous acids when dissolved in the ground water. The composite effect is difficult to determine, but given that the pre-irradiated brine inclusions are

acidic (Moody 1987), an oxic, more acidic brine layer may exist next to the metal barrier with anoxic and less acidic conditions prevailing at increasing distances from the metal barriers. The thickness of this more acidic and oxic layer, if it exists, would be defined by the production and diffusion rates of radiolysis products away from the container surface. The acidic and oxic brine may be incrementally more corrosive; however, the assumed static nature of the system, resulting after brine inflow has reached its maximum, probably limits the corrosion rate in this environment. Assuming the attenuation of  $\gamma$ -radiation by the container is below the levels where radiolysis of brine produces significant oxidizing species in solution, the forward corrosion reaction rate may be governed by the rate of hydrogen, water, and perhaps oxygen diffusion through a static layer. This static layer is made of iron oxyhydroxide corrosion products and the salts remaining after the brine's oxygen and water content has been depleted after prolonged contact with the corroding metal surface. The sources of dissolved oxygen and water and the primary corrosive agents are expected to become depleted as corrosion occurs, however.

Radiolysis and temperature effects, as well as the possibility of corrosion modes other than uniform, are receiving further evaluation for repositories in salt. Studies that may allow better definition of waste package metal barrier requirements specific to selected performance goals are in progress (Simonsen and Kuhn 1984). The salt project is factoring radiolysis into its corrosion studies (ONWI 1984).

#### 2.1.1.3 Tuff

The reference waste package design concept for tuff is that spent-fuel waste containers will be placed in open boreholes, without packing material, in a repository in the unsaturated zone. The gamma-radiation field in a tuff repository will be absorbed by the host rock and by the hot water vapor that will contact the metal barriers as a result of placing the spent-fuel heat source in unsaturated rocks at atmospheric pressure. The host rock is not

susceptible to ionizing radiation damage (USDOE 1986a). Water vapor is not likely to condense on a metal barrier while it is still substantially above the temperature of the surrounding rocks. Therefore, the only water/metal interactions will be vapor/solid interactions until after the temperature decreases below the boiling point of tuff ground water when the gamma field is essentially decayed away.

The tuff project has preliminarily evaluated the short-term corrosion rate of its candidate metal barrier material, 304L stainless steel, immersed in hot ground water under a radiation field of  $3 \times 10^5$  rads/h. Under these extreme conditions, observed uniform corrosion rates suggested that current conceptual waste packages would remain intact in excess of  $10^4$  years. However, the expected lifetime of the waste package may be considerably shorter if corrosion mechanisms other than uniform corrosion become prevalent (USDOE 1986a). Because immersing the steel samples in water would prevent the oxidation of atmospheric nitrogen and the subsequent formation of nitric or nitrous acids, this radiolytic acidification effect was not addressed in this study.

#### 2.1.2 Temperature

Temperature is of interest because of its direct relationship with many reaction rates and solubilities. Temperature may also affect ground-water flow fields, host rock properties and stability, and waste package system behavior. Overall repository temperatures can be controlled by regulating the size and heat content of the spent-fuel waste package and the spacing of the emplacement holes. Ventilation will also remove a substantial portion of the heat generated in the emplaced waste packages (Claiborne, Rickerston and Graham 1980). During the preclosure period, refrigerated, forced-air ventilation will be required to ensure safe working conditions for operators and equipment.

Substantially less heat will be generated at the end of the preclosure period as compared with the end of the emplacement period. Fission-product decay during the remainder of the preclosure retrievability and confirmation testing period (about 50 years) will result in reductions in average container heat generation rates of more than 50%, assuming that 10-year-old (out-of-reactor) spent fuel was placed in the repository over a 25-year period (RRC-IWG 1986).

### 2.1.2.1 Basalt and Crystalline

The ambient, preemplacement, repository-level temperature expected at the candidate site in basalt is 50°C (USDOE 1986b). For crystalline rocks, temperatures have been measured at 1000 m at various locations and range from 17° to 26°C (RRC-IWG 1986). The heat generated by the spent fuel will be absorbed and attenuated by the packing material and the host rocks, but the packing material will act as an insulator, enhancing metal barrier and waste form temperatures. The extent to which smectites and other clays may be affected by enhanced temperatures may be controlled through waste package design and placement engineering.

The temperatures in and near the waste package in basalt or crystalline rock during the preclosure period will be a function of 1) the age, burnup, and mass of spent fuel in the waste package; 2) the thickness of the metal barrier(s); 3) the spacing of the emplacement holes in the repository; 4) the thickness and water content of the packing material; 5) host rock water content and flux; 6) thermal conductivity and heat capacity of the host rock; and 7) the ventilation system's operating characteristics.

Maximum temperatures, as a function of postemplacement time, have been calculated for the near field in crystalline rock (RRC-IWG 1986). The temperature profiles resulting from these calculations are not shown here because they are highly dependent on assumptions regarding the spent-fuel, waste package, repository layout, and the thermal diffusivity of the host rock/ground-water system. These postemplacement temperature profiles also do not recognize the heat-dissipating role of ventilation during the preclosure period. Of some interest here, however, is the timing and progression of temperature maxima.

The RRC-IWG (1986) calculations for crystalline rock suggest that a given container's waste centerline (i.e., the cladding, for practical purposes) reaches its peak temperature at approximately 10 years after emplacement. The container surface temperatures, on the other hand, are at a maximum 25 to 30 years after emplacement, and the emplacement hole wall temperature reaches a maximum about 40 years after emplacement. These maxima are the result of the interactions of increasing temperatures caused by barrier resistance to heat

transfer and decreasing temperatures resulting from radionuclide decay. With ventilation, however, these maxima could be lower and occur later.

Approximate values for maximum temperature increases (assuming one intact fuel assembly with a 550-W heat output per container is placed in the crystalline rock spent-fuel repository) are 170°C, 150°C, and 130°C for the cladding, container surface, and emplacement hole wall, respectively (RRC-IWG 1986). These values are probably useful ballpark figures for expected temperature increases for a crystalline host rock repository, although the emplacement containers with the fuel rods from six assemblies, having a heat output of 3300 W, is to be expected if spent fuel is consolidated before disposal (USDOE 1986b). Assuming the waste packages and repository layout are the same as previously described, the general difference in rock thermal characteristics between crystalline and basalt rocks would lead to somewhat higher temperature increases for a basalt repository. Assumptions regarding the waste package and host rock thermal properties can vary these temperature maxima considerably. More recent estimates (based on the USDOE [1986b] waste package assumption) indicate that the container surface maximum is about 200°C and the average waste package lifetime temperature is about 145°C.

At closure, the internal temperature of the spent-fuel package may have already peaked for virtually all emplaced spent-fuel waste packages; the container surface temperature will be at a maximum for the most recently placed packages and will probably decline for all the others. The emplacement hole wall temperature will begin to decline for the spent-fuel waste packages that were in place the longest and are either at or near their maximum values for all other emplaced spent-fuel waste packages (based on an interpretation of RRC-IWG 1986).

#### 2.1.2.2 Salt

Temperatures are particularly important in a salt repository because of the role of heat in brine migration, salt creep, and host rock and brine susceptibility to radiation damage. Although ventilation during the preclosure period may lower near field host rock temperatures dramatically (by about 25%), the effect is less dramatic (<10%) near or in the waste package (Claiborne, Rickerston and Graham 1980). Over the short period of time represented by the

preclosure period, ventilation may reduce the brine ingress induced by the thermal gradient near the waste package by about 10% (Claiborne, Rickerston and Graham 1980).

Ambient, preemplacement temperatures in salt are a function of the particular salt formation considered and the repository depth. A representative value would be 27°C (USDOE 1986c). Recent estimates of maximum salt temperatures, those occurring at the container/host rock boundary, are about 125°C at 10 to 20 years after emplacement (USDOE 1986c). This estimate is conservative because ventilation cooling is not considered during the operational and retrievability periods that bound this maximum-heat part of the postemplacement period. Thus, temperatures within the waste package and adjoining salt have reached maxima and are beginning to decline as the repository is closed. Temperatures seem to be quite independent of waste package placement because of the high heat conductivity of salt.

#### 2.1.2.3 Tuff

Sinnock, Lin and Brannon (1984) report an estimated 20°C ambient temperature in the unsaturated-zone tuff at repository depth (~500 m). The conceptual design of the waste package emplaced in a tuff repository allows air access to most of the container so that convective air-cooling would be very efficient in a ventilated repository. Because repository sealing in the unsaturated tuff repository involves no backfilling of emplacement holes and rooms, natural air-convection will continue to be a major heat-transfer mechanism during and after permanent closure.

As previously observed, as long as waste package temperatures significantly exceed host rock temperatures, no water will condense on the metal waste package skin. As long as this condition is maintained, hot water vapor will surround the waste package, and the temperature gradient in the rocks surrounding the waste package will maintain a proportional water-content gradient in the rocks. Drier conditions will prevail nearer the heat sources, especially during the preclosure period while the repository is ventilated and both heat and humidity are exhausted. From this perspective, it could be advantageous to maximize spent-fuel waste package thermal loading for disposal in unsaturated tuff. The integrity of waste package components (i.e., a 350°C internal limit

to ensure the stability of the cladding, as in USDOE 1986a) would be a limitation to consider. From another perspective, however, it may be that lower temperatures generally give greater assurance that repository behavior will be more readily predictable.

### 2.1.3 Redox Potential

The degree to which a waste package environment is oxidizing or reducing is largely determined by the amount and reactivity of redox-buffering components (e.g., natural minerals, dissolved species, emplaced metals) that occur within that environment. Polyvalent metal ions or ion complexes can be oxidized or reduced in response to the oxidation-reduction (redox) potential of the environment or in response to highly localized redox conditions resulting from the presence of specific reduced minerals or mineral assemblages. It is this localized control of redox and the kinetic controls on the buffering capacity of a given redox couple or mineral assemblage that make the measurement of a representative redox potential difficult. Because the oxidation state or the charge of a metal ion or ionic complex can determine its solubility or its sorption behavior, the prevailing redox potential will determine the mobility of many metal ions. Also, the presence of reduced aqueous or solid metal sulfides or oxides can result in the precipitation or adsorption of a number of other, especially divalent, metal ions.

During the preclosure period, ventilation will ensure an oxidizing environment in the excavated areas. As waste packages are emplaced, reducing microenvironments could be created, under some circumstances, at metal barrier surfaces. It is also possible that thermophilic, anaerobic, radiation-resistant bacteria may be introduced during preclosure that would control redox conditions in their immediate microenvironment. A review of this possibility and its likely consequences occurs in West et al. 1984. The general improbability of significant consequences, caused by a lack of available carbon as much as the severity of the near field environment, makes further discussion of bacterial effects unnecessary for the purposes of this review.

### 2.1.3.1 Basalt and Crystalline

The expected Eh (redox potential) for ambient conditions within basalt or crystalline rock is estimated from the observed existence of stable minerals or mineral assemblages. For example, an Eh of -0.2 V has been estimated as a representative value for a crystalline host rock at repository depth (RRC-IWG 1986), which coincides with the lower value of the Eh range of amorphous iron oxyhydroxide stability (Deutsch, Jenne and Krupka 1982). In basalt, an early estimate of an ambient Eh of about -0.4 V, based on the observed presence of magnetite and pyrite as apparently stable secondary minerals (Smith et al. 1980; USDOE 1986b), has received support from laboratory experiments using crushed basalt and waters over a range of temperatures, which resulted in similar Eh values (Lane, Jones and West 1984; Jantzen 1984).

During the preclosure phase, ventilation and the placement of well-oxygenated packing materials will ensure an oxidizing environment for spent-fuel waste packages in either basalt or crystalline rock. Less certain is the effect of this oxygen-rich environment on fresh basalt or crystalline rock surfaces, such as those presented by the crushed host rock in the packing material and backfill.

Excavation surfaces, however, may become weathered and well oxygenated during the preclosure period because these surfaces may be wet and in an oxidized environment for a number of years. With a pressure gradient that ranges from hydrostatic in the rock to atmospheric at excavation surfaces, the presence of water films near or on these surfaces seems likely. Experiments on the uptake of dissolved oxygen by fresh basalt surfaces has shown that this is a relatively rapid process (Lane et al. 1984; Lane, Jones and West 1984). Similarly, White and Yee (1984) present data on the uptake rate of dissolved oxygen by fresh basalt surfaces. Their results suggest that aqueous diffusion rates of oxygen controlled the oxygen uptake rate. Oxygen uptake rates for fresh basalt surfaces seemed to be comparable to magnetite uptake rates, suggesting that basalt-surface magnetite was the dominant sink for oxygen. The initial rapidity of these observed oxidation reactions and their decreasing rates over time led the authors to speculate that oxygen uptake on weathered basalt surfaces could be very slow. The preclosure weathering of fresh basalt

surfaces will be controlled by using freshly crushed basalt packing material enclosed in a steel shell and relatively freshly crushed basalt in backfilling rooms (USDOE 1986b). The role of metal barrier materials in returning the repository to reduced conditions has been neglected in this discussion. The removal of oxygen by reaction with metallic surfaces should also be an important determinant of the rate at which oxygen is depleted at depth after closure.

#### 2.1.3.2 Salt

Panno and Czycinski (1984) cite potentiometric and other evidence that suggest mildly reducing conditions generally prevail in brine inclusions within salt. Oxidized and reduced forms of carbon, iron, and sulfur are thought to buffer the Deaf Smith site host rock and deeper formations at an Eh of  $-0.1$  V or lower (USDOE 1986c), suggesting a nonequilibrium, mixed potential (Lindberg and Runnells 1984). Therefore, a case exists for suggesting that undisturbed deep salt formations are generally not oxidizing environments. However, the very near field will become well-oxygenated during the preclosure period, and, since there are no solid phases to buffer this oxygen influx, the waste package metals will be the only significant reduced phases available for oxidation.

The packing material to be used in a salt repository is crushed, well-oxygenated salt. As previously discussed,  $\gamma$ -radiolysis of salt brine inclusions may also produce oxygen. The brines that will first contact the metal barriers are almost certain to be oxic. As corrosion proceeds, however, the production of iron oxyhydroxides will use up the available oxygen and whatever oxygen that may be produced by  $\gamma$ -radiolysis and transported to the heat source. During the preclosure but postemplacement period, therefore, conditions for corrosion will be optimal, as long as salt creep and brine in-migration result in a solid/liquid interface at the metal barrier surface.

### 2.1.3.3 Tuff

The tuff repository will be located in the unsaturated zone so conditions in the host rock will be oxidizing. Also, no major reduced mineral assemblages exist in this host rock (USDOE 1986a). As in the case of salt, the metal barrier(s) (stainless steel, Zircaloy) will control the redox potential in the microenvironment that would be seen by water on or in the waste package. It appears certain, however, that during and beyond the preclosure period, repository conditions will be oxidizing.

### 2.1.4 Ground-Water Flow

Ground-water flux is the rate of ground-water flow, which can mean either the velocity of the ground water or the volume of ground water moving through a specified area in unit time. Because a regulatory requirement specifies a minimum preemplacement ground-water travel time, flux estimates for the U.S. repository program tend to be focused on the ground-water velocity. Volumetric water flux estimates become important when mass transfer calculations are done to estimate radionuclide fluxes. Because estimates of preemplacement ground-water travel times are of special interest, ground-water flux is discussed in greater detail in the preclosure section.

#### 2.1.4.1 Basalt and Crystalline

Ground-water flow in saturated-zone repositories, such as proposed for the basalt and crystalline host rocks, can be estimated from measurements of hydraulic head differences across an area of sufficient size. Problems arise, of course, if the gradient is so low as to be masked by analytical uncertainties in measurement. Also, pressurized, confined aquifers present special difficulty to one attempting to establish flow rates and directions from well measurements.

In basalts, the near field will be the interior of a dense basalt flow. Thus, ground-water flow paths in the near field may not be very different from those expected for a repository in dense but fractured granite. Away from the near field, flow paths will differ more for basalt and crystalline rocks; however, the more similar near fields control the environments and behaviors of the waste packages.

In materials prepared to support the U.S. DOE (1986b), Long (1984) presents preliminary estimates of advective vertical flow rates to a basalt-flow top 40 m above a repository in a dense interior. Their estimates show that the 40-m distance is covered in about 9000 years, corresponding to an equivalent  $10^{-10}$  m/s Darcy water migration rate. The assumed hydraulic properties of the dense interior were (approximately) hydraulic conductivity,  $10^{-13}$  m/s (based on horizontal conductivity measurements); specific storage coefficient,  $10^{-7}$ /m; effective porosity,  $10^{-4}$ ; mass dispersivity, 0.2 m; and a  $10^{-4}$  m/m hydraulic gradient as a driving force. Thermal effects on hydraulic properties were also estimated.

Crystalline rock hydraulic data were compiled from the literature by Harrison et al. (1983), and those measured hydraulic conductivities range from approximately  $10^{-5}$  to  $10^{-14}$  m/s. Rock descriptions and emplacement histories were not compared with these numbers to establish a relationship between rock qualities and hydraulic conductivities. At or near a 1000-m depth, a  $10^{-10}$  m/s hydraulic conductivity seemed a reasonable middle-ground estimate for these reported values. Tammemagi and Chieslar (1985) also reviewed the literature on crystalline rock properties, and their recommended formulation for estimating hydraulic conductivities as a function of depth leads to a value somewhat less than  $10^{-8}$  m/s at 800- to 1000-m depths. Porosities ranged from less than 0.1% to 3%. For porosities at or near a 1000-m depth, a porosity of 0.01% was recommended by Osnes et al. (1984) and Tammemagi and Chieslar (1985). Judging from these two parameters only, the dense interior of the basalt seems to be the rough equivalent of the "tighter" crystalline rocks tested.

A bounding calculation for flux in granite may be instructive. Assuming a 0.1% effective porosity, a cubic meter of saturated rock with a density of  $2.8 \text{ g/cm}^3$  [Isherwood (1981) shows a range of 2.7 to  $2.9 \text{ g/cm}^3$  for crystalline rocks and a  $2.9 \text{ g/cm}^3$  value for a "typical" basalt] may have a water content of about 3 L. To vertically displace these 3 L, a representative cubic meter must be raised by 1 m, which, at a rate of  $10^{-9}$  m/s (an order of magnitude faster than the estimate of the dense interior of the basalt discussed above) takes more than 3 years. This rate corresponds roughly to 100-mL per year passing through a given square meter of the repository, which means 1 L/year will be

flowing through the  $10\text{-m}^2$  horizontal plane of a 1- x 10-m cylindrical waste package hole containing perhaps two metric tons of uranium (MTU). Thus, 0.5 L/year/MTU may flow past the waste packages in this hypothetical, saturated, hard-rock repository. A similar  $0.1\text{-L/m}^2/\text{year}$  flow rate was considered a realistic yet conservative value for three granite locations in Sweden by Andersson, Kjellbert and Forsberg (1984).

The above estimates do not give any indication of the water flow to be expected during the preclosure period. During the preclosure period, the pressure gradient will be steep from atmospheric to hydrostatic across the excavation surfaces. Water flow into excavations could, therefore, be accelerated. At the same time, the heat of the waste packages and the swelling of the clays from the periphery of the packing material inward will likely create a moisture gradient in the waste package that results in the metal barriers staying essentially dry. Only careful simulation or in situ testing will yield answers that can define the preclosure behavior of the hydraulic system at depth. Concerns about the likelihood of wet-dry cycling, which may stress and perhaps cause cracks in the bentonite, need to be experimentally evaluated by careful, realistic simulations.

#### 2.1.4.2 Salt

In the stable interiors of salt beds and domes, the existence of any type of water (brine) flow in the salt itself is problematic and is the subject of some significant controversy. The possibility exists that water may enter salt at one location and diffuse, molecule-by-molecule, as a saturated brine from crystal-to-crystal in response to a water activity gradient. Also, this water may eventually emerge from the salt at another location and contribute to a saline aquifer. A more likely scenario is the flow of brine through interconnected lenses of sedimentary material (clay, silt). The U.S. DOE (1986c) reports about a 9% clay/impurity content for the salt at the candidate location at Deaf Smith. The probability exists that some impurity layers are water-bearing and conductive. The age and current integrity of candidate salt bodies, however, argues that flow through the clay interbeds would not compromise the ability of salt to isolate waste. A heat source in salt will induce the migration of an all-liquid brine inclusion toward that source. The

mechanisms for this migration may be simply described in terms of a greater solubility for major salt components at a higher temperature. Hence, a brine droplet will tend to dissolve salt facing the heat source and precipitate it again in the slightly cooler region pointing away from the heat source. Brine inclusions that contain a vapor phase, on the other hand, migrate away from a heat source if that vapor phase constitutes more than about 10% of the inclusion volume (Olander 1984). This behavior results from vaporization of water at the warmer end of the brine inclusion and its condensation at the cooler end. The condensate dissolves salt in the direction pointing away from the heat source, and this salt is precipitated where the vaporization takes place, resulting in the migration of the inclusion. Water in impurity lenses would be expected to migrate away from a heat source, and it is not clear what the net effect, in terms of brine supply at the waste package, may be.

About one third to one half of the total brine accumulation at the waste package is expected in the first 50 years after emplacement. The range is a function of whether or not a threshold temperature gradient exists below which no migration occurs (USDOE 1986c).

The brine migration rate is reduced about 10% during the air-cooling of the repository. Judging by the estimates given by U.S. DOE (1986c), a few hundred liters of brine could surround each waste container by the time of permanent closure, representing less than 100 mL of brine per square centimeter of metal barrier surface. These are estimates that do not consider the potential movement of brine through clay interbeds. These estimates will be refined during the site characterization process even though the inflow of brine through clay lenses, while there is a steep pressure gradient across opening surfaces, should not be taken to be indicative of flow in the postclosure period.

#### 2.1.4.3 Tuff

The unsaturated tuff host rock represents a different ground-water flow regime. In the unsaturated zone, water will not flow in response to gravity unless the rock matric potential is exceeded. Because matric potentials appear to be high (-5 to -25 bars in one instance) in the welded tuff of interest and moisture content appears to be relatively low [about 5% by weight (USDOE 1986a)], liquid water is not expected to move downward with gravity as the

direct motive force. Current estimates for the average annual flux through the undisturbed candidate repository horizon are well below 1 mm/yr (USDOE 1986a). At a 1-mm/yr flux rate, water volumes of 114 L/yr have been estimated to pass through the repository horizon (USDOE 1986a), assuming an 11 W/m<sup>2</sup> heat loading. This water volume represents approximately 0.1 L/yr per metric ton of emplaced spent fuel.

During the preclosure period, emplaced wastes will create a steep thermal gradient. Increasing the temperature is known to decrease matric potential (Taylor and Ashcroft 1972). A variety of mechanisms have been postulated to explain this behavior, but the direct correlation between water vapor pressure and temperature is sufficient to allow one to visualize the movement of water away from a heat source. During the preclosure period, waste containers will be contacted by warm, moist air but not by liquid water.

#### 2.1.5 Ground-Water Composition

Preemplacement ground-water compositions should not be radically altered by the building of the repository, except that in some cases pressures and temperatures will be reduced before waste emplacement, resulting in solution off-gassing and perhaps some mineral (e.g., calcite) precipitation. When the spent-fuel waste is emplaced, temperatures will be increased markedly. For some dissolved constituents (i.e., NaCl, KCl, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, SiO<sub>2</sub>, etc.) this means a solubility increase. However, dissolved compounds with retrograde solubilities will either precipitate (e.g., CaSO<sub>4</sub> and CaCO<sub>3</sub>) or volatilize out of solution (e.g., H<sub>2</sub>S, CO<sub>2</sub>). If steam is produced, dissolved-solid constituents will likely remain at the location where the vaporization occurred. The solution, if any remains at that locality, would become more concentrated. The introduction of organic compounds before closure should be strictly controlled so as to minimize potential enhancement of radionuclide complexation.

In this section, representative estimates of preemplacement ground-water compositions are presented. Postemplacement ground-water compositions need to be evaluated using thermodynamic calculations that are beyond the scope of the present study. The assumption of thermodynamic equilibrium inherent in current

thermodynamic modeling may lead to estimates that are not exact. Sensitivity and uncertainty analyses may allow the importance of this assumption to be evaluated.

#### 2.1.5.1 Basalt and Crystalline

Measured constituent concentration ranges for Grande Ronde basalt ground-water samples are given in Table 2.1. The Grande Ronde basalt contains the Cohasset flow, which is currently the preferred repository candidate horizon.

The crystalline preemplacement ground-water composition at depth (800 m) is "generic," representing data from a number of U.S. locations. The data

TABLE 2.1. Range of Concentration and Mean Compositions of Major Inorganic Constituents of Grande Ronde Basalt Ground Waters<sup>(a)</sup>

<u>Constituent</u>	<u>Range</u>	<u>Mean</u>
Anions (mg/L)		
HCO <sub>3</sub> <sup>-</sup>	64 to 251	157
Cl <sup>-</sup>	71 to 507	221
SO <sub>4</sub> <sup>-2</sup>	1.7 to 199	92
NO <sub>3</sub> <sup>-</sup>	<0.5	<0.5
F <sup>-</sup>	11 to 44	27
Cations (mg/L)		
Na <sup>+</sup>	161 to 373	269
K <sup>+</sup>	0.4 to 25	9.7
Ca <sup>+</sup>	1.0 to 10	2.7
Mg <sup>+</sup>	0.01 to 0.17	0.04
SiO <sub>2</sub> (mg/L)	82 to 162	103
Total dissolved solids (mg/L)	527 to 1,129	830
pH (field at 25°C)	9.1 to 10.6	9.6

(a) From USDOE 1986b.

shown in Table 2.2 are estimates for a hypothetical location but reflect the likelihood that at-depth water encountered in United States crystalline terrains tends to be of high ionic strength.

#### 2.1.5.2 Salt

The near field will see interstitial salt brines that cannot be described using analytical data for aquifers above or below the salt formation. For the Palo Duro Basin, Lower San Andres Cycle 4 and Cycle 5 salt fluid inclusions have been analyzed, and a representative synthetic brine composition has been formulated for the Cycle 4 salt for use in simulation testing (Table 2.3). The

TABLE 2.2. Composition of a Generic Ground Water in Deep Crystalline Rock <sup>(a)</sup>

<u>Characteristic of Component</u>	<u>Concentration, mg/L</u>
pH	8.0 (units at 25°C)
Eh	-0.25V
Ca <sup>+2</sup>	2,800
Na <sup>+</sup>	2,500
Mg <sup>+2</sup>	150
Fe <sub>tot</sub>	5
K <sup>+</sup>	20
Sr <sup>+2</sup>	50
Mn <sup>+2</sup>	0.5
HCO <sub>3</sub> <sup>-</sup>	25
Cl <sup>-</sup>	9,000
SO <sub>4</sub> <sup>-2</sup>	500
F <sup>-</sup>	2
PO <sub>4</sub> <sup>-2</sup>	0.3
SiO <sub>2</sub>	6
NO <sub>3</sub> <sup>-</sup>	0.2
Br <sup>-</sup>	100

(a) Based on RRC-IWG 1986.

TABLE 2.3. Synthetic Brine Composition for Lower San Andres Cycle 4 Salt Fluid Inclusions<sup>(a)</sup>

<u>Component</u>	<u>Concentration, mg/L<sup>(b)</sup></u>
Na <sup>+</sup>	22,600
Ca <sup>+2</sup>	20,000
Mg <sup>+2</sup>	64,200
K <sup>+</sup>	12,100
Cl <sup>-</sup>	252,000
Br <sup>-</sup>	4,400
SO <sub>4</sub> <sup>-2</sup>	5,380

(a) Moody, J. B. 1987.

(b) Converted from mg/kg values using density of 1.3 kg/L.

brines from fluid inclusions tend to be acidic (Moody 1987) and may be slightly reducing if some methane gas and small amounts of pyrite are present in the salt (USD0E 1986c).

#### 2.1.5.3 Tuff

Ogard and Kerrisk (1984) compare data for waters taken from north of Yucca Mountain (the candidate tuff repository location, well J-13), a few kilometers east of Yucca mountain, and other nearby locations. The ground-water composition data appear to be similar. The analysis shown in Table 2.4 represents the average composition of J-13 well water used as control blanks in experimental work reported by Oversby (1985). An analysis of one of the composite samples from the J-13 well has been chosen as the reference ground-water composition for tuff (Guzowski et al. 1983).

#### 2.1.6 Stress

Repository conditions that could physically stress the waste package are the lithostatic pressure, tectonic stresses, rock stability and the potential for heat-induced rock failure, the swelling pressure of the host rock and

TABLE 2.4. Average Chemical Analysis of Water Samples from Well J-13 Used as Control Blanks in Experimental Work<sup>(a)</sup> (mg/L unless otherwise noted)

<u>Constituent</u>	<u>Concentration</u>
Na <sup>+</sup>	44.7
K <sup>+</sup>	5.11
Ca <sup>+2</sup>	12.7
Mg <sup>+2</sup>	1.92
HCO <sub>3</sub> <sup>-</sup> + CO <sub>3</sub> <sup>-2</sup>	136.0
SO <sub>4</sub> <sup>-2</sup>	18.7
Cl <sup>-</sup>	6.9
NO <sub>3</sub> <sup>-</sup>	9.6
F <sup>-</sup>	2.2
Si (total)	27.1
Fe (total)	0.008
Li <sup>+</sup>	0.044
Al <sup>+3</sup>	0.014
pH	6.9 (units) <sup>(b)</sup>

(a) Oversby 1985.

(b) Ogard and Kerrisk 1984.

certain packing materials, the increased volume of corrosion products, and hydrostatic pressure. The vapor pressure resulting from water contact with a heated container might also, under some circumstances, stress the waste package, and cause hydrothermal alterations in the near field host rock that can further contribute to the increase of pressure.

#### 2.1.6.1 Basalt and Crystalline

Deep underground openings in basalt and crystalline rock will be shaped and sized to maximize rock stability. Nevertheless, spalling or rock failure

is a possibility in vertical boreholes, especially at openings (USDOE 1986b) and when the lower portion of a borehole is heated and compressed by thermal expansion (Brandshaug 1983). These failures are dependent on in situ stress, temperature, and rock quality. The hypothetical consequences of these failures could be a decreased thermal conductivity between the waste package and the ventilated drift and some increased difficulty with retrieval (Brandshaug 1983).

The possibility of steam pressure building up in an emplacement borehole that is well-sealed from the drift is mentioned in the RRC-IWG (1986) report. The maximum pressure during the operational period is the saturation vapor pressure of water at the temperature of the heat source. For a  $20 \text{ W/m}^2$  spent-fuel repository with a  $170^\circ\text{C}$  maximum container surface temperature, the pressure would be 0.6 MPa (RRC-IWG 1986). This value is approximately the pressure equivalent of 62 m of  $\text{H}_2\text{O}$  and is well below the expected hydrostatic pressures that will prevail in basalt or granite repositories after permanent closure. More recent design data for the basalt repository (USDOE 1986b) suggests a hotter waste package will be emplaced. Newer temperature estimates are  $200^\circ\text{C}$  for the container surface and an average of  $145^\circ\text{C}$  for the waste package over its performance life. Still, vapor-pressure stress effects during the pre-closure period are of little concern in terms of waste package integrity.

#### 2.1.6.2 Salt

The expected lithostatic pressure of overburden and salt is 22.6 KPa/m. Therefore, at the 800-m depth, the expected lithostatic load is 18 MPa (USDOE 1986c). Backfilled individual waste package emplacement holes may be resuritized to lithostatic loads within 5 years, and host rock thermal expansion effects may temporarily increase pressures on the waste package above lithostatic. Salt-rock creep is expected to mitigate these higher pressures, however, and readjust lithostatic pressure to ambient.

#### 2.1.6.3 Tuff

The unsaturated tuff has no hydrostatic pressure, and rock properties are such that openings are thought to be stable indefinitely (USDOE 1986a). High

temperatures could possibly induce borehole surface fracturing, but this fracturing is not likely at projected temperatures and would have no impact on waste package integrity (DOE 1986a).

## 2.2 POSTCLOSURE THERMAL PERIOD ENVIRONMENT

At the time of permanent closure, ventilation will have stopped, backfills will be in place, and shafts will be sealed. As soon as the repository is sealed, the underground environment will begin to change, and the long-term postclosure environment will be gradually established.

### 2.2.1 Radiation

High  $\gamma$ -radiation levels from the spent-fuel waste form begin to abate soon after the beginning of the postclosure period. Generally, the surface gamma dose rate from a typical spent-fuel assembly will be reduced by three orders of magnitude from the time of emplacement to 500 years after closure (USDOE 1980). However, even low  $\gamma$ -radiation doses may still result in some ground-water radiolysis that enhances the metal corrosion rate (Christensen and Bjergbakke 1982). In the host rock discussions that follow, the emphasis is on radiation effects. Keep in mind, however, that radiolytic oxidants are not the only possible oxidants in the repository and if reducing conditions exist in the bulk host rock, there may be reduction of oxidizing radiolysis products as they diffuse away from the waste package surface.

#### 2.2.1.1 Basalt and Crystalline

As the postclosure period progresses, gamma dose rates to the near field are reduced over time and the packing materials will receive the bulk of their expected total cumulative gamma dose. Cumulative gamma radiation effects on clays are currently under investigation in the U.S. and Canada. Preliminary results from Canada<sup>(a)</sup> suggested that, to a degree, smectite clay may be transformed to illite and to zeolite if the pH is greater than 9 as doses accumulate. However, the corresponding reductions in cation exchange capacity

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(a) As reported by R. B. Heimann at "The 19th Information Meeting of the Canadian Nuclear Fuel Waste Management Program, Engineered Barriers and Waste Forms," May 14-16, 1985, Toronto.

and swelling potential may be compensated for by corrosion products migrating into the packing material from container corrosion. The dose rate and cumulative dose to the packing material is a function of waste and waste package characteristics. Based on expected waste form and preliminary waste package design characteristics for the basalt repository, Reed, Bonar and Weiner (1985) show that very low dose rates and cumulative doses are expected in the packing material and negligible impacts on packing material characteristics are expected.

The expected mean integrity time for a metal barrier of a basalt repository waste package, assuming general uniform corrosion as the controlling failure process, is currently on the order of 6100 years (USD0E 1986b). Failure time of a waste package metal barrier is defined as the time when the sacrificial metal layer has been corroded, but is not necessarily the time when radionuclide/ground-water interaction actually begins. For the sake of conservatism, the U.S. DOE (1986b) suggested that metal barrier failures begin at a low rate at 4500 years. Gamma radiolysis of ground waters has been calculated to be directly proportional to dose rate, even at such low dose rates as  $10^{-4}$  rad/h. At  $10^{-4}$  rad/h, on the order of  $10^{-6}$  moles of hydrogen could be produced per year (Christensen and Bjergbakke 1982). The production of oxidizing radiolysis products, such as  $O_2$  and  $H_2O_2$ , would be proportional to each other, except that recombination reactions would lower the corrosion potential implied by the production rates. The U.S. DOE (1986c) cites calculations that suggest a square root relationship between dose rates and oxidizing-species production rates in brines, and an experimentally determined threshold of 10 rads/h, below which corrosion rates are negligibly enhanced. If that threshold is also a good approximation for basalt or crystalline repository conditions, radiation enhancement of corrosion rates, assuming at least a 5-cm metal barrier, should cease to be a consideration. At high dose rates, the radiolytic production of organic polymers in synthetic ground waters under methane was reported by Gray (1984a). At lower dose rates (Soo 1985) or in the presence of iron (McGrail 1985), such polymers were not observed.

#### 2.2.1.2 Salt

As discussed for basalt and crystalline, ground-water radiolysis potentially provides a supply of oxidizing species in some proportion to the dose rate, perhaps even at very low dose rates (Gray 1984b). In the case of a repository in salt, the metal barriers of the waste package present the primary, if not the only, material that can reduce these oxidants. Metal barrier corrosion rate estimates that account for enhancement by heat and radiation flux were extrapolated to yield a metal-barrier integrity time of at least 10,000 years (DOE 1986c). At  $10^6$  rads/h the corrosion enhancement was reportedly twentyfold, while at less than 10 rads/h, the contribution of radiation dose to corrosion rate was negligible, as already discussed. With a 12-cm metal container, salt  $\gamma$ -dose rates are expected to be below 10 rads/h at the time of spent-fuel waste package emplacement (USD OE 1986c). However, the effectiveness of the metal barrier in reducing dose, as calculated in Clark and Bradley (1984), suggests that perhaps during the first 50 years after permanent closure, corrosion rates could potentially be enhanced by radiation doses at the brine/metal interface.

#### 2.2.1.3 Tuff

The expected 10,000-year container lifetime in tuff (USD OE 1986a) is based on extrapolating uniform corrosion data obtained under high gamma flux. The postclosure gamma dose rates at the 1-cm-thick, metal barrier surface will not be below 10 rads/h until about 150 years after closure (about 200 years after emplacement), judging from graphical dose rate calculations presented in U.S. DOE (1986c). Corrosion rates could potentially be radiation enhanced for a period after permanent closure, if indeed warm water-vapor corrosion of stainless steel is shown to be enhanced by  $\gamma$ -radiation in an oxidizing, open system. In the tuff's unsaturated environment, nitric/nitrous acid production by the  $\gamma$ -radiolysis of atmospheric nitrogen is likely until the gamma flux is negligible.

#### 2.2.2 Temperature

During the postclosure containment period, the repository, as a whole, will reach its maximum temperatures. As soon as forced ventilation ceases and

backfill is in place, temperature gradients will readjust within a few years after closure. Temperatures and gradients a few years after closure may be nearly indistinguishable from temperatures that would have prevailed had closure been simultaneous with emplacement.

#### 2.2.2.1 Basalt and Crystalline

Recent analyses of expected corrosion rates in a basalt repository assume that for the first 100 years, an air/steam environment would surround the metal barrier surfaces (USDOE 1986b). Hence, the very early postclosure environment may have water vaporizing if it approaches the hot metal barriers. As pressure increases after final closure and temperatures begin to fall, vaporization will cease and a hot-water environment can be seen by metal barrier surfaces (RRC-IWG 1986). In the EA (USDOE 1986b), this hot-water period ( $>125^{\circ}\text{C}$ ) is assumed to last for 200 years, with lower-temperature, aqueous environments prevailing thereafter.

Some repository thermal calculations (RRC-IWG 1986) assume a  $20\text{ W/m}^2$  loading for a spent-fuel repository. These estimates use a waste package heat loading that is less than suggested by more current designs (USDOE 1986b), but the predicted watt/area density is similar to what is currently expected. For example, if the entire basalt repository loading is to be 70,000 MTU of 10-year-old 33,000 MWd/MTU burnup spent fuel at  $1,210\text{ W/MTU}$ , the total watt output,  $8.5 \times 10^7$  (USDOE 1979), spread over the total underground area (800 ha or  $8 \times 10^6\text{ m}^2$ ) gives an  $11\text{ W/m}^2$  thermal loading at emplacement. The acceptance and placement of higher "burnup" or 5-year-old fuel is possible, however, and may result in higher repository heat levels, approaching those assumed for most calculations. There may be significant differences between waste thermal characteristics assumed for planning purposes (i.e., USDOE 1986b) and the character of the waste that may actually be accepted.

One portrayal of expected repository temperatures by U.S. DOE (1986b) is based on a thermal loading of  $8.2\text{ W/m}^2$ . This case loading is realistic because even the  $11\text{-W/m}^2$  estimate (for an assumed 1-m-high waste package zone) assumes an unrealistically high burnup rate and short preemplacement cooling time for the first repository spent-fuel inventory. At this "realistic" thermal loading, the repository level (horizon) is at about  $110^{\circ}\text{C}$  at 100 years after

emplacement, which is 50 years into the postclosure period, given the assumptions made here. The repository horizon is at about 100°C at 500 years (450 years postclosure) and at about 90°C at nearly 5000 years after emplacement (USDOE 1986b).

#### 2.2.2.2 Salt

Near field temperature profiles for a spent-fuel waste package surface in U.S. DOE (1986c) and Claiborne, Rickerston and Graham (1980) are in general agreement for the first 100 years, taking into account differences in assumptions. An ambient, pre-emplacment temperature of about 32°C was assumed by U.S. DOE (1986c). At the time of permanent closure (i.e., 50 years after placement) the spent-fuel waste package (including overpack) was calculated to be at 118°C; at 500 years after placement, it was estimated to be at 79°C.

Maximum salt temperatures close to the spent-fuel waste package should occur at about 50 years after emplacement, according to Claiborne, Rickerston and Graham (1980). The calculations shown in U.S. DOE (1986c) suggest that temperatures in salt will probably peak at about 20 years after placement. This discrepancy is a function of differences in both the models used and the assumptions made regarding waste package heat outputs. In any case, at the time of permanent closure, the maximum temperature of salt nearest the spent-fuel waste package will be at or near 130°C (USDOE 1986c).

#### 2.2.2.3 Tuff

The repository areal thermal loading currently assumed for tuff ranges from 10.0 to 11.9 W/m<sup>2</sup> (O'Neal et al. 1984). However, although other analysts have assumed values as high as 12.4 W/m<sup>2</sup> (Jackson 1984), the repository areal thermal loading is still being evaluated (Johnstone, Peters and Gnirk 1984). O'Neal et al. (1984) reproduced temperature profiles for a conservative thermal loading assumption of near 12 W/m<sup>2</sup>, which suggest that near field temperatures at the start of the postclosure period (about 50 years after emplacement) will range from 200°C at the borehole wall to 230°C at the container surface. Temperatures will drop rather rapidly, with perhaps a 50°C lowering in the next 50 years. At 1000 years, temperatures are expected to be near 100°C throughout the near field.

### 2.2.3 Redox Potential

At the time of permanent closure, the flow of air into a basalt, crystalline, or salt host rock repository ceases. The tuff repository is to be built in the unsaturated zone where air is present by definition. Postclosure oxidation-reduction potentials in the repository may be dramatically different, depending on the choice of host rock.

#### 2.2.3.1 Basalt and Crystalline

Both basalt and crystalline host rocks are expected to take up oxygen after permanent closure and thereby help restore the reducing conditions that prevailed before the repository. Laboratory experiments by Jantzen (1984) showed that water and basalt, at elevated temperature, approached an Eh of  $-0.4$  V; this complements White and Yee's (1984) work and underscores the likelihood that the reducing host rock surfaces exposed by excavation to years of ventilation may become significantly oxidized by the time of permanent closure. Oxygen may diffuse into the host rock, but at a very slow rate. Given this possibility, the mass of reduced metal that constitutes the containers is likely to play an important role in reducing the repository environment.

One method for accelerating or ensuring the reestablishment of reducing conditions is the use of large amounts of relatively freshly crushed host rock as a major packing material and backfill component. Plans are to ensure that the rock can be crushed so that the fresh surfaces are kept dry. The material to be packed around the waste containers is enclosed by a metal shell, and the time between crushing and emplacement is minimized so that the air remaining after the repository is backfilled may be rapidly depleted of its oxygen content. If this rapid oxygen depletion is accomplished, the preliminary prediction for the beginning of containment failure, which was based on uniform corrosion rates assuming the unrestricted availability of atmospheric oxygen (USDOE 1986b), may be lengthened and begin to approach 10,000 years. Of course, if mechanisms other than uniform corrosion are operative, the containment period could be reduced.

### 2.2.3.2 Salt

As discussed in Section 2.1.3, the redox status of a repository in salt is going to be oxidizing at closure. Oxygen introduced during the preclosure period and produced by  $\gamma$ -radiolysis of brines at the surface of the container may be used up as corrosion proceeds or, perhaps, be reduced in the host rock. The brine itself is also assumed to be completely used up in the corrosion process (Jansen et al. 1985). After the brine is used up and brine in-migration stops, corrosion stops and the metal barriers last indefinitely, assuming that only uniform corrosion controls waste package failure. This describes the expected case for a repository in salt (USD0E 1986c). However, this expected case assumes a uniform distribution of available brine over the waste package, resulting in only uniform corrosion. Further site-specific work at depth will allow these assumptions to be experimentally evaluated.

### 2.2.3.3 Tuff

During the period of active corrosion of the metal barriers after gamma flux and thermal output are greatly reduced, it is possible that an oxygen concentration gradient may develop, especially close to metal surfaces. Subsiding temperature gradients will reduce the rate of convective air circulation and will also tend to reduce the air pressure in the excavations and draw small quantities of air and oxygen in from the surrounding rock. It is probable that oxygen diffusion through the host rock will be adequate to allow continued corrosion. Reducing conditions cannot be assumed for the unsaturated tuff repository during the containment period.

### 2.2.4 Ground-Water Flow

Ground-water flow during the postclosure period will be radically different in the four host rock types considered. Hard rock repositories in saturated zones will begin to resaturate after pumping has stopped. In a salt repository, brine migration will begin during the preclosure period and will continue at a reduced rate. In unsaturated tuff, the heat from the waste packages should ensure that the very near field is effectively dry (meaning no mobile liquid water is present) as the postclosure period begins.

#### 2.2.4.1 Basalt and Crystalline

There is no experimental work on which to base an informed estimate of the time involved in resaturating the repository after closure. The RRC-IWG (1986) report on expected repository conditions in crystalline rock gives "a couple of decades" after closure as a likely resaturation time. A 15- to 50-year period has been estimated for the saturation of the basalt repository packing material, not taking into account the effect of clay swelling (Smith et al. 1980). A recent estimate of 300 years, perhaps more fully taking into account the expected hydraulic characteristics of the dense interior of the basalt and the packing material, was used in preliminary analyses shown in U.S. DOE (1986b). The 300-year estimate represented the time to total saturation, however. It appears that some liquid water contact may occur following the 100-year duration assumed for the air/steam period.

After resaturation has begun, water may begin to contact waste package metal barriers. The waste package is engineered so that barriers will be surrounded by an expanding-clay barrier that effectively limits any movement of water or solute to the diffusion process (Smith et al. 1980). Some mineral alterations from hydrothermal effects may also be expected in the packing material and the near field host rock.

After resaturation, a temperature-induced buoyancy effect will drive water upward from the heat source because the density of warmer water is decreased. This force, therefore, is greatest shortly after substantial resaturation has taken place. At the end of the thermal period, the waste will have decayed so that less than 6% of its emplacement-time heat will be generated (USD OE 1980). Temperatures are still expected to be elevated at this point, even though the vertical temperature curve through the repository will be characterized by a broad, gentle, temperature gradient; the buoyancy effect is expected to persist as the thermal period draws to a close.

#### 2.2.4.2 Salt

If the temperature maximum in the very near field is reached at or before closure, the brine migration rate will be near maximum as the postclosure containment period begins. Near 1000 years, brine migration rates will be either

zero or about 1% of the rates at emplacement, depending on flow threshold assumptions. For practical purposes, the brine migration inflow rate becomes negligible. As the thermal period ends at about 1000 years after emplacement, brine may begin diffusing away from the waste packages (USDOE 1986c) in the absence of a steep thermal gradient, or in response to a pressure gradient (ONWI 1984). On the other hand, if there is flow through clay interbeds (USDOE 1986c), the flow that may have been retarded by the presence of the heat source may now again begin to approach the containers.

#### 2.2.4.3 Tuff

During the first 1000 years after emplacement, the near field up to a meter from the waste packages is expected to have temperatures exceeding 95°C (the boiling point for water at the proposed repository location), and no liquid water is expected to contact a waste package surface (Glassley 1986). As wastepackages cool, however, liquid waters in rock pores will migrate toward the waste packages. As the 1000-year thermal period ends, a 120°C temperature will still exist in the near field (O'Neal et al. 1984). Thus, the ground-water flow will not be expected to return to prerepository conditions until long after the thermal output of the waste packages has dropped to low levels. Because rooms, tunnels, and emplacement-hole void spaces will not be backfilled or packed, no capillary continuity will exist whereby unsaturated liquid water can reach the waste except at the bottom of the container, which rests on the tuff.

#### 2.2.5 Ground-Water Composition

During the 1000 years represented by the expected postclosure thermal period, ground water in the very near field will experience a variety of conditions. High heat, possibly high radiation fluxes, and increasing pressure characterize the beginning of this period for some repositories. At the end of the thermal period, prerepository conditions are approached, but not reached. Temperature and radiation may especially affect the ground-water composition early in this period, while accumulations of metal-barrier corrosion products may impact the ground water later in the 1000-year thermal period and beyond.

#### 2.2.5.1 Basalt and Crystalline

As the basalt or crystalline repository resaturates (if resaturation occurs in less than about 100 years) water will be forced against a thermal gradient, which will create a concentration gradient because volatilization of the water will increase closer to the heat source. If the waters have a moderate degree of carbonate saturation, calcite may be expected to precipitate because solubility is decreased at a higher temperature. Even closer to the heat source, especially while pressures are low enough to allow vaporization, other compounds may also be precipitated. As hydrostatic pressures increase, hot liquid water will eventually touch the metal barrier surfaces. The time of contact will be a function of packing material and perhaps backfill properties. Hydrothermal reactions in the backfill or the host rock, involving alumino-silicates or glassy basalt mesostasis, at or near the waste package may result in the formation of hydrated species that could potentially reduce permeabilities.

Over the long term, the ground-water composition described in Tables 2.1 and 2.2 is expected to become temporarily depleted in calcium carbonate and enriched in silica during the thermal period and become more oxygen-poor and iron-rich as corrosion progresses. For the greater part of the thermal period, the packing material/host rock and their hydrothermal alteration products are expected to control the diffusion of oxygen, if there is available oxygen in the near field, to the metal barrier surface. Barrier metals may also be saturated in the water of the very near field. Metal oxide and silicate solid phases may abound because the packing material will also limit the removal of corrosion products. It may be that corrosion products near the container and hydrothermal alteration products in the packing material may accumulate so as to reduce packing material porosity.

#### 2.2.5.2 Salt

The brine composition during the thermal period will initially be affected by high heat and oxidizing radiation, with the effects discussed in Section 2.1.4. As the radiation flux and temperature decrease, the oxygen and brine supply near the waste package may gradually be used up (Jansen et al. 1985). Toward the end of the thermal period, the ground-water composition

described in Table 2.3 may again prevail in brine inclusions far enough from the waste package to avoid the corrosion process. Near the container, iron and other barrier metal components may be saturated in any remaining brine and may be present in a variety of solid phases. As corrosion uses up water, dissolved solids will precipitate very near the container; this may also result in salts near the container being of a different composition than the bulk salt farther from the waste package.

#### 2.2.5.3 Tuff

During the thermal period, ground water could become saturated with iron oxide and hydroxide and other metal solid phases, resulting in increased but low concentrations of iron in solution. However, the composition given in Table 2.4 may still be representative of the ground-water composition that eventually reaches and corrodes the metal barriers during the containment period, although the effects of hydrothermal alteration of the host rock may have influenced ground-water compositions to some extent in the very near field. For example, Oversby (1985) reacted Topopah Spring Tuff with J-13 water at 150°C and found only the silica concentrations were affected to a significant extent. Silica in solution increased approximately fourfold over a 70-day reaction period and solubility control by cristobalite was suggested by the final concentrations obtained.

#### 2.2.6 Stress

During the postclosure containment period, stresses will increase in basalt, crystalline, and salt host rock repositories. These stresses are largely the result of reestablishing hydrostatic pressures, but the waste package may also contribute to the stress environment.

##### 2.2.6.1 Basalt and Crystalline

In a crystalline rock repository at a 1000-m depth, the water table would need to lie at about 940 m or above to suppress any steam formation in the sealed and backfilled repository (based on 60-year spent fuel temperature/vapor space pressure curve in RRC-IWG 1986). At 1000 m, the lithostatic load of a 2.9 g/cm<sup>3</sup> density basalt or crystalline rock is about 28 MPa. After the repository is completely filled with water, the expanding clay packing

materials and backfills will have reached their maximum expansion, and the host rock will have expanded somewhat into the excavation. Then, the total pressure on the waste container should be equal to or somewhat in excess of the hydraulic (hydrostatic) load, depending on the clay composition density and swelling potential in the packing material. The hydrostatic load is calculated to be about 10 MPa for a repository in basalt (Smith et al. 1980). The water and expanded clay matrix should support the rock openings, and as long as these openings are intact they will continue to dissipate and redirect strain energy around the excavations. As the repository cools and the rock contracts slightly, pressures will relax slightly and slowly reach a long-term and stable equilibrium. Any retraction of host rock from the emplacement holes will allow the pressurized, expanded clay matrix of the packing material to relax slightly. The metal barrier corrosion process will produce corrosion products that have higher molar volumes than the uncorroded metals.

#### 2.2.6.2 Salt

At a depth of about 800 m in the candidate salt horizon, minimum horizontal stress is about equal to a vertical stress of 20 or 21 MPa, as in undisturbed salt (based on USDOE 1986c). When backfilling is complete, this uniform level of stress is rapidly restored because salt creep fills voids, and high temperatures probably heal any cracks near the metal barriers. The postclosure temperature rise will probably create a climate that accelerates salt creep and may temporarily disturb near field pressure regimes, but over the long term the salt will likely readjust as temperatures gradually decrease. Well before the end of the thermal period, preconstruction stress conditions should again prevail.

#### 2.2.6.3 Tuff

Although the host rock is stressed, and mining and the thermal period may redistribute or add to that stress in a transitory manner, stress is not expected to be transmitted to the waste containers as long as boreholes remain open (USDOE 1986a). The in situ stress ratio (horizontal/vertical) is expected to be between 1 and 0.5, which is particularly favorable to the stability of

excavations (Scully and Hunter 1984). The expected case, therefore, is that only atmospheric pressure will affect the waste package during the thermal period and beyond.

### 2.3 POSTTHERMAL PERIOD ENVIRONMENTS

As discussed previously, the postthermal period is chosen as beginning at 1000 years after permanent closure. During the postthermal period, conditions in the repository very near field will probably be gradually returning to preemplacement conditions in a number of ways.

#### 2.3.1 Radiation

Gamma dose rates at spent-fuel surfaces at 1000 years after emplacement are expected to be <10 rad/h or 0.03% to 0.02% of what they were at the time of closure (USDOE 1980). These dose rates, assuming intact containers, should be negligible in terms of radiolysis or other corrosion effects at the container surface. It is not currently known if cumulative doses absorbed by metal barriers make them more susceptible to corrosion processes. With eventual breach of the metal barriers allowing brine access to the spent fuel surface, however,  $\alpha$ -radiolysis of ground water commences.

It appears that in the postthermal period, accelerated corrosion of container metals or dissolution of the waste form is a distinct probability once ground water actually contacts the  $UO_2$  matrix. Essentially, direct contact between the  $UO_2$  matrix and water is required for  $\alpha$ -radiolysis because cladding effectively stops  $\alpha$ -radiation.

##### 2.3.1.1 Basalt and Crystalline

Because bentonite clays may be used as part of packing materials and backfills in both basalt and crystalline rock repositories,  $\alpha$ -radiolysis effects on clays need to be known. Haire and Beall (1979) investigated alpha radiation damage on montmorillonite, kaolin, and attapulgite using  $^{253}Es$  (20.5 day half-life, 6.6 MeV  $\alpha$ ) in sodium chloride/acetate buffer solutions at pH 5. At Es loadings of 0.001 to 0.01 meq/100 g of clay (a one part in  $10^4$  loading of the exchange capacity), no structural damage was observed over 2 weeks. However, at 10, 30, and 100 meq/100 g of clay loadings for kaolinite, attapulgite, and

montmorillonite respectively, (clay adsorption sites were completely saturated with Es), extensive structural damage was noted in less than 1 day for montmorillonite and within 2 to 4 days for attapulgite and kaolinite. Despite extensive structural damage, the adsorbent's sorptive capacity did not decrease. In fact, Es adsorption appeared to increase slightly. These results suggest that either Es remained adsorbed on the clay fragments, or Es precipitates or colloids formed that were readily filtered.

Calculations by Beall (1984) [using the results of the work by Haire and Beall (1979)] suggested that a release rate ratio of  $10^{-5}$ /yr of radionuclides from the waste package could structurally destroy the clay fraction of a clay backfill and perhaps render it an amorphous silica-alumina gel in fewer than 200 years. The experimental results suggested that the amorphous gel that was produced still provided a barrier to ground-water flow and still acted as a sorptive medium.

Certain problems must be considered when applying these results to a basalt or crystalline rock repository. First, the saturation of montmorillonite with 100 meq  $^{253}\text{Es}$  per 100 g is extremely unlikely under expected repository conditions, given competitive adsorption between dilute actinides in solution and relatively concentrated dissolved macro cation constituents of the ground water. Second, neither the experimental rate of  $\alpha$ -emission per emitter nor the energy per  $\alpha$ -emission even remotely represent that expected in a repository. Third, kaolin and attapulgite are not likely to be used in repository engineered barriers. Kaolin is reversibly capable of becoming gibbsite, hydrated alumina, and releasing silica even under environmental conditions (Velde 1977). In the same vein, attapulgite (or palygorskite) is a temperature-sensitive clay mineral that breaks down into montmorillonite and quartz at temperatures exceeding  $80^{\circ}\text{C}$  (Velde 1977). It could be that a montmorillonitic phase was formed at the energy input rates to which the attapulgite clay was subjected in Haire and Beall (1979). Fourth, the test solution used does not resemble an expected repository ground water in pH or composition. Nevertheless, these results, and the speculative calculations based on them, do suggest that the behavior of montmorillonite under  $\alpha$ -radiation needs to be established for expected repository conditions.

Alpha radiolysis of ground-water solutions, when such solutions begin to contact spent fuel, may result in oxygen release. Burns et al. (1982) suggest that the lack of gas phase  $N_2$  in a saturated repository should prevent localized nitric acid formation. Others, however, suggest that dissolved  $N_2$  in ground water may allow  $\alpha$ -radiolytic nitric acid production (Rai, Strickert and Ryan 1980). The limited extent to which  $\alpha$ -radiolysis affects water should be appreciated, however. If more than a thin film of water is present as expected in a saturated system, oxidative radiolysis products may diffuse into the bulk solution and be reduced by host rock as well as contribute to container corrosion.

#### 2.3.1.2 Salt

Alpha radiolysis of saturated brine was studied by Pederson et al. (1984). Adding aqueous  $^{244}Cm^{+3}$  to brine under a nitrogen atmosphere resulted in  $H_2$  and  $O_2$  production, a low pH because of nitric acid production, and an extremely high oxidation potential. Rai, Strickert and Ryan (1980) review results which suggest that nitric acid production is possible in air or  $N_2$ -saturated solutions in contact with an alpha-emitting solid. Therefore, if the salt repository environment at postcontainment still has trapped air (oxygen poor, perhaps, because of corrosion) under pressure at depth, localized pH could be significantly lowered as  $\alpha$ -release begins. In a repository, however, the removal of  $N_2$  by diffusion over time could mitigate the extent to which  $N_2$  would be available as  $\alpha$ -radiolysis begins.

Experiments are in progress that more directly apply to predicting expected repository conditions. Alpha radiation effects on saturated, pressurized brines at varying gas composition levels are being studied to allow a better prediction of expected repository conditions in terms of enhanced pressures and oxidation potentials (Gray and Simonson 1985).

#### 2.3.1.3 Tuff

Container failure is not expected for tens of thousands of years after emplacement under uniform corrosion conditions (USDOE 1986a), although localized corrosion modes may cause earlier breaches of containers (Oversby and McCright 1985). When a container has failed in an unsaturated tuff repository

and alpha-emitting solids become accessible to ground water, the potential exists for  $\alpha$ -radiolysis of thin-film contact waters. Because air will be present in the repository, nitric acid can be formed in thin-film contact waters (Burns et al. 1982) and corrosion rates may be enhanced for the remaining metal structures of failed waste packages.

### 2.3.2 Temperature

At 1000 years after permanent closure, a spent-fuel assembly that was emplaced with a thermal power output of 5000 W will have its thermal output reduced to about 25 W (USDOE 1979). Therefore, in the very near field, temperature gradients will be low as the postthermal period begins.

#### 2.3.2.1 Basalt and Crystalline

As the postthermal period begins, the basalt repository will have cooled to about 100°C and will be about 45°C above the preemplacement ambient temperature (USDOE 1986b). Temperatures will fall very slowly during the postthermal period, perhaps 3° or 4°C over the next 5000 years. Therefore, near field radionuclide migration will begin to take place in an environment that is at about 45°C above preemplacement ambient temperatures. This enhanced temperature should be factored into thermodynamic, rock mechanical, or transport calculations affecting the radionuclide flux into the host rock from the engineered barrier system.

#### 2.3.2.2 Salt

When the postthermal period begins, temperatures near 70°C will prevail throughout the repository (DOE 1986c) decreasing to near the preemplacement temperature by 10,000 years after closure. The horizontal thermal gradient is not expected to be significant at the repository horizon during this period. Vertical temperature gradients should still be enhanced at the start of the postthermal period, but decrease gradually to approximate the gradient existing before the repository was built (about 2°C/100 m) by 10,000 years after closure. The higher thermal conductivity of salt [ $\sim 4.5$  W/(m·K)], compared to other candidate host rock types [ $< 3$  W/(m·K)], results in these relatively unique thermal gradient conditions.

### 2.3.2.3 Tuff

From 1,000 years to 10,000 years after closure as radionuclides begin to become accessible to ground water, thermal profiles of Sinnock, Lin and Brannon (1984) indicate that the near field temperature elevation above ambient may have fallen from near 80°C to about 20°C; hence, the 10,000-year temperature gradient will not be very steep. The very near field temperature elevation, at the time uniform corrosion is expected to breach waste packages, will not be much higher than the temperature elevations experienced by the host rock for hundreds of meters in all directions except up. If the repository is built 350 m from the surface, the gradient will be relatively steep in the upward direction from the repository even 50,000 years after closure and beyond.

### 2.3.3 Redox Potential

At the close of the thermal period, redox potentials should be as low as possible. Metal barrier oxidation will have been occurring for 1000 years, and gamma-ray-induced radiolytic production of oxidizing species will probably have ceased. As radionuclides begin to be contacted by ground water,  $\alpha$ -radiolysis of ground water may create oxidizing environments at ground water/waste-form interfaces.

#### 2.3.3.1 Basalt and Crystalline

Neretnieks and Aslund (1983) postulate that as ground water enters a container and contacts the waste form,  $H_2$ ,  $O_2$ ,  $H_2O_2$ , and uranium (VI) could result from radiolysis (largely  $\alpha$ -radiolysis). Being relatively unreactive, it is postulated that  $H_2$  will diffuse away leaving behind an environment relatively enriched in oxidizing species. These reactive oxidizing species could accelerate the corrosion of the waste form or what remains of the container and also greatly increase the solubility of some radionuclides (i.e., U, Np, Tc). As radionuclides dissolve and migrate by diffusion into the packing material and/or host rock,  $\alpha$ -radiolysis continues and a redox front with oxidizing conditions behind it begins to move away from each of the breached waste packages. Neretnieks and Aslund's (1983) analysis showed that release from the spent fuel in a single container could oxidize tens of meters in this manner. This concept was included in radionuclide migration calculations performed for the

KBS-3 safety analysis. Likewise Andersson, Kjellbert and Forsberg (1984) assumed that the entire repository surface area was oxidizing for their calculations. The extent of oxidizing conditions would be a function of the concentration of alpha-emitting radionuclides and the relative availability of reduced iron in the metal barriers, packing material, and host rock.

#### 2.3.3.2 Salt

When metal barriers begin to fail and brine contacts the irradiated  $UO_2$  matrix of the spent fuel, oxidizing conditions will probably develop within the waste package because of radiolysis; this could accelerate further corrosion of the metals and the  $UO_2$  matrix. However, because some limited brine migration (away from the brine collected around the waste package) and diffusion are the only mechanisms considered (USDOE 1986c) to transport the radionuclides, essentially no releases from the repository host rock unit are expected for at least 100,000 years after containment failure (USDOE 1986c).

#### 2.3.3.3 Tuff

For modeling purposes, water is postulated to enter the containers and contact spent fuel during the postthermal period (Oversby and McCright 1985). In the unsaturated setting of the tuff repository, it is expected that cladding and cladding breaches will result in gaseous carbon-14 releases. These releases are expected to be spread over long periods of time, however, corresponding to the time-spread over which canister breaching occurs (Oversby and McCright 1985; Rickertson and Van Luik 1985). Thin films of water in contact with the  $UO_2$  matrix will, perhaps, become a slightly more aggressive corrosive agent in the tuff repository, since it may contain some hydrogen peroxide and nitric acid radiolysis products. The net effect of these radiolytic changes in the chemistry of the ground water, in terms of possible enhancement of radionuclide transport, is unknown. This effect depends on the extent to which radionuclide solubility or ground-water flux is affected by a higher oxidation potential in an already oxic system. The net effect of a slightly more acidic solution that may be a result from a radiolytic nitric acid production may be to enhance radionuclide transport in the very near field.

#### 2.3.4 Ground-Water Flow

As the postthermal period begins, the waste heat that provided the driving force for water flow in the thermal period (i.e., buoyancy, brine migration, vaporization) is or is becoming greatly reduced. During the postthermal period, therefore, ground-water flow may be beginning to reapproach preem-placement conditions, assuming that the transitory temperature increases will not induce chemical or physical rock-property changes that are sufficient to modify the near field environment.

##### 2.3.4.1 Basalt and Crystalline

The postthermal period begins with a reduced temperature gradient across the repository, perhaps lowering the effectiveness of buoyancy as an inducer of ground-water flow. However, no threshold temperature gradient for buoyant flow is known, and perhaps only in situ testing can provide information on whether such a threshold exists.

In the rocks surrounding the repository, ground-water flow rates and directions may be tending toward their preemplacement norms. The packing and backfill materials should still effectively reduce fluxes around the metal barriers so that diffusion controls the rate of movement of materials to and from the metal barriers and the exposed waste form.

##### 2.3.4.2 Salt

After the thermal period, the diffusive redistribution of the brine that has migrated toward the waste packages may continue. Preliminary estimates of a possible water diffusion rate in salt suggest that a 10-m distance could be traversed in 100,000 years (USDOE 1986c). A likely mechanism for radionuclide transport through salt, barring flow in clay lenses, has not been identified. However, pressure, and perhaps concentration gradients, may play a role (ONWI 1984). Experience at the Waste Isolation Pilot Plant in New Mexico shows that water flow may be somewhat likely in sedimentary interbeds. As noted by the U.S. DOE (1986c), the potential for interbed flow needs to be assessed at depth for the candidate site.

#### 2.3.4.3 Tuff

When water-borne radionuclide release becomes possible, either one of two conditions or both must exist to allow radionuclide migration: 1) downward-moving water [less than 0.5 mm/year (USDOE 1986c)] may saturate the ceiling because of the capillary discontinuity presented by the open room, and water drips on the container, or 2) the waste container can collapse and bring spent fuel into intimate contact with the tuff of the borehole wall or bottom. These conditions seem highly unlikely, but even if both of these conditions were to exist, only a small portion of the total flux through the repository horizon may be able to contact the waste form. The entire area of the bottom of 35,000 vertical emplacement holes is less than 0.2% of the total repository area of about  $6 \times 10^6 \text{ m}^2$  (Sinnock, Lin and Brannon 1984).

According to Oversby and McCright (1985), a flux rate of 1 mm/year, or  $10^{-3} \text{ m}^3/(\text{m}^2 \cdot \text{yr})$  and a borehole spacing of 5 to 8 m in a drift 6-m wide, would suggest about a  $40\text{-m}^2$  drift area per waste package, with each borehole area receiving on the order of 40 L/yr. If only water flowing directly onto each borehole is considered likely to enter a borehole, 0.5 L/yr may become available for dissolution and transport per container, if the conservative assumption is made that all of this water contacts the waste form.

In the description of source-term modeling by Oversby and McCright (1985), a dripping water scenario was combined with a scenario assuming a crack in the top of the container to result in a water-filled, spent-fuel container with a 0.3 L/kg water to spent-fuel ratio. Container breach in this scenario is, of necessity, to be followed by nearly 2000 years of water infiltration to provide this 0.3 L/kg ratio, since about a 900-L water-volume capacity is assumed for the container holding 3100 kg of spent fuel. Thus, the period required to fill the container is nearly the same as the 2000 years assumed for the degradation of the spent-fuel cladding within the container after the container is breached. These modeling scenarios are not particularly reflective of the expected futures of waste packages in an unsaturated tuff repository, however, and may be unrealistically conservative with respect to the availability rates of liquid water to corrode, dissolve, and transport.

Oversby and McCright (1985) also discuss the likely airborne release of carbon-14 from crud and cladding surfaces and the spent-fuel cladding. The spent-fuel release modeling being done for the tuff project divides spent fuel into four parts, each of which releases radionuclides at a characteristic rate. This modeling is discussed in Section 4.0.

### 2.3.5 Ground-Water Composition

During the postthermal period, the ground-water composition close to the waste form, if containment has failed, will likely be oxygenated by the  $\alpha$ -radiolysis referred to in Section 2.3.1. After ground water reaches the  $UO_2$  matrix, it should become saturated with respect to alteration products of barrier metals as well as uranium and radionuclides that are released from the  $UO_2$  matrix. The matrix dissolution rate depends on the concentration of dissolved waste form components, that are, in turn, affected by the ability of the aqueous transport system to remove the dissolved uranium that controls  $UO_2$  dissolution (see Section 4.0). Concentrations of nuclides that are not limited by solubility constraints will increase in solution as a function of how their diffusion rate, or the ground-water flux, compares with the matrix dissolution rate. Ground-water compositions at the waste form surface during the postcontainment period will most likely be saturated with respect to sparingly soluble alteration products of barrier metals and radionuclide-bearing solids. Those saturation concentrations have yet to be determined, but preliminary estimates are available.

#### 2.3.5.1 Basalt and Crystalline

Preliminary estimates for radionuclide solubilities in basalt ground water were prepared for U.S. DOE (1986b). These estimates are given as ranges (Table 2.5) and are based on expert judgment with some experimental evidence. The lower values of the ranges are thought to represent likely conditions in the packing material, but do not include  $\alpha$ -radiolysis oxidative effects. The higher values of the ranges represent solubilities in water exposed to air. These values are, therefore, bounding estimates and may also serve as bounds for a crystalline rock repository because chemical characteristics of the host rock and waste package packing material are roughly comparable.

TABLE 2.5. Estimates of Solubility Ranges for Radionuclides in the Basalt Repository Very Near Field<sup>(a)</sup>

<u>Radionuclide</u>	<u>Solubility Range, moles/L</u>
Carbon-14	$4 \times 10^{-6}$ to $4 \times 10^{-9}$
Iodine-129	$1 \times 10^0$ to $1 \times 10^{-2}$
Neptunium-237	$1 \times 10^{-7}$ to $3 \times 10^{-9}$
Plutonium-239	$1 \times 10^{-8}$ to $2 \times 10^{-11}$
Plutonium-240	$6 \times 10^{-9}$ to $9 \times 10^{-12}$
Plutonium-242	$2 \times 10^{-9}$ to $3 \times 10^{-12}$
Technetium-99	$5 \times 10^{-4}$ to $2 \times 10^{-8}$
Selenium-79	$1 \times 10^{-4}$ to $1 \times 10^{-8}$
Tin-126	$3 \times 10^{-6}$ to $3 \times 10^{-11}$

(a) Based on U.S. DOE 1986b.

#### 2.3.5.2 Salt

Radionuclide solubilities for salt brine are also given as expert-judgment-based estimates by U.S. DOE (1986c). Values were given in grams per cubic meter but were changed to moles per liter for Table 2.6.

#### 2.3.5.3 Tuff

Solubilities for 10 selected radionuclides (Table 2.7) have been presented by U.S. DOE (1986a). These values are for water that is characteristic of Yucca Mountain, at pH 7, Eh 700 mV, and 25°C. Kerrisk (1984) was the first to publish these values.

#### 2.3.6 Stress

Postthermal period stresses will be continuations of the near-equilibrium internal pressures that characterized the latter part of the postclosure thermal period.

##### 2.3.6.1 Basalt and Crystalline

Stresses on the waste container that prevail as the container fails during the postthermal period will probably be equal to the hydrostatic (hydraulic)

TABLE 2.6. Estimated Solubilities of Radionuclides in a Saturated Salt Brine<sup>(a)</sup>

<u>Radionuclide</u>	<u>Approximate Solubility, moles/L</u>
Carbon-14	10 <sup>-6</sup>
Selenium-79	10 <sup>-8</sup>
Strontium-90	10 <sup>-5</sup>
Technetium-99	10 <sup>-8</sup>
Tin-126	10 <sup>-9</sup>
Iodine-129	5
Cesium-135	4
Thorium-230	10 <sup>-9</sup>
Uranium-234	10 <sup>-9</sup>
Neptunium-237	10 <sup>-9</sup>
Plutonium-238 to 242	10 <sup>-9</sup>
Americium-241,243	10 <sup>-10</sup>
Curium-244	10 <sup>-9</sup>

(a) Based on U.S. DOE 1986c.

pressure. The pressure created by physical confinement of wet, expanded clays [about 5 MPa (Smith et al. 1980)] should have no role in a 10 MPa environment. In the basalt repository location, the hydraulic pressure at a 1000-m depth is thought to be roughly 100 bars or 10 MPa (Smith et al. 1980). The lithostatic pressure, on the other hand, is approximately the depth (about 1000 m) times the mean density of the overburden (about 2600 kg/m<sup>2</sup>) times the acceleration of gravity (9.8 m/s<sup>2</sup>) or 26 MPa. The horizontal to vertical stress ratio was measured and ranged between 2.1 and 2.6 (Wilde, Ash and Jones 1984). Thus, if the vertical stress component is approximately equivalent to the lithostatic pressure, the horizontal stresses are at or near 60 MPa. Within the excavations, the long-term, near-equilibrium stress on the waste container should remain roughly similar to the hydraulic pressure (i.e., at or somewhat above 10 MPa). As container failures increase, void spaces within containers may become filled with wet, expanded clay, somewhat relieving any pressures in

TABLE 2.7. Expected Solubilities for Selected Radionuclides in Yucca Mountain Ground Water at Neutral pH and 25°C (a)

<u>Element (b)</u>	<u>Solubility, moles/L</u>
Carbon	large
Strontium	$9.4 \times 10^{-4}$
Technetium	large
Tin	$1.0 \times 10^{-9}$
Cesium	large
Radium	$1.0 \times 10^{-7}$
Uranium	$2.1 \times 10^{-4}$
Neptunium	$3.0 \times 10^{-3}$
Plutonium	$1.8 \times 10^{-6}$
Americium	$1.0 \times 10^{-8}$

- 
- (a) Based on U.S. DOE 1986a  
 (b) Selected elements represent 99% of spent-fuel radioactivity 1000 years after closure

excess of the hydraulic pressure caused by the expansion of clay/host rock alteration products and/or corrosion products.

For intrusive crystalline rocks, horizontal and vertical stresses and their ratios cover a wide range (Robinson 1984; Osnes et al. 1984). The basalt stress ratio values appear to be near the middle of the range measured for plutonic crystalline rocks.

#### 2.3.6.2 Salt

Postthermal period stress should be essentially the same as preconstruction stresses within the salt at depth, namely about 21 MPa vertical as well as horizontal (USDOE 1986c).

### 2.3.6.3 Tuff

It is expected that boreholes will be open and stable during the post-thermal period. Hence, intact and failed waste packages will be at atmospheric pressure.

## 2.4 PRELIMINARY SPENT-FUEL WASTE PACKAGE PERFORMANCE EVALUATIONS

One of the numerous requirements of the 10 CFR 960 general siting guidelines is that 100,000-year system performance assessments be done and the results compared for the characterized sites. One of these 100,000-year system performance assessments will include the expected engineered barrier system performance. Therefore, realistic, yet defensibly conservative, estimates must be made of the behavior of engineered barrier system components over long times. These estimates require data gathered as part of the site characterization and testing process. The conceptual models and analytical approaches, however, must be largely defined before site characterization because site characterization will, in part, be guided by the data needs for these models and approaches. Hence, current spent-fuel waste package performance assessment methods and approaches are not likely to be radically different from postcharacterization methods and approaches. It seems, therefore, that preliminary performance assessment treatments of spent fuel as a waste form may be used to help guide preliminary evaluations as to its adequacy as a waste form in present waste package designs.

### 2.4.1 Basalt

The preliminary waste package performance assessment for the basalt site is described in the Hanford Site EA (USDOE 1986b). The failure of a spent-fuel waste package in a basalt repository is defined by the corrosion of 7.5 cm of the 8.3-cm-thick container wall. The remaining 0.8 cm is considered to be vulnerable to stress-induced collapse. Corrosion is assumed uniform, and rate equations are based on ranges observed in short-term laboratory experiments. These rate ranges were statistically sampled by a Monte Carlo simulation routine, and an assumed Gaussian distribution of expected waste container lifetimes was constructed with a mean time to failure of 6100 years and a 600-year

standard deviation. Failures were predicted to begin at a low rate around 4000 years after emplacement, and all containers were predicted to have failed by about 8600 years.

After failure of the spent-fuel container (i.e., only 0.8 cm of the container wall remains), the remaining parts of the container and its corrosion products, spent-fuel cladding, and the  $UO_2$  matrix were assumed to have no further direct influence on the release of radionuclides from the container. In other words, the entire inventory of each radionuclide of interest present at time of failure was assumed to be located within the packing material and available for transport at the time of container failure. Because the packing material was assumed to be intact, it was considered to be a viable barrier that reduced ground-water flux to such a low rate that advective radionuclide transport was considered negligible. Molecular diffusion was considered the primary mechanism transporting radionuclides through the packing material. This assumption indirectly implies that the spent fuel and its container maintain their respective structural integrity (i.e., no shearing of waste packages under stress). In other words, containers and/or spent fuel are assumed to maintain their shape and volume to a sufficient extent so that collapses or depletions can be neglected in terms of potential negative effects on the integrity of the packing material. Packing material shape and volume and density, porosity, and hydraulic conductivity are assumed to remain essentially constant over the functional life of the geologic disposal system; this is expected to be true if the mineralogical makeup of the packing and the temperatures to which it is subjected are properly controlled. However, even if it is not true, and voids and cracks occur, the low water flux in the dense interior of a Basalt flow may still allow diffusion to govern the transport of radionuclides.

For the release rate evaluation, a diffusion coefficient of  $10^{-6}$   $cm^2/s$  was assumed for the packing material, the damaged and/or disturbed host rock zone, and the intact host rock. A 7.5-m zero-concentration boundary was assumed for the equilibrium representative case, and a pathlength from the waste centerline to the waste package system boundary of 44.5 cm was assumed from conceptual design data.

The results for high-solubility, zero sorptivity  $^{129}\text{I}$  given in the EA were just below the 10 CFR 60 release rate requirement for that radionuclide. It was repeatedly emphasized that these preliminary results were highly dependent on the assumptions that were made. The EA notes that the assumption of uniform container corrosion was conservative (in view of the high, oxygen-rich observed rates assumed to apply) unless more rapid, more localized corrosion mechanisms could be operative. The unstated assumption that the volume in the container region is not significantly reduced at or after the time of failure may also be a nonconservative assumption if internal voids occur in the containers at time of emplacement, although water fluxes in the dense interiors of basalt may be sufficiently close to zero that diffusion would still control transport. The basalt project is actively pursuing the development of a probabilistic waste package performance assessment model (Sagar, Elsinger and Baca 1986).

#### 2.4.2 Salt

The salt site EA (USDOE 1986c) presents a series of bounding calculations for its waste package performance assessment because no waste package failure is expected to occur. The bounding calculations are of little interest here except to note that, where spent-fuel behavior is concerned, neither the spent-fuel cladding nor the  $\text{UO}_2$  matrix dissolution rate are considered. Assuming a container failure, the secondary metal barrier of the internal container that is part of the salt repository conceptual waste package design is also considered failed, and brine is assumed to contact the waste form. Waste form radionuclides are then assumed to saturate the volume of stagnant brine that may be available around the waste package. A diffusion rate or low water flow rate is assumed to remove radionuclides from the very near field. However, no likely transport mechanisms for radionuclides in salt have as yet been identified by the salt project (USDOE 1986c; Bloom and Raines 1986).

Thus, the preliminary performance assessment for the salt case really does not take into account any of the waste form's properties. If uniform corrosion, sufficiency of metal barriers against stress, limited volumes of migrating brine, and consumption of the corrosive agents in the available brine can be demonstrated with reasonable assurance, waste packages will maintain their

integrity indefinitely and waste-form characteristics are irrelevant. These assumptions require experimental evaluation.

### 2.4.3 Tuff

Two of the three performance assessments reported by U.S. DOE (1986a) for an engineered barrier system in a tuff repository were based on a representative container case. Expected container lifetimes, assuming only uniform corrosion, are estimated to be on the order of 10,000 years. After 10,000 years, the expected flux rates times the horizontal container area is considered to be the expected volume of water that could contact the waste. This volume may range from 0.1 to about 0.2 L/yr. In the first model, all water flowing through the repository is assumed to become saturated with all inventory radionuclides, while in the second model only water at the waste form surface was assumed saturated with all the inventory radionuclides. In the latter case, diffusion transported radionuclides away from the waste form, resulting in a concentration gradient and, hence, less total radionuclide mass in the downward-moving ground water. Both these models were first reported by Kerrisk (1984). A similar model with yet a different scheme for controlling radionuclide concentrations in the ground water is that by Sinnock, Lin and Brannon (1984), which was not included in the EA discussion of this topic. In this third model, radionuclides entered the ground-water flux at a rate determined by abundance relative to uranium multiplied by the bulk waste form dissolution rate. Cladding was not considered in these preliminary assessments, although distributions in both container and cladding failures were used in the third waste package performance assessment reported in U.S. DOE (1986a), which was based on the work of Oversby and McCright (1985). Batch release rate tests with large, artificially induced cladding defects show that initial release rates are lower by one or two orders of magnitude than release rates for unclad spent  $UO_2$ . If  $UO_2$  solubility is conservatively estimated to be  $5 \times 10^{-2} \text{ kg/m}^3$  (see Sinnock, Lin and Brannon 1984),  $8.3 \times 10^{-6} \text{ kg}$  of the  $UO_2$  matrix may be transported in one year's flux. This represents a fractional mass release rate on the order of  $10^{-9}$  per year, which is well within the 10 CFR 60 performance requirement of  $10^{-5}$  per year.

These bounding calculations are sensitive to the assumed ground-water flux, the assumed fraction of that flux contacting the waste form, and  $UO_2$  solubility. Each value chosen for these three parameters appears to be conservatively estimated for the EA calculations, given the limited data available for the repository horizon. Spent-fuel waste form performance modeling improvements are in progress (O'Connell and Drach 1986).

#### 2.4.4 Conclusions

The bounding or generally conservative preliminary performance assessments shown in the EAs suggest that spent fuel is an adequate waste form for geologic disposal. The governing regulations, however, require that reasonable assurance be demonstrated. Reasonable assurance implies that 1) any data values used either adequately represent the system being evaluated or are demonstrably conservative, 2) models are mathematically correct and conceptually describe the system simulated, and 3) resulting predictions are credible in view of the amount of uncertainty that is nested within each value and assumption. The propagation of uncertainty by each calculation and model must also be assessed. Demonstrating reasonable assurance is the major motivation for the present reevaluation of the spent-fuel data base.

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### 3.0 CONTAINMENT BY CLAD SPENT FUEL

It appears, for the foreseeable future, that spent-fuel rods from U.S. commercial nuclear power plants will not be reprocessed. Thus, the condition of the spent-fuel rods and their ability to contribute toward containment of radioactive wastes under repository conditions has come under greater scrutiny. The spent-fuel waste form (i.e., fuel rods emplaced in containers without removal of the cladding) may contribute toward radionuclide retention through both the cladding and the actual fuel.

Four areas concerning spent-fuel behavior under repository conditions are discussed in Sections 3.1 through 3.4: 1) the expected condition of spent-fuel rods on arrival at a nuclear waste repository, 2) identification of potential failure modes or processes in spent fuel during and after the containment period, 3) the current status/adequacy of performance models for spent fuel under repository conditions, and 4) a summary of the available data in support of performance models for spent fuel in repository environments.

Some of the information provided is based on actual experience, such as the condition of spent fuel after wet storage and limited dry storage. Other information, such as the condition of spent fuel rods after long-term dry storage or performance of spent fuel in a repository environment, is only beginning to be defined by actual data. Thus, prediction of performance of the spent-fuel waste form under repository conditions relies on either extrapolations of short-term data or models that may have limited or no supporting experimental data. Those areas requiring additional supporting data or analyses are discussed in Section 5.

#### 3.1 REVIEW OF EXPECTED RANGE IN SPENT-FUEL AND CLADDING CHARACTERISTICS ON RECEIPT AT A REPOSITORY

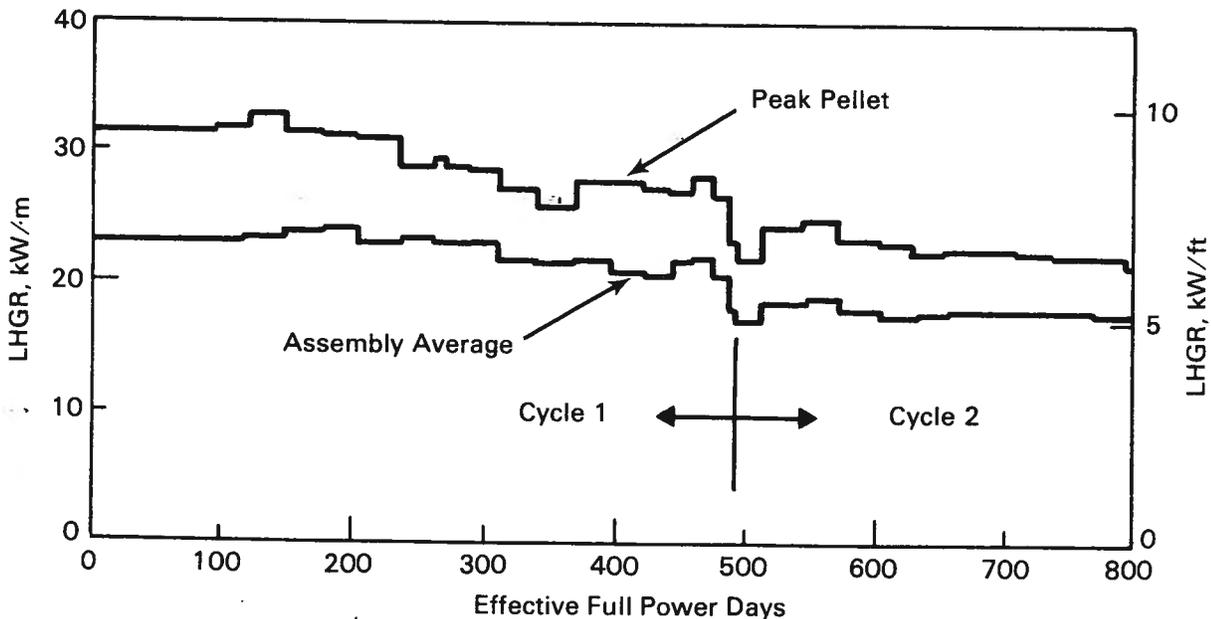
This section provides information on the expected condition of spent-fuel rods on arrival at a repository. Four major concerns are addressed: 1) fuel rod and assembly thermal characteristics, 2) cladding characteristics, 3) cladding integrity, and 4) content and distribution of the solid and gaseous material in the fuel and void space within the fuel rod.

### 3.1.1 Thermal Characteristics of Irradiated Spent-Fuel Rods

The thermal characteristics of spent-fuel rods are discussed in this section. The general power history is described and related to the decay heat and burnup expected from typical pressurized water reactor (PWR) and boiling water reactor (BWR) fuel-rod designs. The effect of age (time since discharge from the reactor) is also included in the discussion.

#### 3.1.1.1 Power History

Fuel assemblies are moved about in the core to achieve the desired burnup and power. As a result, the initial power in a fuel rod is generally higher than later in life. Fuel rods in light water reactors (LWR) typically operate at linear heat generation rates (LHGR) of 19 to 23 kW/m (6 to 7 kW/ft). An example of the power history for fuel assembly B0-5 from the H. B. Robinson, Unit 2 reactor is shown in Figure 3.1 (Barner 1984). This assembly achieved a typical PWR burnup of 28 megawatt days per kg of metal (Mwd/kgM). The peak LHGR of 32.7 kW/m (10.0 kW/ft) occurred in December 1971 after about 150 effective full-power days (EFPD). The LHGR decreased to 21.2 kW/m (6.5 kW/ft) by the end-of-life (EOL), which occurred in May 1974.



**FIGURE 3.1.** Power History for Assembly B0-5 from H. B. Robinson, Unit 2 PWR Reactor (Barner 1984)

### 3.1.1.2 Decay Heat

The decay heat and fuel temperature after nuclear fuel is discharged from the reactor depends on the burnup, power history, and age. Temperatures in the fuel rod also depend on the heat transfer characteristics of the storage medium and/or the waste package. For a typical PWR burnup of 33 MWd/kgM and a specific power of 37.5 kW/kgM, the decrease in decay heat with time is as approximated in Figure 3.2. These curves were calculated by Malbrain, Lester and Deutch (1981) using a simplified equation for spent-fuel decay heat.

The age of a spent-fuel assembly (i.e., the amount of time since the fuel assembly was discharged from the reactor) also plays an important role in determining the fuel rod temperatures during storage. The much slower decrease in decay heat 20 years after discharge is shown in Figure 3.3 for a range of typical PWR and BWR burnups. Storage of fuel rods discharged for 5, 10, or

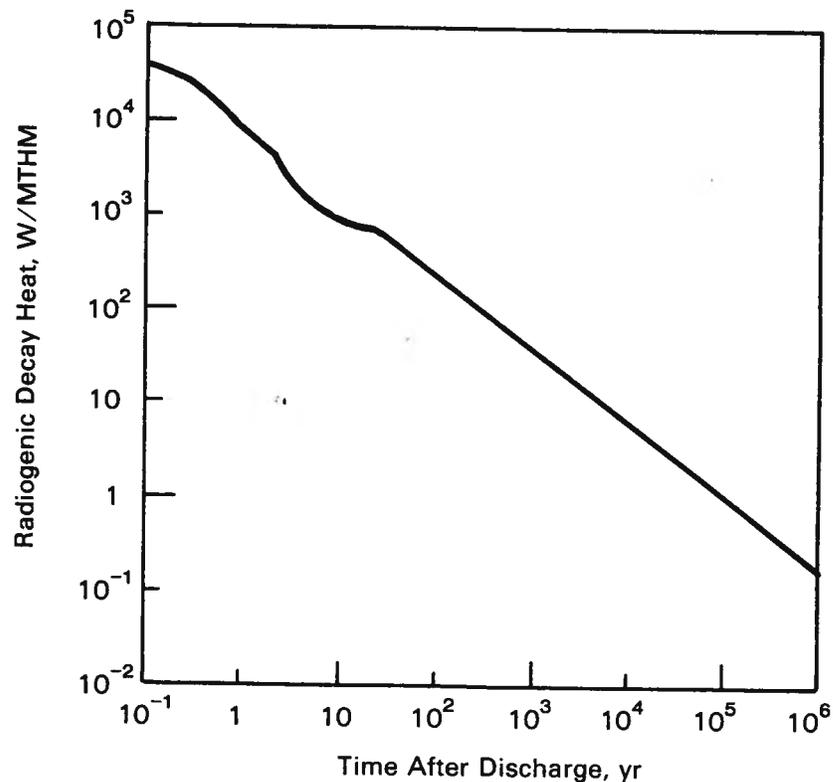


FIGURE 3.2. Analytical Approximation of Decay Heat for Typical PWR Spent Fuel (Malbrain, Lester and Deutch 1981)

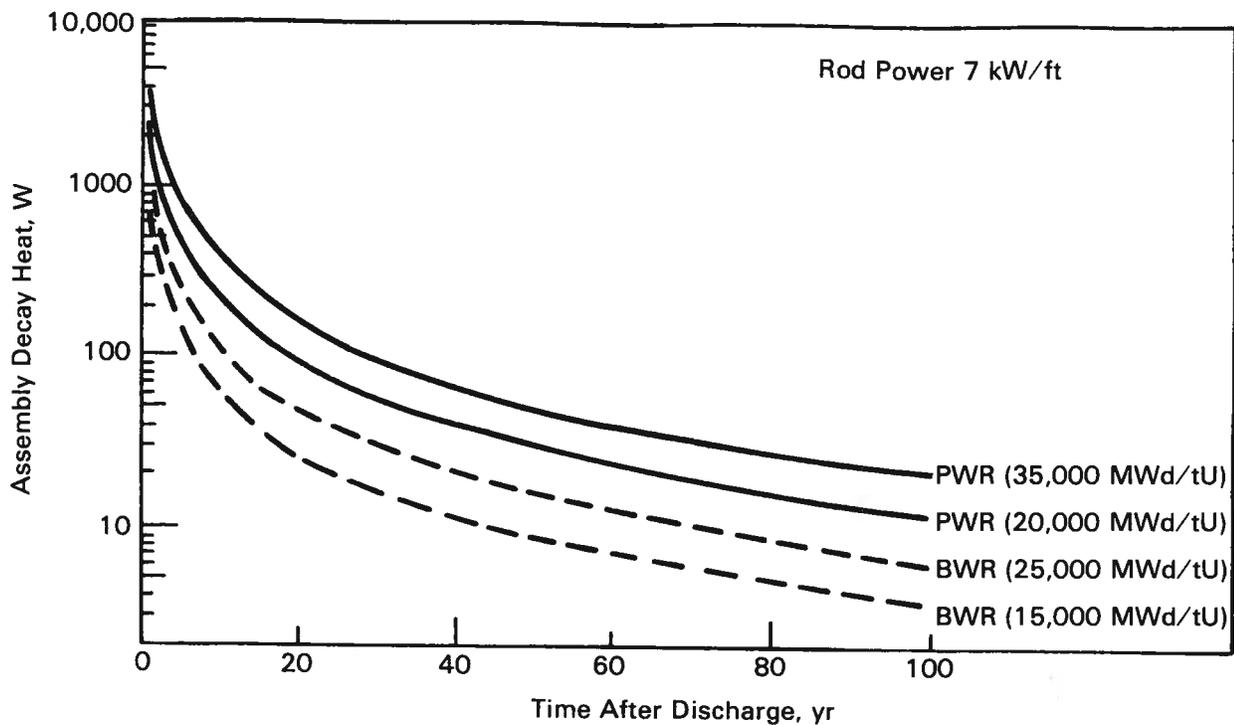


FIGURE 3.3. Decay Heats Calculated for Typical PWR and BWR Burnups (Johnson, Gilbert and Guenther 1982)

15 years can appreciably affect the amount of decay heat and storage temperature; most repository calculations assume that the spent fuel will have been out of the reactor for 10 years.

The assumption of 10-year-old spent fuel could prove to be conservative, because irradiated fuel rods will all reside for some time in pool storage after discharge from the reactor. Pool storage has been as much as 18 years for some spent-fuel rods, but typical times are about 5 to 12 years. This is shown in Figure 3.4 by the distribution of wet storage time for LWR spent fuel discharged as of January 1983 and projected forward to 1986 (Johnson and Gilbert 1983). Because the demand is heavy for storage space at the reactor, some of the spent-fuel rods may also be stored in dry storage, such as metal casks. In addition, Dippold and Wampler (1984) indicate that there is incentive to consider aging the spent fuel before disposal, as well as increase the average burnups, because these changes would lower the cost of disposal. Thus, most of the fuel rods discharged to a repository are likely to be at least 10 years old.

Decay heats, fuel age, and quantities of assemblies containing stainless steel (SS) and Zircaloy-clad fuel rods are compared in Figures 3.4 and 3.5. On the average, stainless-steel-clad spent-fuel rods are about 4 years older than Zircaloy-clad spent-fuel rods. The decay heats for SS-clad and Zircaloy-clad spent-fuel assemblies cover roughly the same range.

### 3.1.2 Cladding Characteristics

This section includes details on the characteristics of the Zircaloy cladding and limited data on SS cladding. Specific information in this section includes: 1) the types of cladding, 2) characteristics of the oxide layer, 3) the crud formed on the exterior of the fuel rod during exposure to reactor coolant water, and 4) the hydrogen content in the cladding and a brief discussion on activation products.

#### 3.1.2.1 Types of Cladding

Spent-fuel rods from LWRs in the United States come from PWRs and BWRs. Of the 33,222 spent-fuel assemblies in storage as of 1982, about one third were from PWRs and two thirds were from BWRs (USDOE 1983). The projected accumulation of spent-fuel assemblies, assuming no future reprocessing, is shown in Table 3.1 for both types of reactors. In 1981, about 95% of the spent-fuel assemblies contained fuel rods with Zircaloy cladding, while the rest had SS cladding (Guenther et al. 1984).

As of January 1984, there were 1303 spent-fuel assemblies with SS cladding from Connecticut Yankee (PWR), San Onofre-1 (PWR), La Crosse (BWR), and Indian Point-1 (PWR) reactors.<sup>(a)</sup> The first three are the only operating U.S. reactors currently using fuel rods with SS cladding. Because of the number of PWR and BWR reactors using SS-clad fuel rods, the normal ratio of spent-fuel types (2/3 BWR and 1/3 PWR) does not hold. About five times as many PWR spent-fuel assemblies contain SS-clad fuel rods (1090 versus 213). A general comparison of the design characteristics of SS-clad and Zircaloy-clad fuel rods is given in Table 3.2. Additional spent-fuel rods with SS cladding will be discharged

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(a) Based on information from the Commercial Spent-Fuel Management (CSFM) Dry Storage Data Base as of the end of 1983 and provided by R. A. Libby at PNL.

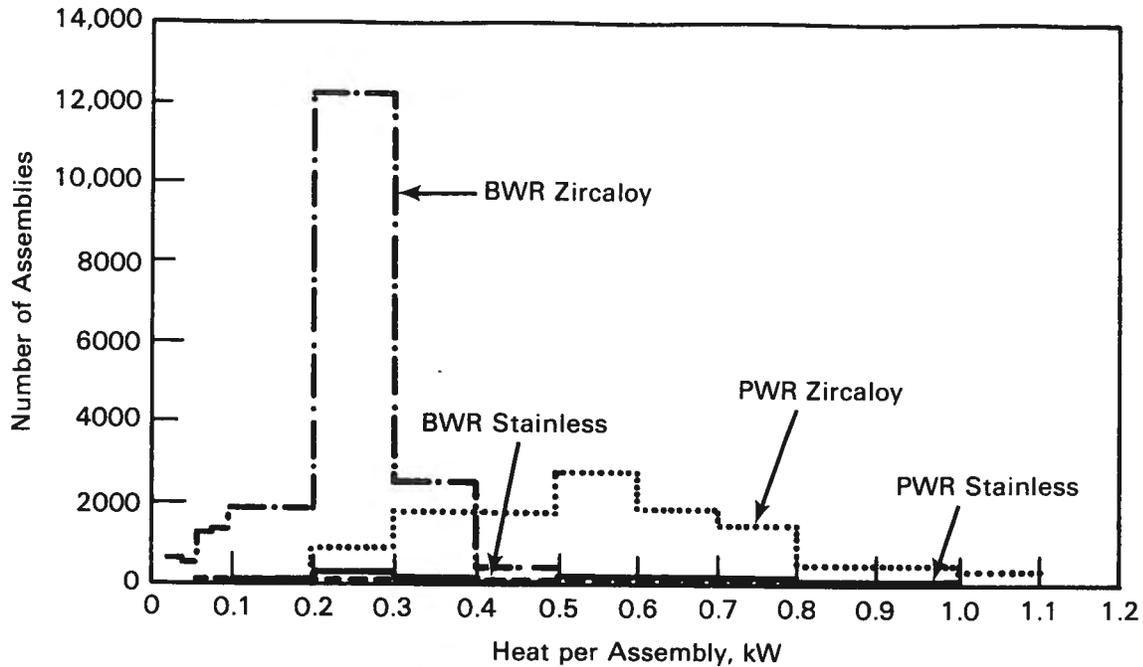


FIGURE 3.4. Distribution of Decay Heats for U.S. LWR Spent-Fuel Inventories Discharged Before January 1983 and Projected to 1986 (Johnson and Gilbert 1983)

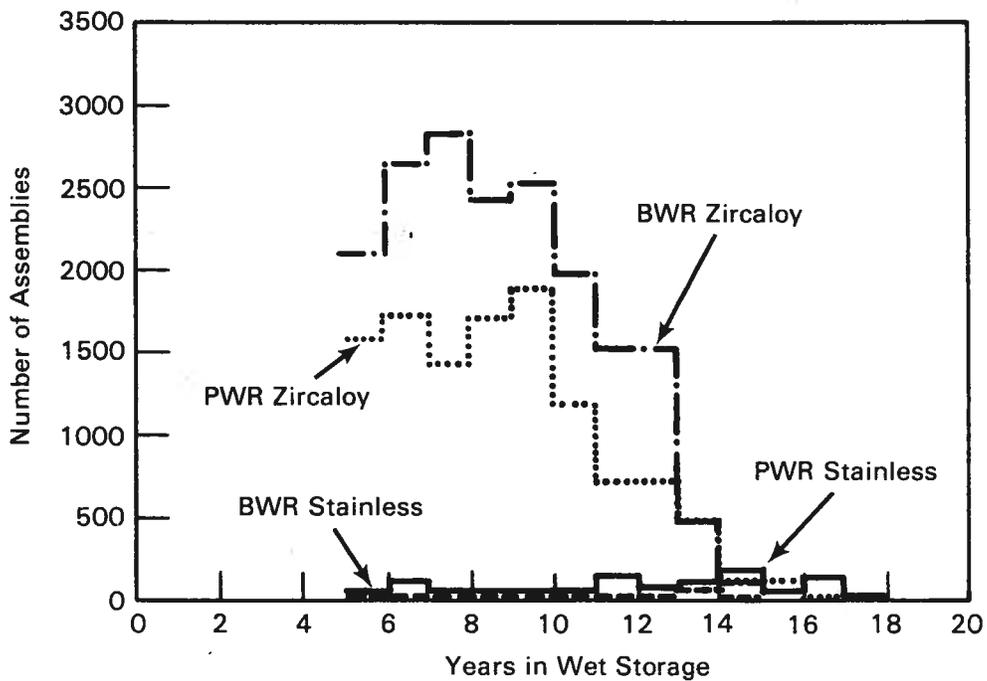


FIGURE 3.5. Distribution of Wet Storage Times for U.S. LWR Spent-Fuel Inventories Discharged Before January 1983 and Projected to 1986 (Johnson and Gilbert 1983)

TABLE 3.1. Projected Number of Fuel Assemblies by Reactor Type Assuming No Future Reprocessing (U.S. DOE 1983) (a)

End of Calendar Year	BWR		PWR		Total	
	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative
1982		20,702		12,520		33,222
1983	2,772	23,474	1,823	14,343	4,595	37,817
1984	3,232	26,706	2,379	16,722	5,611	43,428
1985	3,772	30,478	2,841	19,563	6,613	50,041
1986	4,532	35,010	3,193	22,756	7,725	57,766
1987	5,604	40,614	3,377	26,133	8,981	66,747
1988	5,288	45,902	4,098	30,231	9,386	76,133
1989	4,712	50,614	3,936	34,167	8,648	84,781
1990	6,644	57,258	4,639	38,806	11,283	96,064
1991	5,784	63,042	4,383	43,189	10,167	106,231
1992	5,516	68,558	4,338	47,527	9,854	116,085
1993	6,874	75,432	4,327	51,854	11,201	127,286
1994	5,749	81,181	4,511	56,365	10,260	137,546
1995	6,185	87,366	4,327	60,692	10,512	148,058
1996	6,789	94,155	4,549	65,241	11,338	159,396
1997	5,839	99,994	4,527	69,768	10,366	169,762
1998	6,204	106,198	4,522	74,290	10,726	180,488
1999	6,792	112,990	5,172	79,462	11,964	192,452
2000	6,324	119,314	4,557	84,019	10,881	203,333
2001	5,900	125,214	4,520	88,539	10,420	213,753
2002	7,332	132,546	5,272	93,811	12,604	226,357
2003	6,220	138,766	5,300	99,111	11,520	237,877
2004	6,595	145,362	5,594	104,705	12,190	250,067
2005	7,136	152,498	5,978	110,683	13,114	263,181
2006	7,692	160,190	6,384	117,067	14,076	277,257
2007	7,284	167,474	7,147	124,214	14,431	291,688
2008	9,716	177,190	7,914	132,128	17,630	309,318
2009	5,860	183,050	7,766	139,894	13,626	322,944
2010	6,644	189,694	7,697	147,591	14,341	337,285
2011	7,152	196,846	7,742	155,333	14,894	352,179
2012	6,628	203,474	7,963	163,296	14,591	366,770
2013	6,904	210,378	8,217	171,513	15,121	381,891
2014	7,608	217,986	8,271	179,784	15,879	398,770
2015	8,064	226,050	8,521	188,305	16,585	414,355
2016	5,948	231,998	9,020	197,325	14,968	429,323
2017	7,764	239,762	8,969	206,294	16,733	446,056
2018	6,000	245,762	9,618	215,912	15,618	461,674
2019	5,384	251,146	9,432	225,344	14,816	476,490
2020	5,540	256,686	9,800	235,144	15,340	491,830

(a) Based on a 128.6 gigawatt electric capacity [GW(e)] to be installed by the year 2000 and 218.6 GW(e) to be installed by the year 2020.

from these three reactors: San Onofre (SS304), Connecticut Yankee (SS304), and La Crosse (348H) (Johnson, Gilbert and Guenther 1982).

As noted in Table 3.2, typical burnups for Zircaloy-clad fuel rods from PWRs are 33 to 36 MWd/kgM and about 28 MWd/kgM for BWRs (Bailey and Johnson 1983). Burnups for the SS-clad fuel rods from Connecticut Yankee are typically between 25 and 33 MWd/kgM. The San Onofre-1 spent fuel typically ranges from 18 to 31 MWd/kgM.

### 3.1.2.2 Oxide Layers

Films of  $ZrO_2$  are formed on the cladding during reactor operation. The films on BWR cladding are generally up to 50- $\mu$ m thick at EOL and up to 40  $\mu$ m on typical PWR cladding after three reactor cycles (Johnson, Gilbert and Guenther 1982). Greene (1980) reported post-reactor data for spent fuel and indicated that oxide layers ranged from 1.3 to 27.9  $\mu$ m, depending on reactor residence

**TABLE 3.2.** Comparison of Characteristics of Zircaloy and Stainless Steel-Clad Fuel Rods<sup>(a)</sup>

Characteristic	Zircaloy Clad		SS Clad	
	BWR	PWR	BWR	PWR
Rod Length, m	3.99 - 4.2	3.71 - 4.09	~2.24	3.22
Fueled Length, m	3.66 - 3.81	3.47 - 3.81	2.08	3.05
Rod Diameter, mm	12.27 - 14.30	9.5 - 10.92	9.91	10.72
Wall Thickness, mm	0.813 - 0.914	0.572 - 0.762	0.51	0.42
Pellet Diameter, mm	10.41 - 12.37	8.19 - 9.64	8.75	9.7
Diametral Gap, mm	0.229 - 0.305	0.165 - 0.2134	0.15	0.14
Initial Fill Gas	He	He	He	Air/ He/ Air-He-Ar
Prepressurization, atm	1 - 6	15 - 30	1	1 (some ~13)
EOL Pressure, atm	15	30 - 40	?	2 - 8
Burnups, MWd/kgM	28	33 - 36	7 - 16	5 - 35

(a) Based on information from Guenther et al. (1984), S. Rafferty at La Crosse, and the CSFM Dry Storage Data Base maintained at PNL and provided by R. A. Libby as of December 1984.

time, alloy, and operating conditions. Johnson et al. (1980b) reported that oxide films on SS cladding were too thin to be detected by metallography. A plot of oxide thickness along the length of an H. B. Robinson spent-fuel rod is shown in Figure 3.7.

Oxidation of the cladding can occur during wet or dry storage, depending on the temperatures and the amount of oxidant available. Zircaloy oxidation involves two phases: 1) pretransition, where a black and highly protective  $ZrO_{1.95}$  forms under parabolic or cubic kinetics; and 2) post-transition, where a less protective oxide forms that progresses from a dark (black or mottled gray) to light (beige or white) under linear kinetics (Johnson, Gilbert and Guenther 1982). Hillner (1977) describes equations for these two regimes of cladding oxidation.

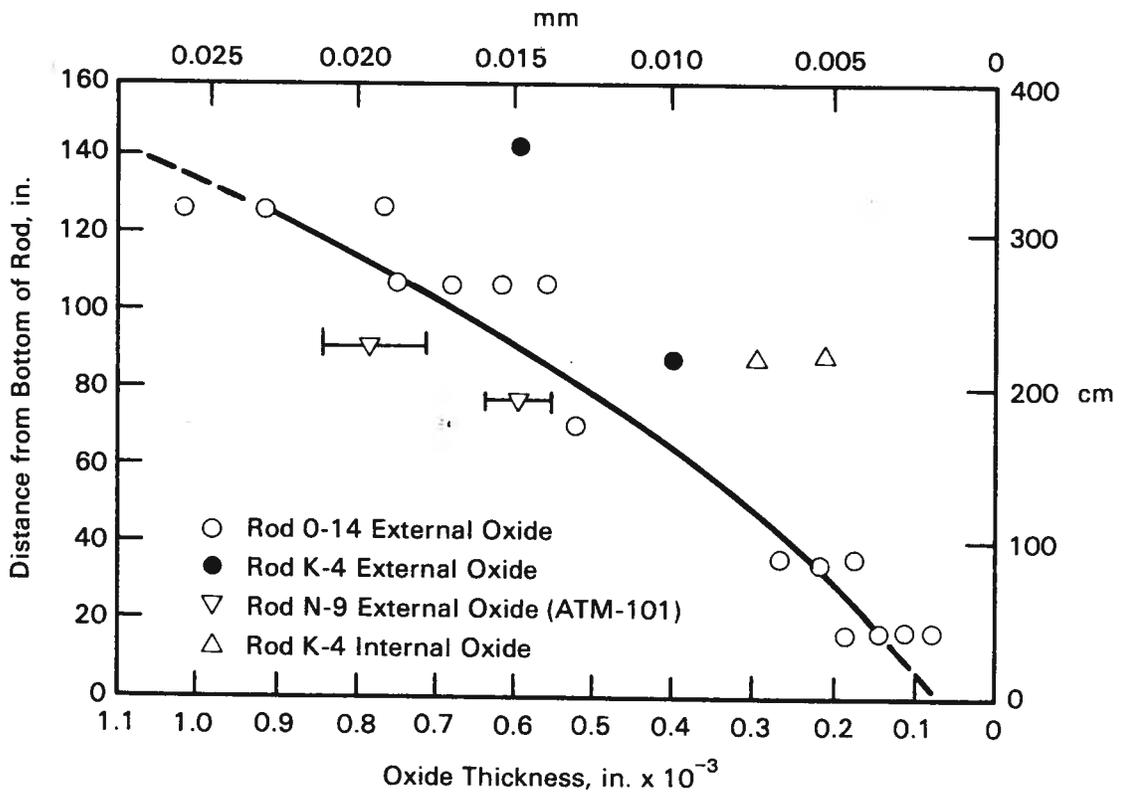


FIGURE 3.6. Oxide Thickness Variations Along Zircaloy Fuel Rods from H. B. Robinson, Unit 2 (Barner 1984)

The amount of cladding oxidation at several temperatures is shown in Figure 3.8 from calculations by Johnson, Gilbert and Guenther (1982) using data from Hillner (1977), Westerman (1964), and Gulbransen and Andrew (1958). These curves were made assuming a prefilm of 10  $\mu\text{m}$  (150  $\text{mg}/\text{dm}^2$ ) and 1 atm of oxidant. Under expected dry storage temperatures of less than 380°C and inert atmospheres, little cladding oxidation would occur. If the Zircaloy cladding is stored in unlimited air at 250°C for 40 years, it is predicted that only 0.3  $\mu\text{m}$  more of the cladding wall would oxidize beyond that previously oxidized. The conditions described above are for controlled environments that do not have any chlorides, fluorides, etc. For oxidation in air or steam as described, the amount of oxidation is conservative because the fuel temperatures would probably decrease, unless the spent fuel was very old and decay was insignificant.

### 3.1.2.3 Crud Formation

Crud is the deposit that develops over the  $\text{ZrO}_2$  film on the cladding surface. Crud develops because most metals in the reactor coolant circuit (iron,

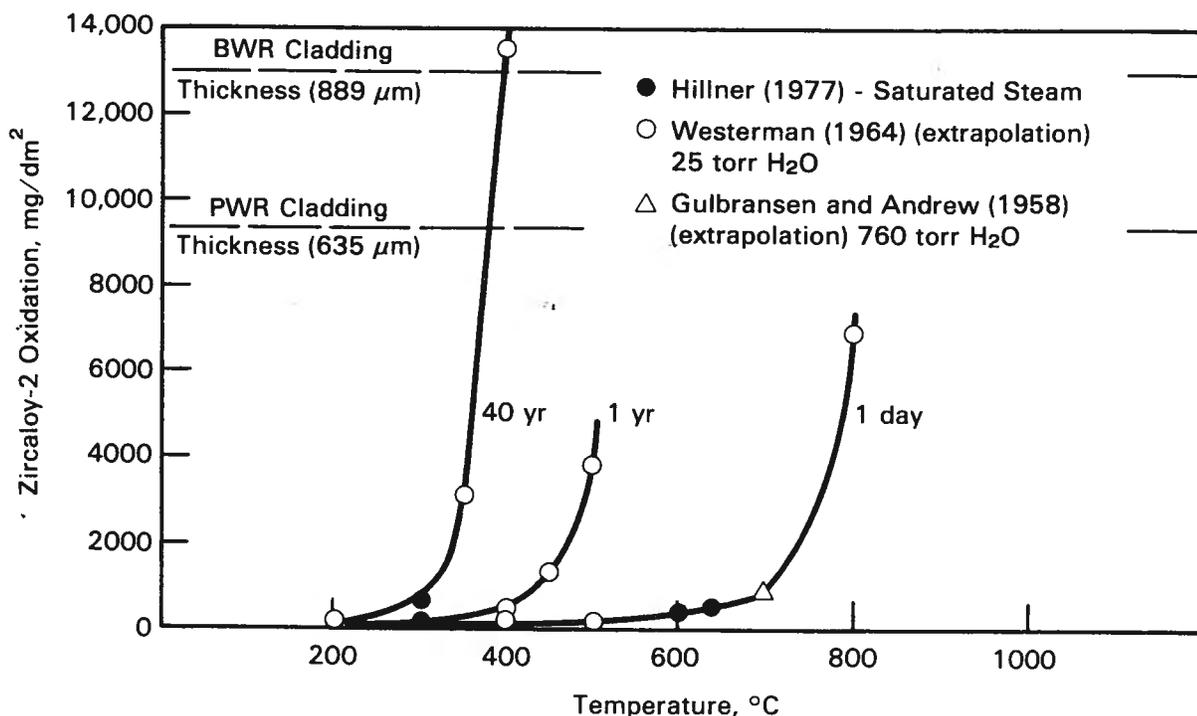


FIGURE 3.7. Projected Corrosion of Zircaloy-2 with an Initial 10- $\mu\text{m}$  Oxide Layer and 1 Atm of Oxidant (Johnson, Gilbert and Guenther 1982)

nickel, and cobalt base alloys) release corrosion products to the circulating coolant that deposit on the fuel rod cladding forming the crud layer. The oxides of zirconium alloys generally remain in place.

The deposits in BWR reactor coolant systems are primarily a reddish-brown  $\text{Fe}_2\text{O}_3$  that forms a tenacious inner layer and a looser outer layer. Thicknesses of these BWR crud deposits range from 6 to 30  $\mu\text{m}$  (100 to 450  $\text{mg}/\text{dm}^2$ ) (Johnson, Gilbert and Guenther 1982).

Crud found on a PWR rod is dark and generally thinner than that found on BWR rods. The deposits in PWR systems are  $\text{Fe}_x\text{Ni}_{3-x}\text{O}_4$  where  $x$  is approximately 0.6 (Johnson, Gilbert and Guenther 1982). Crud from PWRs tends to be heaviest at the top of the rods and is very tenacious. Some PWR rods have so little crud that the shiny  $\text{ZrO}$  is clearly evident.

Two types of radioactive species are present in crud: 1) activation products from exposure of components in the crud to the neutron flux and 2) fission products deposited in the crud from rods that developed defects during reactor operation (Johnson, Gilbert and Guenther 1982). Cobalt-60 is the principal activation product remaining in the crud layers in storage because of its 5.3-year half-life. Other activation products include  $^{54}\text{Mn}$  (310 d half-life) and  $^{65}\text{Zn}$  (243 d). The principal fission products in the crud are  $^{134}\text{Cs}$  (2.1 y) and  $^{137}\text{Cs}$  (30 y). Other moderately long-lived fission products found in the crud include  $^3\text{H}$  (12.3 y),  $^{90}\text{Sr}$  (28.8 y), and  $^{144}\text{Ce}$  (285 d). Because most spent fuel will have been discharged 10 years or more before disposal, the radioactive inventory of crud will have decreased to relatively low values by the time the repository is closed. If the spent fuel has been put in dry storage before disposal, there may be some loosening of the crud because crud spallation has been observed on spent PWR fuel rods heated from 480° to 570°C (Einziger et al. 1982).

#### 3.1.2.4 Hydrogen Content in Cladding

Newly fabricated Zircaloy cladding contains small amounts of hydrogen, usually in the form of thin platelets that run in the circumferential and longitudinal direction in the cladding. Stainless steel has a low solubility for hydrogen and does not form hydrides as do zirconium alloys (Johnson,

Gilbert and Guenther 1982). During exposure to the reactor coolant, the corrosion of the Zircaloy cladding produces free hydrogen from the reaction of the Zr and H<sub>2</sub>O. Some of this hydrogen adheres to the surface and is subsequently absorbed into the cladding. This hydrogen combines with the original hydrogen that was in the cladding during fabrication.

Hydrogen concentrations in irradiated LWR cladding seldom exceed 150 mg/kg and are typically from 80 to 150 mg/kg (Johnson, Gilbert and Guenther 1982). At 30°C, which is the temperature of pool storage, most of the hydrogen has precipitated out because hydrogen has a low terminal solubility in Zircaloy at lower temperature. Below 100°C hydrogen is not appreciably soluble in zirconium alloys (Price 1984). At 250°C, the peak fuel rod temperature in some repository calculations, cladding with the higher concentrations of hydrogen will still have precipitates because the terminal solubility is about 30 mg/kg. At 350°C, the terminal solubility of hydrogen in Zircaloy is 120 mg/kg and most of the the hydrogen would be soluble.

As the fuel rods cool during storage, some of the hydrogen will reprecipitate and may reorient under the tensile stresses caused by fuel rod pressures that are no longer offset by the reactor coolant pressure (Yaggee, Mattas and Neimark 1980). However, the hydride platelets generally remain oriented in the circumferential direction after irradiation or high-temperature and short-time events (Barner 1984; Guenther 1983). How much, if any, reorientation occurs will depend on the peak temperature, the amount of time since discharge, and the internal stresses in the cladding.

Hydrogen tends to degrade the low-temperature impact properties of Zircaloy; however, typical hydrogen levels found in the cladding of spent-fuel rods after discharge from the reactor and reactor pools have apparently not affected the integrity of fuel rods that have been handled or shipped. Theoretical and experimental work by Sawatzky (1975) has shown that hydrogen will migrate to cooler locations in the rod if the thermal gradients are sufficient. Price (1984) has indicated that stress also affects diffusion of hydrogen.

### 3.1.2.5 Activation Products in the Cladding

The highest radiation levels from spent-fuel assemblies come from the fuel rods; however, the spacers and other assembly hardware also become radioactive during irradiation. This results from the accumulation of crud on the metal surfaces of the fuel rods (as discussed previously) and as a result of activation of the original metal in the assembly hardware. The level of activation in fuel assembly hardware and the cladding depends on the neutron flux, irradiation time, the original alloy composition, and the time since discharge. In addition to the radioactive species found in the crud described previously,  $^{60}\text{Co}$  is produced in Zircaloy-2, which initially contains 0.05% Ni along with tin, iron, chromium, and oxygen. Spacers in some fuel assemblies are made of Inconel®, which will activate to higher levels because it contains more nickel.

### 3.1.3 Integrity of Cladding

A small fraction of the fuel rods may become defective (i.e., leak) before receipt at a repository. These defects may result from in-reactor operation, pool storage, transportation and handling, and/or dry storage. Through 1976, a total of 2,290 spent-fuel assemblies were known to have from one to several defected rods; less than 300 of these assemblies have been reprocessed (Bailey and Pankaskie 1982). The number of unreprocessed, defected assemblies represents less than 7% of the assemblies stored as of 1981. The percentage of failed rods out of the total number of spent-fuel rods has been less than 1% and, in some instances, may be less than one rod in 10,000 (Strasser and Lindquist 1977). The percentage of defected assemblies may decrease because earlier LWR fuel rods had a higher incidence of in-reactor cladding failures than more recent designs (Johnson, Gilbert and Guenther 1982). This decrease could be offset to some extent by any additional failures caused by the trend toward higher burnups.

The important aspects of fuel rod integrity are reviewed in the following subsections. The failure rates for fuel rods during in-reactor operation, pool storage, and transportation are given based on available historical

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information. Actual data on the number of fuel rods that would become defected during dry storage are not available because this mode of storage is only beginning to be used. The number of defects expected from each storage mode are discussed below.

#### 3.1.3.1 Fuel Failure Rates In Reactor

Although overall fuel operating experience in reactors continues to be excellent, sporadic events occur involving damage to or failure of fuel rods (Bailey and Tokar 1984). In reviewing information on fuel failure rates, it should be noted that the definition of failed fuel rods is not uniformly applied and the threshold for what constitutes abnormal degradation is not uniform throughout the industry. In many cases, the number of fuel failures is inferred from indirect evidence, and in some cases only directly observed failures are counted (Bailey and Tokar 1984; Bailey et al. 1980). Combining or directly comparing data (i.e., results derived from onsite inspections of fuel systems) from fuel experience reports from different fuel vendors and utilities is difficult for a number of reasons (Bailey et al. 1980): visual examination is not weighted uniformly, sipping<sup>(a)</sup> is a relative measurement, standards are not generally used during poolside gamma scanning, no standard mensural campaign exists, and standardization is lacking for poolside eddy-current and ultrasonic testing. Two other reasons, mentioned earlier, are the variations in the definition of failed fuel and the lack of uniformity in deciding what constitutes abnormal degradation. In addition, four of the five vendors evaluate fuel performance in terms of fuel integrity level (the converse is fuel failure rate) (Bailey and Dunenfeld 1985); however, the fifth fuel vendor, and also one of the four, evaluate fuel performance in terms of reactor primary coolant activity level (Skaritka and Iorii 1984; Matheson et al. 1985).

Some fuel bundles with defective fuel rods may be overlooked unintentionally if visual inspection or sipping of fuel bundles are the only fuel bundle inspection techniques used (Bailey and Tokar 1984; Bailey et al. 1980; Bailey

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(a) Sipping is a method of detecting defected fuels in which the water is sampled near a suspect fuel assembly and analyzed for radioactivity. Dry sipping involves sampling the gas over a fuel assembly that is not in the water.

et al. 1981a). If only fuel bundles are inspected (i.e., if bundles are not disassembled for individual rod inspection), it is difficult to accurately determine the total number of failed fuel rods present. Recently, ultrasonic methods have been developed that detect moisture inside failed rods (Bohmann 1982; Boehm and Foerch 1985; Losh and Ferree 1985); the techniques can be used without disassembling the fuel bundle and can provide clear indications of the exact location of the failed rods. United States utilities have recently used the methods to detect failed fuel rods and find that the results from these methods correlate well with the results from wet sipping (i.e., leak testing) of fuel assemblies.

Occasionally, a group of spent-fuel rods that includes some suspected leakers is discharged and not reused, but is not inspected (Bailey and Tokar 1984). In such cases, the number of failed rods (if any are present) might not be factored into the failure rate estimates. However, one paper indicates that extrapolation of inspection results has been used to estimate the number of leaker rods (Proebstle, Bailey and Klepfer 1977).

Several recent papers by fuel vendors provide information on fuel failure rates in 1984 (Matheson et al. 1985; Andrews and Matzie 1985; Sofer, Van Swam and Exarhos 1985). Combustion Engineering (C&E) states that the percent of leaking rods, as of November 1, 1984, ranged from 0.0175 to 0.0 (Andrews and Matzie 1985). Advanced Nuclear Fuels Corporation [ANFC (formerly EXXON Nuclear Corporation)] states that through December 31, 1984, the failure rate of rods resulting from fuel-related causes was 0.005% and the failure rate resulting from all causes was 0.014% (Sofer, Van Swam and Exarhos 1985).

Information is also available on fuel failure rates in 1983 (Bailey and Dunenfeld 1985). Babcock & Wilcox (B&W) reported fuel failure rates of 0.01% for Zircaloy-clad fuel and 0.0% for stainless steel-clad fuel. Combustion Engineering reported a fuel failure rate of 0.02%. Advanced Nuclear Fuels Corporation reported fuel rod failure rates of 0.002% resulting from fuel-related causes and a total of 0.013% from all causes. General Electric reported fuel failure rates of 0.007% for all 8x8 fuel bundles and zero for barrier 8x8 fuel bundles (Bailey, Marlowe and Proebstle 1985).

Bailey and Tokar (1984) report historical information on fuel failure rates through 1982 for BWRs and PWRs (see Tables 3.3 and 3.4 and Figures 3.8 to 3.10). Garzarolli, von Jan and Stehle (1979) published information on fuel failure rates in water-cooled power reactors (BWR, PWR, and heavy water reactors) in the United States and other countries; they indicated that the average fuel rod failure rate at that time had dropped to near 0.02%, that in the early 1970s failure rates of 0.1% to 1% were experienced at many plants, and some fuel batches had failure rates above 1%.

The majority of in-reactor failures of SS-clad fuel rods have been in BWR environments (Pasupathi and Klingensmith 1981). These failures occurred in highly stressed, unsensitized, austenitic SS (such as Type 304), which are susceptible to stress-assisted, intergranular corrosion in high-purity water environments. The percentage of failures in SS-clad BWR fuel is higher than in PWRs, particularly for earlier spent BWR fuel, although most of the earlier spent BWR fuel was reprocessed. About half of the current 213 spent fuel assemblies at La Crosse (BWR) have failed fuel rods as indicated by visual or sipping examinations.<sup>(a)</sup>

Although the specific number is not well established, it is known that the failure rates for SS-clad PWR rods have been very low, except for one batch of fuel rods at Connecticut Yankee. At that reactor, 36 assemblies out of 48 contained failed fuel rods (Pasupathi and Klingensmith 1981). There appear to be only four documented cases of fuel rod failures under PWR conditions other than in the Connecticut Yankee reactor: 1) the PM-3A portable reactor, 2) a core from an Army reactor, 3) in high burnup rods from the Vulcain reactor, and 4) in the French/Belgian SENA reactor. Only the failures in SENA would be considered comparable with U.S. LWRs based on burnups and reactor conditions, but no data were available on the failures.

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(a) According to S. Rafferty at La Crosse, there were visual indications of failed fuel rods in 50 assemblies, and sipping indicated failed fuel rods in another 53 assemblies stored December 1984. Additional failures have not occurred at La Crosse in the last 2 years, probably as a result of design and material specification changes.

TABLE 3.3. Historical Information on Cumulative Failure Rates in BWRs  
(Bailey and Tokar 1984)

<u>As of Date</u>	<u>Failure Rate, %</u>	<u>Out of This Many Rods</u>	<u>Fuel Vendor</u>
9/72	~0.2	>440,000	GE
9/74	~0.76	>810,000	GE
12/76	(a)	>1,250,000	GE
5/79	(b)	1,583,266	GE
1/1/80	(c)	1,816,147	GE
12/31/80	0.02 (8x8 only)	1,239,000 (8x8 only)	GE
12/31/81	<0.02 (8x8 only) 0.012	1,489,246 (8x8 only) 116,891	GE ANFC
12/31/82	<0.02 (all 8x8) 0.13	1,821,338 (all 8x8) 142,741	GE ANFC

(a) <u>Type</u>	<u>Failure Rate, %</u>	<u>Out of This Many Rods</u>
7x7	no data shown	--
Improved 7x7	~0.05 (47 leakers)	110,100
8x8	no failures	99,500

(b) <u>Type</u>	<u>Failure Rate, %</u>	<u>Out of This Many Rods</u>
7x7	0.98	504,161
7x7 R	0.043	285,376
8x8	0.028	676,053
8x8 R	0.0	117,676
	0.332 (weighted average)	1,583,266 TOTAL

(c) <u>Type</u>	<u>Failure Rate, %</u>	<u>Out of This Many Rods</u>
7x7	~1.01	504,161
7x7 R	0.066	285,572
8x8	0.016	758,016
8x8 R and 8x8 R (PP)	0.002	268,398
	~0.298 (weighted average)	1,816,147 TOTAL

TABLE 3.4. Historical Information on Failure Rates in PWRs  
(Bailey and Tokar 1984)

<u>Date</u>	<u>Failure Rate, %</u>	<u>Out of This Many Rods</u>	<u>Fuel Vendor</u>
12/31/80	(a)	587,110	B&W
12/31/81	(b)	647,728	B&W
1971-1979	See Figures 10 and 11	See Figures 10 and 11	C-E
12/31/81	0.013 (c)	410,965	ENC
1970-1982	See Figure 9	See Figure 9	<u>W</u>

- (a) On a cumulative basis, the failure rates were 0.037% (216 leaker rods) with 586,054 rods (15x15 type) and zero with 1056 rods 17x17 type).
- (b) On a cumulative basis, the failure rates were 0.037% (240 leaker rods) with 646,672 rods (15x15 type) and zero with 1056 rods (17x17 type).
- (c) On a cumulative basis, the failure rate was 0.013% (52 failed rods) with 410,965 rods.

### 3.1.3.2 Fuel Failure Rates In Pool Storage

There have been several comprehensive evaluations of the 40 years of experience with wet storage of spent fuel (IAEA 1980; IAEA 1982; USNRC 1984; USDOE 1980). The NRC has concluded that fuel can be stored safely in a spent-fuel storage pool for at least 30 years (USNRC 1984). A number of investigators have assembled and assessed data on fuel integrity during wet storage, and there continues to be no indication that Zircaloy-clad fuel or SS-clad fuel degrades significantly during wet storage (Johnson 1977; Warner 1977; Flowers 1977; Vesterlund and Olsson 1978; Peehs et al. 1978; Hunt, Wood and Bain 1979; Hillner 1980; Johnson et al. 1980a; Johnson et al. 1980b; Bailey et al. 1981b; Bradley et al. 1981; Johnson et al. 1981; Langstaff et al. 1982; Johnson et al. 1982; Johnson and Bailey 1982; Bailey and Johnson 1983; EPRI 1984; Peehs et al. 1984). One case occurred at Prairie Island in 1981 where stress corrosion cracking (SCC) of SS sleeves in 13 PWR fuel assemblies occurred in the spent-fuel pool. When one of those assemblies was lifted, the top end fitting (nozzle) separated from the remainder of the assembly. The NRC concluded that the corrosion was an isolated event and does not have generic impact.

The behavior of fuel cladding defects during wet storage has also been studied and it was concluded that such defects have little impact during wet

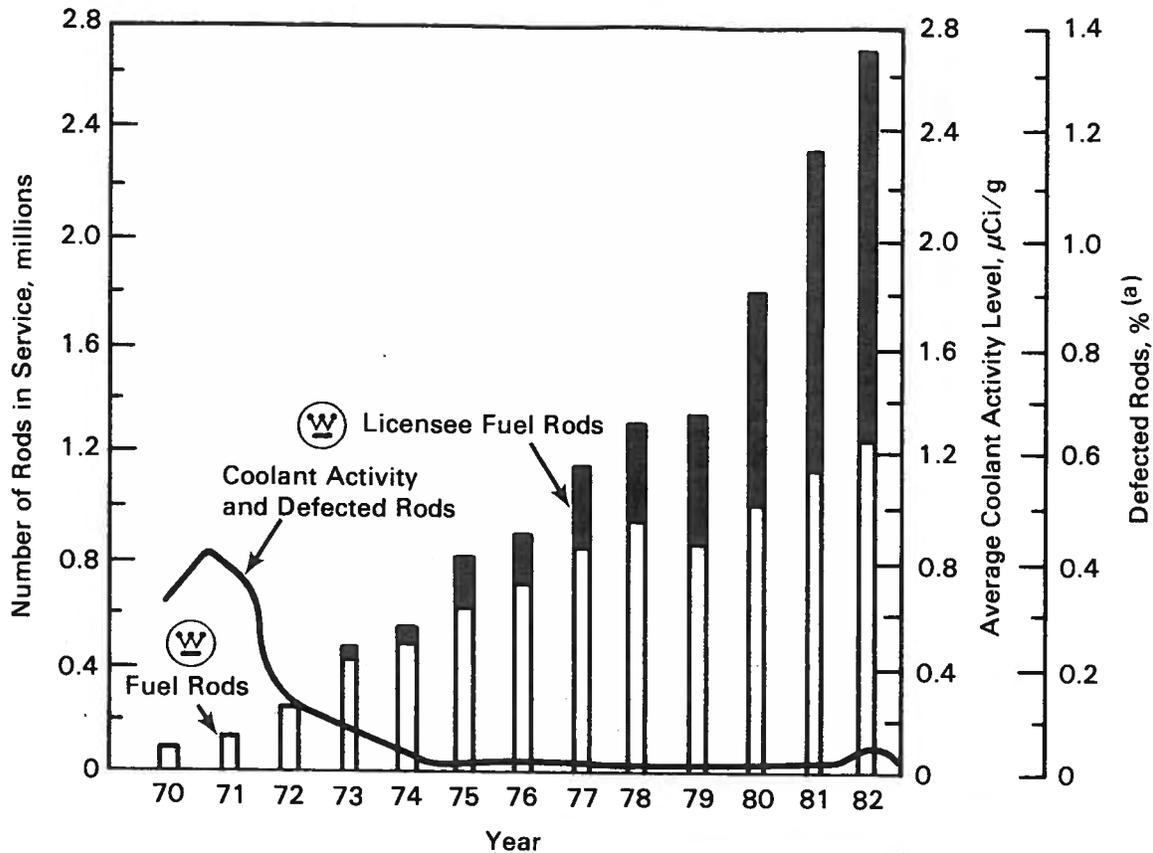
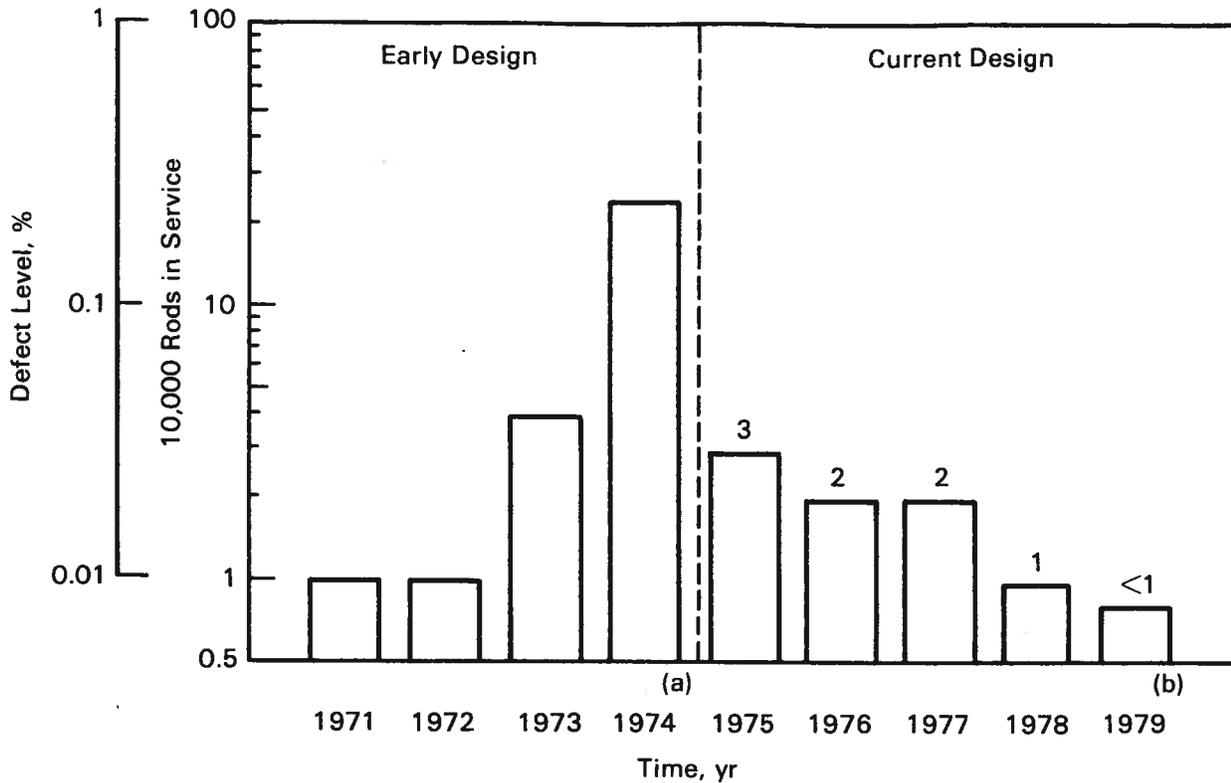


FIGURE 3.8. Westinghouse Zircaloy-Clad Fuel Experience as of December 31, 1982 (Bailey and Tokar 1984)

- (a) Bailey and Tokar (1984) state that "the coolant design basis activity varies somewhat from plant to plant depending on such factors as reactor power and coolant purification flow rate; however, a value of approximately  $2 \mu\text{Ci}$  of iodine-131 per gram of coolant water can be used for comparison. Since the coolant design basis activity was based on an inferred 1-percent defect level, the new basis of reporting (activity) produces a number approximately 100 times larger than the previous basis (inferred defects). That is, 1% of design basis activity would previously have been reported as 0.01% defected rods."



**FIGURE 3.9.** History of Combustion Engineering Fuel Performance (Bailey and Tokar 1984)

storage (Vesterlund and Olsson 1978; Johnson 1978; Hunt, Wood and Bain 1979; Johnson et al. 1982; Bailey and Johnson 1983).

### 3.1.3.3 Fuel Failure Rates During Handling/Consolidation and Transport

Possible damage to fuel rods during handling, rod consolidation operations, and transportation has been evaluated (EPRI 1984; Bailey and Pankaskie 1982; Bailey and Johnson 1982; Bailey 1983; Bailey 1985). It was concluded that the frequency of unusual occurrences involving damage to fuel rods from handling and transporting operations has been low (Bailey 1983). A few rods--approximately 6 out of over 51000 rods--have been broken as a result of handling operations; however, the 6 were known failed rods or came from fuel assemblies that were known to contain failed rods (Bailey 1985; Bailey and Beeman 1985). In most cases, when fuel was damaged during handling operations, there was only minor degradation of fuel assembly components and no breaching

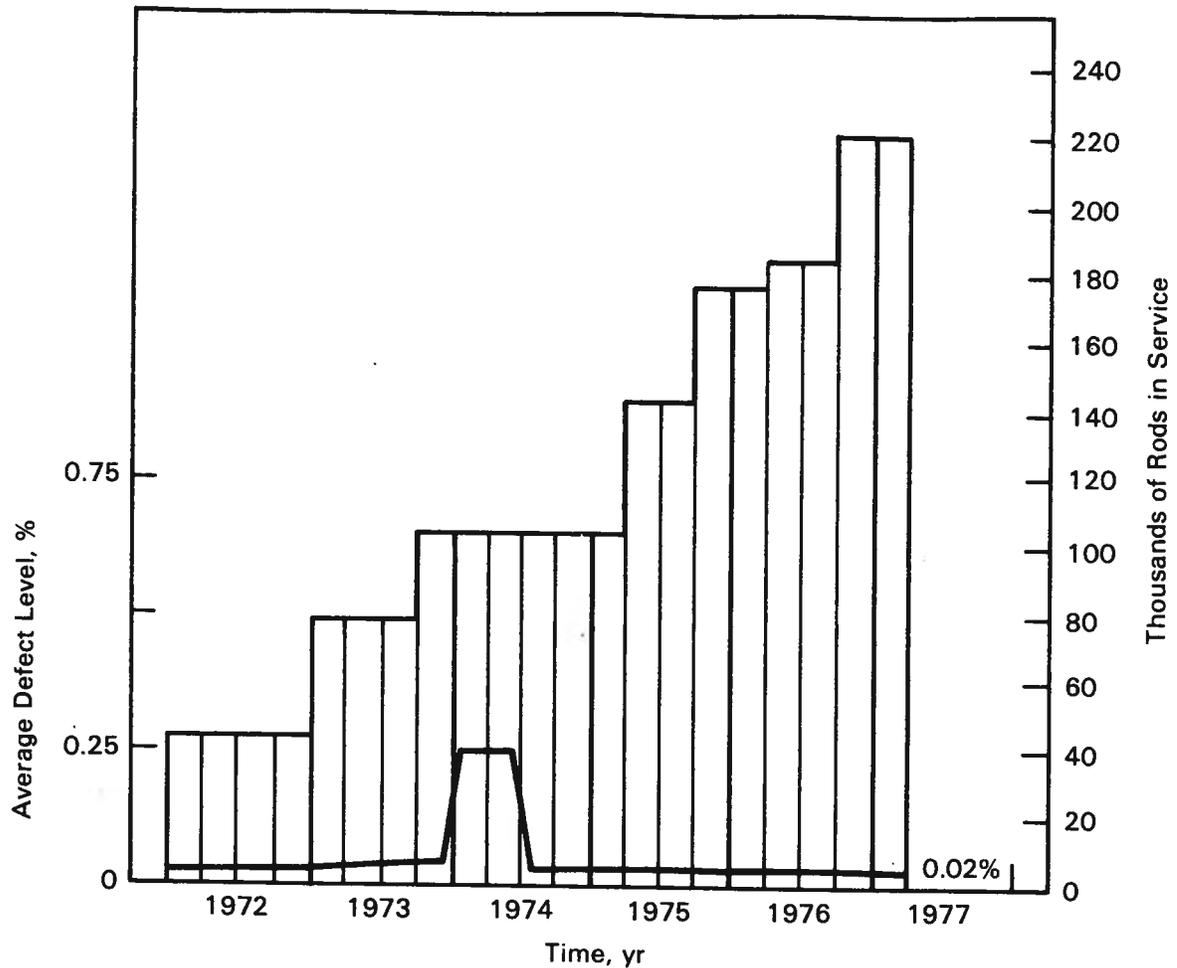


FIGURE 3.10. Combustion Engineering Fuel Performance with Zircaloy-Clad  $UO_2$  Fuel (Bailey and Tokar 1984)

of the fuel cladding or releases of radioactive gases or solids (Bailey 1985). Consolidation operations with extended burnup fuel might encounter a higher incidence of rod breakage, but this is not apparent at present (Anderson and Cholister 1982).

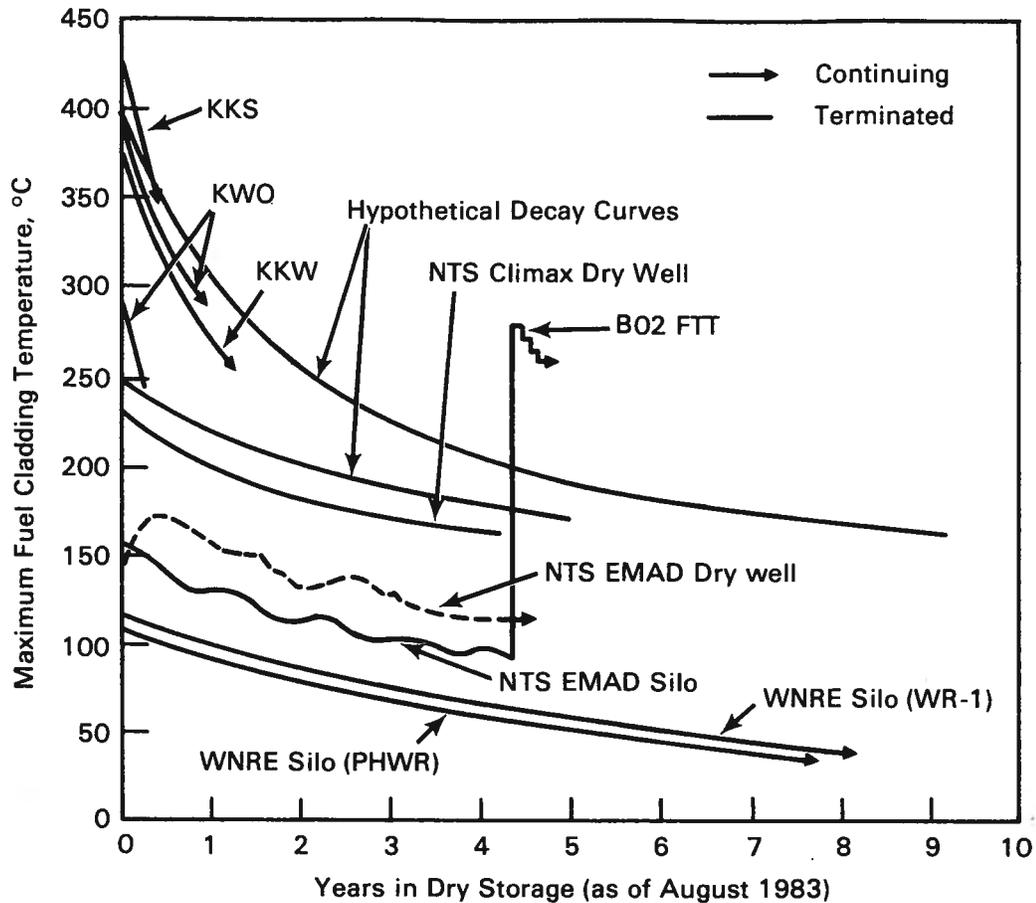
Over 5,100 spent-fuel assemblies have been transported in the United States and damage to previously sound irradiated fuel during transporting operations has apparently been minor; however, little is known on the subject. Fourteen or fewer assemblies (9 domestic, 5 foreign) were found or suspected to have been damaged during transporting operations in the United States and other countries. Five of those had fuel rods that had developed cladding defects

during reactor operation and 6 were unirradiated assemblies being shipped to reactors. In general, nearly all of the unusual occurrences involving handling and transporting operations with spent fuel have had only a minor or negligible effect on spent-fuel storage facility operations (Bailey 1983).

#### 3.1.3.4 Fuel Rod Failures in Dry Storage

The initial characteristics of spent fuel at a repository may also be determined by previous dry storage combined with the characteristics resulting from in-reactor operation, pool storage, and transportation. Interim dry storage will be necessary in the 1980s, and some spent fuel stored in these facilities could eventually be sent to a repository (USD0E 1982a). There is presently no anticipation of a need to store SS-clad spent fuel in dry storage facilities (Johnson, Gilbert and Guenther 1982). Potential methods of dry storage include metal casks, vaults, dry wells, and sealed-storage casks (i.e., silos) (Johnson, Gilbert and Guenther 1982; Guenther et al. 1984).

At the beginning of normal operation in dry interim storage, cladding temperatures will range from 200° to 400°C, based on current potential designs (Johnson, Gilbert and Guenther 1982). Fuel temperatures will decrease depending on the amount of burnup and previous decay as discussed in Section 3.1.1. Data have been collected for several dry storage tests to determine the change in fuel temperature and assess the performance of fuel rods in dry storage as indicated in Figure 3.12 (Johnson and Gilbert 1983). The oscillations in the temperature for the silo tests at the Nevada Test Site (NTS) are seasonal variations. The differences in the peak temperatures during the tests resulted primarily from the age of the fuel or the use of controlled heating to produce higher storage temperatures, such as in the B02 Fuel Temperature Tests (FTT) at the NTS. The other tests and demonstrations shown in Figure 3.11 were Kernkraftwerk Stade (KKS), Kernkraftwerk Wuergassen (KKW), Kernkraftwerk Obrigheim (KWO), NTS dry well tests at the Climax Mine and the Engine Maintenance and Disassembly (EMAD) site, and tests of two types of fuel [WR-1 and PHWR (pressurized heavy water reactor)] at Whiteshell Nuclear Research Establishment (WNRE) in Canada.



**FIGURE 3.11.** Dry Storage Temperatures Experienced in Several Tests and Demonstrations (Johnson and Gilbert 1983)

Current designs that are proposed for interim dry storage and monitored-retrievable storage (MRS) call for storing spent-fuel assemblies in inert cover gases at temperatures less than 380°C. Based on these conditions, few if any additional fuel rods will become defected during storage in these environments. These conclusions were drawn based on a review of possible degradation to the cladding and the fuel for up to 40 to 100 years of dry storage (Johnson and Gilbert 1983; Guenther et al. 1984; Johnson, Gilbert and Guenther 1982). These conclusions presume that oxygen is precluded from the spent fuel and that incipient defects are small enough that premature failure does not occur by creep rupture. Stress corrosion was not considered to be a dominant degradation mechanism for these times and under these conditions.

### 3.1.3.5 Morphology of Cladding Defects

Most of the effort to define defects in spent-fuel cladding has been directed toward evaluating the number of defects. The size and shape of the defect is also important to calculations of release rates. Defects can be perceptibly large, as in the case of fuel rods tested for experiments involving loss-of-coolant conditions, or the defects can be tiny perforations that are similar to those produced at very slow heating rates in experiments simulating abnormal heating events, such as a cask fire (Guenther 1983). The size of the defect typically is very small, if visible at all. Some Zircaloy fuel rods also have been known to have partial, through-wall cracks (i.e., incipient defects). These appear to be even less frequent than through-wall defects; however, there are no statistics on the number of incipient defects (Bailey and Pankaskie 1982).

Primary defects (as from SCC, hydride cracks) generally are small. Larger defects often develop because of secondary defects. In the early years of the nuclear power industry there were secondary failures from hydriding that caused some larger openings in fuel rods. Most of the defects are small and do not change under pool storage conditions even after years of storage. Dry storage in inert atmospheres, such as is proposed for interim storage (10 to 20 years) or for MRS (40 to 100 years), should preclude fuel oxidation in any fuel rods that contain defected cladding (Johnson and Gilbert 1983; Guenther et al. 1984). If the cladding is defected and air has access to the fuel, then fuel oxidation could cause the defect to enlarge. An example of the effect of fuel oxidation on defect size before and after testing in air for 2100 h at 325°C is shown in Johnson and Gilbert (1983).

### 3.1.4 Content and Distribution of Constituents in UO<sub>2</sub> Fuel and Gas in Spent-Fuel Rods

The fuel and fill gas compositions are altered and some of the material is redistributed during irradiation. Available information on physical changes in the fuel, fuel restructuring and redistribution of fission products in the fuel, and fill gas compositional changes are discussed below.

#### 3.1.4.1 Fuel Material

After irradiation, the chemical makeup of spent fuel becomes more complex. Along with the original uranium dioxide, the fuel pellet contains gaseous and solid fission products and reaction products distributed throughout the fuel. Further variations in fuel structure result from the power levels and burnup that a particular fuel rod experiences. Burnups have ranged from 5.4 to 23.2 MWd/kgM for BWRs since the first discharge in 1969 and from 17.4 to 29.5 MWd/kgM for PWRs since the first discharge in 1970 (USDOE 1982b). Information is available from DOE (USDOE 1983) on the accumulative quantities of elements and radionuclides in the spent-fuel rods that are now in storage. Of the 103 known elements, 81 are found in spent fuel and only 24 of those elements do not have radioactive isotopes. One could take the cumulative amounts and determine the amount of radionuclides in an average assembly based on 0.46 kgM for a PWR 17x17 assembly, 0.18 kgM for an 8x8 BWR fuel bundle, and the information in Table 3.1 of this report. However, such an approach would not properly account for the power history and decay time in a particular spent-fuel assembly or bundle. A better approach would be to calculate the inventory for the power history, burnup, and decay time that is of interest. Such calculations were made by Alexander et al. (1977) for a typical PWR and BWR assembly. The listing of elements and radionuclides are extensive and are not repeated here. Wilson and Oversby (1985) have examined the data in Alexander (1977) and made a list of the dominant radionuclides present in a PWR assembly after 1000 years storage (see Table 3.5).

#### 3.1.4.2 Particle Physical Condition

After the first power ascension, the cylindrical fuel pellets in the fuel rod begin to crack into a number of particles. The eventual size of these particles depends on the power level, the number of power ascensions, and the fuel power history. The size distribution of the fuel particles can be important to leaching mechanisms during postcontainment because the surface area affects the leaching of radionuclides from spent fuel (McVay, Bradley and Kircher 1981). Data on the particle sizes of  $UO_2$  from 7 fuel rods used in a loss-of-coolant accident (LOCA) test are provided in Table 3.6 (Rausch 1984). These data are for PWR fuel rods with Zircaloy-4 cladding with a 0.963-cm outside diameter

TABLE 3.5. PWR Spent-Fuel Assembly Inventories at 1000 Years<sup>(a)</sup>  
(Wilson and Oversby 1985)

<u>Radionuclide</u> <sup>(b)</sup>	<u>Percent of Total</u> <u>1000-Year Activity</u>
Am-241	51.84
Am-243	1.75
Pu-240	26.87
Pu-239	17.37
Pu-242	0.10
Pu-238	0.06
Tc-99	0.77
Ni-59	0.252
Ni-63	0.021
Zr-93	0.181
Nb-94	0.074
C-14	0.076 <sup>(c)</sup>
U-234	0.113
U-238	0.018
U-236	0.015
Np-237	0.058
Sn-126	0.045
Se-79	0.023
Cs-135	0.022
Sm-151	0.013
Pd-107	0.006
I-129	0.0018

- (a) Based on ORIGEN reported in Alexander et al. (1977) for 33 MWd/kgM burnup PWR assembly.
- (b) Radionuclides with 1000-year activity less than <sup>129</sup>I or half-life less than 1 year omitted.
- (c) <sup>14</sup>C activity may vary considerably depending on as-fabricated nitrogen impurities.

and 0.841-cm inside diameter. The fuel rods were pressurized with helium to 3.8 MPa (550 psig) and contained 2.93% enriched UO<sub>2</sub> fuel. The fuel pellets were initially 0.825 cm in diameter by 0.953-cm long. As a result of the transient (temporary rapid change in conditions) to a peak centerline temperature of about 777°C, about 96 wt% of the fuel was broken into particles 2.8 mm or larger.

TABLE 3.6. Particle-Size Distribution of Fuel Rods from NRU LOCA Test MT-3  
(Rausch 1984)

Rod Section	Total Weight of Fuel, g	% of Total Sample Weight Retained on Each Sieve Size						
		No. 3-1/2 (5.6 mm or 0.233 in.)	No. 5 (4.00 mm or 0.157 in.)	No. 7 (2.80 mm or 0.111 in.)	No. 10 (2.00 mm or 0.0787 in.)	No. 18 (1.00 mm or 0.0394 in.)	No. 50 (300 $\mu$ m or 0.0117 in.)	Receiver ( $<300 \mu$ m or $<0.0117$ in.)
2D5 (1) <sup>(a)</sup>	243.753	15.98	69.84	12.69	0.71	0.23	0.25	0.31
3B5 (1)	225.212	19.88	65.57	13.35	0.71	0.08	0.19	0.22
3D5 (2)	253.991	18.66	61.03	15.83	2.20	1.13	0.73	0.42
3E5 (3)	254.497	18.88	58.28	20.2	1.53	0.44	0.27	0.31
5C5 (3)	270.867	28.49	54.95	14.92	0.74	0.38	0.24	0.30
5D5 (3)	246.704	20.13	64.58	13.61	0.64	0.31	0.32	0.42
3B5A (3)	136.598	8.43	70.17	18.97	1.22	0.37	0.33	0.52
3B5B (11)	146.223	49.83	45.00	4.52	0	0.07	0.26	0.33

(a) Number in parentheses indicates the number of whole pellets before size analysis.

Particle sizes were also obtained by Katayama, Bradley and Harvey (1980) for H. B. Robinson II spent fuel that reached a burnup of 28 MWd/kgM. The particle sizes were from 2 to 6.73 mm for 86 wt% of the fuel; less than 0.08 wt% had diameters smaller than 0.1 mm. These data are provided in Table 3.7.

Cracking of the fuel pellet increases the surface area as well as the number of particles at which radionuclide release can occur. Barner (1984) estimated the crack surface areas in two specimens of H. B. Robinson II spent fuel with an average burnup of about 28 MWd/kgM. Using photomicrographs, the transverse and longitudinal cracks were counted and used to estimate the surface area per unit length of fuel. In the as-fabricated fuel rods (i.e., before irradiation), there was an estimated 38 mm<sup>2</sup> of surface per millimeter of fuel length. This compares with the surface areas of 114 and 109 mm<sup>2</sup> per millimeter of fuel length estimated for the two samples of H. B. Robinson spent fuel.

TABLE 3.7. Particle-Size Distribution of Fuel Fragments from H. B. Robinson Spent Fuel with a Burnup of 28 MWd/kgM (Katayama, Bradley and Harvey 1980)

<u>Sieve Number</u>	<u>Sieve Opening, mm</u>	<u>Weight, g</u>	<u>Fraction Retained</u>
3	6.73	0	0
4	4.73	192.883	0.1007
5	4.00	634.765	0.3331
10	2.00	1031.170	0.5384
20	0.841	35.205	0.01838
40	0.420	11.242	0.005869
60	0.250	4.979	0.002599
80	0.177	1.424	0.0007434
100	0.149	1.042	0.0005440
140	0.105	1.204	0.0006286
200	0.074	0.769	0.0004015
200	0.074	0.737	0.0003848

#### 3.1.4.3 Fuel Restructuring

Fuel restructuring involves physical and chemical changes in a fuel rod in which the original structure of the fuel may experience grain growth, central void formation, fission-gas bubble formation and release, formation of metallic ingots, and migration of volatile components depending on their vapor pressures.

Fuel rods in LWRs typically operate at LHGRs of 19 to 23 kW/m (6 to 7 kW/ft). At these LHGRs, the fuel temperature at the center of the fuel pellet has been measured to be less than 1200°C for a typical BWR fuel rod design after a burnup of 9.7 MWd/kgM (Guenther and Barner 1981). Olander (1976) has provided an extensive review of fuel rod performance and indicates that equiaxed grain growth requires temperatures of from 1300° to 1650°C according to a range of fuel rod designs. At the typical operating LHGRs, little if any restructuring of the fuel pellet will occur in LWRs. The lack of significant restructuring in LWR spent fuel under normal operating power is supported by metallography and microprobe analyses of H. B. Robinson spent fuel with a burnup of 28 MWd/kgM (Katayama, Bradley and Harvey 1980). There was no significant restructuring in this fuel that had as-irradiated grains of less than about 10  $\mu\text{m}$  in diameter. There was little change in grain size from the center of the pellet to the outer edge. Barner (1984) also reported on the grain size across the fuel pellet radius of the H. B. Robinson spent fuel as shown in Table 3.8. In general, little restructuring occurred in this typical LWR spent fuel.

#### 3.1.5 Distribution of Fission Products

The distribution of fission products within the fuel has not been established as well for LWR spent fuel as for fast reactor fuels because much less fuel restructuring occurs. Information on fission products at the fuel/cladding interface was reviewed by Bailey et al. (1977) to determine potential causes for the pellet-cladding interaction that has caused fuel rod failures under some conditions. Only limited data were found on the actual distribution of the fission products and reaction products within the fuel grains, grain boundaries, or at the fuel/cladding interface.

TABLE 3.8. Results of Fuel Grain-Size Measurements for H. B. Robinson, Unit 2 Spent PWR Fuel (Barner 1984)

Section No.	True Grain Size at Fractional Radius, $\mu\text{m}^{(a)}$			
	Centerline	1/3 Radius	2/3 Radius	Edge
N-9C-C	9.1	8.0	6.2	6.1
N-9C-F	10.1	9.6	8.0	---
N-9C-I	7.8	7.7	6.1	5.9
N-9C-K	9.0	7.8	6.1	5.9

(a) An "intercept" grain size was determined by line intercept method from ASTM E 112. From this, the "true" grain size equals the "intercept" grain size multiplied by 1.57.

Cubicciotti et al. (1976) studied the reaction of fission products at the cladding inner surface and reported that oxygen is slowly transported from the fuel to the inner surface of the cladding during reactor operation. The oxygen potential ranges from -540 kJ/mole of oxygen at the hot fuel center to -460 kJ/mole of oxygen in the fuel at the cladding surface. Cesium (and rubidium, to a lesser extent) can move by vapor transport to cooler parts of the fuel rod, such as the cladding inner surface or plenum area. Gamma scans of spent fuel rods often show higher concentrations of cesium at pellet-pellet interfaces. Other vaporizing fission products that were believed to be able to migrate to the cladding were Cs (Rb) in compounds; I (Br) and Te (Se) in compounds with Cs; elemental Ce, Sb, Ag, Sn, and Pd; Ba, as BaO; and possibly MoO<sub>2</sub>. The impurities and fission products that have been observed at the inner surface of the cladding were also noted by Cubicciotti et al. (1976) and included the following (in elemental form without noting the compounds involved): Te, I, Pd, Ba, Fe, Cl, Si, Al, Ag, Na, and Ca. No information was found on the expected quantities of the elements and compounds in the fuel or at the cladding surface.

Barner (1984) reported the detection of noble metal ingots at the center of some H. B. Robinson spent fuel, but the ingots were about 1  $\mu\text{m}$  or smaller in diameter. In general, metallic fission products, such as molybdenum and ruthenium, and to a lesser extent technetium, palladium, and rhodium develop in oxide fuel irradiated to high burnups (Yang and Olander 1981). These 1- to

10- $\mu\text{m}$  particles are found in the columnar grain regions that form as annular regions toward the center of some fuel rods that achieve higher power or burnup.

Microprobe analyses by Katayama, Bradley and Harvey (1980) indicated that the H. B. Robinson spent fuel had little variation in the fission products across the fuel diameter. The concentrations of several radionuclides are shown in Figures 3.12 through 3.14. Near the fuel surface, plutonium and ruthenium showed distinct enrichment. The plutonium showed the highest

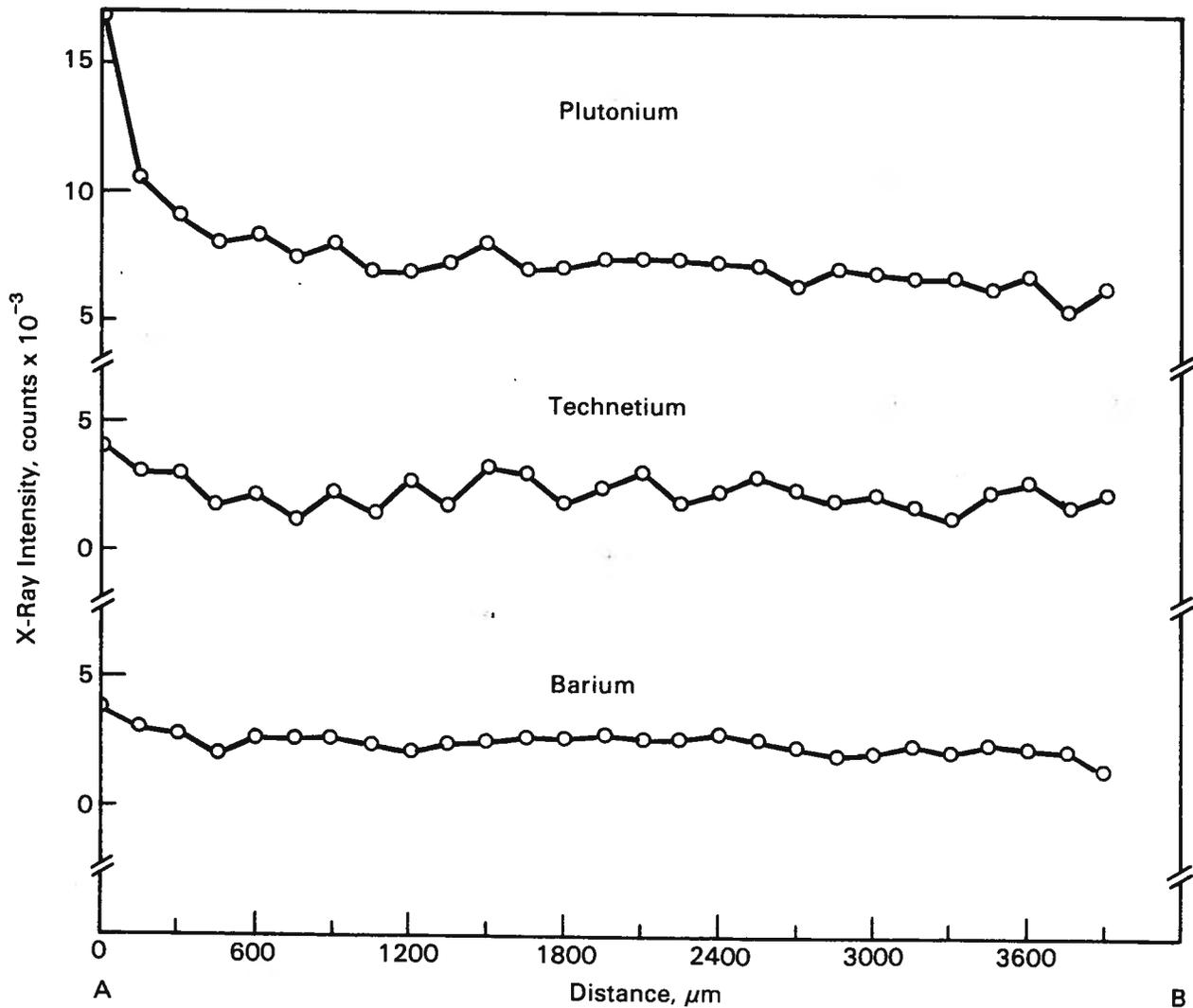


FIGURE 3.12. Microprobe Measured X-Ray Intensities for Plutonium, Technetium, and Barium (Katayama, Bradley and Harvey 1980)

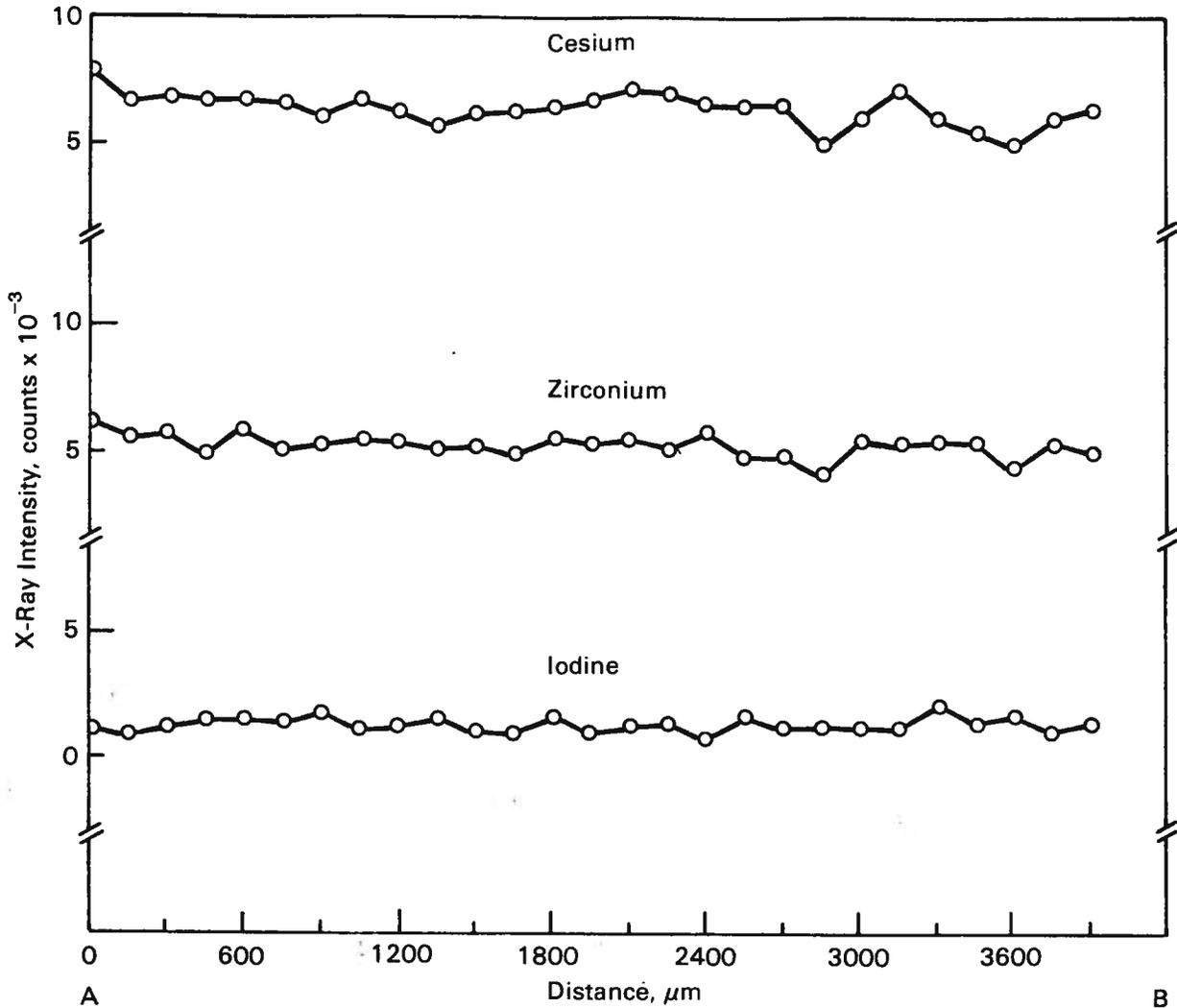
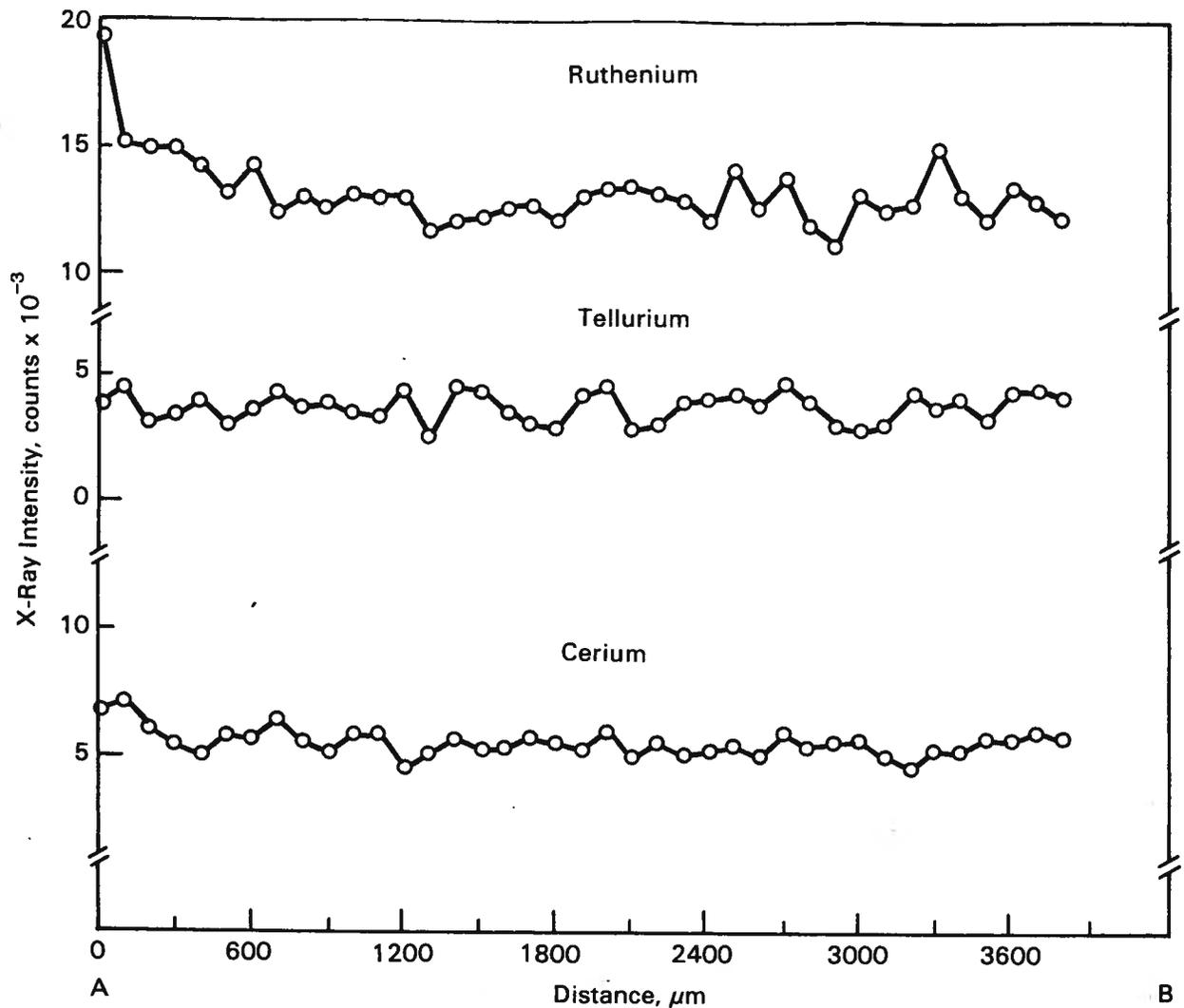


FIGURE 3.13. Microprobe Measured X-Ray Intensities for Cesium, Zirconium, and Iodine (Katayama, Bradley and Harvey 1980)

gradient from edge to center, with a 47% reduction in the x-ray intensity, 300 μm inward from the fuel surface, and an additional 28% drop over the next 3600 μm to the fuel center. Technetium, barium, cerium, and cesium were slightly enriched at the fuel surface. The concentration profiles for tellurium, iodine, and zirconium were essentially flat across the fuel pellet. The amount of release of radionuclides from spent fuel is typically described in terms of a leach rate. In this sense, the releases are determined by the average content in the cracked fuel pellets. Barner (1984) has reported the averaged composition of some radionuclides in H. B. Robinson spent fuel.



**FIGURE 3.14.** Microprobe Measured X-Ray Intensities for Ruthenium, Tellurium, and Cerium (Katayama, Bradley and Harvey 1980)

These data were obtained by inductively coupled plasma spectrometry and are provided in Table 3.9. The data in Table 3.9 represent the concentration of the elements from crushed samples of the PWR spent fuel. The values for the Al and Si under the 250 mesh column probably resulted from the grinding material.

Gause and Soo (1985) reviewed information on the tritium produced during fissioning. About 50% of the tritium produced remains in Zircaloy cladding.

TABLE 3.9. Content of Crushed Spent Fuel from H. B. Robinson, Unit 2 PWR (Barner 1984)<sup>(a)</sup>

Element <sup>(b)</sup>	Concentration, $\mu\text{g/g}$ of fuel <sup>(c)</sup>								
	60 to 115 mesh			115 to 250 mesh			250 mesh		
Al	-	-	(-)	-	-	(-)	1320	690	(1005)
B	220	700	(460)	-	190	(95)	-	-	(-)
Ca	806	-	(403)	350	-	(175)	-	-	(-)
Fe	200	170	(185)	280	32	(156)	170	170	(170)
La	980	900	(940)	980	890	(935)	950	880	(915)
Mn	260	230	(245)	350	320	(335)	210	220	(215)
Mo	2500	2400	(2450)	2500	2450	(2475)	2480	2380	(2430)
Nd	2780	2200	(2490)	2900	1660	(2280)	1920	1950	(1935)
Rh	730	-	(365)	790	-	(395)	-	-	(-)
Ru	1680	1430	(1555)	1580	1260	(1420)	1320	1320	(1320)
Si	-	-	(-)	-	-	(-)	2650	2120	(2385)
Sr	530	510	(520)	520	520	(520)	530	510	(520)
Te	260	80	(170)	-	-	(-)	-	-	(-)
Zr	2330	2130	(2230)	2280	2230	(2255)	2420	2250	(2335)

(a) Fuel fused in KOH in a nickel crucible.

(b) Cr, Dy, Li, and Ti not detected. Regression fit for interference of U not adequate to determine Ba, Ca, Mg, Na, and Zn.

(c) Values shown represent two solutions, prepared at 2000X dilution and at 1000X dilution; averages in parentheses.

The tritium is unevenly distributed in the cladding in concentrations of about 0.07 ppm. As the tritium decays, helium is produced and could degrade the mechanical properties of SS cladding.

### 3.1.5.1 Fission Gas

Two primary aspects need to be considered when assessing fission gas in the spent-fuel rod. These aspects include 1) the amount of fission gas release and its effect on internal fuel rod pressures and 2) the composition of the gas.

3.1.5.1.1 Fission Gas Release and Pressures. Typical end-of-life room-temperature pressures are ~30 to 40 atm (3 to 4 MPa) for PWR fuel rods and 15 atm (1.5 MPa) for BWR fuel rods (Johnson, Gilbert and Guenther 1982). Measured and estimated fission gas releases for nine PWR spent-fuel rods from H. B. Robinson II are given in Table 3.10. These fuel rods were irradiated to a burnup of about 28 MWd/kgM at an initial peak linear heat generation rate (LHGR) of 32.7 kW/m (10 kW/ft); by the end of the irradiation, the LHGR had dropped to 21.2 kW/m (6.5 kW/ft). The fission gas release of 0.2% compared well with analyses of 13 other sibling fuel rods that had an average release of 0.21% (Einziger and Fish 1982).

Other factors, such as storage temperature and actinide decay, can affect the gas pressure. The calculated gas pressures for different fission gas releases and storage temperatures are given in Figure 3.15 (Johnson and Gilbert 1983). Actinide decay could further increase the gas pressure as indicated in Figure 3.16. The two curves in Figure 3.16 represent a conservative peak design temperature (380°C) recommended for interim dry storage and a typical temperature (100°C) calculated for the end of the containment period at a repository. The curves were calculated based on a PWR rod with 36 MWd/kgM burnup and 100% helium release.

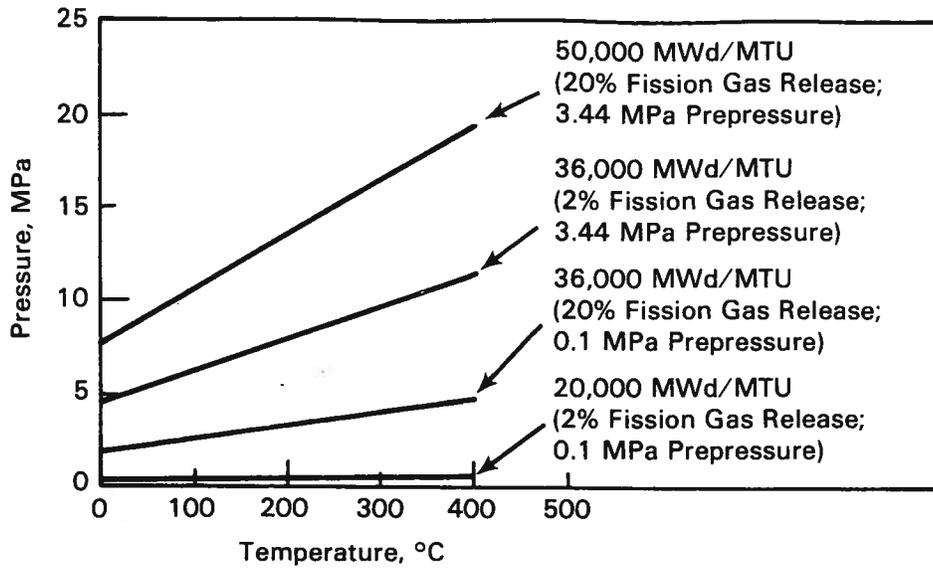
3.1.5.1.2 Composition of Fuel Rod Gas. The isotopic composition of the gas in the plenum, gap, and cracks between the fuel fragments is complex because of a power history dependence and radioactive decay. Most of the gas is composed of xenon, krypton, and helium with a few other gases, such as those listed in Table 3.11 for H. B. Robinson spent fuel. The isotopic distribution of the krypton and xenon gases from this PWR spent fuel is given in Table 3.12. The H. B. Robinson fuel was discharged in May 1974, thus, these results are typical of the 10-year-old PWR fuel rods that are planned for disposal in repositories. Aside from the isotopic changes that result from decay, the

TABLE 3.10. Fission Gas Release Results for PWR Spent-Fuel Rods from H. B. Robinson, Unit 2 (Barner 1984)

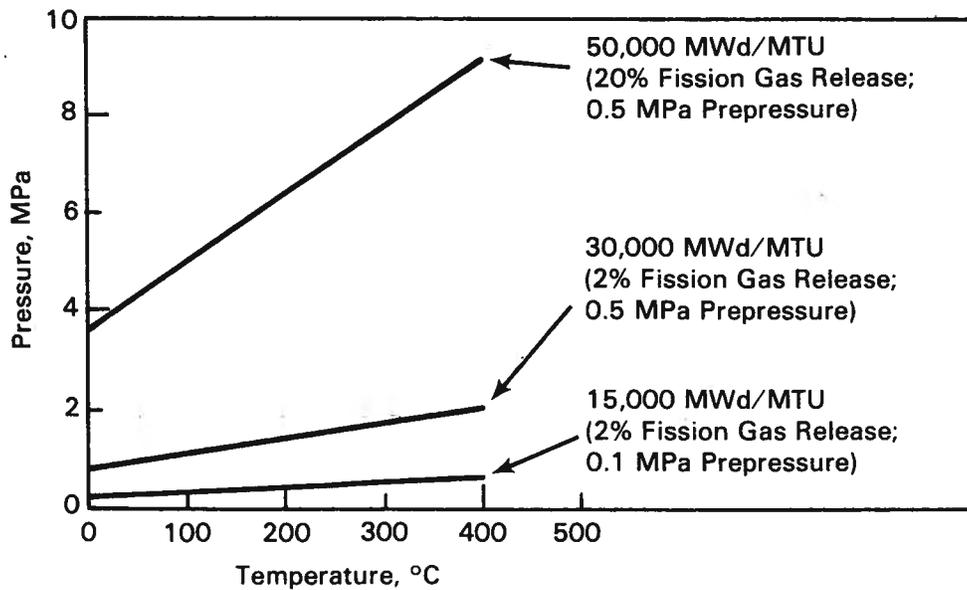
Rod No.	Total Recovered Gas at STP, cm <sup>3</sup>	Xe + Kr, %	Volume of Xe + Kr at STP, cm <sup>3</sup>	Rod-Average Burnup, MWd/kgM <sup>(a)</sup>	Estimated Fission Gas <sup>(a,b)</sup> Produced, cm <sup>3</sup>	Fission Gas <sup>(a)</sup> Released, %
C-5	362	0.99	3.58	28.2	1906	0.19
D-10	369	1.15	4.24	[28.4]	[1919]	[0.22]
G-9	373	0.80	2.98	[28.4]	[1919]	[0.16]
G-13	357	1.09	3.89	[28.4]	[1919]	[0.20]
J-12	368	0.99	3.64	[28.4]	[1919]	[0.19]
L-8	364	1.58	5.75	30.0	2027	0.28
N-4	368	0.82	3.02	[28.4]	[1919]	[0.16]
N-9	371	0.99	3.67	28.4	1919	0.19
N-12	365	0.94	3.43	29.4	1987	0.17
Sibling Rods	--	--	--	--	--	0.21

(a) Values shown in brackets are preliminary pending <sup>137</sup>Cs gamma scan results. For non-scanned rods the burnup is assumed to be the same as N-9.

(b) Calculated from fuel dimensions and density listed in Table 2, and assuming a fuel volume reduction of 1% for dishes, metal to oxide ratio of 0.88, and 31.0 cm<sup>3</sup> fission gas per MWd.



(a)



(b)

**FIGURE 3.15.** Effect of Storage Temperature and Fission Gas Release on (a) PWR and (b) BWR Spent-Fuel Rod Gas Pressures (Johnson and Gilbert 1983)

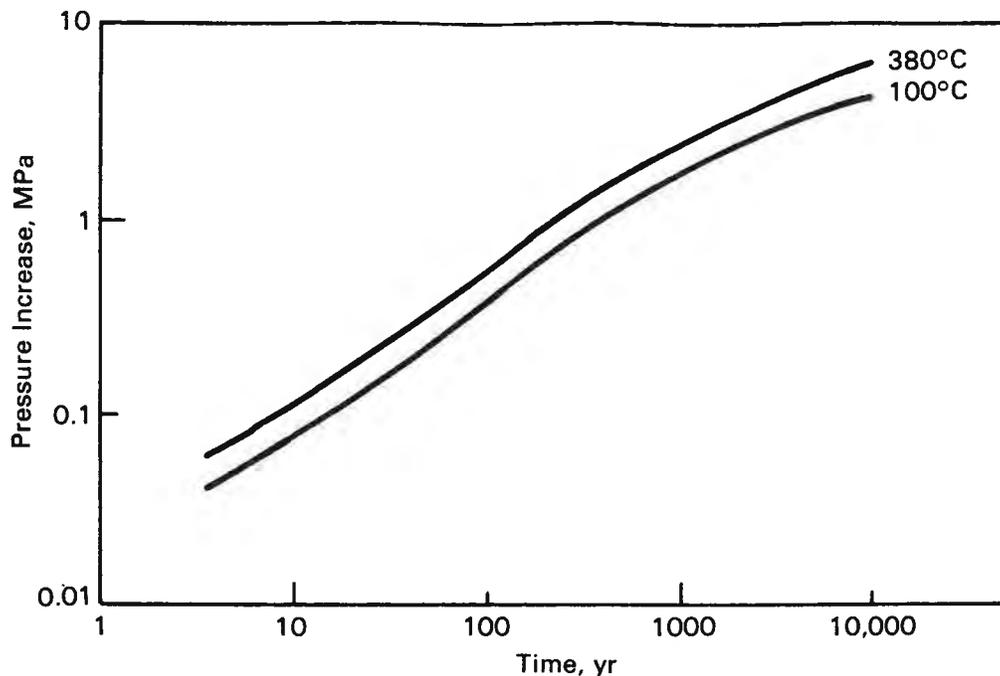


FIGURE 3.16. Calculated Pressure Increase Caused by Helium Production from Actinide Decay (Johnson and Gilbert 1983)

amount of volatile fission products in the free void volume of an intact fuel rod remains constant after discharge as long as the fuel temperature remains below 1000°C (Fish and Einziger 1981). Nearly all of the fission gas is contained in the fuel itself, even after 10 years of pool storage or, possibly, after 40 to 100 years of dry storage before repository closure. Additional fission gas will not be released under typical dry storage temperatures unless the fuel rod cladding fails and  $U_3O_8$  forms, creating a much larger fuel surface area from which the gas can be released. No data were found to indicate the amount of fission gas release as  $UO_2$  converts to  $U_3O_8$ .

### 3.2 IDENTIFICATION OF POTENTIAL FAILURE MODES/PROCESSES

The characteristics of the spent-fuel rods were given in the previous section based on performance during irradiation in a power reactor, wet storage in a reactor pool, handling and transportation operations, and potential dry interim storage and/or monitored retrievable storage. In general, the spent-fuel rods are expected to arrive at the repository with the cladding intact and

TABLE 3.11. Gas Pressure, Gas Composition, and Rod Void Volume for Rods from ATM-101

Rod No.	Measured Void Volume, cm <sup>3</sup>	Total Recovered Gas at STP, cm <sup>3</sup>	Pressure at 0°C, MPa	Gas Composition								
				He	Xe	Kr	Ar	H <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	Organics
C-5	23.9 ±1.1	362 ±8.7	1.54 ±0.07	98.3 ±0.2	0.89 ±0.015	0.10 ±0.044	0.61 ±0.01	<0.01 --	<0.01 --	0.06 ±0.004	<0.01 --	<0.01 --
D-10	22.5 ±1.1	369 ±8.9	1.66 ±0.08	98.2 ±0.2	1.03 ±0.08	0.12 ±0.004	0.61 ±0.01	0.02 ±0.008	<0.01 --	0.05 ±0.004	<0.01 --	0.02 --
G-9	22.2 ±1.0	373 ±8.9	1.70 ±0.08	98.9 ±0.2	0.72 ±0.012	0.08 ±0.003	0.30 ±0.005	<0.01 --	<0.01 --	0.04 ±0.004	<0.01 --	<0.01 --
G-13	20.0 ±0.9	357 ±8.6	1.81 ±0.08	97.9 ±0.2	0.98 ±0.017	0.11 ±0.004	0.91 ±0.016	0.2 ±0.008	<0.01 --	0.05 ±0.004	<0.01 --	<0.02 --
J-12	22.8 ±1.1	368 ±8.8	1.63 ±0.08	98.7 ±0.2	0.88 ±0.015	0.10 ±0.004	0.25 ±0.005	<0.01 --	<0.01 --	±0.004 ±0.004	-- --	-- --
L-8	22.1 ±1.0	364 ±8.7	1.67 ±0.08	96.7 ±0.02	1.42 ±0.024	0.16 ±0.006	0.76 ±0.013	0.03 ±0.008	<0.01 --	0.74 ±0.13	0.12 ±0.004	0.02 --
N-4	20.1 ±0.9	368 ±8.8	1.85 ±0.09	98.7 ±0.2	0.74 ±0.013	0.08 ±0.003	0.33 ±0.003	0.02 ±0.008	<0.01 --	0.08 ±0.004	<0.01 --	0.02 --
N-9	19.7 <sup>(a)</sup> --	371 ±8.9	1.91 <sup>(a)</sup> --	98.3 ±0.2	0.89 ±0.015	0.10 ±0.004	0.63 ±0.01	<0.01 --	<0.01 --	0.08 ±0.005	0.01 ±0.006	<0.01 --
N-12	12.5 <sup>(b)</sup> --	365 ±8.0	2.96 <sup>(b)</sup> --	98.5 ±0.2	0.85 ±0.015	0.09 ±0.003	0.40 ±0.01	<0.01 --	<0.01 --	0.15 ±0.004	0.03 ±0.005	<0.01 --

- (a) Result may be slightly because of incipient valve failure that was discovered during sampling the next fuel rod; however, result is within two standard deviations of results for the first seven rods listed.
- (b) Result in error because of faulty valve.

TABLE 3.12. Isotopic Gas Analyses of PWR Spent Fuel from H. B. Robinson  
(Barner 1984)

Rod No.	Xenon, %						Krypton, %				Xe/Kr Ratio
	128	130	131	132	134	136	83	84	85	86	
C-5	<0.1 --	0.1 ±0.05	8.3 ±0.3	20.6 ±0.4	28.6 ±0.5	42.4 ±0.7	12.0 ±0.5	31.7 ±1.2	3.8 ±0.7	52.4 ±1.9	8.9
D-10	<0.1 --	0.1 ±0.005	8.3 ±0.13	20.5 ±0.4	28.4 ±0.5	42.7 ±0.7	12.1 ±0.6	31.9 ±1.2	3.7 ±0.6	52.5 ±1.9	8.6
G-9	<0.1 --	0.1 ±0.06	8.4 ±0.03	20.5 ±0.4	28.2 ±0.5	42.8 ±0.7	12.1 ±0.8	31.9 ±1.2	3.5 ±0.5	52.4 ±1.9	9.0
G-13	<0.1 --	0.1 ±0.04	8.2 ±0.3	20.4 ±0.4	28.4 ±0.5	42.8 ±0.7	11.9 ±0.7	31.9 ±1.2	3.8 ±0.5	52.4 ±1.9	8.9
J-12	<0.1 --	0.1 ±0.05	8.1 ±0.3	20.6 ±0.4	28.5 ±0.5	42.6 ±0.6	11.6 ±0.4	32.1 ±1.2	3.6 ±0.5	52.7 ±1.9	8.8
L-8	<0.1 --	0.1 ±0.03	7.7 ±0.3	20.9 ±0.4	28.5 ±0.5	42.8 ±0.7	11.5 ±0.4	32.5 ±1.2	3.6 ±0.5	52.4 ±1.9	8.9
N-4	<0.1 --	0.2 ±0.08	8.3 ±0.3	20.7 ±0.4	28.3 ±0.5	42.5 ±0.7	12.2 ±0.9	31.8 ±1.2	3.7 ±0.9	52.3 ±1.9	9.3
N-9	<0.1 --	0.1 ±0.05	8.0 ±0.3	20.8 ±0.4	28.2 ±0.5	42.8 ±0.7	12.0 ±0.7	32.2 ±1.2	4.1 ±0.7	51.8 ±1.9	8.9
N-12	<0.1 --	0.1 ±0.05	8.5 ±0.03	20.5 ±0.4	28.2 ±0.5	42.6 ±0.7	12.2 ±0.8	31.5 ±1.1	3.9 ±0.8	52.3 ±1.9	9.4

the irradiated fuel and gaseous fission products contained in the fuel rod. Only a percent or less of the fuel rods are expected to have breached or incipiently defected cladding.

The spent-fuel rods that arrive at a repository may be shipped in the original assembly configuration in which they existed during irradiation in the reactor. Or, the fuel rods could arrive consolidated in SS boxes or canisters, depending on whether consolidation was accomplished at a reactor site or at an MRS facility. Fuel rods that were stored in dry environments will probably not have been exposed to air during the storage based on present recommendations (Johnson and Gilbert 1983). Canisters of spent-fuel rods from MRS facilities would also contain an inert cover gas. It is not apparent whether the MRS

canister would be over-packed, used in the repository as is (thus becoming the container), or replaced with a container. The following discussion of performance of spent-fuel rods under disposal conditions considers the effect of environmental conditions, such as temperature, cladding stresses, and availability of oxidants to the cladding and fuel. The actual design of the waste package is not considered, although the synergistic effect of waste package materials and their corrosion products are important to the response of the cladding and  $UO_2$  to the repository environment.

The following discussion provides information on the potential performance of Zircaloy- and, to a lesser extent, SS-clad, spent-fuel rods during two time frames: 1) postemplacement involving dry storage and 2) postcontainment with exposure to steam, hot water, and/or water vapor. Expected storage conditions and potential degradation during these time frames are considered.

### 3.2.1 Postemplacement Containment Period: Dry Storage

The first time frame during which spent-fuel rod performance is assessed for repository disposal is the containment period, which should last for 300 to 1000 years according to NRC's 10 CFR Part 60. In reality, this period could be extended if the container continues to perform as a barrier between the spent-fuel rods and the repository environment. Information is provided below on the storage conditions and spent-fuel rod performance during this period.

#### 3.2.1.1 Storage Conditions

During this period, the waste packages are designed to provide essentially complete containment of the radioactive wastes regardless of the condition of the spent-fuel cladding. In waste packages using inert atmospheres inside the container, the spent-fuel rods are exposed to environmental conditions similar to dry storage conditions discussed in Section 3.1.3. Waste packages are designed to have either air or inert cover gases (OCD 1984; Gregg and O'Neal 1983; Anderson 1982; Bolmgren et al. 1983). Regardless of the use of air or inert gases, the cover gas should be relatively pure, although there is a potential for some moisture from fuel rods that breached during reactor operation and absorbed water (i.e., became water-logged).

The peak temperature and temperature history for spent-fuel rods in a repository will be different than that experienced during wet or dry storage. In wet storage, the fuel rods are maintained at a constant temperature of about 30°C or slightly higher. In interim dry storage and MRS, peak temperatures would be less than 380°C followed by a decrease in temperature in a manner similar to that shown before in Figure 3.11 (Johnson and Gilbert 1983). Peak temperatures for spent-fuel rods in repositories would also be less than 380°C; however, the temperature histories will be different than in dry storage as a result of heat transfer characteristics of host rocks, thermal loading of the repository, increased age of the spent-fuel rods, and the number of rods that are emplaced in a waste package.

Peak temperatures have been calculated to range from 255° to 372°C, typically based on 10-year-old spent-fuel rods (ONWI 1980; Bolmgren et al. 1983; RHO/AESD 1982; Hockman and O'Neal 1983). These peak temperatures occur at emplacement or within the first few years. The peak temperature of the fuel rod in a salt repository has been calculated to remain level for about 10 years and decrease slowly to about 100°C by 100 years after emplacement (Bolmgren et al. 1983). In tuff, the temperature would increase slightly to a peak of about 330°C, then decrease to about 100°C within 100 years and 50°C by 1000 years after emplacement (Hockman and O'Neal 1983). The peak temperature is reached in basalt after about 5 years and declines to about 150°C at 100 years and 100°C at 1000 years (Anderson 1982). Section 2.0 discusses temperature in more detail, but the significant point for the purposes of the present discussion is that during the containment period, spent-fuel temperatures are expected to be roughly similar to those encountered in dry storage.

#### 3.2.1.2 Degradation Mechanisms

Several mechanisms could potentially contribute to the degradation of the fuel rod during the containment period, depending on whether the cladding is or is not intact on emplacement. If the cladding has no defects, then degradation to the cladding is the principal concern. If the fuel rod has been breached, then fuel oxidation becomes a problem and further cladding degradation and eventual radionuclide release are of concern. Johnson and Gilbert (1983) summarized information on spent-fuel rod degradation in dry interim storage as

indicated in Table 3.13. Based on the use of an inert cover gas in storage canisters and a peak storage temperature of 380°C followed by a declining temperature history, Johnson and Gilbert concluded that none of the mechanisms outlined in Table 3.13 were expected to cause major degradation for up to 100 years of dry storage. Guenther et al. (1984) reviewed expected dry storage conditions for MRS and concluded that few, if any, additional failures should occur for MRS under similar storage conditions for 40 to 100 years. The two principal degradation modes of concern during dry storage were cladding failure by creep (stress) rupture in intact fuel rods or splitting of the cladding as a result of oxidation of the fuel in defected cladding. Some mechanisms, such as hydride embrittlement or SCC might occur under some circumstances, but these mechanisms were not considered highly probable. Failures by these mechanisms could not be completely ruled out even for dry interim storage because of irradiation effects and possible incipient defects.

#### 3.2.1.3 Unbreached Cladding

If the fuel rods arrive intact at the repository, then the potential for degradation of the cladding is the first consideration in how well the spent-fuel rods will perform in a repository. Because most degradation phenomena are thermally activated, the extent of degradation occurring in a given time depends on the temperature history. Based on previous work on degradation of spent-fuel rods in dry storage there appear to be three processes warranting consideration during repository dry storage: 1) creep rupture, 2) corrosion, and 3) hydriding.

3.2.1.3.1 Creep Rupture. The creep rupture behavior of Zircaloy-clad LWR fuel rods for extended times at elevated temperature has been predicted by the Larsen-Miller parameter method (Blackburn et al. 1978) and by a creep mechanism and failure mechanism mapping approach to modeling (Chin and Madsen 1983; Khan, Madsen and Chin 1984). These predictions depend on the fuel rod plenum pressure, the age of the fuel, and the microstructural features of the cladding.

The fuel rod plenum pressure affects creep rupture because it provides the driving energy for rupture during long disposal times; it also provides the primary driving energy for the growth of reactor-induced incipient cracks during disposal. A fuel rod pressure of 80 atm (~8 MPa), which might be expected

**TABLE 3.13.** Summary of Postulated Cladding Failure Mechanisms in Dry Storage (from Johnson and Gilbert 1983)

Mechanism	Relationship to Dry Storage	Known Consequences	Issues
Rapid stress rupture	Thermal excursions.	Major excursions generate minute defects under postulated dry storage temperature ramp.	What temperature excursions are credible?
	Mechanical overloads, such as fuel handling events.	Has caused no significant impacts during fuel handling operations.	Are overload situations caused by fuel handling in dry storage operations foreseeable?
Stress corrosion cracking	Cladding failures observed in reactor and test thermal regions similar to dry storage conditions.	Requires combination of aggressive fission products and high stresses (> about 180 MPa).	Are fission products aggressive after extended storage?
Strain rate embrittlement	Low ductility specimen failures observed in thermal regions similar to dry storage conditions?	No fission products were present.	Are required stresses and strain rates ever present in fuel under dry storage conditions?
Slow creep rupture	Decreasing dry storage temperature suppress creep.	Observed only at atypical stresses in laboratory tests. Cladding breaches are minute.	Will high-pressure, high-burnup fuel be a candidate for dry storage? Will localized stresses caused by incipient defects lead to creep rupture?
Cladding oxidation (a)	Insignificant in limited air or oxidizing atmospheres below 400°C.	Oxide films are coherent and protective.	None.
Hydride reorientation	Dry storage temperatures eventually decrease below the hydrogen solubility limit.	Radially oriented hydrides reduce the strain for failure.	Do dry storage stresses and temperature conditions cause hydride reorientation?
	Hoop stresses may cause hydrides to become radially oriented.		If so, will cladding creep strains in excess of the failure levels be encountered during dry storage?
Fuel oxidation	Some interest for qualifying air storage.	UO <sub>2</sub> oxidizes to low density U <sub>3</sub> O <sub>8</sub> splits cladding by oxygen ingress through cladding breaches; rates decrease with temperature.	Below what limiting temperature can monitoring of inert gas protection be discontinued? Is air ingress to storage containers credible?

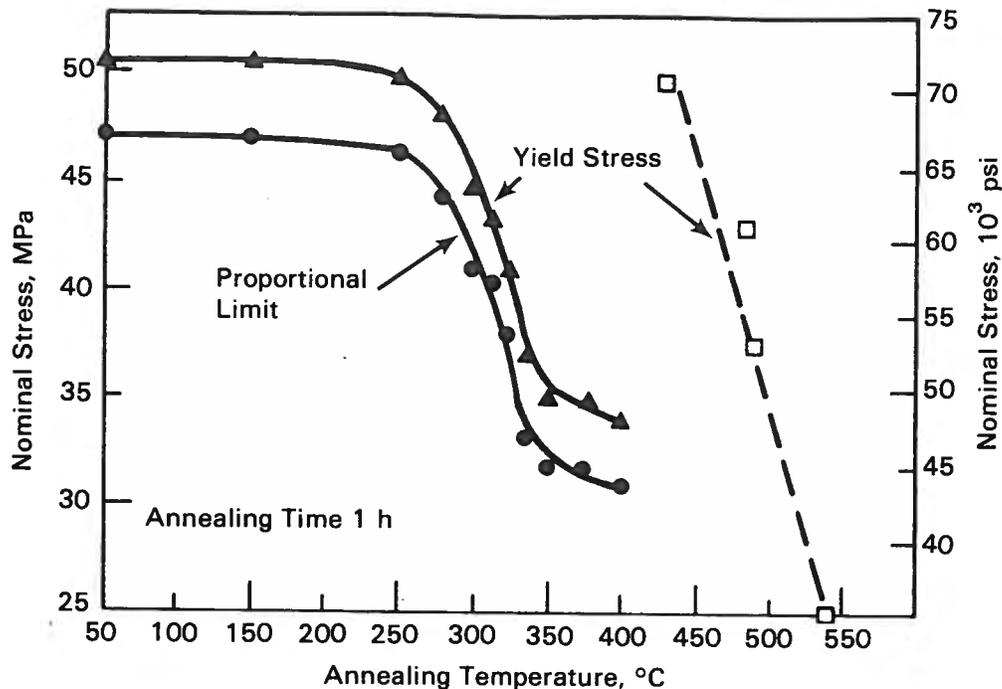
(a) Included to indicate the consequence in the unlikely event that the inert cover gas will degrade because of air ingress.

in a PWR fuel rod fabricated after the 1970s and irradiated to a burnup of 50 MWd/kgM, would be affected by different storage temperatures as shown by the upper line in Figure 3.15a. Based on a cumulative damage model, this level of pressure approaches the limit for creep rupture by a cavitation mechanism in approximately 300 years at a storage temperature of about 275°C (Johnson and Gilbert 1983). Johnson and Gilbert (1983) show that these stresses could increase by nearly a factor of two during the first few thousand years of disposal if the increase from helium production is included (see Figure 3.16).

The cumulative damage models are used to predict the performance of Zircaloy cladding for spent-fuel rods with a declining temperature during interim dry storage (White et al. 1983; Gilbert et al. 1983; Chin and Madsen 1983). However, they have not been applied to the increasing or more slowly decreasing temperatures expected during geologic disposal, nor to SS-clad spent-fuel rods.

Fuel age alters the temperature decrease rate, which directly affects the potential for creep rupture and other failure mechanisms. This, in turn, affects the rate at which damage accumulates for creep rupture. Temperatures of older fuel rods with the same power history will decrease more slowly than younger spent-fuel rods that are stored at the same initial temperature. Thus, fuel rods that have been out of the reactor longer will have to be stored at lower initial peak temperatures to preclude higher cladding damage.

Properties of the cladding also affect the creep behavior of the cladding. Neutron irradiation effects on cladding properties tend to approach an asymptotic level with increasing burnup. Generally, these cladding properties are not expected to limit the performance of spent fuel after disposal. In fact, irradiation of Zircaloy cladding has been found to improve the resistance of the cladding to failure by creep rupture (Blackburn et al. 1978; Peehs et al. 1984). However, if the cladding temperatures are sufficient, thermal recovery and annealing of the irradiation damage in the cladding might occur as shown in Figure 3.17 (Johnson, Gilbert and Guenther 1982). The trend of the data in Figure 3.17 indicates that yield stress and proportional limits can decrease as much as 50% in 1 h. A substantial difference may be apparent between results from these tests on materials and results from tests on actual fuel rods, as



**FIGURE 3.17.** Isochronal Annealing Curve for Annealed Zircaloy-2 Irradiated at 50°C with  $9.1 \times 10^{19}$  neutron/cm<sup>2</sup>. (Open data points represent commercial PWR fuel rods irradiated to burnups of ~30 MWd/kgM for Zircaloy-4 cladding) (Johnson, Gilbert and Guenther 1983)

indicated by the curves in Figure 3.17. Because peak cladding temperatures are expected to be above 250°C for years in several cases, it is reasonable to expect some annealing of the radiation damage and an effect on the creep behavior of the cladding.

Information available on creep of SS suggests that creep rates are very low below 500°C, but data for irradiated SS are very limited for low temperatures (Johnson, Gilbert and Guenther 1983). Because SS-clad fuel rods have thinner cladding, stresses in the cladding may or may not be higher, depending on the internal void volumes.

**3.2.1.3.2 Corrosion.** Zircaloy cladding is susceptible to oxidation resulting from reaction with 1) residual oxygen carried over from packaging operations, 2) radiolysis of moisture carried over from packaging operations and/or released from water-logged spent fuel, and 3) products from component

outgassing. However, an evaluation of the reaction of Zircaloy cladding with residual impurities during interim dry storage in an inert atmosphere has revealed that the inventory of reactive constituents is too small to have an impact on the large surface area of the Zircaloy cladding (Johnson and Gilbert 1983). Stress corrosion cracking of Zircaloy has also been considered, but the stresses are not expected to be high enough for dry storage; it was concluded that further research on this mechanism is required because this mechanism is not well defined (Gause and Soo 1985; Rothman 1984).

Zircaloy cladding will arrive at the repository with oxide layers and crud layers as described in Section 3.1.2. The oxide layers are generally less than 50  $\mu\text{m}$  on a BWR rod and 40  $\mu\text{m}$  on a PWR rod at discharge, although there is some range in these thicknesses (Johnson, Gilbert and Guenther 1982; Gause and Soo 1985). Thus, additional oxidation would occur in the post-transition regime where the kinetics are linear (see discussion on oxide layers in Section 3.1.2). At temperatures below 250°C, the oxidation of Zircaloy cladding is negligible for dry storage up to 40 years: a 0.3- $\mu\text{m}$  oxide layer would form on Zircaloy cladding stored in unlimited air for 40 years (Johnson and Gilbert 1983). If the temperatures are significantly above 250°C or at lower temperatures for long times in unlimited air, then oxidation can become more significant. Oxidation would be about 75  $\mu\text{m}$ , 6% of a BWR cladding or 8% of a PWR cladding wall thickness, if unlimited air were allowed to contact the cladding under a temperature history that consisted of 400°C at the start and decreased to 250°C over a 2-year period (Johnson, Gilbert and Guenther 1983). These calculations presumed an unlimited supply of oxygen for the reaction and a decreasing temperature history, and do not compensate for any unknown effect of the crud in limiting cladding oxidation.

Evaluation of the corrosion of SS under dry storage conditions has not been of great interest because the inventory of spent-fuel rods with SS cladding is small and there has not been a need to provide dry storage for them. There is storage experience with SS-clad spent-fuel rods from other than LWRs at the Idaho National Engineering Laboratory, but only limited performance data exists for these spent-fuel rods. In an inert atmosphere or in air, uniform corrosion of the SS cladding is expected to be low, but SS cladding is more

sensitive to water storage regimes as a result of its greater sensitivity to SCC on the water side. Stainless steel is susceptible to SCC if stress, a corrosive environment, and sensitization are present. There is a known potential for SCC in SS in water and moisture; however, little information exists specific to dry storage conditions. Gause and Soo (1985) summarized current information on corrosion of SS and related this information to repository conditions, but the information was pertinent to postcontainment conditions.

3.2.1.3.3 Cladding Hydriding. As discussed in Section 3.1.2, Zircaloy cladding typically contains thin, circumferentially oriented hydrides before and after irradiation. At wet-storage temperatures (30°C), most of the hydrogen is insoluble, whereas at dry-storage temperatures of 250° to 370°C, between 30 and 120 mg/kg would dissolve in the cladding. At these temperatures, the hydrogen could move under thermal gradients to lower temperature regions at the ends of the rods (Sawatzky 1975) or to regions of high stress (Price 1984).

Two factors enhance hydride formation in Zircaloy cladding during disposal: 1) increasing hydrogen concentration from reactions with hydrogen formed by radiolysis of moisture and migration of hydrogen to cool regions of the Zircaloy cladding; and 2) reduced solubility as a result of decreasing temperature with time associated with the declining decay heat of the spent fuel.

No specific assessment has been made on the importance of hydride movement under repository conditions, but that hydrides can reorient under stress. If the zirconium hydrides remain oriented in the circumferential direction (the preferred orientation under the manufactured crystalline texture), then no serious degradation of mechanical properties is predicted. However, if the hydrides become oriented in the radial direction (preferred direction under the influence of the tangential stresses imposed by the internal rod gas pressure), then degradation of the mechanical properties is likely (Marshall and Louthan 1963). The primary results of this degradation would be to enhance cracking by creep rupture and propagation of reactor-induced incipient defects. Radial hydride orientation in tests designed to simulate dry-storage conditions was induced by pressure-induced tangential stress (Einziger and Kohli 1983).

#### 3.2.1.4 Breached Cladding

If a fuel rod is breached when emplaced in the waste package, or becomes breached during the containment period, then fuel oxidation becomes important to the condition of the cladding. Several factors are important once a fuel rod has become defected, including fuel oxidation, moisture in the fuel rod or cover gas, and changes in the defect size. In addition to the fuel oxidation in breached rods, cladding corrosion continues as a competing process for the available oxygen.

3.2.1.4.1 Fuel Oxidation. Oxidation of  $UO_2$  spent fuel can occur only if 1) the cladding is breached and 2) the atmosphere contains sufficient oxygen to produce low-density uranium oxide products. Given enough oxygen, the oxidation behavior depends primarily on storage temperature and fuel burnup (Gilbert, White and Knox 1985).

The duration of exposures to elevated temperatures required for spent fuel to form low density uranium oxides in air is not yet established, but tests are in progress for spent LWR fuel to identify the design basis for interim dry storage in air (Knox, White and Gilbert 1985). When  $UO_2$  oxidizes to  $U_3O_8$ , the fuel begins to fragment into a powder. White et al. (1983) have collected data on fuel oxidation. For a hypothetical storage cask with a decreasing storage temperature, preliminary calculations indicate that the initial peak temperature should be less than about  $150^\circ C$  to prevent the formation of powder for 100 years in irradiated fuel that was 5 years old (Guenther et al. 1984). These calculations indicated that the potential for fuel oxidation was the greatest during the first 10 years because of the decreasing storage temperature; the majority of the temperature decline occurred in 20 years. Because the temperatures increase and remain higher for longer times in a repository, breached fuel rods would experience fuel oxidation limited by the amount of oxygen ingress to the fuel and the consumption of oxygen by cladding corrosion.

Burnup appears to affect the amount of fuel oxidation (Gilbert, White and Knox 1985; Gilbert et al. 1985). At burnups of 15 MWd/kgM or less, such as in CANDU (for pressurized heavy water reactors) and high-temperature gas reactor spent fuels or at the ends of LWR spent fuel rods, fuel oxidation is similar to or slightly more than for nonirradiated  $UO_2$  (Novak and Hastings 1983; Novak

et al. 1983; Hastings and Novak 1983; Simpson and Wood 1983; Einziger and Cook 1983; Gilbert et al. 1985). However, at higher burnups, the increasing concentrations of fission products in the spent fuel affect fuel oxidation and appear to delay and prolong the time to form low density oxides of uranium (Gilbert, White, and Knox 1985; Gilbert et al. 1985).

3.2.1.4.2 Moisture Effects. Water-logged spent fuel may be disposed of if fuel is transferred directly from pool storage to the repository. Fuel transferred from dry storage to the repository is expected to contain very little residual moisture (Gilbert, Knox and White 1985). Water-logged spent fuel can be a source of oxygen for oxidation of spent fuel at cladding breach sites and may generate hydrogen for reaction with the Zircaloy cladding. The reaction of oxygen with the Zircaloy cladding will provide negligible increase in oxide thickness because the moisture inventory is small compared to the large surface area of Zircaloy cladding (Johnson and Gilbert 1983). The moisture is not expected to be sufficient to cause over-pressurization of the canisters (Woodley 1984).

3.2.1.4.3 Defect Size. The size of the defect from creep rupture would be too small to allow release of spent-fuel particulate matter (Guenther 1983). If the breached rod were in an oxidizing atmosphere and the temperature were sufficiently high for oxidation of the spent-fuel, then enlargement of the breach could potentially lead to release of spent-fuel particulates. Provided enough air, defected cladding will split under the pressure of the oxidizing, expanding fuel. The release of fuel particles of  $U_3O_8$  to the container is not a problem during the containment period, but the increased surface area could affect subsequent leach rates. No information was found on the amount of fission gas released from fuel as it oxidized to  $U_3O_8$  or what effect the formation of  $U_3O_8$  would have on the leach rates.

#### 3.2.1.5 Summary of Potential Degradation During Containment Period

Spent-fuel rods are not expected to experience a great deal of degradation during the containment period before intrusion of water or steam from the repository environment. Cladding that arrives intact at the repository might fail as a result of incipient defects that are exposed to normal storage stresses. Undefected fuel rods may also experience degradation by creep

rupture, hydride embrittlement, and general corrosion during 300 to 1000 years of containment. Stress corrosion cracking on the fuel side is not believed to be of major concern under the expected dry-storage conditions because the stresses appear too low even though the amounts of aggressive species required for SCC initiation under stress, such as iodine, appear available (Gause and Soo 1985). However, the possibility of such failures is not ruled out. Fuel rods that are breached on entry into the repository or are subsequently breached and exposed to dry storage atmospheres may also experience fuel oxidation if sufficient oxidant is available from either the cover gas or from moisture in the fuel rods.

Although none of the degradation processes are expected to be of major concern during dry storage, no attempts have been made to sum up the degradation from each process and determine a net effect for all of the potential degradation modes. Similarly, no attempt has been made here or previously to determine the total effect of degradation from all the stages of the waste management cycle. For example, failure from general corrosion should be based on the amount of corrosion in the repository plus previous corrosion in interim dry storage, MRS, wet storage, and in-reactor operation. Analyses of the cumulative damage fraction for the cladding during disposal should also account for heat dissipated during interim dry storage and MRS. Such considerations are complicated because not every fuel rod will experience the same storage history, and no codes are set up to calculate or consider these factors.

### 3.2.2 Postcontainment Period: Steam, Hot Water, or Water Vapor Environments

The first environment that the spent-fuel rods experience during disposal is that of dry storage. Once the canister fails, 300 to 1000 years or later, then the fuel rods will be exposed to the repository environment. The cladding and/or the fuel will be exposed to a number of environmental conditions and an increased number of simultaneous and competing processes, as described below. This particular discussion deals with degradation mechanisms after the container fails and the environment consists of steam, hot water, and/or water vapor with a potential range of additional elements from the ground water all of which are at temperatures of about 100°C to ambient.

### 3.2.2.1 Storage Conditions

Once the canister fails, the spent-fuel rods become exposed to a more complicated environment. During the containment period, the container prevents the ingress of a large variety of ions in the ground water as well as corrosion products from the waste package. Gause and Soo (1985) point out that specific ions, such as silicon and chlorides, radiolysis, pH, and temperatures, all affect the corrosion rates of Zircaloy.

The pressure inside the waste package could be a few atmospheres, depending on the package temperature, the initial pressure, and any releases of gases or moisture from the fuel rods. These pressures could remain relatively unchanged after the waste package fails or could be affected by the repository hydrostatic pressures that are expected to be between 0.1 and 11 MPa for typical repository depths of 500 to 1000 m. Pressures are important in determining the phase of the corroding liquid at any given repository temperature.

Temperatures would still be determined by the decay heat in the fuel rods but might be affected by convective cooling depending on the repository environment. Temperatures in the fuel and cladding during the postcontainment period would be about 100°C or less. It is assumed for the discussion below that the waste package has failed and that steam, hot water, and/or water vapor have contacted the spent fuel. It is conceivable that a failed canister would permit part of the fuel rods to be exposed to a liquid while another portion of the fuel is exposed to steam.

### 3.2.2.2 Degradation Mechanisms

Interest in the effect of the repository environment on the cladding has prompted reviews of degradation mechanisms for the postcontainment period (Gause and Soo 1985; Rothman 1984). Degradation mechanisms were considered for Zircaloy-clad spent-fuel rods including 1) uniform corrosion, 2) SCC on the fuelside and waterside (inside and outside of cladding in pool storage), 3) hydriding, and 4) creep rupture. Degradation mechanisms considered for SS-clad, spent-fuel rods included 1) uniform, pitting, and crevice corrosion, 2) SCC, and 3) hydrogen/helium embrittlement.

### 3.2.2.3 Unbreached Fuel Rods

If the fuel rod has not been breached before the end of the containment period, then degradation by creep rupture and reprecipitation of hydrides will continue as described above. Corrosion rates will be affected by the availability of oxygen and the types and levels of impurities in the ground water. Hydrogen may also be produced and would increase the availability of hydrogen for pickup in the cladding.

3.2.2.3.1 Cladding Corrosion. Cladding corrosion may proceed by a variety of rates, depending on the specific environment. Corrosion data exist for water and steam environments under reactor or pool storage conditions, but few data exist for Zircaloy cladding under expected repository conditions because this material is not being considered as a waste package material. Gause and Soo (1985) reviewed the data that exist for various storage conditions as indicated in Table 3.14. In general, a number of environmental conditions indicate that uniform corrosion could consume the cladding in 300 years if the temperatures remain above 250°C. These corrosion rates are based on limited data over short test periods and were, for constant temperatures, above those expected during the postcontainment period. For a steam environment at about 100°C, the corrosion would be much less, but no data are available to confirm or confidently project the corrosion expected in steam with impurities for hundreds or thousands of years.

Rothman (1984) has used existing corrosion data for air and steam to determine the amount of uniform corrosion on Zircaloy cladding exposed to a tuff repository environment for 9000 years using a very conservative initial temperature of 180°C at the time of container failure at 1000 years. Using equations from Hillner (1977), 5  $\mu\text{m}$  of corrosion was calculated. The results indicate that uniform corrosion does not appear to be of significance, although ground-water impurities, pH, or radiolytical effects are not factored into such a calculation.

Uniform, pitting, and crevice corrosion of SS were also reviewed by Gause and Soo (1985). The uniform corrosion rates indicate both high and low corrosion rates for a variety of brine and salt environments; in some cases, the cladding would be consumed in less than 300 years while other data indicate

TABLE 3.14. Summary of Zircaloy Uniform Corrosion Data (Gause and Soo 1985)

Test Temperature, °C	Test Time, d	Environmental Conditions	Rate of Weight Increase, mg/dm	Metal Loss Rate, cm/y	300 year Metal Loss, mm
250	Varies	Aqueous	$4.45 \times 10^{-3}$	---	0.02
300	Varies	Aqueous	$3.60 \times 10^{-2}$	---	0.2
350	Varies	Aqueous	$2.08 \times 10^{-1}$	---	1.0
400	Varies	Aqueous	$9.25 \times 10^{-1}$	---	4.4
250	Varies	Air or Steam	$1.75 \times 10^{-3}$	---	0.008
300	Varies	Air or Steam	$2.35 \times 10^{-2}$	---	0.1
350	Varies	Air or Steam	$2.09 \times 10^{-1}$	---	1.0
400	Varies	Air or Steam	1.34	---	6.3
250	90	Anoxic basaltic water (pH 7.7 to 8.5)	0.26	---	1.2
250	28	Deoxygenated WIPP Brine A (pH 6.5)	---	0.0001	0.3
250	58	MgCl-NaCl solution (ph 9)	0.14	---	0.6
250	1134	Air/natural salt	0.11	---	0.5

only a fraction of the cladding wall would be removed. Gause and Soo (1985) estimated the corrosion rate of  $0.079 \text{ mg/dm}^2\text{-d}$  for type 304L SS from corrosion data obtained from a test with a  $1.5 \times 10^5$  rad/hr gamma field at 30°C for 96 days. This rate was estimated to be equivalent to a loss of 0.1 mm in 300 years. From these data, it appears that the SS-clad, spent-fuel rods would require about 1500 years to be consumed based on wall thicknesses reported in Table 3.2. Gamma fields affect the corrosion rate and would be several orders of magnitude lower in the postcontainment period. Crevice corrosion of SS can remove material equivalent to the cladding wall thickness within months. However, data for SS corrosion also exist indicating crevice corrosion might not be significant in deaerated solutions.

3.2.2.3.2 Stress Corrosion Cracking. The research on SCC of Zircaloy-clad spent-fuel rods has focused on reactor operating conditions (Cubicciotti, Jones and Syrett 1980), because Zircaloy has not been considered as part of the waste package. Gause and Soo (1985) reviewed information on fuelside SCC and determined that stresses would probably not be high enough to cause failure by this mechanism, even though the supply of aggressive substances, such as iodine, cadmium, and cesium, appeared to be sufficient. They point out that the substances that cause SCC are not well known. Thus, it is not possible to determine whether quantities of these materials are sufficient to cause SCC during repository disposal. Rothman (1984) has also concluded that SCC will probably not be an issue under repository conditions; however, he recommends further study because the mechanism is not well understood.

Stress corrosion cracking of Zircaloy from the waterside may be caused by chloride ions (Gause and Soo 1985). Zircaloy-2 has failed by SCC in acidic ferric chloride solutions and may warrant research for some repository environments.

Stress corrosion cracking of SS-clad, spent-fuel rods is a possibility as indicated previously in Section 3.1.3. Chloride and caustic solutions are known to cause SCC of SS (Gause and Soo 1984). Chloride solutions at temperatures above 60°C cause SCC of SS if exposed for very long times. Gause and Soo (1985) also reported research that indicated that SCC in SS is possible at 100°C in caustic solutions, in brines where radiation fields may cause the formation of colloidal sodium, and in liquid and steam conditions in the presence of O<sub>2</sub> and Cl<sup>-</sup>.

3.2.2.3.3 Hydriding. The hydriding characteristics of Zircaloy cladding were discussed in Section 3.1.2 and in the previous discussion of the containment period. As the temperature decreases, more and more of the hydrogen reprecipitates. If the initial hydrogen and the hydrogen accumulated during corrosion reach high levels, then there is the potential for hydrogen embrittlement. Rothman (1984) has estimated the hydrogen pickup in Zircaloy cladding and determined that less than 250 mg/kg would be in the cladding at 10,000 years based on a predicted corrosion thickness of 17 μm.

Additional hydrogen may also be picked in the fuel rod as a result of the temperature gradient formed between the higher power region of the fuel rod and the nonfueled region in the plenum. This may degrade the fracture toughness at the cooler plenum more than may be expected based on the average hydrogen content in the cladding.

Rothman (1984) has estimated failure by hydriding, and indicates that this mechanism does not appear to be a likely form of premature failure for expected temperature gradients, hydrogen contents of 250 mg/kg projected after 10,000 years, and cracks of less than 20% of the cladding wall; crack depths of 50% of the cladding wall thickness might pose problems for some fuel rods. However, he indicated that the amount of hydrogen redistribution and reorientation requires further study.

Rothman (1984) apparently did not factor loss of the cladding wall through corrosion into his assessment of hydride failure. Based on the information in Table 3.14 and the discussion on corrosion above, it might be possible to lose about 20% of the wall thickness from corrosion during in-reactor operation and subsequent storage. This loss of thickness would reduce the acceptable crack size for failure in a fuel rod.

Hydrogen is generally not considered an issue with austenitic SS, although some instances of hydrogen embrittlement were covered in the review by Gause and Soo (1985). However, the eventual decay of tritium ( $^3\text{H}$ ) to helium has been known to degrade the mechanical properties of SS at temperatures higher than those anticipated for geologic disposal.

3.2.2.3.4 Creep Rupture. Creep rupture is not expected to be a factor in fuel rod degradation after the first few decades after discharge from the reactor. However, damage to the cladding by creep during that period plus losses in the wall thicknesses from previous corrosion and corrosion during the post-containment period might combine to cause premature failure of the cladding. Creep at slow heating rates was generally observed to cause uniform thinning of the cladding wall in unirradiated PWR fuel rods. Failure, however, occurred at an isolated site on the fuel rod (Guenther 1983). No apparent account has been made for the loss of the wall thickness from creep, although it is probably small for many conditions. The effects of lithostatic and hydrostatic loads

that would be applied to the cladding some time after failure of the waste package and any canister should also be included in such an evaluation.

#### 3.2.2.4 Breached Fuel Rods

Once the fuel rod cladding is breached, the degradation mechanisms that involve stress, such as creep rupture and SCC, are eliminated except for possible effects of residual stresses. However, the gases will have been released from the void volume in the fuel rod and leaching of the fuel can begin by the repository liquids. At the same time, all of the types of corrosion discussed above will continue even after the fuel rod has failed. Thus, the entire cladding surface will be competing for oxygen and will continue to lose wall thickness.

Gause and Soo (1985) reviewed work on release from bare fuel, defected fuel rods, and undefected fuel rods in deionized and tuff ground water. In general, release occurred from all waste forms, but the release rates from defected fuel rods were lower than release rates for bare fuel except for  $^{137}\text{Cs}$  after 100 days. Undefected fuel rods were found to have release rates two to three orders of magnitude lower than those for defected fuel rods.

#### 3.2.2.5 Summary of Potential Degradation During Postcontainment Period

Degradation mechanisms that could operate during the postcontainment period, when steam, hot water, and/or water vapor are present at temperatures of 100°C or less, include corrosion, SCC, and hydride embrittlement. Once the fuel rods fail, the stress-related mechanisms become of little or no importance. Uniform corrosion in Zircaloy cladding is expected to be low during 10,000 years under some environments, but could consume substantial portions of the cladding at higher temperatures or in environments with aggressive species, such as ferric chlorides. Stainless steel cladding corrodes significantly in some environments, particularly by crevice corrosion. Stress corrosion cracking is not as prevalent in Zircaloy and may not be a significant factor based on estimated stresses. However, stainless steel materials are susceptible to SCC in a number of environments plausible for repository conditions. Hydriding is not believed to be an issue in failure of fuel rods, but no account has been

made for the cumulative effects of corrosion, creep rupture, and hydriding during and before repository disposal.

### 3.3 CURRENT STATUS/ADEQUACY OF PERFORMANCE MODELS DESCRIBING CONTAINMENT

This section deals with the status and adequacy of the models that exist for predicting the performance of spent-fuel cladding under repository conditions. Information on the existing codes is given in Section 3.3.1, and potential ways of modeling cladding performance are given in Section 3.3.2.

#### 3.3.1 Existing Models for Cladding Performance

Waste package performance codes were reviewed by Coffman, Vogt and Mills (1984). Some of the more pertinent information from that review is summarized in Tables 3.15 and 3.16. Their review indicates that existing performance codes are, in general, somewhat limited to analysis of the outer containment structures, such as low-carbon steel canisters. Few codes appear to be able to address the performance of fuel rod cladding in the thermal and chemical environments characteristic of geologic waste applications; exceptions are the codes BARIER, WAPPA, and the PANDORA code being developed for the tuff project. The WAPPA and BARIER codes, however, incorporate semi-empirical submodels for some aspects of Zircaloy performance, and those submodels appear to be limited by the lack of relevant data for calibration, benchmarking, and verification. The PANDORA code is not yet fully developed, but is to address cladding as a barrier (O'Connell and Drach 1986). The preliminary description of the corrosion model within PANDORA indicates that it is based on the WAPPA corrosion model. It remains to be seen if the PANDORA treatment of cladding corrosion presents an improvement over the WAPPA treatment.

Most of the data and submodels available for cladding performance are limited to reactor applications, with the following general characteristics. Reactor temperatures are usually substantially higher than expected in those geologic environments. The reactor environment is limited to hot water at 1000 psi (BWR) to 2000 psi (PWR), whereas geologic pressures at the Zircaloy surface are much less (i.e., as low as 1 atm). Reactor water chemistries are

TABLE 3.15. Principal Features of Waste Package Codes  
(Coffman, Vogt and Mills 1984)

<u>Code</u>	<u>Processes Modeled</u>
ADINA	Static and dynamic elastic and plastic continuum mechanics
ADINAT	General purpose thermal analyses
ANSYS	Static and dynamic, elastic and plastic continuum mechanics, thermal analyses
BARIER	Waste package performance--radiation, structural, thermal, corrosion, leaching
BOSOR 5	Buckling of shell structures
BUCKLE	Buckling of shells because of revolution, elastic and plastic continuum mechanics
COVE-1	Buckling of cylinders
HEATING 6	General purpose thermal analyses
HYDRA-1	Thermal analyses (special purpose for waste package)
IMPAC 2	Impact transient loads for shipping containers
KENO	Nuclear criticality
NONSAP	Static and dynamic elastic and plastic continuum mechanics
SAP	Static and dynamic elastic continuum mechanics
SINDA	General purpose thermal analyses
STAGS	Buckling of shells of revolution, elastic and plastic continuum mechanics
STEALTH	Dynamic, elastic and plastic continuum mechanics, and thermal analyses (steady-state analysis is done using transient mathematical model)
WAPPA	Waste package performance--radiation, structural, thermal, corrosion, leaching

TABLE 3.16. Principal Features of Other Codes Useful for Waste Package Analysis (Coffman, Vogt and Mills 1984)

Code	Processes Modeled
ANISN	One-dimensional neutron/gamma transport, criticality
DOT	Two-dimensional neutron/gamma transport, criticality
MORSE-SGC/S	Three-dimensional neutron/gamma transport, Monte Carlo method
ORIGEN-S	Point model of radionuclide production and decay, including decay gamma spectra and decay heat rates
PHREEQE	Geochemical reactions
EQ3/EQ6	Geochemical reactions including mass transfer from solids
WATEQF	Geochemical reactions
SHAFT 79	Two-phase fluid flow and heat transport in a porous geologic media

closely controlled, whereas geologic environments have a myriad of impurities with currently ill-characterized effects on the long-term integrity of Zircaloy.

### 3.3.2 Modeling Cladding Performance

The data and models needed to describe cladding performance under the conditions of geologic disposal fall under three major categories representing three dominant modes of degradation: 1) chemical degradation by corrosion mechanisms (uniform, pitting, crevice, etc.); 2) mechanical degradation by creep, overload yielding, or fracture; and 3) combined chemical and mechanical degradation mechanisms, such as stress corrosion cracking or delayed hydrogen cracking.

#### 3.3.2.1 Bases for Modeling Cladding Behavior

The foundations for submodels describing relevant chemical degradation mechanisms are currently being developed. Some short-term scoping data by Pitman, Griggs and Elmore (1981); Braithwaite and Molecke (1980); Griess (1982); Anderson (1981); and Rothman (1984) have been used to develop semi-empirical models with relatively short-time-span applications (<1000 y)

compared to the long-time predictions (10,000 y) desired for geologic repository modeling. A summary of models developed or being developed for creep (stress) rupture, SCC, and fuel oxidation is given in Table 3.17 (Johnson and Gilbert 1983). Semi-empirical models are prudent for the current stage but may have insufficient scope for performing sensitivity analyses concerning cladding response to various repository conditions and histories.

The foundations for mechanical degradation submodels seem to exist in a suitable form, although they are dispersed throughout the nuclear science and metallurgical literature. Examples of the models available include relatively recent reviews of metallurgical phenomena, such as grain boundary cavitation (Nix 1983) and creep-related mechanisms (Chin, Madsen and Gilbert 1983). These submodels are more mechanistic than empirical, and consequently offer the potential advantage of improved estimates of the rates of mechanical degradation processes. The importance of this feature is discussed below.

The foundations for submodels of combined chemical and mechanical degradation mechanisms, such as SCC, also seem to exist in the nuclear and metallurgical literature. These submodels are also frequently semi-empirical in some aspects; however, some models attempt to make maximum use of mechanistic features in order to maintain a maximum range of application.

#### 3.3.2.2 Modeling Approach

Recent models by Williford (1984 and 1985) for SCC of Zircaloy cladding in a reactor environment may be used as mechanistic models to indicate the required data for a range of conditions. The models (Williford 1984 and 1985) assume that fission product iodine is the active chemical species. The same models can be adapted for some geologic applications by collecting the proper data for fluoride or iron chloride environments. The specific data needed are 1) plots of stress versus time to failure and 2) strain to failure versus strain rate, both as functions of fluoride or iron chloride concentration. These data can be used to develop semi-empirical embrittlement factors in an adsorption-induced embrittlement model based on creep-controlled fracture. The model can be verified by experiments using standard surface-science techniques, coupled with the necessary diffusion data if protective layers (i.e., oxides, etc.) occur at the crack tip. The most desirable feature of this approach is

**TABLE 3.17. Models for Predicting LWR Spent-Fuel Performance  
(Johnson and Gilbert 1983)**

<u>Mechanism and Model</u>	<u>Benefits</u>	<u>Limitations</u>	<u>Predicted Temperature Limit, (a) °C</u>
<u>Stress Rupture</u>			
• Larson-Miller parameter	Allows for simplicity and broad experience in applications.	Data base is limited to high stresses and unirradiated cladding that is atypical of spent fuel.	380
• Deformation and failure mapping	Accommodates changes in mechanisms and accounts for differences in metallurgical properties such as grain size.	Data base on irradiated Zircaloy is limited to 140-h duration.	300 to 430 (b)
• Strain limit	Requires knowledge of ductility limit of Zircaloy cladding.	Description of strain-time behavior must be accurate.	400
<u>Stress Corrosion Cracking</u>			
• SCCIG model	Predicts crack initiation and growth as a function of metallurgical condition and environment.	Input on metallurgical condition and environment is not now well defined.	150 to 400 <sup>(b)</sup>
• Crack growth model	Predicts incipient crack behavior.	Input on incipient cracks is not now well defined.	150 to 400 <sup>(b)</sup>
<u>Fuel Oxidation (c)</u>			
• Cumulative oxidation before power induction	Predicts storage time under variable temperature conditions.	Model not verified by variable temperature conditions. Data base on irradiated UO <sub>2</sub> limited, but expanding.	150 to 180 <sup>(b)</sup>

(a) Temperature below which cladding failures are unlikely.

(b) Depends on fuel condition.

(c) Fuel oxidation is a consideration in the unlikely event of air ingress.

that mechanistic modeling of long-term degradation phenomena is possible. The foundations are diffusion processes, which are particularly suited for long, slow degradation process modeling. Such a model could account for changing chemistry, loads, and temperatures in geologic environments.

The application is only one incomplete example of how mechanistic models can clearly define data needs. An important point is that such models provide more useful descriptions of the rates of degradation processes than empirical models because they are able to respond to changing temperatures, chemistries, and loads in geologic repositories. These descriptions yield valuable and statistically significant information about what particular aspects (variables or parameters) of the overall phenomenon are most important. In the case of Zircaloy degradation in geologic repositories, the most important piece of information describes the state of the Zircaloy after 10,000 years. The data are obviously not attainable in the time frame allowed. Thus, the rate of damage accumulation must be estimated, so that the degradation can be predicted by multiplying the rate by the time. Because this rate may change with time, nonlinear models of degradation rates are required. The concluding point is that mechanistic models usually provide more useful and versatile estimations of these rates than do empirical models; therefore, the most viable modeling approach with maximum yield in the near future will be to 1) select mechanistic degradation models from the available literature and 2) let those models define the detailed data needs.

This approach is intended to complement the existing scoping tests, which in fact help to identify the most important degradation systems and phenomena, albeit under limited environmental conditions. The main thrust of the approach is that it can yield useful and versatile modeling results while the repository thermal-mechanical-chemical systems are defined. That is, progress can be made before the repository environment is fully defined. Because the model foundations are mechanistic formulations accepted by the appropriate technical communities, the submodels can be changed with more confidence than for empirical models as the definition of repository conditions evolves and matures.

### 3.4 SUMMARY OF DATA RELEVANT TO SPENT-FUEL CLADDING CONTAINMENT

As indicated in Section 3.2, potential failure mechanisms for spent-fuel cladding in repository environments include uniform corrosion under air, steam, and aqueous conditions; localized nonuniform corrosion, such as pitting and crevice corrosion; waterside and fuelside stress corrosion cracking; creep rupture; and hydriding.

Data that can be used to support predictions of cladding behavior under the above degradation mechanisms are limited. Those data that do exist, such as given in Table 3.14 for uniform corrosion of Zircaloy cladding, were obtained during scoping tests over short times in quasi-typical repository conditions or in other environments, such as reactor coolants or storage pools.

Most of the data for corrosion of Zircaloy come from in-reactor and pool storage experience with Zircaloy cladding and pressure tubes. The aqueous environments of these studies, which consist of deionized water with a low oxygen content and a neutral or slightly acidic pH are likely to be less aggressive than that of a repository. Based on the in-reactor and pool storage corrosion data, models have been developed for corrosion in aqueous and steam/air environments (see Section 3.3, Tables 3.15 and 3.17). These equations are used to predict some types of corrosion under repository conditions, but no information has been developed on the effect of ground-water impurities, pH, or radiation fields on the corrosion rates in actual repository environments.

Corrosion of SS-clad, spent-fuel rods from LWRs has not been treated in detail because they represent a small fraction of the LWR inventory. The data that exist come primarily from scoping tests conducted for potential waste package materials. However, a large amount of data is available for SS in other environments that might provide insight into repository corrosion. Tests are also being conducted on SS waste canisters, which may be applicable to the cladding (Gause and Soo 1984).

Some of the most relevant data for the containment period in a repository, where the environment is essentially controlled, are from work on dry interim storage. This research is developing data and models applicable to fuel oxidation in air and inert atmospheres and could be used to analyze the performance

of defected fuel rods (Gilbert, White and Knox 1985). Data are being developed for the rate of oxidation in air under conditions that can be expected in a repository during the containment period or other times when air might have access to the fuel. Predicting fuel oxidation in a repository will require a knowledge of fuel temperature history. Because such temperature histories may not feasibly be collected for all the fuel expected in a repository, bounding assumptions will need to be made based on studies of representative fuels.

Some predictive methods have been used for creep (stress) rupture of Zircaloy cladding but not for SS-clad LWR fuel rods. The main deficiency in these models is the use of data for unirradiated cladding because of the lack of creep rupture data for irradiated Zircaloy or SS cladding at the temperatures of interest [i.e., less than 380°C (Johnson and Gilbert 1983)].

The uptake of hydrogen in Zircaloy is fairly well established, but subsequent migration of the hydrogen along temperature gradients and stress-related reorientation of hydrides are not as well understood (Gause and Soo 1985; Rothman 1984; Price 1984). Only approximations of the behavior of hydrogen can be made for repository conditions because the factors that affect hydrogen movement and reorientation (i.e., grain size, texture, thermal and concentration gradients, and stress) are not understood well enough.

Current data for SCC of Zircaloy and SS cladding are not adequate to assess the performance of these materials under repository conditions. Available data are primarily for in-reactor conditions and the fuelside of the cladding: conditions other than those expected for repositories. New data are being obtained under some repository conditions in tuff (Gause and Soo 1985), but no known tests are being conducted in other repository environments.

Sufficient quantities of germane data do not exist to allow the net effect of multiple degradation to fuel rods to be taken into account. The accumulation of damage resulting from all portions of storage subsequent to discharge from the reactor also needs to be considered. This type of multiple-process modeling will probably not be possible until each mechanism is quantitatively defined through testing. Once this is done, the net effect of degradation by the several competing and complementing mechanisms can be modeled to predict performance under actual repository conditions.

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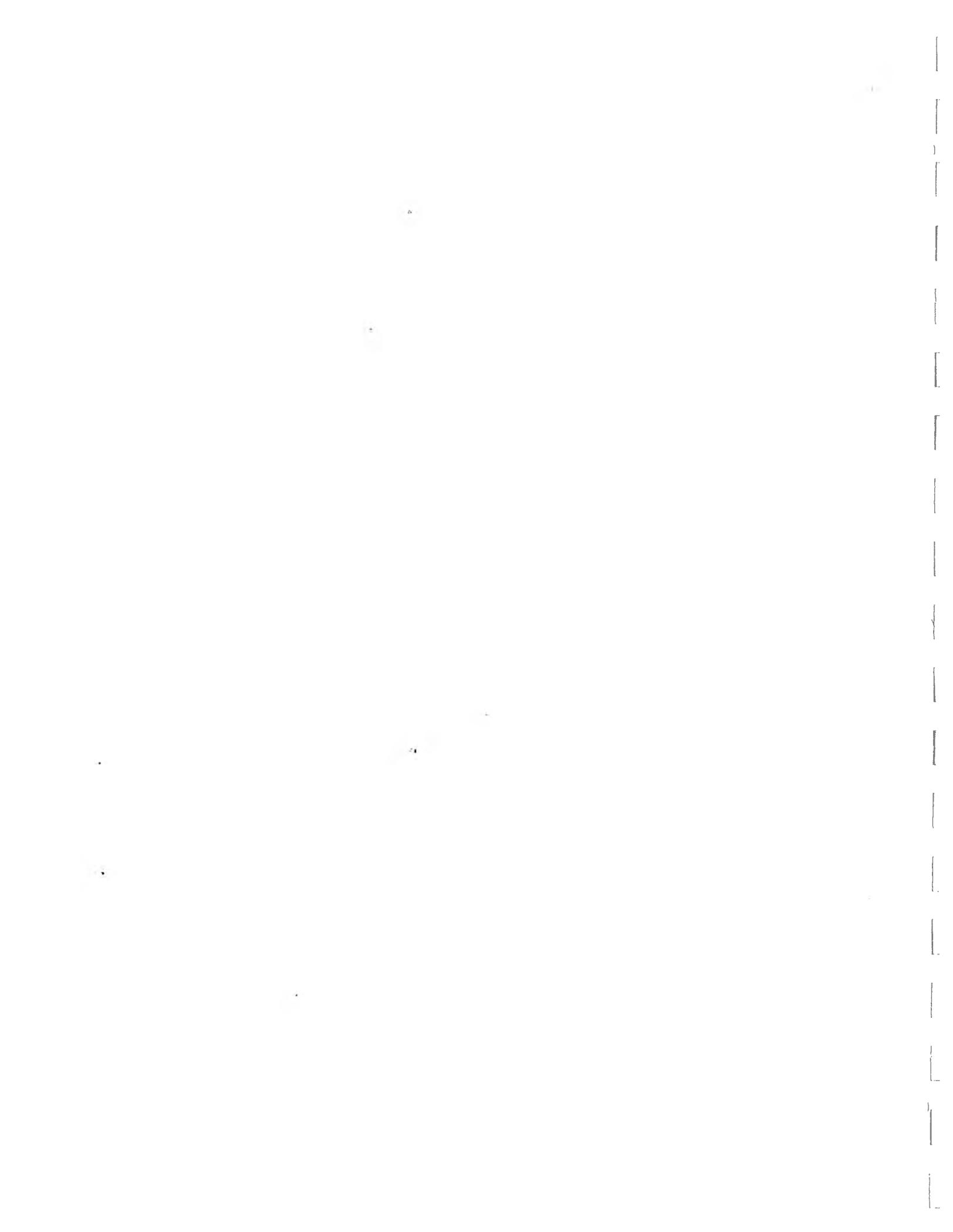
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#### 4.0 POSTCONTAINMENT RELEASES FROM SPENT FUEL

The NRC (USNRC 1983; see Section 1.2) has established a release rate criterion for the performance of the engineered barrier system<sup>(a)</sup> after the period of substantially complete containment of radionuclides. This criterion specifies that the fractional release rates of an individual radionuclide not exceed one part in 100,000 per year of that radionuclide inventory calculated to be present at 1000 years after permanent closure. Higher release rates are allowed for radionuclides that are present as extremely low fractions of the total inventory, and all nuclides present at  $<10^{-8}$  of the total activity at 1000 years may be excluded from analysis (USNRC 1983). In addition, the NRC leaves open the option of considering an alternate set of performance criteria "as may be approved or specified by the Commission" (USNRC 1983). The quantitative release rate criterion is evaluated at the boundary of the engineered barrier system. The release rate is also the primary source term needed for evaluation of migration of radionuclides through the repository to the accessible environment, at which boundary the EPA has established a separate cumulative release criterion (USEPA 1985; see Section 1.0).

#### 4.1 CONCEPTUAL MODELS FOR RELEASE FROM SPENT FUEL

A conceptual model for assessing time-dependent, radionuclide release rates can be divided into two parts: 1) radionuclide release from the waste form (spent fuel) itself and 2) release from the waste package/engineered barrier system containing spent fuel. It must be stressed that no criterion is imposed on the release rate from the waste form per se. Attempts to evaluate compliance with respect to the  $10^{-5}$  per year criterion based on waste-form test results alone are misleading and potentially invalid from both a regulatory and scientific viewpoint. Release data from tests on only waste forms are not even

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(a) The principal part of the engineered barrier system designed to limit release is the waste package system, and these terms are used interchangeably in this text unless explicitly stated otherwise. Similarly, the term spent fuel is used to denote all of the different parts of the spent-fuel assembly that will be disposed of in a geologic repository: the fuel itself, the cladding, any trapped material in the gap between the fuel and the cladding, and any associated hardware.

a reliable bounding case; the presence of actual barrier materials and host rocks have shown significant changes to waste form release behavior (McVay and Buckwalter 1983; Rawson et al. 1987). It is also clear, however, that evaluation of release behavior of the waste form is central to the calculation of the release rate of radionuclides from the waste package/engineered barrier system and that the two cannot be fully decoupled (see Section 4.1.5).

Accordingly, the following sections review the conceptual models for the release of radionuclides from both spent fuel and waste packages containing spent fuel. Section 4.1.1 reviews the two limiting mechanisms that control the release of radionuclides from spent fuel: transport-controlled (including solubility-limited and colloid formation) release and surface-reaction controlled ("leach rate") release. From this, separate sources of radionuclides from spent fuel are identified based on their release mechanism and release rate. Sections 4.1.2 through 4.1.4 discuss detailed aspects of radionuclide release from these separate sources within spent fuel including the  $UO_2$  matrix, the fuel/cladding gap, the grain boundaries, and the cladding. Section 4.1.5 considers the effect of barrier materials in addition to spent fuel on the migration and release of radionuclides from the waste package system. Section 4.1.6 details the role of sorption of radionuclides on primary and altered waste package barrier materials.

#### 4.1.1 Release Processes for Spent Fuel

On contact with ingressing ground waters, spent fuel will immediately undergo a dissolution reaction. This dissolution is called "congruent" if all of the components in the dissolving solid are released in their stoichiometric proportions. "Incongruent" dissolution arises when certain components are preferentially dissolved or leached from the solid. Distinguishing between true incongruent dissolution and apparent incongruent dissolution is important. Incongruent dissolution often arises from congruent dissolution followed by precipitation of selected components from the congruent dissolution of two or more solids. The dissolution reaction is driven by the difference in chemical potentials of all components between the solution and the waste form (Dibble

and Tiller 1981; Giggenbach 1981). The pathway and progress of continued reaction depends on whether spent fuel/water is treated as a closed or open system.

#### 4.1.1.1 Closed System

A closed system is a system in which the dissolving phase (solid, liquid, or gas) and coexisting solution cannot exchange matter with the surrounding environment. Although all repository systems will not be strictly closed systems, the expected diffusion-limited transport within waste packages can be used to justify consideration of that subsystem as quasi-closed (Chambre and Pigford 1984). Continued dissolution under closed-system conditions necessarily leads to an increase in concentration of dissolved (waste) components in the solution surrounding the dissolving phase (spent fuel). The rate of change in solution concentration (i.e., dissolution or leach rate) decreases with time, however, as the concentration approaches a saturation limit with respect to some solid. This period could be called the "transient," during which the release of radionuclides is time-dependent because the chemical reaction rates controlling release are time-dependent. Eventually, a saturation limit is exceeded and the dissolved components begin to precipitate. This saturation precipitate may be the original solid (e.g.,  $UO_2$  matrix) itself or a new, alteration solid. As dissolution and precipitation continue, the net change in solution concentration eventually becomes zero. This period could be called the "steady state," during which the concentration of radionuclides is time-independent.

Several key points should be stressed in this closed-system analysis of radionuclide release. The first is that true solubility is a special equilibrium case of steady state in which the dissolving and precipitating solids are the same; the general nonequilibrium steady-state case arises when dissolving and precipitating solids are different. Also, under nonequilibrium steady-state conditions one or more dissolved components may be at steady state, while the concentrations of other components continue to change. Second, a steady-state condition (including true solubility) does not imply that the rates of dissolution and precipitation are zero, only that these rates are opposite and equal. A third key point is that this analysis assumes that the concentration

of a component released from a dissolving waste form is not inventory-limited before a solubility limit is reached. That is, if a component occurs in the waste form as a small (trace) quantity or has a tremendously high solubility limit (or both), then the concentration of that component may not be controlled by its own solubility-limited solid. Assuming other components do form, however, nonsolubility-limited trace components will be partitioned between the solution and these other solids, as described by Henry's Law (Hodder 1983; Volfinger and Robert 1980). This copartitioning/coprecipitation will exert a variable effect on release, depending on the bonding energetics and the size and charge matching between the trace component and the structural position into which the component is incorporated.

Although a strictly closed system is a physically unrealistic representation of a geologic repository, the bulk of waste form testing has been performed under such conditions. Closed-system tests are operationally less difficult and expensive than open-system tests. When the influx of water is extremely low, closed-system tests can also provide meaningful waste form performance data for expected diffusion-limited flow conditions at all repositories (Apted 1982; Chambre and Pigford 1984), if they are conducted for sufficient duration. Emphasis for glass forms, in particular, has been given to short-term, 28-day tests that attempt to measure the transient, time-dependent dissolution, or leach rates of waste forms (Hench, Clark and Yen-Bower 1980; McVay, Bradley and Kircher 1981; Pederson et al. 1983; Wicks et al. 1982). In addition, considerable effort has been devoted to developing mathematical models describing this time-dependent behavior (Kuhn, Peters and Simonsen 1983; Wallace and Wicks 1983; Sullivan and Machiels 1984). Subsequent closed-system tests performed for longer time periods (>1 year) have confirmed, however, that saturation (solubility) concentration limits are commonly obtained for most radionuclides released from waste forms (Apted 1982; Grambow 1982; Savage and Robbins 1982; Strachan 1982). Such solubility limits are essentially time-independent for constant repository conditions.

The situation for testing spent fuel as a waste form are somewhat better with regard to long-term experiments. Most of the studies on spent fuel (e.g., Johnson, Garisto and Stroes-Gascoyne 1985; Wilson and Oversby 1985; Forsyth and

Werme 1985; Gray and McVay 1986; Rawson, Neal and Burnell 1987) involve tests of over 1 year. Many of these tests often include additional engineered barriers to examine their effect on release.

#### 4.1.1.2 Open System

An open system condition applies when reacting phases (waste form and solution) can undergo mass exchange, or transfer, with their surrounding environment. This is clearly a more realistic representation of an actual nuclear waste package than the closed-system model discussed previously. Dissolution and precipitation/saturation continue to be important processes under open system conditions, as will be demonstrated. The crucial aspect of an open system is that mass transfer through the solution to the surrounding environment, rather than the rate of chemical reaction of the waste form, may become the limiting process that will control the time-dependent release rate of most radionuclides under expected waste package conditions.

The initial interaction between ground-water solution and a waste form (spent fuel) is identical for open- and closed-system conditions. The solution is initially undersaturated with respect to waste components, so the forward rate of dissolution is initially high. As the concentration of dissolved waste components increases in solution, two processes come into play. The first process decreases the rate of dissolution as saturation is approached, with respect to waste form solid(s) or alteration products. This process is identical to the closed-system case. The second process is a diffusive/convective current (i.e., mass-transfer rate) of these dissolved components that is away from the waste form surface. This mass transfer is driven by diffusion, which is developed from the gradient in chemical potential (concentration) surrounding the waste form, or diffusion combined with convective flow of ground water.

There is a competition with respect to solution concentration at the waste form surface between the rate of these two processes: the rate at which a waste component detaches from spent fuel and the rate at which a detached component moves away from the surface. The relative importance of these two processes can be evaluated (Zavoshy, Chambre and Pigford 1984) by defining a ratio,  $R$ , such that

$$R = \frac{\text{forward dissolution rate per unit area}}{\text{diffusive/convective mass transfer rate}}$$

This so-called flux ratio,  $R$ , is evaluated at the waste form surface. Note that the forward dissolution rate here is assumed to be first order with respect to concentration of matrix components of the waste form.

When  $R \ll 1$ , the dissolved waste components migrate away from the surface of spent fuel so rapidly that the concentration of such components cannot build up; therefore, the concentration at the surface is always less than the saturation concentration. In this case, the release rate can be called surface-reaction controlled (Berner 1978). As shown in Figure 4.1, the concentration profile surrounding the spent-fuel waste form is essentially flat for the surface-reaction controlled case. Calculation of time-dependent fractional release rates for this case are based on dissolution (leach) rate models similar to those discussed under closed-system conditions where no saturation limit is reached.

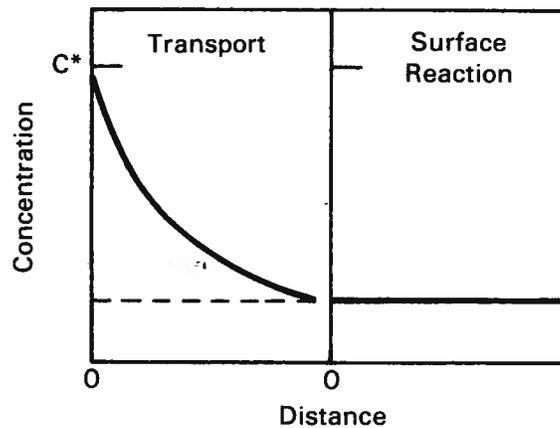


FIGURE 4.1. Schematic of Bounding Case for Radionuclide Concentration Profiles Surrounding a Waste Form (modified from Berner 1978). ("0" distance corresponds to the surface of the waste form, "C\*" represents a solubility limit for a given radionuclide.)

When the mass transfer rate is low ( $R \gg 1$ ), the concentration of dissolved waste components will build up at the surface of spent fuel. Concentration will continue to increase, finally attaining a saturation/solubility limit identical to the closed-system case. The release rate in this case can be called transport controlled (see similar treatment by Berner 1978). The concentration profile developed around a spent-fuel waste form for this case is shown in Figure 4.1. Analytical equations for the time-dependent, fractional release rate of radionuclides under open-system, transport-limited ( $R \gg 1$ ) conditions have been developed (Chambre and Pigford 1984). In this approach, it is assumed that a waste form is in contact with a surrounding porous medium (or a medium that can be modeled as an equivalent porous medium) with a fixed boundary concentration at the waste form surface. This boundary concentration is most commonly set equal to the solubility of a stated radionuclide-bearing solid. Note that intermediate cases ( $R \sim 1$ ) exist in which there is mixed transport- and reaction-control. In these cases, slight concentration gradients are developed and the surface concentration remains below the saturation value.

Two separate transport-limited cases can, in turn, be identified. The first case relies on a determination of the separate solubility limit for each radionuclide of interest. This approach is data intensive and relies on difficult and costly analysis of waste form tests. The second case is based on the assumption of congruent dissolution of a chemically homogeneous waste form. In this case, only the solubility of the waste form matrix ( $UO_2$  for example) needs to be determined; from this solubility, the release rate of the matrix component can be calculated and the release rate of incorporated radionuclides is scaled to this calculated release rate according to their congruent proportion in the waste matrix. This second case also permits the option of considering subsequent solubility limits for any given radionuclide, thereby reducing to the first case. Such subsequent precipitation of a radionuclide-bearing solid can only lower the calculated release rate for that radionuclide from the matrix-controlled value.

Table 4.1 summarizes the possible processes controlling radionuclide release from spent fuel under closed- and open-repository conditions.

TABLE 4.1. Summary of Possible Processes Controlling Radionuclide Release from the Waste Form (Spent Fuel)

- I. Closed System
  - A. Leach Rate Control
    - 1. High-solubility radionuclides
    - 2. Limited inventory radionuclides
  - B. Steady-State Control
    - 1. Nonequilibrium
    - 2. Equilibrium
    - 3. Henry's Law Partitioning/Coprecipitation
- II. Open System
  - A. Surface Reaction Control
  - B. Transport Control
    - 1. Matrix solubility
    - 2. Individual radionuclide solubility

Realistic evaluation of spent fuel requires additional information on the identity and location of radionuclides within spent fuel.

#### 4.1.1.3 Spent-Fuel Release Model

The release of radionuclides from spent fuel is dependent on the physical and chemical properties of the various components of the spent fuel (Johnson, Garisto and Stroes-Gascoyne 1985). During fuel irradiation, the physicochemical properties of the fuel change primarily as a function of initial composition and reactor operating conditions. Chemical changes arise from uranium fissioning (fission products), neutron-capture (production of heavier actinides), and neutron-activation (production of activation products). Neutron-capture and neutron-activation may affect trace impurities, notably the formation of  $^{14}\text{C}$  from  $^{14}\text{N}$ . Absolute abundance of fission products is a function of fuel burnup, while the production of neutron-activated higher actinides and other activation products depends on the flux and the energy spectrum of neutrons within the fuel.

Spent-fuel radionuclide inventories are often estimated through calculation. Johnson et al. (1982) used the CANIGEN code to estimate inventories; Forsyth, Svanberg and Werme (1984) used the BEGAFID code, and Wilson (1985) based inventory calculations on the ORIGEN-2 code. In other leach tests (Gray et al. 1984; Gray and McVay 1984), inventories were determined by direct analysis of dissolved fuel fragments. As an example of inventory distribution, Wilson (1985) has calculated that  $^{241}\text{Am}$ ,  $^{240}\text{Pu}$ , and  $^{239}\text{Pu}$  may represent about 98% of the 1000-year inventory of a moderate burnup fuel (Table 4.2). His calculations were based on the ORIGEN-2 results of Alexander et al. (1977).

Spatial distribution of radionuclides depends on reactor operating conditions and physical properties of specific elements. Gaseous fission products accumulate into gas bubbles or migrate completely out of the  $\text{UO}_2$  matrix to the boundary (gap) between the fuel and cladding. Other elements that are relatively volatile at the high centerline temperatures of a fuel pin ( $800^\circ$  to  $1600^\circ\text{C}$ ), such as Tc, Cs, and I, will also migrate out of the  $\text{UO}_2$  matrix by volume diffusion. Once these elements reach the boundaries between  $\text{UO}_2$  grains, they may remain there or continue to migrate by grain boundary diffusion to the fuel-cladding gap. Other fission products are stabilized as metals at the temperature-oxygen fugacity conditions of the fuel pin and form their own grain boundaries with  $\text{UO}_2$  grains. Temperature cycling of the fuel during operations can lead to thermal stress cracking of the fuel (Katayama, Bradley and Harvey 1980), enhancing migration of volatile species, as well as recrystallization of the  $\text{UO}_2$  grains (Barner 1984a,b). Finally,  $^{241}\text{Am}$ ,  $^{240}\text{Pu}$ , and  $^{239}\text{Pu}$  are likely to remain in the  $\text{UO}_2$  grains without redistribution (Alexander et al. 1977).

Studies of the interaction of spent fuel with ground-water solutions (Johnson et al. 1983; Johnson and Joling 1984; Forsyth, Svanberg and Werme 1984; Gray and McVay 1984; Oversby 1984; Johnson, Garisto and Stroes-Gascoyne 1985) indicate that release of radionuclides from spent fuel can be divided into four distinct sources: the gap between the fuel and the cladding, the boundaries between the  $\text{UO}_2$  grains, the matrix of  $\text{UO}_2$  grains, and the cladding. These sources can be distinguished on the basis of different processes controlling release, as well as the different physical forms and chemical

TABLE 4.2. PWR Spent-Fuel Assembly Radionuclide Inventories at 1000 Years<sup>(a)</sup>  
(Alexander et al. 1977; Wilson 1985)

<u>Radionuclide<sup>(b)</sup></u>	<u>Percent of Total 1000-Year Activity</u>	<u>Cumulative Percent</u>
<sup>241</sup> Am	51.84	51.84
<sup>243</sup> Am	1.75 <sup>(c)</sup>	53.59
<sup>240</sup> Pu	26.87	80.46
<sup>239</sup> Pu	17.37	97.83
<sup>242</sup> Pu	0.10	97.93
<sup>238</sup> Pu	0.06	97.99
<sup>99</sup> Tc	0.77	98.76
<sup>59</sup> Ni	0.252	99.01
<sup>63</sup> Ni	0.021	
<sup>93</sup> Zr	0.181	
<sup>94</sup> Nb	0.074	
<sup>14</sup> C	0.076 <sup>(d)</sup>	
<sup>234</sup> U	0.113	
<sup>238</sup> U	0.018	
<sup>236</sup> U	0.015	
<sup>237</sup> Np	0.058	
<sup>126</sup> Sn	0.045	
<sup>79</sup> Se	0.023	
<sup>135</sup> Cs	0.022	
<sup>151</sup> Sm	0.013	
<sup>107</sup> Pd	0.006	
<sup>129</sup> I	0.0018	

- (a) Based on ORIGEN-2 data for 33,000 MWd/MTM burnup PWR Assembly
- (b) Radionuclides with 1000-year activity less than <sup>129</sup>I or half-life less than 1 year omitted.
- (c) Includes activity of <sup>239</sup>Np daughter products.
- (d) <sup>14</sup>C activity may vary considerably depending on as-fabricated nitrogen impurities.

compositions/radionuclide inventories of these sources. Details of the release of radionuclides from these separate sources are reviewed in Sections 4.1.2 to 4.1.4.

#### 4.1.2 UO<sub>2</sub> Matrix Dissolution

More than 90% of the radionuclides in spent UO<sub>2</sub> fuel are contained within the UO<sub>2</sub> matrix grains; therefore, attention has been directed toward the rate at which the matrix dissolves and the mechanism under which dissolution occurs under a variety of repository conditions. The results of spent-fuel leach tests conducted during the past several years (Johnson et al. 1982; Johnson, Garisto and Stroes-Gascoyne 1985; Forsyth, Svanberg and Werme 1984; Wilson 1985) show that <sup>240</sup>Pu, <sup>239</sup>Pu, and <sup>241</sup>Am may occur as solid solution components within the UO<sub>2</sub> structure, possibly as substitutes for uranium atoms. This conclusion is based on the observation that these actinides exhibit leach rates that are congruent with respect to calculated inventories and are released in fixed proportion to uranium dissolution rates. This concept is partly supported by chemical analysis on a transverse (edge to center) section of H. B. Robinson spent fuel with an average burnup of 28 MWd/kgM (Katayama, Bradley and Harvey 1980). Point counts of nine radioelements (Ba, Ce, Cs, I, Pu, Ru, Tc, Te, Zr) showed essentially flat concentration profiles across the bulk of the spent fuel, with some enrichment of all elements except I and Te at the outer edge of the fuel pellet. Accordingly, additional effort has been directed toward unirradiated UO<sub>2</sub> dissolution studies in repository environments with the expectation that these may be an alternate and less expensive means of understanding spent fuel dissolution. As discussed below, unirradiated UO<sub>2</sub> studies may be useful to obtain baseline data for comparison with actual spent fuel investigations, but these studies will probably not eliminate the need to test the behavior of actual spent fuel.

Some of the spent-fuel properties discussed earlier can potentially influence matrix dissolution and can possibly account for differences in leaching behavior between spent fuel and unirradiated UO<sub>2</sub> fuel pellets. Sintered UO<sub>2</sub> pellets are a hard ceramic material of about 98% theoretical density and, when fractured, tend to exhibit transgranular cleavage indicating strong grain boundary properties. The oxygen-to-metal (O/M) molar ratio is very close to

2.00. In general, spent PWR fuel with a typical burnup range of about 25 to 40 MWd/KgM tends to be friable and fractures readily along grain boundaries. Accumulation of fission products and possibly some change in O/M along these boundaries may contribute to intergranular weakening. In addition, fission gas generation may contribute to increased porosity. Although most PWR and LWR fuels are operated rather conservatively at moderate burnup and generally at less than 1300°C, some volatile fission products may migrate toward grain boundaries and may influence microstructural integrity. Alpha recoil might also affect crystalline integrity. Wilson (1985) has suggested that bulk oxidation to O/M of 2.25 or 2.33 may be sufficient to open up grain boundaries so that grain boundary phases could become more susceptible to leaching relative to unirradiated UO<sub>2</sub>.

Johnson et al. (1982) have shown that <sup>239</sup>Pu and <sup>240</sup>Pu in clad spent fuel appear to leach congruently with U at 25°C. Wilson (1985), also observed that U, Pu, Am, and Cm exhibit congruent release behavior in clad spent fuel at 25°C. Forsyth, Svanberg and Werme (1984) noted similar behavior for U, Pu, and Cm but also observed that a significant colloidal fraction of these nuclides occurred in the leachates. These measurements imply that for those nuclides released congruently, U release rates indicate release rates of fission products contained in the UO<sub>2</sub> matrix. This relationship is probably valid within the limits imposed by accuracies in leachate analyses and initial inventory. For example, Wilson (1985) noted that <sup>237</sup>Np may leach incongruently, although it is expected to be a matrix element, but inaccuracies in inventory calculation and chemical analyses may also be responsible for the apparent incongruency. Note that apparent incongruent release of certain radionuclides may be attributable to precipitation reactions after congruent release, resulting in an apparent incongruent, albeit lower, release of that radionuclide. Also note that congruent leaching behavior of actinides from spent fuel may be difficult to demonstrate based on the analogy of the U dissolution behavior of unirradiated UO<sub>2</sub>. For example, in comparing U released from unclad spent fuel and UO<sub>2</sub>, Gray and McVay (1984) determined that U was released from spent fuel to a level about two orders of magnitude greater than that from unirradiated UO<sub>2</sub> under the same conditions. Radiolysis, surface oxidation of spent-fuel samples before

testing, and a larger surface area of spent fuel may all have played a role in these observed differences between U release from spent fuel as compared with unirradiated  $UO_2$ .

Results from spent-fuel leach tests imply that the controlling factor for the release of radionuclides contained within the matrix is the dissolution rate of  $UO_2$ , which may, in turn, be controlled by  $UO_2$  solubility under certain flow and chemical (e.g., reducing) conditions. These approaches include electrochemical studies; leach tests over ranges of pH, ligand concentrations, and redox conditions; and hydrothermal investigations were used in an attempt to understand  $UO_2$  dissolution rates and mechanisms. It is generally agreed that under oxygenated conditions in deionized water,  $UO_2$  undergoes sequential oxidation from  $UO_2$  to  $UO_{2+x}$  to  $U_4O_9$  to  $U_3O_7$  with the eventual formation of U(VI) species in solution (Wang and Katayama 1982; Thomas and Till 1984; Johnson et al. 1982). Uranium oxide dissolution rates increase according to a first-order dependence with dissolved oxygen and also with dissolved carbonate (Thomas and Till 1984; Grandstaff 1976; and Johnson et al. 1981) in both deionized water and low-ionic-strength ground water. However, note that the results of McVay, Bradley and Kircher (1981) suggest less than a first-order reaction, and the results of Shoesmith et al. (1985) suggest that no significant increase in dissolution rates occurs until after oxidation to  $U_4O_9$  is attained. The evidence is suggestive of the rate of dissolution being at least partly controlled by the rate of  $UO_2$  oxidation under oxidizing conditions.

At temperatures below  $100^\circ C$ , activation energies for  $UO_2$  dissolution have been reported at about 20 kJ/mol (Thomas and Till 1984) but at 56 kJ/mol by others (Grandstaff 1976). At higher temperatures, up to  $150^\circ C$ , using spent fuel, Johnson et al. (1981) estimated activation energies of 15 to 30 kJ/mol. Some of these discrepancies may involve different reaction paths and alteration products. For example, Thomas and Till (1984) found a decrease in temperature with the dissolution rate in ground water when compared with deionized water, although the magnitude of activation energies was the same. Thomas and Till suggest the decreasing rate in ground water may be the result of formation of a sodium uranyl passivating phase. At higher temperatures, Johnson et al. (1981) state that the formation of oxidized phases, such as  $UO_3 \cdot 0.8H_2O$  or  $UO_2(OH)_2$ ,

could affect measured activation energies; whereas at temperatures below 100°C, Wang and Katayama (1982) invoke the formation of  $UO_3 \cdot 2H_2O$  as an alteration product. Thus, the temperature dependence of spent-fuel dissolution and alteration is still uncertain.

Mass transfer models applicable to low-solubility nuclear waste systems (Chambre, Pigford and Zavoshy 1982; Chambre, Zavoshy and Pigford 1982; Berner 1978) require steady-state saturation values or solubility products for radionuclide species as input parameters. Recently, Zavoshy, Chambre and Pigford (1985) derived analytical expressions that contrast mass transfer rates under diffusional transport with forward dissolution rate data to distinguish between transport or reaction control of the radionuclide release rate.

Zavoshy, Chambre and Pigford (1985) derive a flux ratio,

$$R = \frac{J_o \cdot r_o}{\epsilon \cdot D \cdot C_s} \quad (4.1)$$

where  $J_o$  = the forward dissolution rate, assuming a zero-order dissolution rate and a first-order (with respect to a dissolved waste component) precipitation rate

$r_o$  = the waste form radius

$\epsilon$  = the porosity of the surrounding medium

$D$  = the liquid diffusion coefficient

$C_s$  = the saturation value (or solubility) of the element.

$C_s$  values can be obtained either from long-term matrix dissolution studies to determine individual solubilities of specific radionuclide-bearing solids (e.g.,  $Am(OH)_3$ ,  $PuO_2$ ) or from assuming congruent dissolution of the  $UO_2$  matrix and  $UO_2$  solubility control and proportioning radionuclide releases to their relative abundance in the  $UO_2$  matrix. The latter assumption is not valid under conditions where  $UO_2$  is not stable, such as may occur in oxidizing environments or through effects of radiolysis. In addition,  $C_s$  values for  $UO_2$  can be calculated from thermochemical data (Langmuir 1978; Lemire and Tremaine 1980) or evaluated from other analytical expressions (Garisto and Garisto 1985). When the flux ratio is large ( $R \gg 1$ ), concentrations adjacent to the waste form are

at saturation and the net dissolution rate is controlled by molecular diffusion in the exterior field (transport control in terms of Berner 1978). At high flow rates, when  $R \ll 1$ , net mass transfer is surface-reaction controlled.

Table 4.3 shows some estimated values for  $J_0$  derived from the literature. In many cases, these are not true forward rates because they were obtained from concentrations near  $UO_2$  saturation; however, these data are the best available for spent fuel. Furthermore, because dissolution rates decrease with increasing degree of saturation, these apparent forward dissolution rates should be conservative with respect to the following analysis. A range of  $UO_2$  saturation values is considered using  $2.51 \times 10^{-8} \text{ gm/m}^3$  at pH 6 and  $2.39 \times 10^{-2} \text{ gm/m}^3$  at pH 11 from Johnson et al. (1982). Flux ratios were calculated assuming the following values of  $J_0 = 5.0 \times 10^{-3} \text{ g/(m}^2 \cdot \text{d)}$  (Table 4.3),  $D = 5.2 \times 10^{-4} \text{ m}^2/\text{d}$  (Zavoshy et al. 1985),  $r_0 = 0.005 \text{ m}$  (radius of a fuel pin), and  $\epsilon = 0.1$ . The resulting flux ratios for these two solubilities were  $1.9 \times 10^7$  and  $2.0 \times 10^1$  for  $2.51 \times 10^{-8} \text{ g/m}^3$  and  $2.39 \times 10^{-2} \text{ g/m}^3$ , respectively. These R values imply that release from the  $UO_2$  matrix of spent fuel should be dominated by transport control over a broad range of postulated repository conditions.

In summary, studies on the dissolution of  $UO_2$  show that the release rate of radionuclides from the matrix will be controlled by the solubility of  $UO_2$  under mildly reducing repository conditions (Johnson et al. 1982; Johnson, Garisto and Stroes-Gascoyne 1985) and under more oxidizing conditions. Releases of radionuclides with relatively low solubilities are expected to be controlled by the solubility of individual radionuclide oxide/hydroxide solids (Rai and Ryan 1984). Release rates of more soluble radionuclides will be controlled by the forward dissolution rate of the  $UO_2$  matrix. Accordingly, the equations developed for transport-limited release (Chambre and Pigford 1984) should be applied to radionuclide release from the spent-fuel matrix, assuming the model can be applied as at least a bounding approach for all repository environments under characterization (Lieberman 1985). For example, all three Environmental Assessment Reports (USDOE 1986a,b,c) for the candidate sites in basalt, tuff, and salt adopt, as at least one model for performance assessment, models based on solubility limits combined with mass transport control (also see Kerrisk 1985 for a specific application of a bounding, mass-transfer model

TABLE 4.3. Summary of Dissolution Rate Data from Irradiated and Unirradiated UO<sub>2</sub>

Material	Dissolution Rate, J <sub>0</sub> (x 10 <sup>-4</sup> gmU/m <sup>2</sup> ·d)	Temperature, °C	Solvent	Source(a)
UO <sub>2</sub> (irradiated)	900	25	J-13 ground water	1
	6000	25	Brine	4
	330	25	Brine + Fe coupon	4
UO <sub>2</sub> (unirradiated)	6.3 to 2500	23	Deionized water	2
	2.5 to 790	2	Deionized water	2
	50	70	Deionized water	3
	20	30 (P <sub>O<sub>2</sub></sub> = 0.2 atm)	Deionized water	3
	32	30 (P <sub>O<sub>2</sub></sub> = 0.75 atm)	Deionized water	3
	33	25	Brine	4
	17	25	Brine + Fe coupon	4
	7	150	Brine	4
	14	150	Brine + Fe Coupon	4

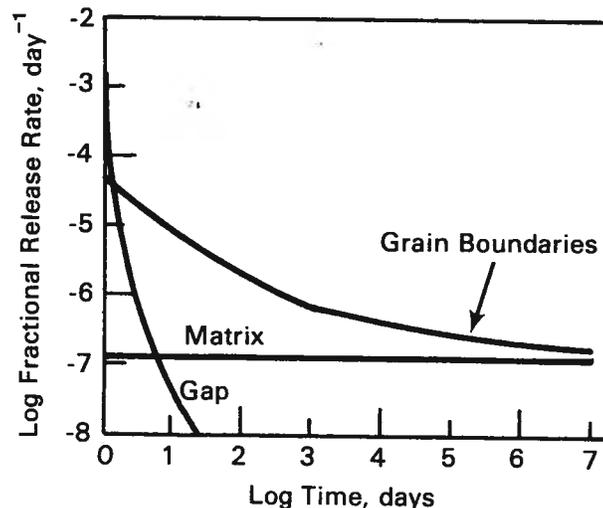
- (a) 1 = Wilson and Oversby 1985  
 2 = Grandstaff 1976  
 3 = Thomas and Till 1984.  
 4 = Gray and McVay 1984.

to the tuff site). The expected matrix release rate from the waste form as a function of time is shown in Figure 4.2, in conjunction with release rates from the spent fuel for the gap and grain boundary sources. Note that the matrix release as plotted is assumed to reach a steady-state value immediately (<1 day) on contact with water.

#### 4.1.3 Gap and Grain Boundaries

In contrast to the actinides, which tend to be produced within the matrix of spent fuel and remain there, the volatile and more mobile fission products and activation products, such as  $^{137}\text{Cs}$ ,  $^{135}\text{Cs}$ ,  $^{129}\text{I}$ ,  $^{99}\text{Tc}$ ,  $^{93}\text{Mo}$ ,  $^{79}\text{Se}$ , and possibly  $^{90}\text{Sr}$ , tend to migrate out of the  $\text{UO}_2$  matrix and down thermal gradients in fuel pins. These radionuclides tend to accumulate in grain boundaries and the gap (the interconnected void space within the fuel, including the space between the fuel and cladding).

Early leach studies of clad spent fuel indicated an initially high release rate of fission products, such as Cs and I, during the first few days of leaching (Vandergraaf 1980; Johnson et al. 1983; Johnson et al. 1984). Later studies using different spent fuels confirmed this behavior (Forsyth, Svanberg and Werme 1984; Wilson 1985). Nuclide release rates of Cs, I, etc., based on



**FIGURE 4.2.** Schematic Release Behavior of Different Sources Within Spent Fuel as a Function of Time (based on Johnson, Garisto and Stroes-Gascoyne 1985)

inventory fraction during this initial stage, are much higher than matrix element (e.g., U, Pu) release rates indicating that the fission products are not in matrix lattice sites. The fraction of inventory released during this initial stage is thus considered to represent the readily accessible gap inventory.

After the initial rapid release of gap fission products, release rates of many of these same elements are expected to gradually decrease and eventually tend to approach the release rate of uranium. A considerable amount of time may be required (months to years), depending on the power history of the fuel, before this approach to the matrix release rate is achieved (Johnson, Garisto and Stroes-Gascoyne 1985). The inventory that is gradually released during this period is considered to represent the fission products located along grain boundaries. The individual release contribution of the gap and grain boundaries cannot be easily separated because the same mechanisms, such as grain growth, bubble formation, and diffusion, lead to the accumulation of both gap and grain boundary inventories. Furthermore, essentially no data are available on the chemical nature and proportion of grain boundary phases. Consequently, Johnson, Garisto and Stroes-Gascoyne (1985) suggested that, in lieu of more detailed information, these inventories be combined to yield a single instant release parameter for modeling purposes.

The combined gap plus grain boundary inventory can represent from 1 to 10% (with the distribution weighted strongly to the lower end for U.S. LWR fuels) of fission product activity, depending on burnup and history, and also contains some of the more mobile nuclides. Several studies have included attempts to determine these inventories and predict their release rates. In general, release rates are a direct function of gap inventory because of the essentially instantaneous release of these elements. Thus, Johnson et al. (1984) were able to roughly correlate stable xenon release with the fraction of  $^{137}\text{Cs}$  and  $^{129}\text{I}$  released, although the fraction of xenon released was slightly higher than the Cs fraction. As an alternative, Johnson et al. (1984) attempted to calculate the average gap and grain boundary inventories. They were able to calculate a probability distribution of the instant release fraction based on calculated fuel bundle power histories.

At present, little is known or understood about grain boundary leaching kinetics and the rate at which radionuclides other than Cs and I are released. In some cases, the initial release rates as discussed here appear to be four orders of magnitude greater than matrix release rates. For the time being, however, the idea of treating the combined gap and grain boundary inventory as an instantaneous release contribution seems the most viable conservative alternative.

#### 4.1.4 Cladding

The cladding sheath of spent fuel and associated hardware are not typically considered as sources for radionuclide release. The cladding does, however, contain a limited amount of radionuclides produced through neutron activation of the original cladding (see Section 4.1.1; Table 4.4). None of these radionuclides presented in Table 4.4, with the exception of  $^3\text{H}$ , fall below the cutoff of 0.1% of the calculated total release rate limit set by the NRC [10 CFR 60, Section 113 subpart (a)] for consideration in performance evaluations. In particular, the cladding does contain an appreciable fraction of the total  $^{14}\text{C}$  inventory of spent fuel (Van Konyenburg et al. 1985), making cladding the dominant waste form of this important and mobile radionuclide. It must be stressed that this source of radionuclides contained within the cladding is different in both radionuclide inventory and release behavior than gap release (see Section 4.1.3).

Spent-fuel cladding may degrade by physical or chemical processes. Because physical disruption/fracturing of the cladding would lead to negligible amounts of released radionuclides, release by this type of mechanism is not considered. Chemical degradation of the cladding can be divided into uniform and nonuniform (localized) corrosion. Because a limited mass of cladding undergoes dissolution in nonuniform attack, radionuclide release from this type of mechanism can also be neglected.

Uniform corrosion, then, should be the dominant process controlling the release of radionuclides from cladding. Fortunately, models for uniform corrosion are perhaps better understood and accepted than other corrosion mechanisms. For radionuclides occurring within the cladding alloy matrix, release

TABLE 4.4. The Activation Products in Curies of the Metallic Components of a PWR Assembly Predicted by the ORIGEN-2 Code (Alexander et al. 1977)

Nuclides	1 Year	10 Years	100 Years	1000 Years	10,000 Years
<sup>3</sup> H	1.48E 02 (a)	6.911E 01	4.334E-01	4.077E-23	0.0
<sup>14</sup> C	6.852E-01	6.844E-01	6.770E-01	6.072E-01	2.044E-01
<sup>36</sup> Cl	5.126E-03	5.126E-03	5.125E-03	5.115E-03	5.013E-03
<sup>54</sup> Mn	1.965E 01	1.066E-02	0.0	0.0	0.0
<sup>55</sup> Fe	1.970E 03	1.788E 02	6.793E-09	0.0	0.0
<sup>58</sup> Co	9.062E 01	1.198E-12	0.0	0.0	0.0
<sup>60</sup> Co	3.181E 03	9.716E 02	6.867E-03	0.0	0.0
<sup>59</sup> Ni	2.118E 00	2.117E 00	2.116E 00	2.099E 00	1.942E 00
<sup>63</sup> Ni	3.038E 02	2.839E 02	1.441E 02	1.637E-01	0.0
<sup>65</sup> Zn	2.259E 01	2.068E-03	0.0	0.0	0.0
<sup>93</sup> Zr	1.049E-01	1.049E-01	1.049E-01	1.049E-01	1.042E-01
<sup>95</sup> Zr	4.489E 02	3.498E-13	0.0	0.0	0.0
<sup>93m</sup> Nb	1.181E-02	4.746E-02	9.940E-02	9.962E-02	9.897E-02
<sup>94</sup> Nb	6.242E-01	6.240E-01	6.220E-01		4.413E-01
<sup>95</sup> Nb	9.494E 02	7.543E-13	0.0	6.029E-01	0.0
<sup>93</sup> Mo	1.396E-02	1.393E-02	1.364E-02	0.0	1.385E-03
<sup>99</sup> Tc	2.589E-03	2.589E-03	2.588E-03	1.108E-02	2.505E-03
<sup>113m</sup> In	4.568E 01	1.105E-07	0.0	2.580E-03	0.0
<sup>113</sup> Sn	4.565E 01	1.104E-07	0.0	0.0	0.0
<sup>119m</sup> Sn	1.097E 03	1.005E-01	0.0	0.0	0.0
<sup>123</sup> Sn	2.094E 01	4.484E-07	0.0	0.0	0.0
<sup>125</sup> Sn	6.187E 02	6.296E 01	7.501E-09	0.0	0.0
<sup>125m</sup> Te	1.507E 02	1.538E 01	1.832E-09	0.0	0.0
Sum Total	9.082E 03	1.585E 03	1.482E 02	3.696E 01	2.800E 00

(a) 1.48E 02 = 1.48 x 10<sup>2</sup>.

can be conservatively considered as congruent with the corrosion rate of the cladding matrix. If some radionuclides preferentially occur along grain boundaries within the cladding, it may be possible (although unwarranted at this time) to further modify the congruent dissolution model.

A far more important consideration is the potential for solubility to constrain release. The cladding is a complex alloy, thermodynamically unstable (i.e., reactive) under geologic conditions, and incapable of undergoing a reversible dissolution/precipitation reaction (i.e., the precipitation of metallic Zircaloy out of solution). Therefore, the release of radionuclides from cladding cannot be modeled as controlled by any solubility constraint of the cladding itself. New radionuclide-bearing solids (e.g., metal oxides and hydroxides), however, may precipitate as corrosion products. If these phases incorporate radionuclides directly into their structure, solubility constraints would be imposed on radionuclide release.

#### 4.1.5 Barrier Interactions

The calculation of the time-dependent release rate of radionuclides from a waste package system containing spent fuel is conceptually identical to that developed for release from spent fuel alone (Chambre and Pigford 1984; Chambre et al. 1985). As with waste form release, two processes limit release from the waste package system: transport control and surface reaction control. Essentially any number of nested barriers, each possessing distinct chemical and physical properties, can be incorporated within either of these models.

The release of most radionuclides from waste package systems can be modeled as transport controlled under expected conditions for all current repository sites (National Academy of Sciences 1983; Chambre and Pigford 1984; Lieberman 1985). The strict applicability of this model to the expected hydrological characteristics of all proposed repository environments is open to question; however, conservative bounding calculations in support of waste package performance assessment conducted by DOE repository programs have used a similar modeling approach (e.g., Sagar, Eslinger and Baca 1985; Kerrisk 1985; Lieberman 1985). For this model, the time-dependent release rates from the waste package system will be directly proportional to the solubility-limited concentration at the surface of the  $UO_2$  matrix. The transport-controlled

release illustrates the central role of spent-fuel performance in the evaluation of waste package performance. This correspondence between spent-fuel and waste package performance is further supported by the fact that if the release of a given radionuclide from spent fuel is surface-reaction limited (e.g., gap and grain boundary release), the release of this same radionuclide from the waste package system must also be modeled as surface-reaction limited.

The properties of other barriers in addition to the waste form, however, will also affect the time dependency of release rates from the waste package. For example, assume a waste package system containing spent fuel within a packing material (backfill) having different physical and chemical properties than the surrounding host rock, with diffusional mass transport only. The space- and time-dependent release rate of a low-solubility (i.e., transport-controlled) radionuclide from such a system will be a function of at least eleven parameters. These parameters include (Chambre et al. 1985)

- solubility-limited concentration at the waste form surface
- radioactive decay constant
- diffusion coefficient
- physical dimensions of the waste form and the packing
- geometric (shape) factors for the packing and the host rock
- sorption coefficients of the (altered) packing and the host rock
- porosity of the (altered) packing and the host rock.

Because of the large amount of detailed work on sorption, the sorption process is reviewed more fully in Section 4.1.6.

Additional factors affect the release of radionuclides from waste package systems. The failure of containment distributed over time has been demonstrated to have a profound positive effect on limiting radionuclide release rates to values below the NRC criterion (Sagar, Eslinger and Baca 1985; KBS 1983). Furthermore, the access of ground water to the surface of the  $UO_2$  matrix may be greatly limited by the restricted nature and geometry of cladding and containment barrier failure, thus potentially decreasing the radionuclide release rate from spent fuel (Cheung and Chan 1983). Another possibility is that synergistic interaction may occur among the barrier materials themselves, and this may affect their individual performance. For example, the presence of

metallic barriers and associated corrosion products may affect the solubility of radionuclide-bearing solids, such as  $UO_2$ . The reactivity of packing material or host rock may change as a result of prolonged exposure to the radiation field associated with spent fuel. Chemical reaction between metallic barriers and packing material may alter the mechanism or rate of corrosion of the metallic barriers.

In addition to synergistic interactions, calculation of radionuclide release from waste package systems may be complicated by physical, chemical, and biological processes. Formation of colloids containing radionuclides represents a transport mechanism that is separate from, and additive to, the mass transfer mechanism discussed previously. Chemical reaction of migrating radionuclides with barrier materials (an entirely different process than the reversible sorption process accounted for in Section 4.1.6) is also probable. This process is especially important if a strongly oxidizing plume of radionuclides forms via alpha radiolysis of ground water at the surface of spent fuel and begins to move through the waste package system (Neretnieks 1984).

Under certain conditions, the release of radionuclides may not be limited by the solubility of the  $UO_2$  matrix. The presence of additional barrier materials may contribute dissolved components that will alter the spent fuel/ground-water reaction to the point that  $UO_2$  is not the thermodynamically stable solid under expected waste package conditions. For example, the formation of uranium carbonate or uranium silicate compounds from the dissolution of the initial  $UO_2$  would invalidate the concept of radionuclide release controlled by the congruent dissolution of the  $UO_2$ . This is not to say that a similar solubility approach to controlled radionuclide release would not apply; it merely complicates the modeling, necessitating experimental information regarding both initial and secondary uranium phases, as well as information on the partitioning of released radionuclides between the ground water and the secondary uranium phase.

#### 4.1.6 Potential Sorption Properties of Cladding and Container Corrosion Products

Loss of containment may occur by corrosion processes that oxidize the steel container and Zircaloy cladding. Probable corrosion products for these

metals include magnetite  $\text{Fe}_3\text{O}_4$ , hematite  $\text{Fe}_2\text{O}_3$ , goethite  $\text{FeOOH}$ , amorphous ferric hydroxides, and zirconium oxide  $\text{ZrO}_2$  and amorphous zirconium hydroxides [e.g.,  $\text{Zr}(\text{OH})_4$ ]. Many of these oxide solids are high-capacity adsorbents that exhibit both anion and cation adsorption properties, depending on the pH of the system.

As mentioned in Sections 3.1 and 3.2, the surface of spent-fuel rods leaving the reactor have a thin film of oxidation/crud that consists of  $\text{ZrO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and Fe and Ni oxides. These films are generally between 30 and 50  $\mu\text{m}$  in thickness (about 5 to 10% of the overall cladding thickness). Table 4.5 shows the mass of U, Zr, fission, and activation productions present in spent-fuel rods. As can be seen, Zr mass represents 21% by weight of the spent-fuel rod. Should this zirconium be oxidized during containment, depending on the surface area and crystallinity of the oxide corrosion product, substantial numbers of adsorption sites will be available to retard the migration of radionuclides. Furthermore, the metal container may consume large quantities of oxidizing agents, which might be formed via radiolysis (Neretnieks 1983; McKinley 1985).

Kraus et al. (1958) found hydrous Zr oxides are capable of adsorbing up to 0.4 to 1 mole of monovalent species/kg of  $\text{ZrO}_2$ . For each metric ton of spent-fuel heavy metal,  $1.3 \times 10^3$  kg of Zr oxides can form. Therefore, the corrosion products could adsorb between 500 and 1300 equivalents of elements leached from the waste package. Table 4.5 shows that, after 1000 years of storage, the following elements would be present in each metric ton of heavy metal: 11 moles of C, 0.6 moles of Se, 8 moles of Tc, 2 moles of I, 2.2 moles of Cs, 6 moles of Np, 29 moles of Pu, and  $4 \times 10^3$  moles of U. Thus, the zirconium corrosion products of the cladding have the capacity to adsorb most of the radionuclides present. Note that the capacity to adsorb and the selectivity, or preference, for one element over another are two separate issues. That is, a high capacity is helpful, but it does not ensure that the elements of concern will be readily adsorbed.

Depending on the thickness used, a low-carbon, steel container should also provide a substantial mass of iron so that when corrosion proceeds, another high-capacity adsorbent, iron oxide, also forms. Together the corrosion products of zirconium and iron have the capacity to adsorb most of the

TABLE 4.5. Element Mass Inventory (grams/MTHM) in Spent Fuel  
(taken from USDOE 1980)

Element	Time After Closure			
	$10^3$ Years	$10^4$ Years	$10^5$ Years	$10^6$ Years
C	132	132	132	132
Ni	$10^4$	$10^4$	$10^4$	$10^4$
Se	45	45	45	45
Zr	$2.6 \times 10^5$	$2.6 \times 10^5$	$2.6 \times 10^5$	$2.6 \times 10^5$
Tc	750	750	750	750
Pd	1250	1250	1250	1250
Sn	4300	4300	4300	4300
I	240	240	240	240
Cs	300	300	300	300
Sm	788	788	788	788
Cm	1	0.47	$1.7 \times 10^{-3}$	$1.4 \times 10^{-3}$
Am	309	29.4	$8.5 \times 10^{-3}$	$6.1 \times 10^{-7}$
Pu	6900	4800	630	67
Np	1400	1600	1500	1200
U	$9.6 \times 10^5$	$9.6 \times 10^5$	$9.6 \times 10^5$	$9.6 \times 10^5$
Pa	$7.4 \times 10^{-3}$	$7.1 \times 10^{-2}$	0.45	0.56
Th	0.41	4.63	38.6	178
Ac	$4.8 \times 10^{-6}$	$4.7 \times 10^{-5}$	$3 \times 10^{-4}$	$3.8 \times 10^{-4}$
Ra	$1 \times 10^{-3}$	0.05	0.43	0.36
Pb	$8.7 \times 10^{-4}$	0.092	10.2	184

radionuclides present in spent fuel. If the adsorption is totally reversible, the corrosion products will release the adsorbed nuclides as the leachate plume diminishes. Thus, the adsorption may only act as a delay mechanism, which, for long-lived nuclides, will not allow much mass reduction by decay. On the other hand, if the adsorption mechanism is partially irreversible, the corrosion products can permanently lower the mass leaving the waste package.

At low pH values, these oxide surfaces exhibit a net positive charge caused by protonation of surface hydroxyl groups, and at higher pH, these oxide surfaces exhibit a net negative charge caused by loss of protons. Each solid

exhibits a characteristic pH value at which the net surface charge is zero, the  $pH_{pzc}$ . Below this characteristic pH, the solid is positively charged and acts like an anion exchanger, while above this pH, the solid acts like a cation exchanger because it has a net negative charge.

Table 4.6 lists  $pH_{pzc}$  values for many known oxide surfaces. The iron and zirconium oxides all show a  $pH_{pzc}$  near neutrality or under slightly alkaline conditions; they could be expected to strongly adsorb anions at low pH values and continue to adsorb anions in neutral to slightly alkaline solutions. In alkaline solutions, these oxides are expected to adsorb cations.

Trace metal adsorption onto these oxide surfaces, which exhibit this amphoteric behavior dependent on pH, has been successfully predicted using the site-binding surface complexation or triple-layer adsorption conceptual model discussed in the following paragraphs. Surface complexation adsorption models treat the adsorbent surface as a plane of hydroxyl groups, X-OH, where X represents structural Al, Fe, Zr, Si, or other atoms. The adsorption sites, -OH or hydroxyl groups, are considered ligands that are acid/base sensitive and form complexes with solutes in solution. The model assumes that 1) adsorption occurs on the sites with no interactions (neither chemical nor electrostatic) between adsorbed species; 2) all of the adsorption sites have equal binding energies (each site is identical); 3) no matter how many sites are full, each remaining site has the same probability of adsorbing the next solute ion (the

TABLE 4.6. pH Values for Zero Charge

<u>Solid</u>	<u>pH Value</u>
SiO <sub>2</sub>	2
Al <sub>2</sub> O <sub>3</sub>	8.4 to 9.0
TiO <sub>2</sub>	5.9 to 7.0
ZrO <sub>2</sub>	6.2 to 6.8
ThO <sub>2</sub>	6.6 to 7.0
Fe <sub>3</sub> O <sub>4</sub> (Magnetite)	6.8 to 7.0
α-Fe <sub>2</sub> O <sub>3</sub>	8.5 to 9.3
α-FeOOH (Leipidocrocite)	7.3 to 7.7
Fe <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O am	7.5

binding energy does not depend on sorption density); and 4) the adsorption maximum (capacity) allows only a monolayer coverage of each site. All four of these assumptions are also invoked for the Langmuir isotherm and ideal ion-exchange approach, two other conceptual models used to describe trace metal adsorption.

Adsorption reactions in the surface complexation model are considered analogous to soluble complex reactions in solution with one fundamental difference. The adsorption reaction includes an electrostatic energy term to account for the interaction of the charged adsorbing ion and the surface charge on the solid. The conceptual model is schematically shown in Figure 4.1. For the surface complexation model, dubbed the triple-layer model [originally suggested by James and Healy (1972 and 1975), and applied by Davis, James and Leckie (1978), Davis and Leckie (1978, 1980) and Leckie et al. (1980)], the space around the solid surface (usually represented as a semi-infinite planar surface) is arbitrarily broken into three zones, the o plane, b plane, and d plane, as shown in Figure 4.3. The o plane represents the solid surface. Only hydrogen and hydroxyl ions can approach the o plane to interact with the solid. Just beyond the o plane is the b plane, which extends out farther from the surface and ends at the boundary of the diffuse zone. Solution ions, such as the macro cations and anions ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , etc.) and the trace constituents [ $\text{Sr}^{2+}$ ,  $\text{PuO}_2^+$ ,  $\text{Cs}^+$ ,  $\text{I}^-$ ,  $\text{TcO}_4^-$ ,  $\text{Am}(\text{OH})_2^+$ , etc.] that are adsorbing onto the solid surface, are found in this plane. The plane represents the diffuse layer where ions are not influenced strongly by electrostatic forces emanating from the solid surface. The ions in this region are considered counter-ions that neutralize any residual charge caused by the surface and specifically adsorbed ions in the b plane. The d plane blends into the bulk solution zone farther from the surface.

The electrostatic interactions modify the thermodynamic activities of ions as they move from the bulk solution to the various adsorption planes. Ion activity of a species near the surface [ $\text{Ion}_S$ ] is related to its activity in the bulk solution [ $\text{Ion}_B$ ] by the following relationship

$$[\text{Ion}_S] = [\text{Ion}_B] e^{-ZF\psi/RT} \quad (4.2)$$

where  $Z$  = charge of ion (e.g.,  $\text{Sr}^{2+} = +2$ ,  $\text{SO}_4^{2-} = -2$ )

$F$  = Faraday constant

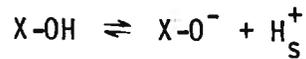
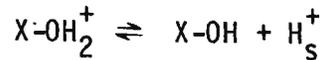
$R$  = gas constant

$T$  = temperature (K)

$\psi$  = electrostatic potential for the designated plane.

Figure 4.3 also shows the shape of the potential curve as an ion approaches the surface and defines two capacitance terms and three surface charges. Using the relationships between surface charges, capacitances, and potentials (see James and Healy 1972) and equations for each species adsorbed onto the solid surface [combinations of Equation (4.2)], adsorption reactions onto oxide surfaces have been successfully described.

Adsorption dependence on acid/base reactions is explicitly accommodated by the following two reactions:

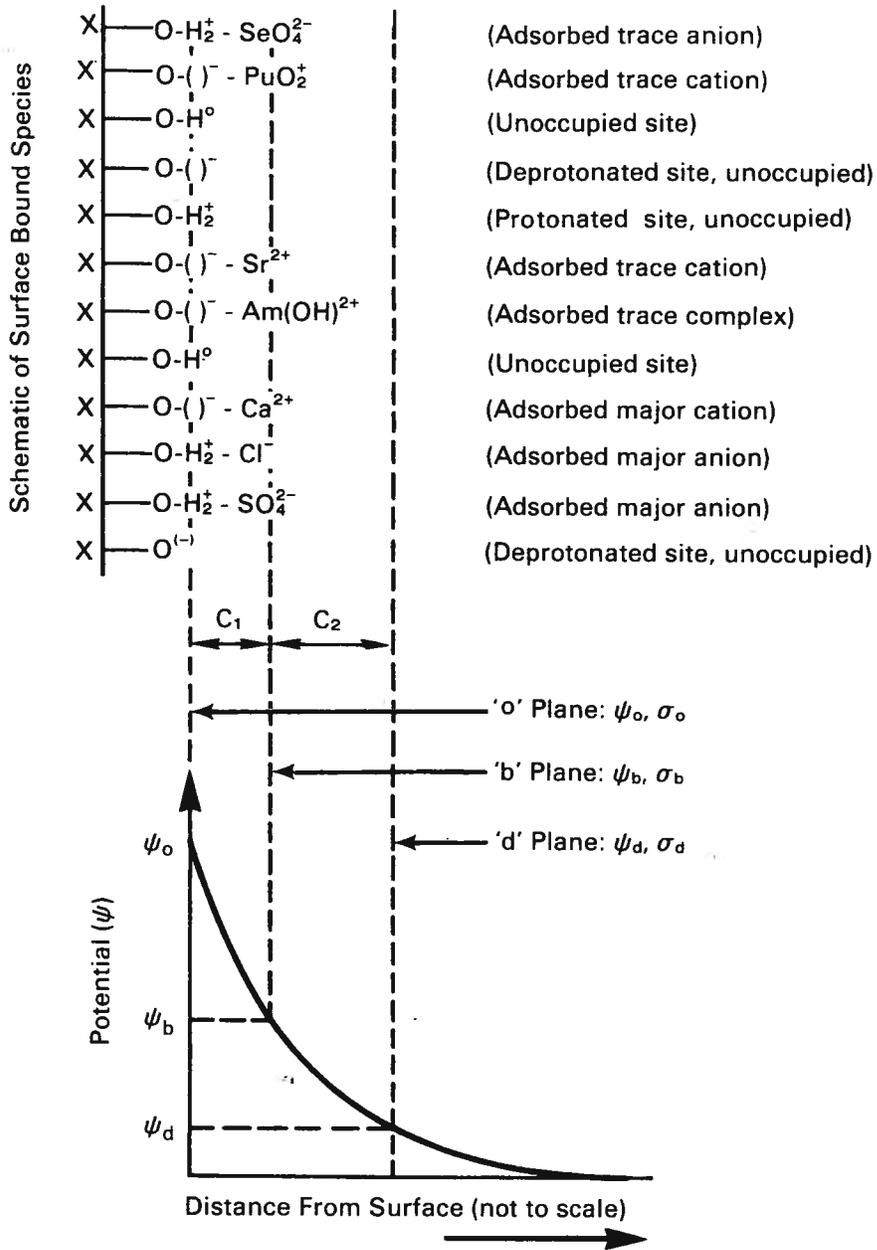


by

$$K_{a_1}^{\text{int}} = \frac{[\text{X-OH}] [\text{H}_s^+]}{[\text{X-OH}_2^+]} = \frac{[\text{X-OH}] [\text{H}^+] e^{(-F\psi_o/RT)}}{[\text{X-OH}_2^+]} \quad (4.3)$$

and

$$K_{a_2}^{\text{int}} = \frac{[\text{X-O}^-] [\text{H}_s^+]}{[\text{X-OH}]} = \frac{[\text{X-O}^-] [\text{H}^+] e^{(-F\psi_o/RT)}}{[\text{X-OH}]} \quad (4.4)$$

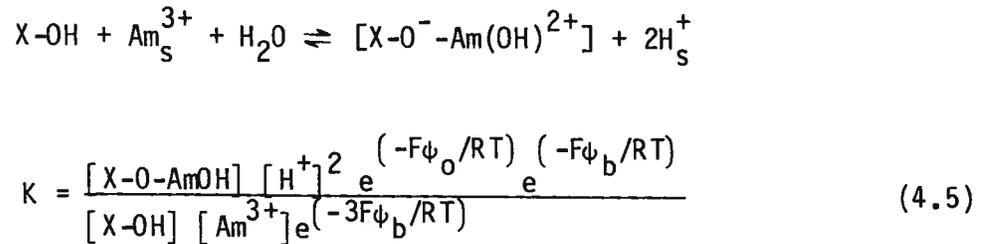


Electroneutrality requires  $\sigma_o + \sigma_b + \sigma_d = 0$   
 Where  $\sigma_i$  = Surface charge at designated plane  
 Charge-potential relationships  
 $\psi_o - \psi_b = \sigma_o / C_1$   
 $\psi_b - \psi_d = -\sigma_d / C_2$

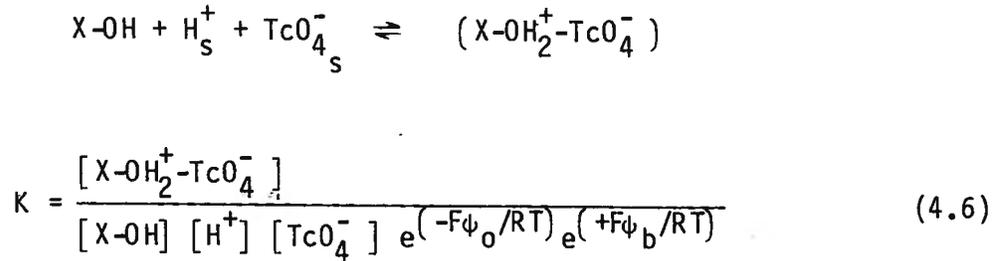
FIGURE 4.3. Schematic Representation of Triple-Layer Adsorption Model

where the equilibrium constants,  $K_{a1}^{int}$  and  $K_{a2}^{int}$ , are similar to dissociation constants for soluble complex formation and can be determined in the laboratory by systematic acid/base titrations (see Davis, James and Leckie 1978).

Examples of cation and anion adsorption reactions for trace contaminants, such as radionuclides, are shown in Equations (4.5) and (4.6). Recall that these ions and the macro cations and anions are bound in the b plane, not the o plane; therefore, the electrostatic terms differ from those in Equations (4.3) and (4.4). The first reaction shows the adsorption of the first hydrolysis species for americium:



while the second reaction shows the adsorption of the pertechnetate anion:



The triple-layer conceptual model explicitly accommodates pH effects, speciation (allows for adsorption of free cations/anions and hydrolyzed species), macro cation/anion competition [reactions similar to Equations (4.5) and (4.6) for major constituents are included], and, when incorporated into a thermodynamic code, can explicitly address oxidation/reduction effects on ion speciation and stability of solid adsorbents, such as iron oxides. The

individual reactions [e.g., Equations (4.5) and (4.6)] are solved simultaneously such that the effect of differing concentrations of each aqueous species on each other is explicitly addressed.

The use of the surface complexation model requires detailed characterization of the adsorbent's adsorption capacity (number of sites or site density and surface area), dependency on pH (acid-base titrations), dependency on major cations/anions that compete for adsorption sites and electrical properties of the surface (electrokinetic potential, specific conductivity, etc.) as well as detailed studies of the adsorption of trace constituents.

Currently, data are available for adsorption of the trace constituents As(V), As(III),  $\text{Cd}^{2+}$ , Cr(VI),  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , Se(VI), Se(IV),  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$ , and  $\text{H}_3\text{BO}_3^-$  and major ions  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  onto hydrous ferric oxides. Of these, only selenium has direct relevance to long-lived radionuclide disposal issues. For scoping studies, it is useful to assume similar adsorption tendencies for chemically similar elements. For example,  $\text{I}^-$  may behave similarly to  $\text{Cl}^-$ , and  $\text{Cs}^+$  may behave similar to  $\text{K}^+$ . Thus, from available data one can estimate the probable adsorption tendencies of several radionuclides onto hydrous iron oxides, although actual data are more desirable than chemical analog data.

Regazzoni, Blesa and Marato (1983) and Blesa, Marato and Regazzoni (1984) have reported the intrinsic acidity properties of  $\text{ZrO}_2$  and the adsorption of boric acid onto  $\text{ZrO}_2$ , respectively. The former article gives most of the solids characterization data for  $\text{ZrO}_2$  (baddelyite form) such that only specific experiments on trace metal (radionuclide) and additional macro cations and anions adsorption versus pH would be required to use the triple-layer adsorption conceptual model. Furthermore, from the values for the intrinsic acidity constants [see Equations (4.3) and (4.4)] and intrinsic constants for the major cation,  $\text{K}^+$ , and anion,  $\text{NO}_3^-$ , one can make some qualitative statements about probable adsorption potential onto  $\text{ZrO}_2$  versus iron oxides.

As early as 1958 (Kraus et al. 1958), the adsorption properties of hydrous zirconium oxides were discussed for applications in the purification of nuclear waste streams and the separation/isolation/purification of selected species. Kraus et al. (1958) discuss the amphoteric nature of hydrous Zr oxides  $[\text{Zr}(\text{OH})_4$

amorphous] and the fact that the solid exhibits a large capacity for adsorbing anions under acid conditions and a slightly lower capacity for adsorbing cations under basic conditions. At pH = 2, hydrous Zr oxide is capable of adsorbing 1 mole of anions ( $\text{Cl}^-$ )/kg of solid. The capacity diminishes as the pH is raised such that at pH 7, virtually no chloride is adsorbed. Conversely, at pH 10.5, the Zr oxide adsorbs up to 0.4 mole of cations ( $\text{Na}^+$ )/kg of solid and diminishes to virtually zero cation adsorption at pH 6.

Such adsorption characteristics suggest that the  $\text{pH}_{\text{PZC}}$  of the amorphous zirconium oxide would be in the neighborhood of pH = 6.5, which agrees well with the value for the crystalline  $\text{ZrO}_2$  shown in Table 4.6. Furthermore, the observed capacity [0.4 mole to 1 mole/kg of solid] is as high as most clays and ten times as large as most soils. Also recall that most clays and soils adsorb only cations at pH values normally found in the geosphere, pH 3.5 to 10.5. Kraus et al. (1958) found that the adsorption was reversible and reproducible in that changing the pH from 2 up to 10.5 and then back down to 2 etc., gave the same anion and cation adsorption curves through numerous cycles.

The effect of temperature on adsorption by the hydrous zirconium oxide was also studied. The amount of anion or cation adsorbed increased between 27°C and 85°C, and one test to 150°C showed further increases. Anion adsorption increases with temperature more than cation adsorption. On the other hand, drying the hydrous oxide at elevated temperatures before contact with adsorbate-bearing solutions lowers the apparent capacity as shown by data in Table 4.7 for Cr(VI) adsorption. The decrease in capacity is attributed to crystal growth and lowering of effective surface area.

Kraus et al. (1958) state that hydrous zirconium oxides (and most hydrous oxides in general) are unusually selective in adsorbing polyvalent oxyanions, such as  $\text{BO}_4^{3-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{AsO}_3^{3-}$ ,  $\text{AsO}_4^{3-}$ , and  $\text{MoO}_4^{2-}$ , and also exhibit a small degree (~5%) of irreversibility. If the near-container environment becomes slightly oxidizing and acidic (pH = 4 to 5), one might expect significant anion adsorption for  $^{79}\text{Se}$  as selenite or selenate and measurable adsorption of  $^{99}\text{Tc}$  as  $\text{TcO}_4^-$  and  $^{129}\text{I}$  as  $\text{IO}_3^-$ .

TABLE 4.7. Effect of Drying Temperature on Hydrous Zr Oxide Adsorption

<u>Drying T, °C</u>	<u>Adsorbed/kg Solid Mole Cr(VI)</u>
32	1.38
105	1.25
202	0.91
320	0.45

In the alkaline pH regime, the hydrous oxides act as cation exchangers and strongly adsorb polyvalent cations. Elution generally requires switching to acid eluants. Leckie et al. (1980) present data on trace metal adsorption onto hydrous ferric oxide,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  am. The solutions studied ranged from simple electrolytes (0.001 to 0.1 M  $\text{KNO}_3$ ) to complicated coal-fired power plant waste streams with ionic strengths up to 0.1 M. In general, cation adsorption onto hydrous oxides is quite sensitive to pH around the point of zero charge. The percentage adsorption of trace metals rapidly increases from zero at acid pH values to essentially complete (~100% adsorption) at pH values more alkaline than the  $\text{pH}_{\text{pzc}}$ . For instance, data presented by Leckie et al. (1980) and Davis and Leckie (1978) show that adsorption of various trace metals onto amorphous iron oxide follows trends depicted in Table 4.8.

The rapid rise from negligible adsorption to almost quantitative adsorption occurs over a small pH range of about 2 units. The steep rise is often

TABLE 4.8. pH Value at Which Designated Percent Adsorption Occurs

<u>Percent Adsorbed</u>	<u>Zn</u>	<u>Cd</u>	<u>Cu</u>	<u>Pb</u>	<u>Ag</u>
0	~5.0	~5.5	~4.1	<3.5	<4
20	6.0	6.2	4.7	3.7	6.2
40	6.2	6.5	4.9	4.0	6.8
60	6.5	6.8	5.2	4.2	7.2
80	6.7	7.0	5.5	4.5	7.7
>95	7.2	7.8	6.2	5.2	8.7

Note: Trace Metal Total Concentration  $\sim 10^{-7}$  M (trace range).

called the adsorption edge. Also note that adsorption begins and becomes significant for most cationic trace metals at pH values below the pH of zero charge for amorphous iron oxide. This phenomenon of adsorption of cations onto the oxide surface at a pH value where the surface should also be positively charged and thus be an anion adsorber, is called specific adsorption. As long as the system's pH does not drop below pH 4.5, metals such as Cu and Pb remain tightly bound, and for Zn and Cd, little desorption is observed as long as the pH remains above 6. It appears that trace metals that form stable hydrolysis species (Cu, Pb) in natural waters are preferentially adsorbed by hydrous iron oxides at lower pH values than trace metals that form only weak hydrolysis species (Zn, Cd, Ag). As the actinides and lanthanides form stable hydrolysis species, one could speculate that they will be readily adsorbed by amorphous iron oxides at pH values above 5. Furthermore, because the hydrous zirconium oxides have a similar  $pH_{pzc}$ , one could speculate that they will act as strong scavengers of cationic forms of radionuclides in leachate from nuclear waste forms.

Paterson and Rahman (1985) report on the anion and cation exchange properties of microcrystals of zirconia ( $ZrO_2$ ). Their materials had a reported surface area of  $143 \text{ m}^2/\text{g}$ , which is quite high for a crystalline material, suggesting it should have a high adsorption capacity. The capacity of the zirconia for adsorbing anions ( $Cl^-$ ) and cations ( $Na^+$ ) was determined versus pH. The results are shown in Table 4.9. The values agree nicely with Kraus et al. (1958) capacity values for amorphous zirconium oxides.

TABLE 4.9. Exchange Capacity (mmols/g  $ZrO_2$ )

<u>pH</u>	<u>Anions</u>	<u>Cations</u>
3	0.6 to 0.8	---
5	0.25 to 0.4	---
7	0.1	---
9	---	0.1
11	---	0.2 to 0.5

Paterson and Rahman remark that the capacities are qualitatively similar to those of  $\alpha$ -FeOOH, but the capacities are significantly larger. The capacity determinations were also performed varying the salt content (as well as pH) of the solutions. As predicted by the Donnan theory for the exclusion of salt from the charged pores within crystals, the anion capacity is directly related to total acid activity, which can be expressed as  $pA = pH + pCl$  (when the system is chloride-based and  $pCl = -\log$  of the chloride activity in solution). Similarly, the cation exchange capacity is directly related to the total basicity  $pB = pOH + pNa$  (when the system is sodium based). The major consequences of these relationships are that the capacity-pH relationship will not be unique. The concentration of the major anions or major cations are equally important in determining anion and cation exchange capacities, respectively. For anion exchange on zirconia as one increases the anion concentration, for example chloride ( $pCl$  decreases), either the capacity must increase or the pH must go up to keep the capacity fixed. For cation exchange, increasing the cation concentration, such as sodium, either increases the capacity or lowers the pH. Thus, if the ionic strength is increased at a fixed pH, zirconia should exhibit larger sorption capacity.

Regazzoni, Blesa and Marato (1983) and Blesa, Marato and Regazzoni (1984) have measured the surface properties of zirconia ( $ZrO_2$ ) and its adsorption properties for boric acid using the conceptual constructs of the aforementioned surface complexation model. Generally, oxide surfaces show maximum adsorption for polybasic acids at pH values close to the  $pK_a$  values of the acids; therefore, the qualitative anion adsorption trends should be predictable. Furthermore, knowing the adsorption attributes of trace anions and cations onto iron oxide surfaces and some attributes of the zirconia should allow qualitative description of zirconia's probable adsorption characteristics.

These two reports used a high purity  $ZrO_2$ . The  $ZrO_2$  average particle size was  $0.18 \mu m$ , and the surface area was  $5.72 m^2/g$ , 25 times smaller than the surface area of the material used by Paterson and Rahman (1985). The intrinsic stability constants ( $K_{a_1}^{int}, K_{a_2}^{int}$ ) and stability constants for adsorption of

potassium and nitrate, the major cation and anion used in triple-layer adsorption studies, determined by Regazzoni, Blesa and Marato (1983) suggest the following:

1. At a given pH, zirconia ( $ZrO_2$ ) has more neutral sites, has more X-OH, and forms fewer complexes with the major cations and anions in the solution than crystalline or amorphous iron oxides.
2. The zirconia also has more surface sites than crystalline iron oxides and thus probably has more capacity to adsorb trace contaminants.
3. Zirconia and amorphous zirconium adsorption would be less sensitive to increasing ionic strength and should thus show even greater selectivity than iron oxides for trace contaminant adsorption in high ionic strength solutions.

Blesa, Marato and Regazzoni (1984) measured the adsorption of boric acid ( $H_3BO_3$ ) onto magnetite and zirconia. The data suggest that boric acid adsorption actually occurs in the o plane, and maximum adsorption occurs for both magnetite and zirconia at pH 8.5 to 9.0. The zirconia's capacity for boric acid adsorption is 30 times greater than that of magnetite. The pH of maximum adsorption falls very near the pH where  $H_3BO_3$  hydrolyzes to form  $B(OH)_4^-$ . Adsorption in the o plane suggests a strong chemical bonding.

In summary, although few of the available data are directly germane to adsorption of trace radionuclides onto zirconium hydrous oxides, related data can be used to infer probable behavior. The following inferences are supported by the data that has been referenced. Actual experimentation is suggested to gather data to assess directly zirconium hydrous oxide adsorption properties and to corroborate these inferences. Corroboration of these inferences would validate the underlying surface complexation model.

Available data on hydrous and crystalline iron and zirconium oxide's adsorption properties suggest the following:

1. Zirconium oxides have a significantly larger adsorption capacity than iron oxides for anions at acidic pH values and for cations at basic pH values. The amount of Zr present in spent fuel (~20% by weight) is significant and could affect the release of radionuclides present

by sorption if converted to oxides. Note that Gray et al. (1984) placed oxidized Zircaloy coupons in some  $UO_2$ -salt brine leach tests to study the effects on solution concentrations. Uranium solution concentrations were the same in systems with or without Zircaloy coupons for experiments performed between 25° and 150°C. The inference could be made that the oxidized Zircaloy is showing no effect (i.e., adsorption).

There are two possible explanations why Gray et al. (1984) do not show that oxidized Zircaloy is a significant adsorbent in the cited tests. First, because the system is a salt brine, it is possible that the high salt concentrations are out-competing uranium (probably  $UO_2^{2+}$ ) for adsorption sites. Second, no pH values are given; if the leach tests are slightly acidic, little cationic adsorption would be expected because the oxide surface would exhibit a net positive charge. Barner et al. (1985) reported coupon tests using iron and Zircaloy in brines and deionized water. In deionized water, iron sorbed more uranium than oxidized Zircaloy. Because iron has a higher  $pH_{pZC}$  than Zircaloy, the possibility of cation sorption onto Zircaloy in brines is suggested, yet only iron sorption of uranium was observed in brines. Values for pH were given in Barner et al. (1985) and ranged from 4.4 to 7.5. Thus, it appears that high salt concentration competition is excluding uranium from adsorption sites on the oxidized Zircaloy in the near-neutral pH tests. However, inasmuch as these relative sorptions of U observed in deionized water were not accompanied by quantitative surface characterization data, no conclusions can be reached regarding relative U-sorptive capacities for equivalent iron and zirconium oxide surface areas.

2. Kraus et al. (1958) suggest that adsorption increases with temperature from 27° to 150°C.
3. Polyvalent oxyanions, such as  $CO_3^{2-}$ ,  $PO_4^{2-}$ ,  $SO_4^{2-}$ ,  $CrO_4^{2-}$ ,  $SeO_4^{2-}$ , etc., show that adsorption is largest at pH values near their pKa. Thus, significant adsorption of  $CO_3^{2-}$  (pKa = 6.4),  $SeO_3^{2-}$  (pKa = 8.6),  $H_3BO_3$  (pKa = 9.2), and  $CrO_4^{2-}$  (pKa = 6.5) might be expected under probable

repository conditions. Technetium, iodide, iodate, fluoride, and molybdate anions are formed from strong acids with pKa values <4 and often less than 1. Thus, maximum adsorption of these anions would occur at very acidic pH values probably not relevant to the repository.

Radiolysis-induced acid formation could influence the corrosion products environment by creating acid conditions. If acid conditions prevail, the corrosion products would be more likely to adsorb anions, such as  $I^-$ ,  $IO_3^-$  and  $TcO_4^-$ . Oxides may then become more soluble, dissolve, and buffer the pH back toward neutral conditions. Thus, aside from weak acid anions, such as  $CO_3^{2-}$ , significant adsorption by zirconia of radioactive anionic contaminants, such as  $TcO_4^-$  and  $I^-$ , is not expected at probable repository conditions after loss of containment. However, hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), with  $pH_{pZC}$  values of pH 8.5 to 9.3, might adsorb significant amounts of anions at the expected repository pH values.

4. Cation adsorption properties of the iron and zirconium oxides are quite favorable in expected repository environments. The corrosion products should adsorb significant quantities of actinide, lanthanide, and other fission products that form predominantly cationic species, especially hydrolysis  $M(OH)_Z^{X-Z}$  species. The adsorption of trace cations onto metal oxides is quite strong at neutral to slightly alkaline pH values. Desorption of significant quantities might require acidification, thus the adsorption under neutral conditions might appear irreversible. Irreversibly adsorbed species would appear to be permanently removed from further transport.
5. Regazzoni, Blesa and Marato (1983) suggest that zirconium oxides' adsorption capacity for trace contaminants might remain high even in high-ionic-strength ground waters because the adsorbent forms relatively weaker complexes with the major cations and anions present compared to iron oxide adsorbents. Paterson and Rahman (1985) suggest that at constant pH, increasing the ionic strength of the solution should increase the adsorption capacity of zirconium

dioxide. Of course, increasing capacity does not mean increased trace contaminant adsorption because more sites could be filled by the higher concentration macroconstituents, as appears to be suggested by the results of Barner et al. (1985) discussed above.

#### 4.2 HIGHLY SOLUBLE RADIONUCLIDES AS SPECIAL CASES

Portions of the following relatively long-lived radionuclides (i.e.,  $^{79}\text{Se}$ ,  $^{129}\text{I}$ ,  $^{99}\text{Tc}$ ,  $^{14}\text{C}$ ,  $^{135}\text{Cs}$ ,  $^{137}\text{Cs}$ ) are either known to or are expected to leach from spent fuel very rapidly and appear not to form relatively insoluble compounds. Further, the dominant species of  $^{129}\text{I}$ ,  $^{14}\text{C}$ ,  $^{79}\text{Se}$ , and  $^{99}\text{Tc}$  (under oxidizing conditions) in expected repository conditions are anionic. In general, for most geologic materials under expected repository conditions, adsorption of anions is minimal. Thus, these elements that show rapid leaching, high solubility, and minimal adsorption represent problem elements from the performance assessment standpoint. It must be added, however, that from 1 to 10% of such highly soluble fission products are likely to be readily accessible for release to ground water; the remaining 90 to 99% are associated with the  $\text{UO}_2$  matrix of the spent fuel or the cladding (see Sections 4.1.3 and 4.1.4). Also, if mass transfer resistance into the host rock is extremely high, these nuclides may not be rapidly released. The geochemistry of each of these long-lived isotopes, excepting  $^{79}\text{Se}$ , is briefly described, and available data on retardation in geologic media are reviewed. Also, note that large portions of the radionuclides are bound within the spent-fuel matrix and likely leach congruently with the  $\text{UO}_2$ . Thus, it is a fraction of total inventory (1 to 10%) that is of most concern.

As mentioned in Section 4.1, Canadian researchers (e.g., Johnson, Garisto and Stroes-Gascoyne 1985) have developed a conceptual spent-fuel leach model that differentiates three regions: a) the gap between the fuel and the cladding, b) the grain boundary (cracks, etc.) between the spent-fuel fragments, and c) the intact  $\text{UO}_2$  matrix.

Volatile elements, such as Se, Cs, I, and perhaps C and Tc, migrate toward the gap and grain boundaries during irradiation at the high temperatures found in reactor cores. The larger the fuel "burn up" and the higher the operating

temperature the more reordering of volatiles and cracking of the  $UO_2$  grains is expected. Because CANDU fuel is operated at higher temperatures than LWR fuel, although at lower EOL burnup (see Section 3.0), the reordering and concentration of volatiles in the gap and grain boundary cracks observed in Canadian fuel likely overestimate what may be expected in LWR fuel. Johnson, Garisto and Stroes-Gascoyne (1985) note that the percent of the total volatile elements inventory expected to mobilize is similar to the percentage of fission gases (e.g., Xe) released during operation of the reactor. The Canadian fuels regularly release several percent whereas typical U.S. LWR fuels release a few tenths of a percent. This difference, roughly a factor of 10, suggests that only 1% of the volatiles in LWR should be rapidly mobilized. Johnson, Garisto and Stroes-Gascoyne (1985) estimate a maximum of 10% of the Cs inventory in CANDU fuel is readily mobilized from the gap and grain boundary regions.

In the following discussion, the reader should consider that the reported experimental data often reflect different concepts. Some researchers have emphasized measuring total concentrations of radionuclides in unfiltered and filtered solutions. Other researchers have also evaluated the amount of radionuclides that "plate-out", precipitate, or adsorb on the leach container walls. The two approaches can give very different results because for some nuclides, especially actinides, >90% of the total mass removed from spent fuel is found in the "plate-out" fraction. If one considers only solution-phase and filterable "colloidal" fractions as the mass leached, leach rates are much smaller. On the other hand, if the plate-out represents solubility-controlled precipitation and the true flux of radionuclides away from the waste-form into the migrating ground water, the solution portion may represent a more realistic source term. It must be added, however, that potential resistance to mass transfer into the host rock could also act to control radionuclide release from the spent fuel.

#### 4.2.1 Cesium

As mentioned earlier (see Section 4.1), a percentage of the Cs in spent fuel leaches very rapidly on contact with water. Forsyth, Svanberg and Werme (1984) found Cs leach rates  $10^2$  to  $10^3$  times higher for at least the first year than U from Swedish spent fuel leached in granite ground water. Werme and

Forsyth (1985) discuss further Swedish spent-fuel leach tests using distilled water and synthetic granite ground water for up to 900 days; they report only the fraction in the aqueous phase. Apparent leach rates for Cs show a very rapid initial release of Cs (~1% of the total inventory) followed by a slow release. Even after 2 years, the apparent accumulative percentage leached per day for Cs is larger than Sr by a factor of 3 to 4. Yet, if you look at the "incremental" leach rate of their data and the slope of their accumulative fractions leached versus days, there is little difference. That is, the leach rates from one sampling time to the next show similar rates after the initial Cs flush.

After 2 years of leaching, approximately 1% Cs, 0.08% Sr, 0.02% U, 0.001% Pu, and 0.0008% Cm have been removed based on analyses of the solution. If considerable plate-out occurred, the actinide values would not represent true leach rates. In fact, it would appear that the difference in Sr and U suggests that some uranium phase may be removing U from solution after release. Alternatively, a portion ~0.06% of the total inventory of Sr may be in the gap or grain boundaries. The lower accumulative release of Pu and Cm relative to uranium suggests that they are controlled by a lower solubility compound than uranium or that some uranium is more leachable than the bulk matrix.

Johnson, Garisto and Stroes-Gascoyne (1985) suggest that the observed release (dubbed the instantaneous release period) represents Cs that has migrated to the gap between the spent fuel and cladding. Even after this short period of high release, Cs leach rates remain three to five times higher than other radionuclides for several months. For one high-burnup CANDU fuel, the Cs leach rate remained two orders of magnitude higher than that of U after 7 years. This longer-term elevated leach rate is hypothesized to include material in the gap and in the grain boundaries. The combined gap and grain boundary inventory is estimated to average 2.2% (with a maximum estimate of 10%) of the total spent-fuel inventory for volatile elements, such as Cs, I, and Se. The remaining 90 to 98% or more of these elements are contained within the UO<sub>2</sub> grain and should leach congruently with the uranium (see Section 4.0). Johnson, Garisto and Stroes-Gascoyne (1985) include plate-out material in their calculations.

Wilson and Oversby (1985) discuss leach studies of spent fuel from two U.S. PWR reactors. The leachants used were deionized water and J-13 tuff ground water. The experiments were performed in the presence of hot cell air at room temperature. Data for the first 223 days are reported for bare fuel fragments in split cladding hulls, clad rods with a 2.5-cm-long slit, 150- $\mu\text{m}$ -wide clad rods with two 200- $\mu\text{m}$  holes in the cladding, and undefected rods. Each test vessel contained 250 mL of leachant and between 43 and 80 g of spent fuel. Periodically 10 to 25 mL of leachate were removed and replaced with fresh leachant. Quartz rods were present and periodically removed and stripped. At the end of the test, the quartz rods, fuel, and apparatus were rinsed. Finally, at the completion of the test, the test apparatus was stripped with 8 M  $\text{HNO}_3$ . Selected leachate samples were also filtered through 0.4- $\mu\text{m}$  and 0.0018- $\mu\text{m}$  (18A) membranes to distinguish colloidal material.

Table 4.10 summarizes the fraction of the total inventory (based on ORIGEN-2 calculations) that leached from the bare fuel sample after 223 days. The fraction leached includes mass found in solution, suspended as colloids and plated-out within the leach container. Table 4.11 gives similar data for the intact fuel pin with the slit in the cladding.

Table 4.12 shows the percentages of the leached material for the bare spent fuel-tuff ground water tests that were found a) in solution (dissolved and colloidal), b) weakly bound to the sample surface, or c) acid strippable from the leach containers.

Tables 4.10 and 4.11 show that, excepting cesium, these radionuclides show greater release when deionized water is used as the leachant. Solids characterization of the bare fuel after leaching shows that deionized water attacked the grain boundaries more significantly than did the tuff ground water, perhaps because the resultant pH was more acid. They also suggest that the leaching of the actinides U, Pu, Am, Cm, and Np is congruent. In ground water, the leaching of cesium is about 100 times greater than the actinides for the bare fuel and nearly 10,000 times greater for the slit defect samples. In fact, almost as much cesium is leached from the slit defect sample as the bare sample, suggesting that the cesium source was predominantly the gap between the cladding and fuel and nearby grain boundary (cracks) area. Using the aforementioned

TABLE 4.10. Fraction of Total Inventory Leached from Bare Spent Fuel

<u>Nuclide</u>	<u>Tuff Ground Water</u>	<u>Deionized Water</u>
<sup>137</sup> Cs	683 x 10 <sup>-5</sup>	230 x 10 <sup>-5</sup>
<sup>129</sup> I	7.5 x 10 <sup>-5</sup> (a)	---
<sup>99</sup> Tc	20.2 x 10 <sup>-5</sup>	152 x 10 <sup>-5</sup>
U	5.42 x 10 <sup>-5</sup>	21.2 x 10 <sup>-5</sup>
<sup>239,240</sup> Pu	7.04 x 10 <sup>-5</sup>	22.4 x 10 <sup>-5</sup>
<sup>241</sup> Am	7.76 x 10 <sup>-5</sup>	17.2 x 10 <sup>-5</sup>
<sup>244</sup> Cm	6.54 x 10 <sup>-5</sup>	21.5 x 10 <sup>-5</sup>
<sup>237</sup> Np	~6.4 x 10 <sup>-5</sup>	~18 x 10 <sup>-5</sup>

(a) Solution analyses only - no plate-out included.

TABLE 4.11. Fraction of Total Inventory Leached from "Slit Defect" Spent Fuel

<u>Nuclide</u>	<u>Tuff Ground Water</u>	<u>Deionized Water</u>
<sup>137</sup> Cs	567 x 10 <sup>-5</sup>	110 x 10 <sup>-5</sup>
<sup>129</sup> I	4.0 x 10 <sup>-5</sup> (a)	---
<sup>99</sup> Tc	2.46 x 10 <sup>-5</sup>	8.1 x 10 <sup>-5</sup>
U	0.044 x 10 <sup>-5</sup>	0.065 x 10 <sup>-5</sup>
<sup>239,240</sup> Pu	0.0082 x 10 <sup>-5</sup>	0.20 x 10 <sup>-5</sup>
<sup>241</sup> Am	0.0082 x 10 <sup>-5</sup>	0.15 x 10 <sup>-5</sup>
<sup>244</sup> Cm	0.0073 x 10 <sup>-5</sup>	0.35 x 10 <sup>-5</sup>
<sup>237</sup> Np	---	0.20 x 10 <sup>-5</sup>

(a) Solution analyses only - no plate-out included.

conceptual model and leach data versus time [shown in Wilson and Oversby (1985)], it appears <0.6% of the Cs inventory is released in the first 30 days of leaching and then the rate drops dramatically. This 0.6% agrees with estimates of <1.0% of the total Cs inventory in the gap.

TABLE 4.12. Percentage Distribution Among Solution, Waste Form Surface, and Container

	<u>Solution</u>	<u>Sample Rinse</u>	<u>Acid Strip of Container</u>
$^{137}\text{Cs}$	---	---	---
$^{129}\text{I}$	---	---	---
$^{99}\text{Tc}$	74.3	10.2	15.5
U	13.5	15.5	71.0
$^{239,240}\text{Pu}$	1.6	7.4	91.0
$^{241}\text{Am}$	0.7	7.3	92.0
$^{244}\text{Cm}$	2.3	6.7	91.0
$^{237}\text{Np}$	---	---	---

Ames and Rai (1978) and Rai and Serne (1978) have reviewed the geochemistry of Cs. In all known solid compounds and solution species, Cs occurs as a monovalent cation. Cesium has little, if any, tendency to form complexes in natural environments. Most common solid phases, hydroxides, oxides, chlorides, sulfates, nitrates, and carbonates of cesium are highly soluble and will not act as a solubility control under expected repository conditions. It is probable that given long time frames, Cs could substitute into clays, zeolites, and feldspars that contain alkali metals. Clays, zeolites, and perhaps feldspars probably form under relatively low temperatures (<150°C) and would incorporate some Cs, thus becoming capable of controlling the solution concentration. At high temperatures, the aluminosilicate pollucite ( $\text{Cs}_4\text{Al}_4\text{Si}_9\text{O}_{26} \cdot \text{H}_2\text{O}$ ) could form in a waste package environment but this is not considered likely in expected conditions with spent fuel as the waste form.

As there appears to be no solubility control for cesium in the expected waste package environment and because the solution chemistry of cesium shows the monocationic species  $\text{Cs}^+$  as the only expected species, adsorption would appear to be only viable retardation mechanism. A large amount of data has been collected on the cesium adsorption properties of soils, sediments, and rocks. Review articles include Ames and Rai (1978), Onishi et al. (1981), and Gee, Rai and Serne (1983). In general,  $\text{Cs}^+$  is adsorbed readily by most soils, sediments, and rocks.

The adsorption appears ion-exchange-like for many adsorbents. Mica-like minerals, such as illite, tend to "fix" Cs between sheets in the crystal structure (see Sawhney 1964; Tamura and Jacobs 1961). Cesium adsorption, similar to many exchangeable trace elements, shows a strong dependence on the solution ionic strength and composition. We expect the adsorption of Cs<sup>+</sup> in highly saline waters and brines to be significantly lower than adsorption from low-ionic-strength ground waters expected in basalt, tuff, and crystalline rock environments. This fact is corroborated by various laboratory experiments referenced in Table 4.13.

Using the distribution coefficient (K<sub>d</sub>) approach to quantifying radionuclide adsorption, the following values can be considered representative for candidate U.S. repository sites. These values have likely been superseded by recent site investigations that are in the process of being published; therefore, the values should be considered as generally applicable and representative but not necessarily the most defensible or most probable values to use in specific site assessments.

Table 4.13 shows that, except in the salt repository sites, significant adsorption (K<sub>d</sub> > 50) should occur. Cesium adsorption in nonsaline environments will most likely minimize the amount of Cs reaching the accessible environment to levels below concern.

#### 4.2.2 Technetium

Katayama, Bradley and Harvey (1980) found only a very slight increase in Tc concentration at the gap between the spent fuel and cladding when analyzing spent-fuel fragments, but since they also found only a slightly elevated concentration of Cs, the implications of finding only a slightly enriched surface on Tc leach rates from spent fuel are undeterminable. Johnson, Garisto and Stroes-Gascoyne (1985), however, definitely show a faster leach rate for Cs than U, and Wilson and Oversby (1985) show Tc release a factor of 3 greater than actinide release, while Cs release was 100 times the actinide release. Similarly, Barner et al. (1985) observed that Cs release was greater than Tc release over a 7- to 60-day period. Wilson and Oversby and Barner et al. used

TABLE 4.13. Representative Kd (mL/g) Values for Cs in Host Rocks<sup>(a)</sup>

<u>Host Rock</u>	<u>Kd (Cs)</u>
Tuff	
• devitrified	100 - 500
• zeolitized	500 - >1000
Basalt	
• fresh rock	100 - 500
• altered, weathered	200 - 500
Salt	
• quartz sediments	0 - 20
• clay-rich sediments	0 - 100
Granite	
• nonsaline waters	50 - 150

(a) See the following references: Ames and McGarrah 1980a,b; Ames, McGarrah and Walker 1981; Ames et al. 1982; Ames et al. 1983; Barney 1982; Salter, Ames and McGarrah 1981a,b; Guzowski et al. 1983; Erdal et al. 1980, Erdal, Daniels and Wolfsberg 1981; Erdal et al. 1981; Vine et al. 1980; Wolfsberg et al. 1979, 1980, 1982a,b; Daniels et al. 1982; Coles, Weed and Tewhey 1980; Dosch and Lynch 1978; Harwell et al. 1980; Relyea et al. 1978, 1979; Serne, Rai and Mason 1977; Allard, Kipatsi and Ryberg 1977; Andersson and Allard 1983; Andersson, Torstenfelt and Allard 1983; Eriksen 1983.

the same fuel as Katayama, Bradley and Harvey. The expectation is, therefore, that Tc will be preferentially located in the spent-fuel gap and/or grain boundaries and will be available for early rapid release upon containment failure.

Wilson and Oversby (1985) show that the fractional release of <sup>99</sup>Tc from spent fuel in contact with tuff ground water or deionized water after 223 days is about 4 to 7 times greater than U and other actinides but less than the cesium release. Further, the difference in the quantity leached from the bare spent fuel and the "split-defect" samples is much larger than for cesium. The split-defect data for Tc show a decrease of 10 to almost 20 times, whereas

cesium leach rates decreased only by a factor of 2. Perhaps this decrease suggests that Tc is found more in the grain boundary area than in the gap. When Tc is leached, three quarters of the Tc remains in the solution phase, compared to between 1 and 13% for actinides. Once leached, Tc seems to remain soluble in these tests, which were conducted in the presence of hot cell air. In all the leach tests reported, no more than 0.1% of the total Tc inventory was leached in the first 223 days.

Technetium is a redox-sensitive element that is readily soluble under oxidizing conditions but relatively insoluble under reducing conditions. Leached Tc could precipitate outside the waste package near field if reducing conditions occur there. As discussed in Section 2.0, the basalt and granite and possibly salt repository environments will be reducing. Thus, even if radiolysis or waste emplacement creates oxidizing conditions within the container, reducing conditions could predominate outside this region.

Technetium exists in valence states from +7 to -1, but a clear understanding and accurate thermochemical data for many compounds and probable aqueous species are lacking. Oxidized Tc(+7) compounds and species are most thoroughly characterized. Two likely solubility-controlling phases,  $TcO_2(c)$  and hydrated  $TcO_2(am)$ , are not sufficiently characterized to allow the calculation of thermochemical data ( $\Delta G_f^\circ$ ,  $\Delta H_f^\circ$ ,  $S^\circ$ ) necessary to fabricate predominance diagrams and solubility values. An estimate for the  $\Delta G_f^\circ$  of  $TcO_2 \cdot 2H_2O(am)$  is provided in Rard (1983).

Many solid pertechnetates (e.g.,  $KTcO_4$ ,  $NaTcO_4$ ) and sulfides (e.g.,  $TcS_2$ ,  $Tc_2S_7$ ) are also well characterized. The former are very soluble, while the latter are only stable in highly reducing environments. It is, therefore, difficult to quantify the solubility of Tc in geologic environments other than to say qualitatively that technetium is very soluble under oxidizing conditions and rather insoluble under strongly reducing conditions. Most researchers conclude that reduction of the solution species  $TcO_4^-$  forms aqueous Tc(V) or Tc(IV) species that require consumption of two and three electrons, respectively. In acid solution, reduction of  $TcO_4^-$  leads generally to Tc(IV) species that precipitate to  $TcO_2 \cdot 2H_2O(am)$  or a similar compound. The actual aqueous species present (at pH >2.7) are likely  $TcO(OH)_2^\circ$  or the dimer  $[TcO(OH)_2^\circ]_2$ . In alkaline

solutions, reduction of  $TcO_4^-$  is thought to proceed to a Tc(V) species ( $TcO_4^{3-}$ ) and perhaps the Tc(IV) species ( $TcO_3^{2-}$ ).

The key issue for determining the migration of Tc from the waste package is the redox state of the environment directly in contact with the breached spent fuel and the redox state near the outside perimeter of the waste package. If the redox state at the spent-fuel surface is oxidizing, Tc release from the gap and grain boundaries may be as rapid as that observed for Cs. If the outer package has a more reduced redox condition, the Tc concentration may become solubility limited. At room temperature, Bondietti and Francis (1979) and Meyer, Arnold and Case (1984) found that fresh basalt rock appeared capable of reducing  $TcO_4^-$  in ground waters such that Tc retardation via precipitation or adsorption was greatly increased. Bondietti and Francis (1979) found similar decreases in Tc solution concentration when granite rocks were immersed in ground water laden with  $TcO_4^-$  in an  $N_2$ -controlled atmosphere. The Tc was brought back into solution only by addition of oxidants. Adding competing ions to the system did not increase Tc solution concentrations as one might expect if adsorption processes originally caused the Tc removal. Vandergraaf, Ticknor and George (1984) found Tc adsorption under anoxic conditions occurred not on the ferrous minerals within granite, but on iron-oxide coatings in granite microfractures. Other ferrous-iron-bearing minerals (biotite, olivine, pyroxene, hornblende, and magnetite) also adsorb Tc under anoxic conditions.

The adsorption properties of technetium onto soils, sediments, and rocks are reviewed in Ames and Rai (1978) and Onishi et al. (1981). In general, only insignificant amounts of Tc adsorb onto geologic media under oxidizing conditions. Significant adsorption is only observed for soils or sediments with high organic matter, and the retardation could actually result from a reduction/precipitation reaction rather than adsorption.

Experimenters have also studied Tc adsorption under anoxic conditions in controlled atmosphere chambers or by using reducing reagents added to the ground water. Much of the work has been performed on basalt rock and interbed sedimentary materials (see Salter, Ames and McGarrah 1981a,b; Barney 1981, 1982; Meyer et al. 1983; Meyer, Arnold and Case 1984, 1985; Kelmers et al. 1984a,b, 1985).

Some observations from these studies are that Tc adsorption is quite sensitive to the ground-water and rock compositions. Adsorption of Tc from synthetic ground waters is significantly lower than from simple NaCl solutions. When a rock specimen does show significant adsorption, the Tc appears to be bound to the rock surface in a reduced valence state. Further desorption off the rock is minimal, suggesting a precipitation process. Because the experimental results are quite variable and sensitive to the  $O_2$  content in the system and the pretreatment of the basalt (crushing in air versus argon, etc.), predicting the actual process that removes Tc from solution is difficult. The reduction of  $TcO_4^-$  entails consumption of at least two to three if not more electrons so the process may be quite complicated. Also, the reactivity of the surface of the rock appears to be a key parameter. If a thin oxidized layer is present at the rock surface, Tc reduction may be hindered.

Distribution coefficient values for Tc adsorption onto rocks and sediments of interest to proposed U.S. repository sites are listed in Table 4.14. As noted above, the  $K_d$  value is quite sensitive to the experimental conditions ( $O_2$  content) and rock surface condition.

As mentioned in Section 4.1.6, under slightly acidic conditions the hydrous oxides of zirconium and iron are expected to adsorb anions. Furthermore, as shown by Coles et al. (1985) the presence of iron (and by inference Zr) metal in a hydrothermal leach experiment lowers the solution concentration of Tc by three orders of magnitude compared to a hydrothermal leach test with only the waste form (PNL76-68 glass). Barner et al. (1985) observed similar behavior. The hypothesis is that the metal can reduce  $TcO_4^-$  to a lower valence state that forms insoluble compounds.

In conclusion, the fate of Tc in spent fuel seems to lie between Cs (most leachable) and the actinides (least leachable). At most, 0.1% was released from bare spent fuel in 223 days. Ample evidence indicates that under reducing conditions Tc can be immobilized, but under oxidizing conditions Tc appears to be very mobile. The ambient far field conditions at a basalt and perhaps granite repository should be reducing enough to sequester Tc. No data are available for Tc adsorption in a salt environment under reducing conditions.

TABLE 4.14. Representative Kd (mL/g) Values for Tc in Host Rocks<sup>(a)</sup>

<u>Host Rock</u>	<u>Oxidizing Conditions</u>	<u>Reducing Conditions</u>
Tuff		
• devitrified	0-1	2-3
• zeolitized	0-1	3-10
Basalt		
• fresh rock	0-2	3-20
• altered, weathered	0-3	0-90
Salt		
• quartz sediments	0	--
• clay-rich sediments	0	--
Granite		
• nonsaline waters	0-0.2	20

(a) See the following references: Ames and McGarrah 1980a,b; Ames, McGarrah and Walker 1981; Ames et al. 1982; Ames et al. 1983; Barney 1982; Salter, Ames and McGarrah 1981a,b; Guzowski et al. 1983; Erdal et al. 1980, Erdal, Daniels and Wolfsberg 1981; Erdal et al. 1981; Vine et al. 1980; Wolfsberg et al. 1979, 1980, 1982a,b; Daniels et al. 1982; Coles, Weed and Tewhey 1980; Dosch and Lynch 1978; Harwell et al. 1980; Relyea et al. 1978, 1979; Serne, Rai and Mason 1977; Allard, Kipatsi and Ryberg 1977; Andersson and Allard 1983; Andersson, Torstenfelt and Allard 1983; Eriksen 1983.

#### 4.2.3 Iodine

Spent-fuel leaching studies by Johnson, Garisto and Stroes-Gascoyne (1985), Wilson and Oversby (1985), and Wilson (1985) suggest that a portion of the I inventory is rapidly leached in a manner similar to Cs. Johnson, Garisto and Stroes-Gascoyne (1985) suggest that the rapid release represents release from the gap and grain boundary.

Interestingly, Wilson and Oversby (1985) (as shown in Tables 4.10 and 4.11) found that, for bare spent fuel, the percent leached in 223 days was no more than the amount for the actinides. Conversely, for the slit-defect samples, <sup>129</sup>I release was twice as high as Tc, 500 times higher than the actinides, and 100 times lower than Cs. The ratio of iodine release for bare

spent fuel versus slit defect spent fuel is about 2, similar to cesium. This finding suggests that the leachable iodine is found in the gap, but the quantity is much smaller than the relative amount of cesium found in the gap. At most, 0.008% of the total iodine inventory was leached in the first 223 days, provided the amount that plated-out was not significant (as it was not measured or included in these calculations).

The geochemistry of iodine is briefly reviewed in Ames and Rai (1978). In general, I is found in sedimentary rocks and sediments at low ppm concentrations, whereas in igneous and metamorphic rocks, I contents are 75 to 150 ppb. In soils and sediments, high iodide contents often correlate with high organic contents. Naturally occurring iodine minerals are found only in unusual environments and include marshite (CuI), iodargyrite (AgI), coccinite (HgI<sub>2</sub>), bellingerite [Cu(IO<sub>3</sub>)<sub>2</sub>], salesite [CuIO<sub>3</sub>(OH)], and lautarite [Ca(IO<sub>3</sub>)<sub>2</sub>]. None of these minerals are expected to form under probable repository/near field conditions, and thus there are no likely candidate solubility controlling solids. The Swedish KBS staff has also come to this conclusion and assumes that when spent-fuel containment is lost, the iodine inventory is immediately available for transport.

Brown and Grutzeck (1985), Burger, Scheele and Weimers (1981), Clark (1977), Morgan et al. (1979), and Barnes et al. (1982) discuss the stability and leachability of various cementitious and iodine-bearing minerals that can be generated via planned reprocessing of the waste stream. These reports would be useful should investigators decide to explore iodine-sorbing waste package alternatives.

The aqueous speciation distribution of iodine is not clearly known. Pourbaix (1966) suggests that the species I<sup>-</sup> (iodide) predominates over the entire pH range of natural waters and at all but the most oxidized redox states. Sugawara and Terada (1958) and Liss, Herring and Goldberg (1973) suggest that the IO<sub>3</sub><sup>-</sup> (iodate) species predominates in certain seawater regimes. As discussed in the next several paragraphs, the sorption behavior of these two species differ such that it is important to determine which species actually is present in waste package environments and in the far field environments around

a deep geologic repository. At present, it is unclear which form,  $I^-$  or  $IO_3^-$ , will predominate in deep geologic repositories, and we suggest that this issue be addressed.

The adsorption of iodine species on soils, sediments, and rocks is reviewed in Ames and Rai (1978) and Onishi et al. (1981). In general, iodide ( $I^-$ ) adsorbs only weakly onto soils and sediments, except for a few soils with high organic content. Goldberg et al. (1962) measured a  $K_d(I)$  value of 1.1 mL/g for  $I^-$  adsorption onto Rainier tuff from a simulated ground water.

Allard et al. (1980) performed batch tests on iodide using numerous sulfide minerals, AgCl, numerous metal oxides and silicate minerals, and both a synthetic ground water and 4 M NaCl. The experiments were run from pH 4 to about pH 9. Lead, copper, and mercury sulfides as well as silver chloride adsorbed iodide readily at all pH values from synthetic ground water --  $K_d(I) = 10$  to 100 mL/g. Adsorption onto these minerals from 4 M NaCl was less --  $K_d(I) = 2$  to 20 mL/g -- perhaps reflecting the increased mass of I present as an impurity in the NaCl. Iron, aluminum, and hydroxides adsorb some  $I^-$  --  $K_d(I) = 10$  to 50 mL/g at neutral pH values. At more acidic conditions, adsorption increased as would be expected for hydrous oxide adsorption of anions. Little if any decrease occurred in adsorption from 4 M NaCl. Lead hydroxide in neutral synthetic ground water adsorbed I strongly --  $K_d = 1000$  mL/g. Silicates, such as olivine, serpentine, attapulgite, halloysite, and montmorillonite, adsorbed I from both solutions with a  $K_d(I) = 5$  to 20 mL/g. Adsorption tended to decrease as pH increased. Allard et al. (1980) suggest that copper or lead containers may be beneficial to  $I^-$  adsorption should the waste form lose containment. Although Allard et al.'s (1980) data suggest  $I^-$  might be adsorbed by minerals commonly found in granite rock, iodide was found to move with minimal retardation in a field experiment in granite (Landstrom et al. 1978).

Whitehead (1973, 1974a,b) discuss the sorption properties of iodide ( $I^-$ ) and iodate ( $IO_3^-$ ) onto English soils and pure minerals. Iodide is adsorbed only by soil organic matter and aluminum and iron oxides (under acidic conditions). Iodate is more strongly adsorbed by aluminum and iron oxides/hydroxides.

Recently, Couture and Seitz (1983) reported on the adsorption of iodide, iodate, and periodate ( $\text{IO}_4^-$ ). Solid adsorbents used included hematite ( $\text{Fe}_2\text{O}_3$ ), kaolinite clay, and pelagic red clay (actually a mixture of clay, iron oxides, organic matter, and other phases) from the Pacific Ocean with both hematite and goethite ( $\text{FeOOH}$ ) present (total Fe content 4.3% as  $\text{Fe}_2\text{O}_3$ ). Hematite (with a  $\text{pH}_{\text{pzc}} = 8.5$  to 9.3) readily adsorbed (>99.9%)  $\text{IO}_3^-$  from a 0.001 M  $\text{NaHCO}_3$  solution at pH values 6.7 to 7.0. Iodide adsorption under the same conditions was less (30%, equivalent  $\text{Kd}(\text{I}) \sim 0.8$ ). For kaolinite,  $\text{IO}_3^-$  adsorption was 20 to 28%,  $\text{Kd}(\text{IO}_3^-) \sim 1.6$  mL/g, and  $\text{I}^-$  adsorption was minimal, <5%.

Additional experiments in acetate buffer solutions (0.1 M  $\text{CH}_3\text{COOH}$  to 0.1 M  $\text{CH}_3\text{COONa}$ ) with variable pH values of 2.9 to 8.7 show that adsorption of periodate and iodate onto hematite decreases as pH increases, as expected for oxide surfaces (see triple-layer conceptual model description in Section 4.1.6). At pH 5.8, the  $\text{Kd}$  has dropped to 20 mL/g and at pH 8.7 the iodate  $\text{Kd}$  is only 0.6 mL/g.

Hematite placed in seawater adsorbs iodate ( $\text{Kd} \sim 30$  mL/g) about as well as it does from acetate buffer solutions at an equivalent pH value. Pelagic red clay adsorbs about the same amount of iodate as hematite does from seawater at various pH values. Thus, even though the "red clay" is only 4.3% iron oxide, it appears as efficient as pure iron oxide in adsorbing  $\text{IO}_3^-$ .

It would be interesting to conduct iodine adsorption studies with other zirconium and iron oxides and hydroxides that have lower  $\text{pH}_{\text{pzc}}$  values to see whether significant  $\text{IO}_3^-$  adsorption occurs in the pH range 6 to 8. Note that Couture and Seitz's (1983) data show a rapidly decreasing  $\text{Kd}$  value with increasing pH for  $\text{IO}_3^-$  adsorption onto hematite in the pH range 6 to 9. A key point presented by Couture and Seitz is that past adsorption studies that make no attempt to define iodine speciation must be viewed carefully because  $\text{IO}_3^-$  and  $\text{I}^-$  adsorb differently. Therefore, identifying which species is present in a test is important.

Despite the potential for some iodine adsorption onto selected pure minerals, rocks, sediments, and soils, most researchers performing work on repository-relevant materials have concluded that iodine adsorption is insignificant and have recommended that the range  $\text{Kd}(\text{I}) = 0$  to 2 mL/g be used in far field

transport calculations. Table 4.15 lists typical values used in high-level waste performance assessments and references.

#### 4.2.4 Carbon-14

Carbon-14 is an activation product formed mainly by the following two reactions:  $^{14}\text{N}(n,p) \rightarrow ^{14}\text{C}$  and  $^{17}\text{O}(n,\alpha) \rightarrow ^{14}\text{C}$ . The former equation is most important for LWR. Therefore, a key to estimating the production of carbon-14

TABLE 4.15. Representative Kd (mL/g) Values for I in Host Rocks(a)

<u>Host Rock</u>	<u>Kd(I)</u>
Tuff	
• devitrified	0
• zeolitized	0
Basalt	
• fresh rock	0
• altered, weathered	0-2
Salt	
• quartz sediments	0
• clay-rich sediments	0
Granite	
• nonsaline waters	0

(a) See the following references: Ames and McGarrah 1980a,b; Ames, McGarrah and Walker 1981; Ames et al. 1982; Ames et al. 1983; Barney 1982; Salter, Ames and McGarrah 1981a,b; Guzowski et al. 1983; Erdal et al. 1980; Erdal, Daniels and Wolfsberg 1981; Erdal et al. 1981; Vine et al. 1980; Wolfsberg et al. 1979, 1980, 1982a,b; Daniels et al. 1982; Coles, Weed and Tewhey 1980; Dosch and Lynch 1978; Harwell et al. 1980; Relyea et al. 1978, 1979; Serne, Rai and Mason 1977; Allard, Kipatsi and Ryberg 1977; Andersson and Allard 1983; Andersson, Torstenfelt and Allard 1983; Eriksen 1983.

is knowledge of the nitrogen content (as an impurity) in the UO<sub>2</sub> fuel, cladding and assembly hardware, and cooling water. Numerous reports are available that describe calculations performed to estimate the <sup>14</sup>C production in LWRs (see Braun et al. 1983; Bush 1984; Croff and Alexander 1980; Davis 1977; NCRP 1985).

The National Council on Radiation Protection and Measurements (NCRP 1985) discussion presents <sup>14</sup>C production calculations in terms of Ci/GW(e)y (curies of <sup>14</sup>C produced/gigawatt electrical years power production). Table 4.16 summarizes their findings for BWR and PWR reactors using an average burnup value.

In general, only the <sup>14</sup>C associated with the fuel and hardware should be of importance for geologic disposal options, although adsorption of <sup>14</sup>C from the cooling water onto the cladding/hardware surfaces cannot be totally discounted. Van Konynenburg et al. (1985) report similar data for the fuel and hardware but use Ci/MTU units (curies of <sup>14</sup>C produced/metric ton of uranium in the fuel assembly); they also report the data shown in Table 4.17 (Barner 1985). Recall that all of the values discussed represent calculations rather than actual measurements.

Einzigler and Fish (1982) and Barner (1984a,b) report on the fission gases released from spent-fuel rods when breaching the cladding before dismantling the rods to perform detailed analyses. The amount of CO<sub>2</sub> gas removed when breaching the cladding and collecting all offgas in a vacuum was less than 0.01% mole fraction. Gases released were He (98%), Xe (1%), Kr (0.1%), Ar (0.6%), H<sub>2</sub> (<0.01%), N<sub>2</sub> (0.06%), and O<sub>2</sub> (<0.01%). The total gas recovered was about 370 cm<sup>3</sup> at STP out of a total 1920 cm<sup>3</sup> calculated as being produced. The release represents an instantaneous release of only 0.19%. If we assume the <sup>14</sup>CO<sub>2</sub> content was 0.01%, then the 370 cm<sup>3</sup> at STP would yield 1.65 x 10<sup>-6</sup> moles or 2.31 x 10<sup>-5</sup> g of <sup>14</sup>C, which equates to 0.10 mCi. This quantity is a few percent of the total <sup>14</sup>C activity calculated to be present in the rod.

Recently, Van Konynenburg et al. (1985) measured the release of <sup>14</sup>C from a spent-fuel assembly placed in an air atmosphere and temperature elevated up to 260° to 275°C. Gas samples were taken periodically by opening small vacuumed sample bottles that were connected to the main chamber. Chemical and radio-metric analyses of the gases suggest that up to 1.5 mCi <sup>14</sup>C as CO<sub>2</sub> could be removed from the exterior surfaces of the rods (from the cladding) and assembly

TABLE 4.16.  $^{14}\text{C}$  Production for Various Reactor Components [Ci/GW(e)yr]

<u>Reactor Components</u>	<u>BWR</u>	<u>PWR</u>
Fuel	20	20
Hardware	52 to 72	30 to 43
Cooling Water	6	10 to 15
TOTAL	78 to 98	60 to 78

TABLE 4.17.  $^{14}\text{C}$  Production in Spent Nuclear Fuel (Ci/MTU)

<u>Fuel Component</u>	<u>BWR</u>	<u>PWR</u>
Fuel	0.58	0.60
Hardware	1.08	0.95

hardware. Furthermore, the authors suggest that a later sample releasing an additional 0.3 mCi of  $^{14}\text{C}$  might represent a breach of one fuel rod because  $^{85}\text{Kr}$  was also found in the gas sample. The quantity, 0.3 mCi  $^{14}\text{C}$ , could also partly consist of additional  $^{14}\text{C}$  released from the external cladding and hardware surfaces, or conversely some  $^{14}\text{C}$  could be adsorbed or exchanged with C in the sample bottle and the larger container in which the whole experiment was performed. Therefore, it is not possible to quantify whether the 0.3 mCi represents the total amount of  $^{14}\text{C}$  that is expected to be rapidly released as gaseous  $\text{CO}_2$  per fuel rod. It is interesting that this value, 0.3 mCi, is similar to the 0.1 mCi maximum release calculated from Barner's (1985) data. For comparison, the overall 225-fuel-rod assembly used in the experiment was calculated to contain 690 mCi of  $^{14}\text{C}$ . If the release (0.3 mCi) represents one fuel rod, then about 10% of the inventory in one rod was "instantly" released by the breach. The fact that 1.5 mCi of  $^{14}\text{C}$  appears to be released from the external surface before any breach needs further consideration.

The  $^{14}\text{C}$  released as  $\text{CO}_2$  gas or perhaps leached from spent fuel that is breached by ground water (likely species  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ), probably will react in the geosphere identically to stable carbon or bomb fallout  $^{14}\text{C}$ . The geochemistry of carbon is discussed in numerous textbooks, such as Garrells and Christ

(1965) and Stumm and Morgan (1981). In general, inorganic carbon species of interest include  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  and solid compounds, such as  $\text{CaCO}_3$  (calcite, aragonite) and  $(\text{Ca},\text{Mg})\text{CO}_3$  (dolomite).

Carbon also enters the biosphere as the major building block of all plant and animal tissue. The National Council on Radiation Protection and Measurements (1985) reviews the distribution of  $^{14}\text{C}$  in the biosphere: the global carbon cycle. Existing  $^{14}\text{C}$  in the natural environment is distributed as shown in Table 4.18.

The data in Table 4.18 represent "active" carbon that is continually exchanging from one reservoir to another. The ultimate fate of stable carbon is to enter deep ocean sediments. The  $^{14}\text{C}$  of deep ocean sediments (the ultimate carbon sink) is negligible because of decay.

Carbon-14 is thus expected to mimic the fate of natural carbon in the geosphere. In almost all nuclear waste transport predictions,  $^{14}\text{C}$  is assumed to move as a water-coincident tracer (i.e.,  $K_d = 0$ ). This assumption is usually made because of the lack of actual data and the fact that the predominant aqueous species,  $\text{HCO}_3^-$ , is an anion and thus should not readily adsorb. The use of  $^{14}\text{C}$  to age-date water also leads to its being considered a nonsorbing constituent. After careful analyses of the  $^{14}\text{C}$  age-dating literature, one finds

TABLE 4.18. Distribution of  $^{14}\text{C}$  in Biosphere

<u>Biosphere Component</u>	<u><math>^{14}\text{C}</math> (MCi)</u>	<u>Percent Total</u>
Atmosphere	4.0	~2
Ocean		
inorganic ions	210.0	85
biota	0.02	~0
detritus	5 to 15	~4
sediment	10.0	~4
Terrestrial		
biota	2 to 3	~1
soil humus	5 to 10	~3
Fresh Water		
inorganic ions	4.0	~2

several acknowledgments that  $^{14}\text{C}$  is not, strictly speaking, a water-coincident tracer. Both chemical processes (precipitation of carbonate minerals, isotopic exchange with natural carbon, incorporation into biological tissue) and physical processes (diffusion into rock matrix and neighboring aquitards) are shown to lower the  $^{14}\text{C}$  concentration in a plume. Some specific references discussing these processes include Wigley (1975), Fritz, Gale and Reardon (1979) and Sudicky and Frind (1981).

Most of these processes can lower actually observed  $^{14}\text{C}$  concentrations in a plume by a factor of at least two to three over the values expected for water-coincident tracers even after radioactive decay is considered. The data from the age-dating literature are not readily converted to Kd type data so it is difficult to develop quantitative estimates of  $^{14}\text{C}$  retardation. The physical process of diffusion into neighboring media, matrix pore spaces in crystalline rock, or dead-end pore spaces, can be quantified using simple transport models [e.g., Sudicky and Frind (1981) and Neretnieks (1980)]. Also, note that these physical processes lower the concentrations of all nuclides, not just  $^{14}\text{C}$ .

Allard, Torstenfelt and Andersson (1981) and Hietanen, Jaakkola and Miettinen (1985) have performed batch and column adsorption tests on concrete, sands, granite, montmorillonite, calcite, and glacial moraine sediments using granitic ground waters traced with  $^{14}\text{C}$  as  $\text{NaHCO}_3$ . The highly alkaline, calcareous materials--cement, calcite, and concrete--showed strong  $^{14}\text{C}$  adsorption Kd values of ~100 to 10,000 mL/g. The probable retardation mechanism is not adsorption, but actually precipitation of calcium carbonate bearing solids. Granite rock, montmorillonite, and crushed aggregate rock showed very low Kd values (0 to 2 mL/g). Glacial moraine sediment showed small Kd values (~2 mL/g). Column experiments with glacial moraine sediments and calcite showed a little  $^{14}\text{C}$  retention but less than that observed for the same materials under batch conditions.

The retardation increased as the flow rate in the column decreased, suggesting the reaction was slower than usual surface adsorption reactions. Allard, Torstenfelt and Andersson (1981) conclude that alkaline solids containing high concentrations of calcium can retain  $^{14}\text{C}$ . The observed retardation

requires longer residence times (low flow rates) than normal laboratory adsorption tests. Such low flow rates are expected in the repository environments and calcite (a good  $^{14}\text{C}$  scavenger) is a common fracture-filling mineral in crystalline rock environments.

On the other hand, Andrews and Pearson (1984) compare a computer modeling prediction with the observed  $^{14}\text{C}$  concentrations in the Carrizo aquifer of South Texas. Using a simple, one-dimensional advective/dispersive ground-water model, they found that  $^{14}\text{C}$  concentrations are best predicted assuming a  $K_d(\text{C}) = 0$ . The computer predictions using a  $K_d = 0$  fit the  $^{14}\text{C}$  concentration profile from the recharge zone downgradient for at least 60 km. Age-dating suggests it takes 30,000 years for the water to travel this distance. Using even a small retardation  $K_d$  of 0.1 or 0.5 mL/g gives dramatically poorer predictions. Thus, in this environment, it appears that  $^{14}\text{C}$  is not retarded. One can speculate that this occurs because the aquifer sediments and ground water are not sufficiently calcareous to allow calcite precipitation or  $^{14}\text{C}$  exchange with stable carbon in carbonate minerals.

Geochemical knowledge/predictions on the existence of or potential for formation of carbonate minerals downgradient from the waste package appear to be a key in estimating the fate of  $^{14}\text{C}$  in spent fuel. It is interesting to note that most carbonate minerals are less soluble at higher temperatures (retrograde solubility). Thus, elevated temperatures in the near field might promote sequestration of  $^{14}\text{C}$  by formation of carbonate minerals. Conversely, as the repository cools, carbonate minerals will be less stable and some  $^{14}\text{C}$  will be released.

#### 4.3 CURRENT STATUS OF PERFORMANCE MODELS FOR RELEASE

##### 4.3.1 U.S. Repository Projects

###### 4.3.1.1 Basalt Waste Isolation Project (BWIP)

The analysis methodology adopted by BWIP is described by Sagar, Eslinger and Baca (1985) and USDOE (1986a) and involves two basic calculations: 1) the distribution (versus time after closure) of failures for the large (i.e., >20,000) population of waste package containers and 2) the release rate from

single waste packages after their containers have failed. The results from these two calculations are then integrated to provide the time-dependant release from all waste packages in the repository. The failure distribution as well as release rates are treated stochastically by random sampling of variable input parameters, such as corrosion rate or solubility. Within the stated uncertainties and assumptions of this analysis, it was demonstrated that spent fuel in the current waste package system is adequate to fully meet the NRC fractional release rate criterion for all radionuclides.

The individual containers in the repository are subjected to certain conditions that lead to eventual degradation and failure. The enclosed waste then becomes available for dissolution and radionuclides are thus released. The containers will differ in age of enclosed waste, thermal and chemical exposure history and perhaps variations associated with fabrication. Ideally, the distribution of these conditions over the container population would be provided, along with relationships that describe failure time as a function of these conditions. However, the required information on repository conditions and the effect on container lifetime is currently not available. For the purposes of preliminary calculations, which appear in the Environmental Assessment (USDOE 1986a), variations in experimentally determined parameters that define container corrosion are used in lieu of specific information about variations between individual waste packages.

The waste package failure distribution is based on empirical corrosion models applicable to either the air/steam environment or the saturated aqueous environment. Up to three parameters are used in empirical corrosion rate equations. The experimental variation in these fitted parameters is assumed to define the range of variability for these parameters in the stochastic model that predicts the failure distribution in the repository. In other words, variations between laboratory specimens (i.e., corrosion coupons) are assumed to represent variations in actual waste packages. This approach is recognized by its developers as simplistic; however, as more extensive data about corrosion and environmental variations become available, the model will be refined.

Release rates from failed waste packages are calculated based on diffusion and convection near the waste package. The code CHAINT-MC is used, which

solves multidimensional mass transport equations using finite element methods (Baca et al. 1984). In an analysis described by Sagar, Eslinger and Baca (1985), molecular diffusion through the packing material and host rock was identified as the factor controlling movement of radionuclides away from the waste package. To account for variations and uncertainty in factors influencing transport, several governing parameters are defined as random variables. Key input parameters that are varied for each radionuclide are the solubilities and adsorption coefficients for the packing. Uniform, loguniform, and log-normal probability distributions for solubility and adsorption were used in the report by Sagar, Eslinger and Baca (1985).

In the predictions of waste package subsystem performance as described in the Environmental Assessment (USDOE 1986a), several assumptions regarding the container and waste form were made. Containers were considered to be failed after 7.5 cm of container wall was depleted, rather than the design thickness of 8.3 cm. The remaining thickness corresponds to the minimum yield strength of the container material. This portion of the remaining container, as well as the residue from corrosion of 7.5 cm, would likely provide a barrier to movement of radionuclides but was not considered during calculations of radionuclide release. Credit was not taken for the containment time and possible impediment to radionuclide release afforded by spent-fuel cladding. The gross dissolution behavior of the waste form was also not explicitly modeled for performance credit; such a consideration would affect release rates of the more soluble radionuclides, such as  $^{129}\text{I}$  and  $^{14}\text{C}$ . These assumptions are recognized by BWIP as conservative, and as further studies are conducted and as more data become available, more realistic predictions can be developed.

#### 4.3.1.2 Salt Repository Project (SRP)

An important consideration for a repository in salt formations is the amount of water that will reach waste packages. In an unbreached salt repository, small brine inclusions can migrate toward waste packages because solubility varies with temperature. In addition, appreciable water may be derived from available water of hydration from clay layers associated with some salt environments. Analyses indicate that the migrating water will be consumed in corrosion reactions with waste package materials, and little or no water will

remain to dissolve radionuclides (Jansen, Raines and Kircher 1984). The generally expected condition for a salt repository is that there will be insufficient water available to cause release of radioactivity to the accessible environment. Release rate across the boundary of the engineered barrier system, however, was only modeled in a preliminary manner.

A preliminary postclosure evaluation presented in the Environmental Assessment (USDOE 1986c) for the proposed Deaf Smith site considers three scenarios for water ingress to waste packages: 1) thermally migrating brine with a temperature gradient threshold below which brine will not migrate, 2) thermally migrating brine with no brine flow threshold, and 3) an intrusive salt dissolution brine in which there is an unlimited flow of brine. The expected condition is given by 1); the latter two cases are not expected. Spent-fuel containers for the salt repository are designed with a 2.5-cm corrosion allowance for their walls. In the first two scenarios discussed above, less than 0.5 cm is predicted to corrode considering the limited amount of brine available and assuming uniform corrosion. The waste package is thus predicted to last indefinitely, and there is no release of radionuclides. In the third scenario, which corresponds to an unlikely breached repository, the container is projected to last for 4800 years, and shortly thereafter the waste form would potentially come into contact with brine.

Radionuclide release calculations are presented in the Environmental Assessment (USDOE 1986c) assuming that brine migrates to waste packages according to the first scenario and that it is available for dissolution of radionuclides. The stoichiometric consumption of brine associated with the corrosion reaction with the container is ignored. The rate of supply of brine to waste packages limits the rate of release of radionuclides. The influent brine is assumed to become chemically saturated with elements from the waste, with no consideration given to mass transfer resistances. Radionuclide releases in this case are simply calculated by multiplying solubility times the rate of influx water to waste packages. Important mass transfer resistances that are identified, but not quantitatively considered, in the Environmental Assessment (USDOE 1986c) are diffusion resistances through stagnant liquid films near the waste form and through layers of accumulated corrosion products.

Other factors identified that may limit radionuclide releases, but are not incorporated into their preliminary analysis, include protection of spent fuel from cladding and the dissolution rate of spent fuel.

The interacting phenomena that influence the behavior of the waste package are linked in the WAPPA (Waste Package Performance Assessment) code (INTERA 1983), which is being used by the Salt Repository Project (SRP). The code predicts the degradation of waste package components with time as a result of the major operative processes. The degradation processes are driven by the presence of radioactive waste, which generates heat and radiation, and by ground water, which corrodes metallic barriers and dissolves the waste form. Five basic submodels are in the WAPPA code. These submodels can interact simultaneously and account for radiation, heat flow, mechanical influences, corrosion, and leaching.

The WAPPA code provides a mathematical framework for implementing the submodels, but the user must provide various constants or factors to proceed with calculations. Many of the mathematical forms are simplified so that phenomena like irradiation are represented through use of an "enhancement factor." For example, generalized corrosion is represented as a reference corrosion rate multiplied by an enhancement factor. Both the corrosion rate and the enhancement factor must be determined independently from the WAPPA code, either through experimentation or through theoretical analysis. Similarly, an enhancement factor is used to represent the effects that alpha damage and radiolysis have on waste form leaching.

The waste form leaching model presented in the report by INTERA assumes that the governing phenomena are matrix diffusion (with a half-power time dependence) and matrix dissolution (linear time dependence). Additionally, the rate is allowed to decrease as leach products accumulate in solution, and this is represented as a reversible, first-order process. The utility of this type of model for spent-fuel dissolution has not been demonstrated, and the WAPPA code will perhaps be revised as more data on this process are generated and as the understanding of controlling mechanisms increases.

#### 4.3.1.3 Nevada Nuclear Waste Site Investigation (NNWSI) Project

A preliminary, bounding method for calculating releases from spent fuel disposed in a tuff repository is described in the Environmental Assessment for the Yucca Mt. site (USDOE 1986b). Congruent dissolution of spent fuel is assumed and is determined by the volumetric flow rate through the repository as the result of rainfall times the solubility of  $UO_2$  under oxidizing conditions. Thus, the spent-fuel matrix, and all the constituents therein, are assumed to dissolve at a rate given by uranium solubility times flow through the waste package cross-sectional area. In the Environmental Assessment (USDOE 1986b), this approach is recognized as simple yet reasonable, considering the current knowledge on spent-fuel dissolution and considering the hydrological complexities of the unsaturated zone. This analysis also indicates that within noted uncertainties in site characterization data, current waste package designs incorporating spent fuel as a waste form appear to be adequate to fully meet the NRC release rate criterion for all radionuclides.

The Environmental Assessment (USDOE 1986b) identifies the approach to be conservative (overestimates release rates) from the standpoint that no mass transfer or kinetic limitations are considered and some radionuclides may have solubilities lower than uranium. Also, the cladding surrounding the fuel is not considered. The approach may be nonconservative, in part, if the  $UO_2$  matrix is not the most thermodynamically stable solid under expected waste package conditions (Johnson, Garisto and Stroes-Gascoyne 1985). In this case, the alteration of  $UO_2$  to a more stable solid would invalidate the concept of  $UO_2$ -solubility control to the congruent release of other radionuclides. Additionally, it is recognized by NNWSI that some fission products in the fuel pellets will undergo segregation and alterations at the high temperatures and radiation fluxes in the reactor (see Sections 4.1.2 and 4.1.3). The result is a heterogeneous assemblage of phases, which when exposed to water, will cause some radionuclides to escape faster than the fuel matrix dissolves (Oversby 1984; Wilson and Oversby 1984; Wilson and Oversby 1985).

The potential effects of mass transfer limitations on release rate from packages in a tuff repository were examined by Kerrisk (1985). The waste form

was modeled as a flat plate oriented parallel to saturated ground-water flow. The concentration at the surface was that of the solubility of the diffusing species.

Kerrisk calculated release rates of solubility-limited species for the same recharge rate both with and without mass transfer resistance. He found that consideration of mass transfer resistances lowers release rate by a factor of 400. Even the mass transfer approach used by Kerrisk is perhaps conservative because the waste form is assumed to be immersed in water-saturated porous rock, whereas the host rock in a tuff repository is expected to be unsaturated.

A waste package performance assessment model more detailed than that appearing in the Environmental Assessment (USDOE 1986b) is currently under development by the NNWSI project. Included will be quantitative predictions of waste-package failure times that are based on experimentally determined corrosion rates. A waste form release model will consider elements controlled by matrix dissolution, elements present in the pellet-cladding gap, and activation products in the spent-fuel assembly components and cladding. Transport away from the package will be based on convection, diffusion, and adsorption onto host rock or packing materials. PANDORA, a code that integrates simultaneous phenomena similarly to WAPPA, is being developed for waste package performance calculations (O'Connell and Drach 1986).

#### 4.3.2 Foreign Countries

##### 4.3.2.1 Swedish KBS Release Models

The KBS concept for disposal involves spent fuel in copper containers buried in granite and surrounded by a compact bentonite clay (KBS 1983). The copper container is corroded at a rate determined by the transport rate of reactants to the copper surface (Neretnieks and Rasmuson 1984). Similarly the release of radionuclides and the dissolution rate of the fuel is governed by mass transport rates. Mass transport rates are based on steady-state conditions and take into account both the diffusion in the clay and the diffusion and convection through water-bearing fractures in the host rock (Neretnieks 1978; Anderson, Rasmuson and Neretnieks 1982).

It is assumed that the mass transport rate of uranium will determine the dissolution rate of the spent-fuel matrix (Neretnieks and Rasmuson 1984). This assumption is similar to that for the analysis in the tuff Draft Environmental Assessment (USDOE 1986c), except that mass transport limitations are invoked and the release rate of nuclides with solubilities lower than uranium are correspondingly reduced. The KBS analysis also accounts for the local oxidizing conditions caused by radiolysis from the container in the otherwise reducing granite and predicts the movement of a "redox front" (Neretnieks 1984). Oxidizing species created by radiolysis will diffuse and disperse into the host rock and mitigate the reducing capability of the granite by conversion of divalent iron minerals to trivalent iron. Radionuclide species leaving spent fuel in an oxidized state will remain that way until they pass through the redox front and into pristine granite rock. Release rate increases with the spatial dimensions of the redox front, which is limited in size by the space between containers.

The KBS analysis assumes that carbon, iodine, and cesium are predominantly located in the fuel-to-cladding gap, and are 100% released to a bentonite clay backfill buffer (i.e., packing material equivalent) on penetration of containers. The release criterion for long-lived  $^{129}\text{I}$  was successfully met in the KBS design by consideration of a uniform distribution of container failure times rather than unrealistically assuming that all containers fail simultaneously. The release rate of the associated radionuclides is given by the water turnover rate in the buffer zone, as predicted by pore water diffusion (KBS 1983).

#### 4.3.2.2 SYstems Variability Analysis Code (SYVAC)

In the Canadian Nuclear Fuel Waste Management Program, the assessment of nuclear fuel disposal is being carried out using the probabilistic assessment code, SYVAC: SYstems Variability Analysis Code (Dormouth and Quick 1981). SYstems Variability Analysis Code has three principal components, or system models: the Vault (i.e., engineered barrier system), the Geosphere, and the Biosphere. The Vault submodel of SYVAC is used to calculate the time distribution of radionuclide releases as a source term to the Geosphere model, using input parameter distributions that take account of uncertainty and variability.

The release of radionuclides from used fuel (reference case for the Canadian program) and subsequent migration through the vault and into the geosphere, is represented in SYVAC by one-dimensional transport equations. These equations include consideration of diffusion, convection, sorption (linear), radioactive decay, and buildup (Garisto and Lyon 1984). Two different boundary conditions representing two distinct release mechanisms operating at different timescales are used in the Vault submodel (Johnson, Garisto and Stroes-Gascoyne 1985): 1) instant release on contact with ground water of gap and grain boundary inventories, and 2) slow, solubility-controlled, congruent release resulting from dissolution of the  $UO_2$  matrix. Because congruent dissolution of the  $UO_2$  matrix plays a dominant role in the release of the majority of radionuclides, the SYVAC Vault Submodel contains a process algorithm or function that calculates the solubility of  $UO_2$  under a variety of repository conditions (Garisto and Garisto 1985). In addition to temperature, pH, and redox conditions, this solubility function calculates  $UO_2$  solubility as a function of anion (carbonate, phosphate, sulfate, and chloride) concentrations based on thermodynamic principles. Thus, the solubility of the  $UO_2$  matrix under a range of repository conditions can be determined without the need to repeatedly run complex thermodynamic equilibrium computer programs.

#### 4.3.3 Additional Waste Release Models

##### 4.3.3.1 Berkeley Mass Transfer Models

Analytical equations for the time-dependent, fractional release rate of radionuclides from nuclear waste forms under open system, transport-limited conditions have been developed (Chambre and Pigford 1984; Chambre et al. 1985; Zavoshy et al. 1985). This approach assumes a waste form in contact with a surrounding porous medium with a fixed-boundary concentration at the waste form surface. The fixed-boundary concentration is most commonly set equal to the solubility of a stated radionuclide-bearing solid. The current level of development in the analytical model permits inclusion of sorption and radioactive decay effects; consideration of any number of nested barrier materials encapsulating a spent-fuel waste form; variation in dimensions, shape, and properties of these nested barriers; and temporal variation of solubility, diffusion, and sorption parameters for individual radionuclides.

At its simplest application, the model can be used to calculate steady-state (i.e., time-independent) fractional release rates ( $f_j$ ) of a given radionuclide  $j$  (Chambre and Pigford 1984) and thus conservatively bound radionuclide release by ignoring the time to attain steady-state conditions. For diffusion-convection flow, the steady-state, fractional release rate is

$$f_j = \frac{\alpha \epsilon (DU)^{1/2} C_j^*}{n_j} \quad (4.7)$$

where  $\epsilon$  = porosity

$D$  = the diffusion coefficient

$U$  = the pore velocity

$C_j^*$  = saturation/solubility concentration of radionuclide  $j$  at the waste form surface

$n_j$  = bulk density (inventory) of radionuclide  $j$  in the waste form

$\alpha$  = a geometrical factor.

For diffusion-only flow, the steady-state, fractional release rate is

$$f_j = \frac{\beta \epsilon D C_j^*}{n_j} \quad (4.8)$$

where  $\beta$  is a different geometrical factor and all other terms have the same meanings. Note that release rates are directly proportional to solubility limits imposed at the waste form surface (i.e., transport control is assumed). The time to reach steady-state release for an individual waste form (i.e., the duration of time-dependent release rates) has also been calculated (Chambre and Pigford 1984; Zavoshy et al. 1984). This time to reach steady state is a function of the degree of radionuclide sorption (i.e., sorption coefficient) on the surrounding porous media, pore velocity, diffusion coefficient, and radioactive decay constant. These same parameters also affect the rate of radionuclide release from the overall waste package system. Even at steady-state conditions, a limited degree of time dependency may arise from the variation in solubility, diffusion, and sorption parameters as a function of temperature (Chambre et al. 1985). Note, however, that the post-1000-year temperature

decrease with time is slight (approximately  $0.6^{\circ}\text{C}/100$  years). Furthermore, solubilities and diffusion coefficients generally decrease with decreasing temperature. Therefore, time-dependent release arising from post containment temperature variation is expected to be conservatively modeled by assuming time-independent values for solubilities and sorption coefficients based on conditions at 1000 years (or longer, if justified) after emplacement.

#### 4.3.3.2 AREST Code

The AREST code is being developed as a series of deterministic process submodels, which are coupled with a stochastic treatment of input parameters to provide a probabilistically sound and quantifiable assessment of waste package performance. The AREST code (Alexander et al. 1985; Liebetrau and Apted 1985) is divided into three subcomponents:

- Waste Package Containment Model
- Waste Package Release Model
- Engineered System (Repository) Release Model

The Waste Package Containment (WPC) model simulates those corrosion processes and degradation mechanisms (e.g., mechanical failure) that ultimately result in loss of complete containment of radionuclides. When ground water (or steam) comes into contact with the waste form, the Waste Package Release (WPR) model simulates the release of radionuclides from the waste form and their migration outward through the waste package. Finally, the Engineered System Release (ESR) model integrates the releases of individual waste packages to provide the distribution of total system release over space and time.

The radionuclide release rate calculations made by the AREST code (Alexander et al. 1985; Liebetrau and Apted 1985) are based on the analytical mass transfer equations reviewed in the previous section and developed in detail elsewhere (Chambre and Pigford 1984; Chambre et al. 1985). These analytical expressions relate release as a function of several relevant chemical and physical properties of a waste package system. In particular, any solubility constraints on radionuclides imposed at the surface of a waste form are key parameters. The thickness, sorption properties, and porosity of several nested barriers also can be explicitly defined and used in release rate calculations. Several features of AREST allow realistic evaluation of the time dependence for

radionuclide release. First, there are two phenomenological sources for time-dependent release rates. The primary source is the inherent time-dependent rate of many processes, such as corrosion of metallic barriers, dissolution of waste forms, transport of radionuclides, and ground-water flow. Related to this is time variation in important physical parameters, such as temperature, pressure, and/or radiation level, that can, in turn, affect the magnitude and rate of change of important degradation processes. Next, time dependence is introduced in a fundamental way by treating input parameters (e.g., temperature, ground-water flowrate, radiation level) stochastically. This treatment results in a distribution of corrosion/failure rates over all of the waste packages of a repository, leading to a distribution over time of containment loss for individual packages. By integrating the releases of individual waste packages with respect to this stochastically generated series of failure times, a time-dependent release rate (source term) from the engineered barrier system is generated.

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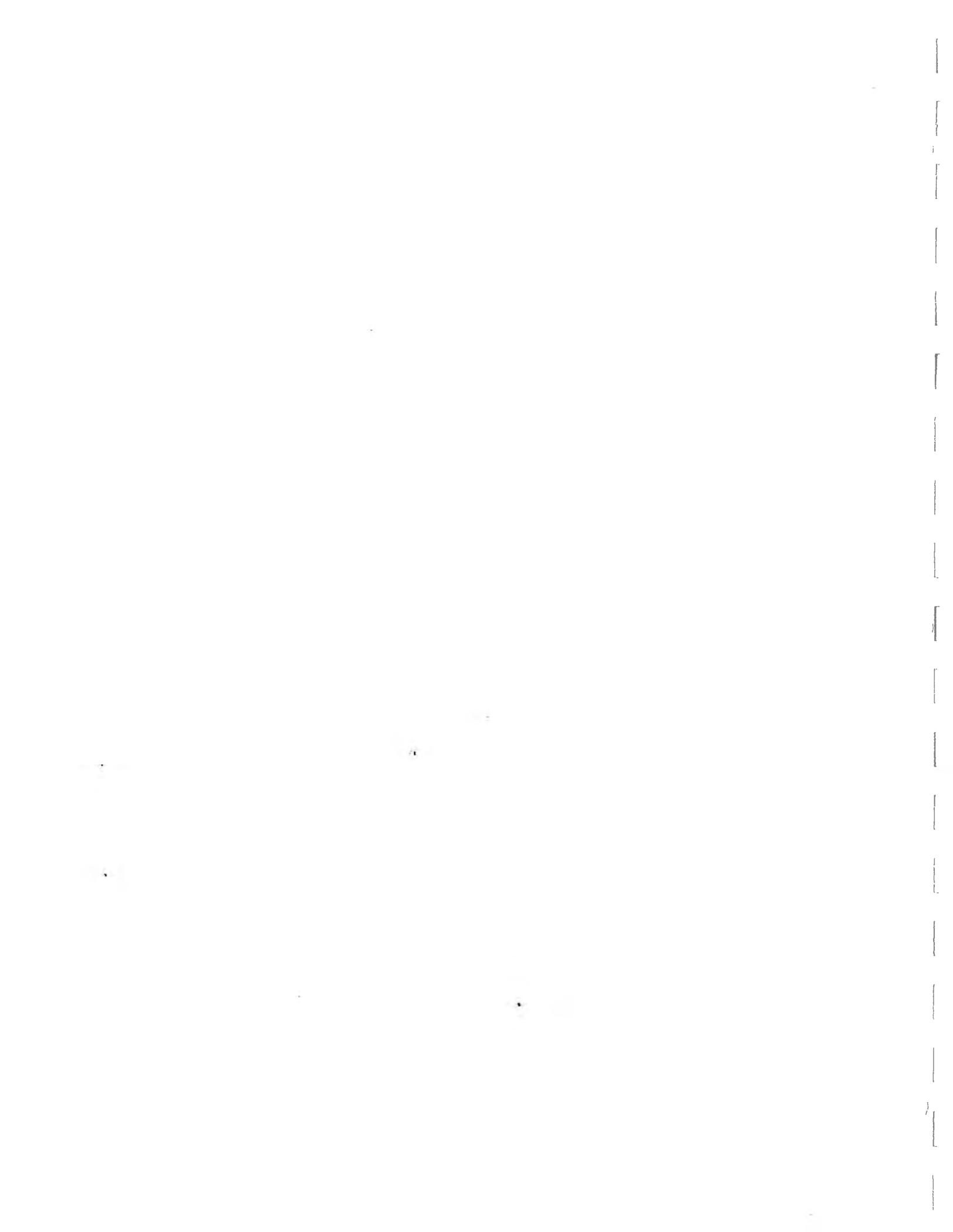
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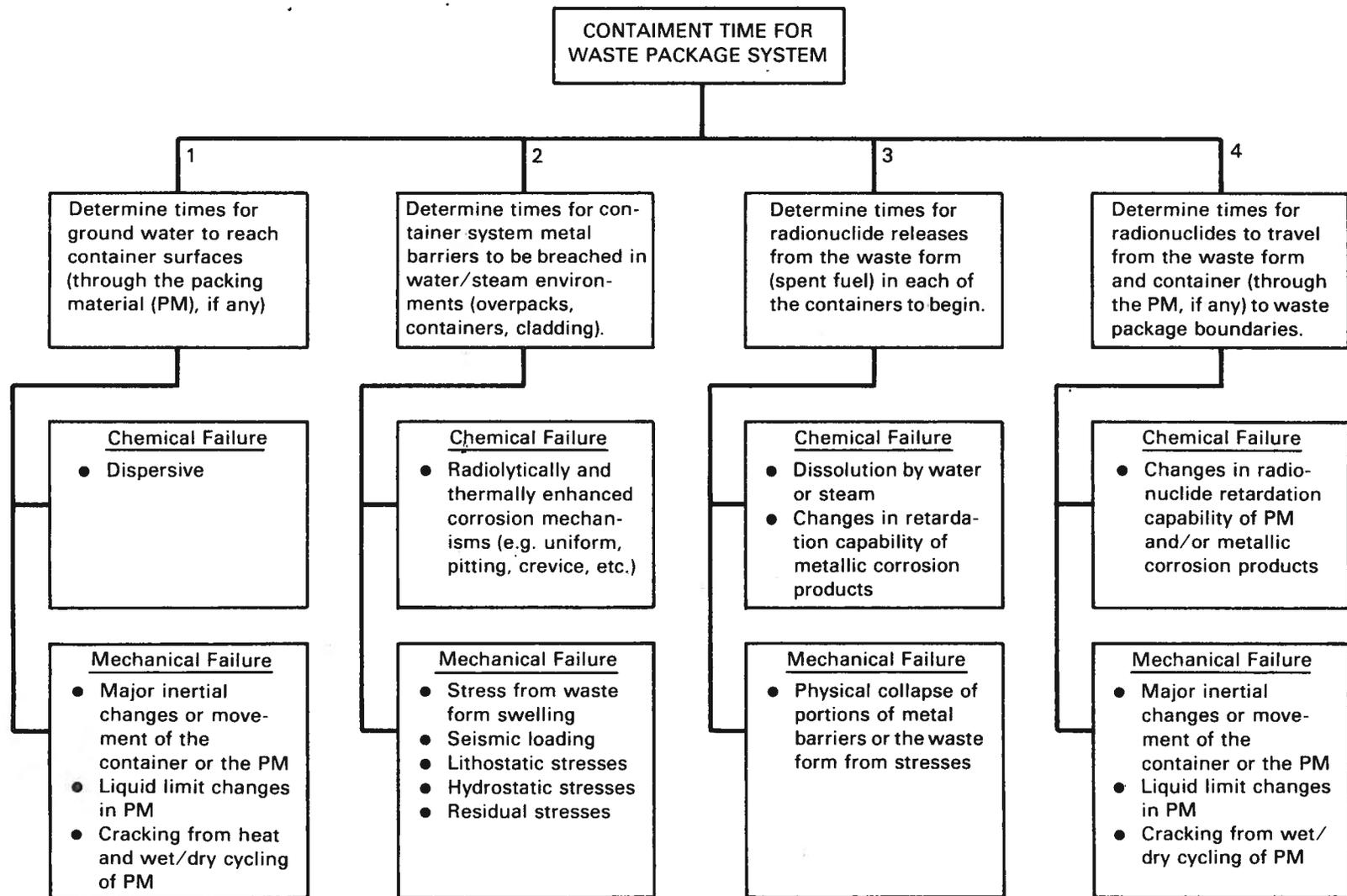
## 5.0 SUMMARY AND RECOMMENDATIONS

This section summarizes Sections 1.0 through 4.0. The data and modeling needs identified in those sections are emphasized here and expressed in terms of research recommendations. Section 5.1 summarizes Sections 1.0 and 2.0. Sections 5.2 and 5.3 summarize Sections 3.0 and 4.0, respectively.

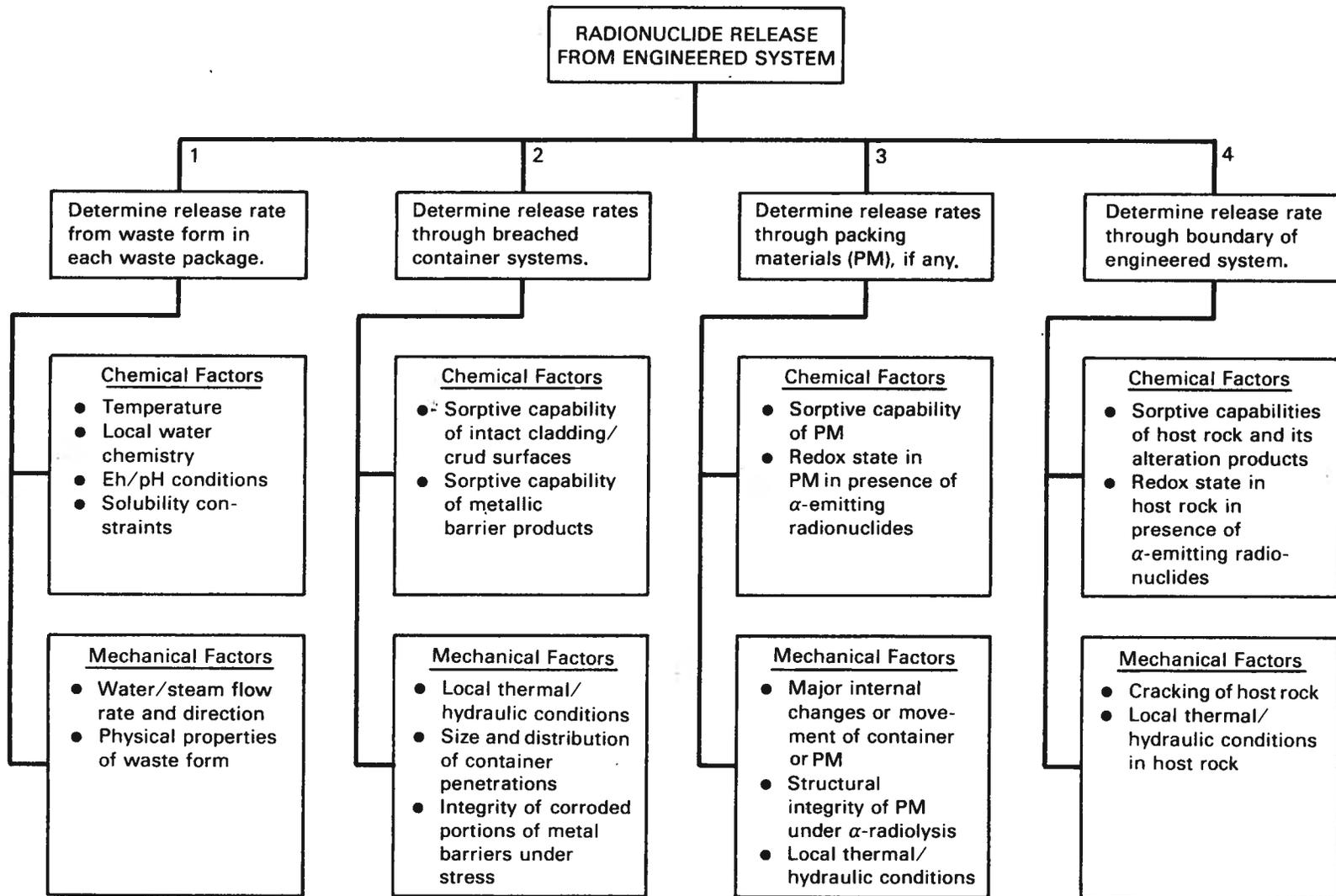
### 5.1 REGULATORY AND ENVIRONMENTAL BACKGROUND

Certain regulations must be addressed in evaluating the suitability of spent fuel as a waste form for geologic disposal. The NRC's 10 CFR Part 60 provides the most applicable performance objectives: the containment and the release rate objectives. The containment objective specifies that radionuclide "...containment within the waste packages will be substantially complete for a period to be determined by the Commission ... provided that such period shall not be less than 300 years nor more than 1000 years after permanent closure of the geologic repository..." The release rate objective specifies in part that "the release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1000 years following permanent closure" with the caveat that "this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1000 years of radioactive decay."

Gause and Soo (1985) (see Section 3.5) tabulated information that may be needed to fully address these two performance objectives. Their information was slightly modified for this report and is shown in Figures 5.1 and 5.2. Figure 5.1 represents a general summary of containment time information needs and Figure 5.2 similarly summarizes general release-rate information needs. The failure modes listed would need to be addressed experimentally in such a way as to allow the controlling mode or modes to be identified, after which the other modes would need no further evaluation. Gause and Soo (1985) note that



**FIGURE 5.1.** Chemical and Mechanical Failure/Degradation Modes Affecting Containment of Radionuclides by the Waste Package System (adapted from Gause and Soo 1985)



**FIGURE 5.2.** Factors Affecting Radionuclide Release from the Engineered Barrier System (adapted from Gause and Soo 1985)

the DOE licensing strategy would determine the extent to which individual component failure modes would have to be characterized. For example, if waste package containment beyond 10,000 years can be demonstrated with "reasonable assurance," the release rate performance objective is satisfied, and the characteristics of the waste form are moot. Of course, DOE must still demonstrate that the behavior of the geologic disposal system and each of its components under expected and unexpected event conditions are understood in order to demonstrate its findings with reasonable assurance. Also, the 100,000 year cumulative release calculation, to be used in site selection only (10 CFR 960), requires some degree of knowledge concerning the behavior of spent fuel as a waste form.

In this report, the second and third columns of Figure 5.1 and the first and second columns of Figure 5.2 are generally addressed. The emphasis of this report is on clad spent fuel, which means that the metal barrier (Column 2 of Figure 5.1 and Figure 5.2) that is specifically addressed is the cladding. The waste form (Columns 3 and 1 of Figures 5.1 and 5.2, respectively) addressed is the irradiated  $UO_2$  matrix of spent fuel. Other aspects of the engineered barrier system are only superficially addressed as part of the very near field that determines the time when containment by the primary metal barrier(s) is lost and clad spent fuel becomes accessible by ground water.

Preliminary performance assessments by the DOE Office of Geologic Repositories projects estimated containment by the primary metal barrier(s) in multiple thousands of years. If subsequent assessments can confirm these estimates with reasonable assurance, the containment properties of spent-fuel cladding are not important because the NRC containment requirement has been amply met. The influence of cladding on the waste form release rate may remain important, however, unless a primary metal barrier containment period greater than  $10^4$  years can be demonstrated. This is not to say that cladding performance must be part of a repository performance assessment strategy for it to be successful, only that it may potentially be a useful part of a performance assessment strategy. If primary metal barrier containment for  $10^4$  years cannot be demonstrated, the ability of cladding to keep the  $UO_2$  matrix inaccessible to ground water could potentially become part of a repository-wide integrated

release rate calculation. These two approaches are equivalent in terms of data needs and modeling approaches; the only difference hinges on the definition of "substantially complete" containment.

If substantially complete containment means that release rates for all radionuclides remain below 0.1% of the calculated total release rate limit, for example, then as long as release rates do not exceed this limit, cladding could provide containment. If, on the other hand, substantially complete containment means that no  $UO_2$  is accessible to ground water, then the somewhat less-than-total inaccessibility provided by cladding becomes a part of the radionuclide-specific release rate calculation for the engineered barrier system. Either way, the calculational approach is one resulting in a release rate curve, initially zero, that slowly rises over time.

The expected very near field environments that determine the length of the containment period and ultimately control the release rates are further summarized in Table 5.1. Table 5.1 gives some ranges for selected major variables for the four potential host rock types. The DOE Site Characterization Plan currently being prepared for each proposed candidate site, and required for future proposed candidate sites by the Nuclear Waste Policy Act of 1982, is to address the issues and data needs pertaining to these environmental variables. Therefore, this report does not address very near field or near field environmental data needs.

## 5.2 DATA AND MODELING NEEDS FOR CONTAINMENT BY CLAD SPENT FUEL

The following areas concerning spent-fuel behavior under repository conditions are addressed in terms of data and modeling needs: 1) the expected condition of spent-fuel rods on arrival at a nuclear waste repository, which may be important if cladding is to be used as a containment barrier, 2) identification of potential failure modes or processes in spent-fuel cladding during and after the containment period, 3) identification of potential failure models or processes for irradiated  $UO_2$  fuel, and 4) the current status/adequacy of performance models for spent fuel under repository conditions.

**TABLE 5.1. Estimates of Expected Spent-Fuel Waste Package Very Near Field Environments for Hypothetical Repositories in Basalt, Crystalline, Salt, and Tuff Host Rocks (a)**

Radiation to Nearest Host Rock	Preclosure (up to 100 years)				Postclosure (from ~100 yr to 1000 yr)				Postthermal (>1,000 to 10,000 yr)			
	Basalt	Crystalline	Salt	Tuff	Basalt	Crystalline	Salt	Tuff	Basalt	Crystalline	Salt	Tuff
$\gamma$ -dose rate (rad/hr)	$\sim 10^4 - 10^3$	$\sim 10^4 - 10^3$	$\sim 10^3 - 10^1$	$\sim 10^4 - 10^3$	$\sim 10^2$ to negligible	$\sim 10^2$ to negligible	$\sim 10$ to negligible	$\sim 10^2$ to negligible	negligible	negligible	negligible	negligible
total $\gamma$ -dose (rads)	$<10^9$	$<10^9$	$<10^6$	$<10^{10}$	$\sim 10^9$	$\sim 10^9$	$\sim 10^6$	$\sim 10^{10}$	$\sim 10^9$	$\sim 10^9$	$\sim 10^6$	$\sim 10^{10}$
$\alpha$ -radiation	contained	contained	contained	contained	contained	contained	contained	contained	slow release	slow release	slow release	slow release
<u>Temperature Maxima</u>												
Cladding ( $^{\circ}\text{C}$ )	230	190	190 <sup>(b)</sup>	250 <sup>(b)</sup>	$<140$ <sup>(b)</sup>	$<140$ <sup>(b)</sup>	$<120$ <sup>(b)</sup>	$<160$ <sup>(b)</sup>	$<100$ <sup>(b)</sup>	$<80$ <sup>(b)</sup>	$<50$ <sup>(b)</sup>	$<60$ <sup>(b)</sup>
Emplacement hole wall ( $^{\circ}\text{C}$ )	180	150	140	190 <sup>(b)</sup>	$\sim 170$ <sup>(b)</sup>	$\sim 140$ <sup>(b)</sup>	$\sim 130$ <sup>(b)</sup>	$\sim 140$ <sup>(b)</sup>	$\sim 90$	$\sim 60$ <sup>(b)</sup>	$\sim 27$	$\sim 40$
<u>Ground Water/Brine</u>												
Redox	oxidizing	oxidizing	oxidizing	oxidizing	oxidizing, then reducing	oxidizing, then reducing	indetermi- <sup>(b)</sup> nate, tending to reduce	oxidizing	reducing, <sup>(d)</sup>	reducing, <sup>(d)</sup>	reducing, <sup>(d)</sup>	oxidizing
Acidity (pH)	$\sim 9$	$\sim 9$	$<5$	$\sim 7$	$\sim 6$ <sup>(b)</sup> to $\sim 9$	$\sim 6$ <sup>(b)</sup> to $\sim 9$	$<5$	$\sim 5$ <sup>(b)</sup> to $\sim 7$	$\sim 6$ <sup>(b)</sup> to $\sim 9$	$\sim 6$ <sup>(b)</sup> to $\sim 9$	$<5$	$\sim 5$ <sup>(b)</sup> to $\sim 7$
Flux	not applicable	not applicable	maximum brine inflow rate; ( $<50$ L/MTU)	$<<1$ mm/yr	$\sim 0.1$ L/ $(\text{m}^2\text{-yr})$ <sup>(b)</sup>	$\sim 0.1$ L/ $(\text{m}^2\text{-yr})$	brine inflow decreases ( $\sim 100$ L/MTU total inflow)	$<1$ mm/yr	$<0.1$ L/ $(\text{m}^2\text{-yr})$ <sup>(b)</sup>	$<0.1$ L/ $(\text{m}^2\text{-yr})$	no further brine inflow	$<1$ mm/yr
<u>Stress</u>												
Hydraulic (MPa)	not applicable	not applicable	not applicable	0.1	10	10 <sup>(b)</sup>	not applicable	0.1	10	10 <sup>(b)</sup>	not applicable	0.1
Lithostatic <sup>(c)</sup> (MPa)	$\sim 26$	$\sim 28$	21	$<10$ <sup>(b)</sup>	$\sim 26$	$\sim 28$	21	$<10$ <sup>(b)</sup>	$\sim 26$	$\sim 28$	21	$<10^6$
Waste Package (MPa)	0.1	0.1	0.1 to $<21$	0.1	10-15 <sup>(b)</sup>	10 <sup>(b)</sup> -15	21	0.1	10-15	10-15 <sup>(b)</sup>	21	0.1

(a) Estimates based on sources discussed and cited in Chapter 2. Because most of these estimates reflect interpolations and interpretations of very preliminary work, using very preliminary design and field data estimates, these numbers should not be used for any purpose except 1) to convey a general impression of expected conditions and 2) to suggest areas where the site characterization activity needs to focus. Comparing this table with Tables 3.7, 3.8, and 3.9 in Soo and Gause (1985) may be especially instructive to those planning characterization activities.

(b) Values based on technical judgment or estimates from analogous calculations rather than on sources cited in Chapter 2.

(c) Vertical lithostatic stress.

(d) Locally oxidizing conditions arising from more rapid escape of radiolytically produced reducing species (e.g.,  $\text{H}_2$ ) leaving behind a net increase in oxidizing species. The oxidizing species produced from radiolysis has been proposed (Neretnieks 1983) but has not been substantiated or disproven by field or laboratory tests.

5.6

### 5.2.1 Condition of Spent-Fuel Rods

The condition of the spent-fuel rod depends on reactor operation, pool storage, and subsequent dry storage before receipt at the repository. A summary of information on thermal and cladding characteristics of spent fuel, cladding integrity, and distribution of constituents in the fuel rod are given below.

#### 5.2.1.1 Thermal and Cladding Characteristics

Most of the spent-fuel rods that will arrive at a repository will be clad with Zircaloy-2 or Zircaloy-4, but 5% or less of the fuel rods will have stainless steel (SS) cladding. About two thirds of the spent-fuel assemblies with Zircaloy cladding are from BWRs while about one sixth of the spent-fuel assemblies with SS cladding are from BWRs. These fuel rods have operated at rod powers of about 19 to 23 kW/m (6 to 7 kW/ft) to burnups of between 5 and 35 MWd/kgM, depending on the type of reactor and when the fuel rod was fabricated. The typical spent-fuel rod has been in storage from 5 to 12 years and has a decay heat covering a broad range that results from the power history and amount of time since discharge from the reactor.

Several general characteristics of the cladding of spent-fuel rods are important. These general characteristics include the presence and extent of oxide layers, crud layers, constituents of the crud, and hydrogen in the cladding. Spent-fuel rods with Zircaloy cladding have oxide and crud layers over the base metal. Oxide layers are less than about 50  $\mu\text{m}$  on BWRs and about 40  $\mu\text{m}$  on PWRs. Oxide layers have been very thin on SS cladding. Crud forms a reddish-brown layer over the oxide layer in thicknesses of 6 to 30  $\mu\text{m}$  on BWR spent-fuel rods while the crud is thinner and more tenacious on PWR rods. The constituents in the crud include both activation and fission products transported in the reactor coolant. Cobalt-60 is the primary activation product, but  $^{54}\text{Mn}$  and  $^{65}\text{Zn}$  are also important. Fission products in the crud include cesium isotopes as well as tritium, strontium, and cerium. Hydrogen levels in Zircaloy cladding range from 80 to 150 mg/kg and form hydride grains generally oriented in the circumferential direction. These hydrides can reorient to a less favorable radial position if the cladding stresses and temperatures are high enough, and the hydrogen can migrate under temperature gradients.

### 5.2.1.2 Cladding Integrity

More than 99% of the spent-fuel rods that will arrive at a repository are expected to have intact cladding. Most of the defects will have occurred in-reactor, although there is a potential for a few additional breaches during handling, transportation, dry storage, or consolidation. Experience indicates that pool storage will not cause any appreciable increase in the number of breaches. The limits proposed for dry storage (i.e., temperatures less than 380°C and use of an inert cover gas in the storage container) are expected to substantially prevent further cladding breaches or degradation of already breached fuel rods. Defects will range in size depending on any secondary defects or the availability of oxygen to cause splitting of the cladding.

### 5.2.1.3 Distribution of Constituents in the Fuel Rod

After irradiation, the  $\text{UO}_2$  fuel changes substantially. In place of the cylindrical fuel pellet are fragments typically between 2 and 6 mm, which increase the fuel surface by about a factor of 3 based on limited examinations. Radioactive elements and compounds are formed in the fuel depending on the power history and the fuel age. Computer codes are available to calculate the amounts of these radionuclides but are not used to report the specific location and/or chemistry of these materials.

The distribution of the radionuclides in the fuel has not been investigated extensively, because there is little restructuring in LWR fuels. Oxygen does slowly transport to the outer edge during irradiation and cesium moves by vapor transport to cooler regions. Noble metals, such as molybdenum or ruthenium, may form 1- to 10- $\mu\text{m}$  ingots in the equiangular grain growth region (at about two thirds the distance from the fuel pellet center to the cladding) of some fuel of higher burnup. There may also be a slight enrichment of technetium, barium, cerium, and cesium at the outer fuel edge, but the data are very limited. About 50% of the  $^3\text{H}$  produced during irradiation is retained in the cladding. In general, only limited data are available on the specific quantities of different elements in the grains, at the grain boundaries, or at the fuel/cladding interface.

The amount and composition of the fission gas released to the void space in the fuel rod has been studied because it is of interest to reactor operations. The gas pressures in PWR fuel rods range from 30 to 40 atm at the end of life at room temperatures. Typically, about 99% of the fission gas is retained in the fuel after discharge from the reactor. Unless temperatures were very high, the gas will remain in the fuel. However, actinide decay produces helium gas that will increase the fuel-rod pressures during long-term storage. The composition of the gas in the fuel rod after irradiation consists primarily of helium, xenon, krypton, and a few other gases.

#### 5.2.2 Potential Failure Modes/Processes for Spent-Fuel Cladding

Limited degradation is expected to the spent-fuel rods during the containment period in a container before intrusion of water or steam from the repository environment. During the containment period, the environment consists basically of dry storage, probably using an inert atmosphere inside the container. Cladding that arrives intact at the repository might fail as a result of incipient defects that are exposed to normal storage stresses. Undeformed fuel rods may also experience degradation by creep rupture, hydride embrittlement, and general corrosion during the 1000 years or more of containment. Stress corrosion cracking on the fuel side is not believed to be of major concern under the expected dry storage conditions because the stresses appear too low. However, the possibility of such failures is not ruled out. Fuel rods that are breached on entry into the repository or are subsequently breached and exposed to dry storage atmospheres may also experience fuel oxidation if enough oxidant is available.

Degradation mechanisms that could be operable during the postcontainment period when steam, hot water, and/or water vapor are present at temperatures of 100°C or less could include corrosion, SCC, and hydride embrittlement. Once the fuel rods fail, the stress-related mechanisms become of little or no importance. Uniform corrosion in Zircaloy cladding is expected to be low during 10,000 years under some environments, but could consume substantial portions of the cladding at higher temperatures or in environments with aggressive species. Stainless steel cladding corrodes significantly in some environments, particularly by crevice corrosion. Stress corrosion cracking is not as

prevalent in Zircaloy and may not be a significant factor, based on estimated stresses. However, SS materials are susceptible to SCC in a number of environments plausible for repository conditions. Hydriding is not believed to be an issue in failure of fuel rods, but no account has been made for cumulative effects of corrosion, creep rupture, and hydriding during and before repository disposal.

As mentioned in Section 3, the condition of spent-fuel rods is well enough established to define the number of defects and the cladding characteristics after reactor operation and pool storage. However, there are fewer data on the cladding condition during and after dry storage. Several areas require further development of data and models for the cladding of spent-fuel rods under repository conditions: 1) creep rupture, 2) corrosion, 3) SCC, 4) long-term annealing, and 5) hydride distribution.

#### 5.2.2.1 Creep Rupture

The amount of creep rupture has been calculated for Zircaloy cladding under a decreasing temperature history postulated for dry interim storage and MRS. These calculations are based on analytical methods and are supported by limited data for irradiated Zircaloy cladding tested over short times. While the peak temperature history in a repository may be comparable to that expected in dry interim storage or MRS, the cladding temperature in the repository will decrease more slowly and, in some cases, actually increase for a short while. Once the container fails, the hydrostatic pressures of up to about 11 MPa might then cause the cladding to creep inward as a result of the difference in the internal and external pressures. As a first approach, creep rupture should be calculated for the expected repository conditions and combined with the cladding creep from previous storage to determine the cumulative damage to the cladding. Then, because the time frame for disposal exceeds that of any previous storage mode, additional, long-term (3 to 5 years) creep rupture data should be collected to benchmark these calculations and provide confidence in such predictions. No low-temperature creep rupture data are available for irradiated SS cladding, and calculations have not been made for creep rupture under either dry-storage or repository temperature histories. While creep

rupture is not expected to be significant in SS cladding, a complete assessment of cladding degradation should include such an analysis for SS clad spent-fuel rods.

#### 5.2.2.2 Corrosion

Most of the corrosion data for zirconium alloys are for in-reactor conditions in controlled water or steam environments. The addition of a host of other chemicals found in repository ground waters increases the complexity of the system and will alter the corrosion tendencies. Actual corrosion data for Zircaloy and SS cladding under expected repository conditions are needed to adequately predict the performance of intact spent-fuel rods once the container fails and the fuel rod is exposed to repository liquids. General corrosion, pitting, and crevice corrosion should all be considered when a test matrix is developed for both Zircaloy and SS cladding material. These new data could be used to determine the combined effect of corrosion, creep rupture, and other mechanisms on the integrity of the cladding.

#### 5.2.2.3 Stress Corrosion Cracking

Stress corrosion cracking has been considered extensively for nuclear fuel rods, but the years of research have been primarily on the SCC that occurs on the fuelside and is still unresolved. Stresses during dry storage and geologic disposal are not expected to be high enough to cause SCC on the fuelside; however, SCC could occur on the water side once the repository environment comes in contact with the cladding. Stress corrosion cracking is considered more likely for sensitized SS cladding than for Zircaloy-clad spent-fuel rods. Some of the data and modeling efforts for SS-clad spent-fuel rods may come from work on waste package containers, but an improved understanding of SCC of Zircaloy cladding will be required to adequately predict performance under the range of expected repository conditions.

#### 5.2.2.4 Long-Term Annealing

Data for annealing of Zircaloy cladding irradiated at low temperatures (<50°C) indicated that the yield strength can be reduced substantially in short time periods (1 h) at peak temperatures that might occur under dry-storage conditions. However, fuel-rod cladding is typically irradiated at about 300°C,

and the temperature at which the cladding is irradiated appears to affect the amount of annealing. Data are needed to determine the amount of annealing of radiation damage under expected repository temperature histories because the mechanical properties of the cladding are important to calculations of stress-related phenomena.

#### 5.2.2.5 Hydride Distribution

The average amount of hydrogen in Zircaloy cladding is expected to be low enough to preclude failure by embrittlement; however, the hydrogen could migrate to cooler regions of the fuel rods where the mechanical properties might be unfavorably affected. Models have been used for predicting hydrogen migration in other conditions but need to be adapted and applied to the specific conditions of the repository waste packages. Additional data will also be required to confirm long-term projections.

#### 5.2.3 Potential Failure Modes/Processes for Irradiated UO<sub>2</sub> Fuel

The data on spent-fuel performance under repository conditions are limited. For the dry storage conditions of the containment period, germane data are being generated on fuel oxidation; however, the use of an inert atmosphere will preclude such a problem. After the UO<sub>2</sub> is exposed to the repository environment, moist air or steam could potentially enter the container and contact exposed fuel. Limited oxidation data for these conditions indicate that moisture adversely affects fuel oxidation rates, but data are insufficient to adequately predict such oxidation for specific repository environments.

Most of the other data are very limited or are for unirradiated material. The corrosion data are generally for in-reactor or pool storage conditions where the water has neutral to slightly acidic pH (deionized water with low oxygen content).

In several areas, additional data are required to support existing models or develop models for predicting the performance of clad spent fuel placed in a repository for final disposal. Recommendations for further analytical and experimental work are summarized in Table 5.2. These data are based on the condition and performance of Zircaloy-clad and SS-clad spent-fuel rods described in Section 3. The model development recommended below should

TABLE 5.2. Summary of Recommendations for Irradiated Zircaloy and Stainless Steel Cladding and for Irradiated UO<sub>2</sub>

<u>Material</u>	<u>Mechanism To Address</u>	<u>Data Requirements</u>
Cladding	Creep rupture	Creep rupture data are required for the applicable storage conditions.
	Corrosion	Corrosion data exist for Zircalloys and SS in a number of environments, but not for the expected ground waters and radiation environments.
	SCC	Waterside <sup>(a)</sup> SCC is an issue for SS and may be for Zircalloys in some environments. Need to establish the propensity for SCC and what species are factors.
	Long-term annealing	Annealing data are required for actual irradiated cladding under expected storage conditions to define limits below which storage temperatures will not affect mechanical properties.
	Hydride distribution	Data on hydrogen migration are required and models should be developed to determine potential for degradation of cladding mechanical properties.
Fuel	Radionuclide distribution	Determine elemental and compound composition of fuel in grains, at grain boundaries, and at interface between fuel and cladding.
	Oxidation	Oxidation rates in moist air and steam are required.
	Effects of fuel oxidation	Determine effect of fuel oxidation on fission gas release, fuel particle size, and the chemical composition on leach rates.

(a) Waterside refers to the exterior of the cladding in pool storage. The interior of the cladding in contact with the irradiated UO<sub>2</sub> is referred to as the fuelside.

eventually be included in a performance code for spent-fuel rods to determine the net effect of all of the degradation mechanisms as well as the cumulative damage from in-reactor, pool, dry interim, and monitored retrievable storage that may occur before ultimate disposal.

If the cladding loses its integrity, oxidation of the fuel becomes important to the eventual size of the cladding defect and to the ultimate leachability of the fuel. Much of the data on oxidation of irradiated fuel is being developed as part of ongoing dry storage programs and can be applied to dry storage of  $UO_2$  contained in defected fuel rods that might be in a repository waste package. However, a few areas require further investigation to assist in defining the performance of spent-fuel rods in a repository: 1) the distribution of radionuclides in the fuel, 2) oxidation in moisture or steam, and 3) the effect of fuel oxidation on fission gas release and leach rates.

#### 5.2.3.1 Radionuclide Distribution

Unlike fast breeder fuel or high-power test fuel rods, there is relatively little restructuring in  $UO_2$  fuel used in LWRs. Thus, information on the distribution of radionuclides is typically provided on an average basis rather than in terms of specific locations, such as at grain boundaries or at the fuel/cladding gap. To properly model radionuclide release from irradiated fuel during the postcontainment period, additional data are required on the amounts and location of specific radionuclides and their compounds in the fuel. A range of fuel burnups should be studied to establish the expected range in radionuclide distributions in LWR fuel rods with a variety of power histories.

#### 5.2.3.2 Fuel Oxidation in Moisture or Steam

Oxidation tests for  $UO_2$  fuel are being conducted primarily in air and controlled redox cover gases with and without radiation fields. These data are particularly germane to the containment period where defected cladding might expose fuel to a basically dry storage environment. If, when the container fails, the fuel temperature is at or below  $100^\circ C$ , fuel oxidation is not expected to be significant if the air is dry. However, moist air or steam in contact with exposed fuel, especially at temperatures above  $100^\circ C$ , could adversely affect fuel oxidation rates, but data are insufficient to adequately predict such oxidation for specific repository environments.

#### 5.2.3.3 Effect of Oxidation on Fission Gas Release and Leach Rates

If the cladding becomes defected during the 1000 or more years of dry storage or after the containment period, when only air or steam is present,

then the fuel may gradually convert from  $UO_2$  to  $U_3O_7$  or  $U_3O_8$  in the presence of air or oxygen in the steam phase. The  $U_3O_8$  has a lower density than  $UO_2$  and causes the cladding to split if there is sufficient oxygen. It is expected that as the fuel oxidizes, smaller particles are formed, which will increase the amount of fission gas released and the surface area of the fuel. Sufficient data are not available on the effect of fuel oxidation on fission gas release, on the change in the leachability of fuel when part or all of it converts to  $U_3O_7$  or  $U_3O_8$ , or on the change in particle size from fuel oxidation and its effect on radionuclide release. These data should be obtained and incorporated into models for predicting radionuclide releases during the post-containment period.

#### 5.2.4 Current Status/Adequacy of Performance Models

Existing codes for analyzing performance in repository environments are generally limited to the containment structures rather than spent-fuel rods. The BARIER and WAPPA codes do consider spent-fuel cladding performance, but only with semiempirical submodels for which there is a lack of relevant data for calibration, benchmarking, and verification. It remains to be seen if the PANDORA code under development improves the WAPPA cladding performance model. A mechanistic approach, in which chemical, mechanical, or combined mechanisms are used to analyze the performance of spent-fuel rods, will be required, if it is desired to develop models that can predict beyond specific environments and limited time periods. There are the theoretical foundations for such approaches but only limited data exist to support such an effort.

A performance code also needs to be developed to consider the net effect of previous and current degradation mechanisms. Although none of the degradation processes are expected to be of major concern during dry storage, no attempts have been made to sum up the degradation from each process and determine a net effect for all of the potential degradation modes. Similarly, the total effect of degradation from all of the stages of the waste management cycle should be considered in predicting performance. Such considerations are complicated because not every fuel rod will experience the same storage history and no codes are currently set up to accomplish this.

### 5.3 DATA AND MODELING NEEDS FOR RADIONUCLIDE RELEASES FROM SPENT FUEL

The mechanistic models and supporting data needs for calculating the release rate performance of spent fuel are reviewed in Section 4. Because the proposed deep geologic repositories have different environmental conditions (reviewed in Section 2) and different waste package designs, several approaches have been developed to calculate radionuclide release rates for spent fuel. This report has focused on the common aspects of such modeling approaches, and identified areas of research that require additional study or characterization to support these approaches.

Note that these recommendations are not exhaustive in scope nor universal in application to different types of host rocks or different waste-package designs. The recommendations are based, however, on evaluation of model development and data needs that are viewed as broadly supporting and enhancing the analyses of the suitability of spent fuel as a waste form in any host rock repository. In some noted cases, data needs are suggested that may be obviated by selection of a more conservative assumption or bounding approximation; it must also be cautioned, however, that in proving an assumption conservative, the same data needs suggested here are often required. In addition, overly conservative assumptions can lead to physically unrealistic scenarios. Assessments based on such unrealistic situations will not establish a viable measure of conservatism, nor will it provide guidance for testing and design development.

#### 5.3.1 Spent-Fuel Characterization

The calculation of total radionuclide inventory for a given spent-fuel assembly as a function of burnup is clearly inadequate for the purposes of defensible performance assessment of radionuclide release. We must also know 1) the spatial distribution of a given radionuclide and 2) the physical state (gas, liquid, solid) and chemical composition of the phase in which a given radionuclide occurs.

Spent-fuel characterizations should be guided by consideration of the four separate sources of radionuclides within spent fuel based on their release behavior (see Section 4.1.1). These sources are 1) the  $UO_2$  matrix, 2) the

cladding, 3) the fuel-cladding gap, and 4) the grain boundary phases. Particular emphasis must be given to the location and form of highly soluble radionuclides and spatial zoning of composition in  $UO_2$ , which is expected to contain (and control the release of) over 90% of the total radionuclide inventory. The Material Characterization Center (MCC) is currently investigating the effects of burnup and measured fission gas release on the characteristics of spent fuel (Mendel 1985; Barner 1984).

A key concern of DOE should be reaching an understanding, with appropriate regulatory organizations, on the definition of spent fuel from a testing and performance assessment point of view. Because performance tests on spent fuel are expensive and lengthy and because the spent-fuel properties vary as a function of reactor history, a uniform and carefully considered approach to this matter is needed. Another problem is that the actual spent fuel that can be tested is not a close analog to spent fuel as it will exist 1000 years or more after emplacement in a repository. Short-lived isotopes will have decayed away, daughter isotopes will have grown in, and the gamma radiation field will be greatly attenuated after this time. These differences could make it difficult to relate expected spent-fuel performance to the results of tests on available spent fuel.

### 5.3.2 Highly Soluble Radionuclides

The release of some highly soluble radionuclides from the engineered barrier system may be difficult to control for any repository. The greatest difficulties come from highly soluble radionuclides that are long-lived (e.g., cesium-135), form anionic solution species (e.g., carbon-14, technetium-99), or are both long-lived and form anionic solution species (e.g., iodine-129). Because of the absence of primary control on the release of such radionuclides by spent fuel, determining the fate of these radionuclides during migration through the engineered barrier system should be given particular emphasis.

Reversible sorption on engineered barrier materials is not an effective mechanism for attenuating release because such radionuclides are either essentially nonsorbing or have extremely long half-lives in relation to the relatively short path length across the waste package. However, if it can be demonstrated that sorption hysteresis occurs (i.e., the rate of desorption is

less than the rate of sorption) or if a proportion of a sorbed radionuclide is sorbed irreversibly by the cladding or some engineered barrier, these processes could reduce the release rate of highly soluble radionuclides. Solid-solution substitutions (i.e., coprecipitation) of highly soluble radionuclides in alteration/corrosion products could also effectively attenuate release. In an analogous manner, specialized tailoring agents or chemical buffers (McKay Shoemith and Bailey 1983) added into packing materials (or inside the container) could be used to form low-solubility products of radionuclides that would otherwise be highly soluble. Isotopic dilution by natural, stable isotopes in ground waters or co-released from the waste form (e.g., carbon-12 released from cladding in conjunction with carbon-14) may also play a role in minimizing the fractional release rate of some highly soluble radionuclides. Careful consideration should be given to all of these potential processes in assessing the performance of spent fuel.

Beyond these technical considerations, there is also the prospect that the time-distributed nature of container failures will greatly alleviate potential release rates of highly soluble radionuclides. This modeling concept follows that of the successful Swedish KBS-3 study (KBS 1983). The KBS-3 report showed that even after one million years containment, assumption of instantaneous failure of all waste containers would lead to an unacceptably high pulsed-release of some highly soluble radionuclides, particularly iodine-129. By considering that container failures were uniformly distributed, conservatively starting at 100,000 years and ending at one million years, an acceptably low iodine release rate over time was obtained. A similar preliminary analysis of time-distributed container failures for a U.S. repository project also demonstrated the attenuating effect on release rates of highly soluble radionuclides (Sagar, Eslinger and Baca 1985; Oversby and Wilson 1985). This attenuation arises because of the interpretation of NRC's 10 CFR 60, Section 113(a)(1)(ii)(B) that the release rate is considered relative to the inventory of that radionuclide within the entire engineered barrier system (i.e., the release from any failed containers is normalized over the entire inventory contained in the repository). Therefore, the time-dependent degradation of containment barriers is potentially important to the evaluation of the release rate performance of spent fuel or any other waste form.

### 5.3.3 Spent-Fuel/Ground-Water Tests

The relevant types of spent-fuel/ground-water tests designed to produce information on primary mechanisms of radionuclide release need to be based on proper consideration of expected (and unexpected) waste package conditions. A key parameter in justifying either dissolution leach-rate studies or steady-state/solubility studies is the flux ratio (Zavoshy, Chambre and Pigford 1985), which depends on the comparison of chemical reaction rates (assumed to be first-order kinetics) with mass transport rates (see Section 4.1.1). Different sources of radionuclides within spent fuel can be identified on the basis of different processes controlling release. It is apparent, however, that all U.S. Repository Projects are relying on solubility limits of most radionuclides to control their release.

The control of radionuclides contained within the  $UO_2$  matrix (perhaps as much as 99% of the total fission product inventory and all of the actinide inventory) by the congruent dissolution and solubility of  $UO_2$  (Johnson, Garisto and Stroes-Gascoyne 1985) is a concept that would make the task of obtaining performance data on spent fuel comparatively easier. By adopting this model in preliminary tests, it is not necessary to attempt to demonstrate and characterize the separate solubility control of each radionuclide contained in  $UO_2$ . The rigorous application of this simple concept relies on the stability of  $UO_2$  under reducing and oxidizing waste package conditions. It may be possible, however, to relate the congruent release of radionuclides contained in the matrix to the measurable rate of conversion of metastable  $UO_2$  to a more stable form. It is recommended, therefore, that the role of congruent dissolution of  $UO_2$  and the solubility of  $UO_2$  as a control to radionuclide release be experimentally investigated and incorporated into spent-fuel modeling and validation testing in U.S. programs as appropriate. Specifically, it is recommended that those repository projects that expect reducing conditions during the release period, such that  $UO_2$  (or  $U_4O_9$ ) would be stable, investigate the mechanism of  $UO_2$  dissolution under expected conditions. Basalt, crystalline, and possibly salt host rock are expected to provide a reducing postclosure environment.

#### 5.3.4 Cladding

The metallic cladding of spent fuel has been identified previously as potentially contributing to the containment of radionuclides and as a source for the limited release of certain radionuclides. The difficulty and expense of establishing containment credit for irradiated cladding that has experienced a broad range of temperature and chemical environments has led some researchers to embrace a conservative approach to performance assessment and neglect cladding performance. Two important caveats should be added to this conservative approach. First, the cladding itself contains radionuclides, and the release of these radionuclides, and hence their release mechanism, must be determined. Second, the cladding may play an important chemical and physical role in attenuating the release of radionuclides; neglecting this role may represent a conservatism bordering on physical unreality. This latter point does not require a mechanistic understanding of cladding corrosion per se, but does indicate that chemical reactions between cladding and ground water must be understood, as outlined below.

The considerable redox buffering capacity of cladding and its close proximity to the  $UO_2$  matrix make this pair of materials an important one for study. In particular, it has been proposed that under some conditions, the production of reactive oxidizing species by alpha radiolysis (Neretnieks 1984) may locally raise the redox potential (Eh) at the surface of the  $UO_2$ , leading to tremendous enhancement of the solubility of many radionuclides, including the alpha-generators. Subsequently, this self-sustaining plume of alpha-generating radionuclides could migrate through the engineered barrier system. A key factor not considered by Neretnieks is the role of reducing metallic barriers adjacent to the  $UO_2$  surface and along the initial migration pathway. The relative rates of radiolytic production of oxidizing (and an equal amount of reducing) species, the rates of chemical buffering of redox species by metal barriers (and  $UO_2$ , which is relatively reduced form of uranium), and the rates of mass transport of redox species within the waste package environment are a key concern. Resolution of the actual importance of this postulated process will require both experimental and modeling efforts.

Cladding may also physically restrict the release rate of radionuclides from  $UO_2$ . Loss of physical containment by the cladding does not imply that the cladding material disappears, leaving bare fuel exposed. Rather, the access of ground-water solutions will be restricted to fractures or crevices penetrating through the cladding. This effect of limited-access has been modeled for certain sets of bounding hydrological assumptions (Cheung and Chan 1983). These modeled results indicate that integrated flux, or release rates, scale with the percentage of exposed surface area of the waste form in an approximately linear relationship under certain repository conditions. Further work in modeling and validating this effect is recommended. Recent experiments on clad spent fuel with laser-induced penetrations (Wilson and Oversby 1985) show that the releases of gap radionuclides are not likely to be significantly restricted by limited-access considerations. The radionuclides within the gap are highly soluble and highly mobile.

Finally, the corrosion of the cladding will cause many of these accessways to be lined with corrosion products of the cladding, or perhaps packing material if present. Oxides and hydroxides of iron have been shown to have high exchange capacities for many radioelements (Couture and Seitz 1983; Vandergraaf, Ticknor and George 1984), and it is expected that oxides/hydroxides of zirconium may have even a greater exchange capacity than analog iron compounds under some environmental conditions (Section 4.1.6). It is recommended, therefore, that the interactions of radionuclides (especially those that are highly soluble or mobile) with expected corrosion products of cladding be evaluated. Furthermore, such studies should provide data compatible with phenomenologically based interaction models, such as the triple-layer model (Davis, James and Leckie 1978). This type of model explicitly incorporates effects of variable repository conditions, such as pH, Eh, and competing ions.

#### 5.3.5 Colloids, Coupled Processes, and Design

Additional factors could be listed that might affect the assessment of spent fuel as a suitable waste form for disposal in a geologic repository. Radiolysis and the presence of additional barrier materials have been mentioned previously. Other factors that may need to be addressed are colloids, coupled processes, and designs.

The release of some portion of radionuclides as colloids may be another area of concern. Colloidal fractions represent contributions to radionuclide release that are not accounted for by assumption of solubility limits. Analyses of colloids in certain waste package designs have evaluated the mechanism (Champ, Merritt and Young 1982; Apps et al. 1983; Avogadro and de Marsily 1984) and relative importance (National Academy of Sciences 1983) of colloid transport; however, experiments on spent-fuel/ground-water interactions should attempt to separate and quantify colloidal fractions from true solution fractions of released radionuclides. There are several reasons for stressing these experiments. First, attempts to model experimental results from chemical reaction codes (Wolery 1980) without such a separation would be misleading at best. Second, it is also important that the true solubilities be used to provide a reliable basis for waste package design and performance assessment. Third, the fraction of a radionuclide present as a colloid will migrate at a different rate (National Academy of Sciences 1983) and in a different manner than the same radionuclide present as a truly dissolved species. Analysis of radionuclide-bearing colloids must be kept distinct from analysis of dissolved radionuclides, and this begins with making the appropriate measurements in spent-fuel interaction tests.

It has been pointed out that in the waste package region, thermodynamically coupled flows of solute and solvent can occur in addition to the independent flows (i.e., Darcy's law, Fick's law) because of local gradients in temperature, hydraulic gradient, and composition (Carnahan 1984). Analysis of these potential coupled flow effects is limited by the lack of data on phenomenological coefficients of appropriate waste package materials. The use of data from analog materials (Carnahan 1984, 1985), however, suggests that certain of these coupled flow effects may be of equal or greater magnitude and in the opposite direction to solvent/solute flow based solely on Darcy's and Fick's laws. The same analyses also show that other coupled flow effects (e.g., Soret or "thermal" diffusion) are expected to be relatively minor compared to conventionally modeled flows under realistic repository conditions. It is urged, assuming these calculations are even approximately correct, that

relevant phenomenological coefficients be experimentally obtained so that a more defensible evaluation of the absolute effect of such coupled flow processes can be established.

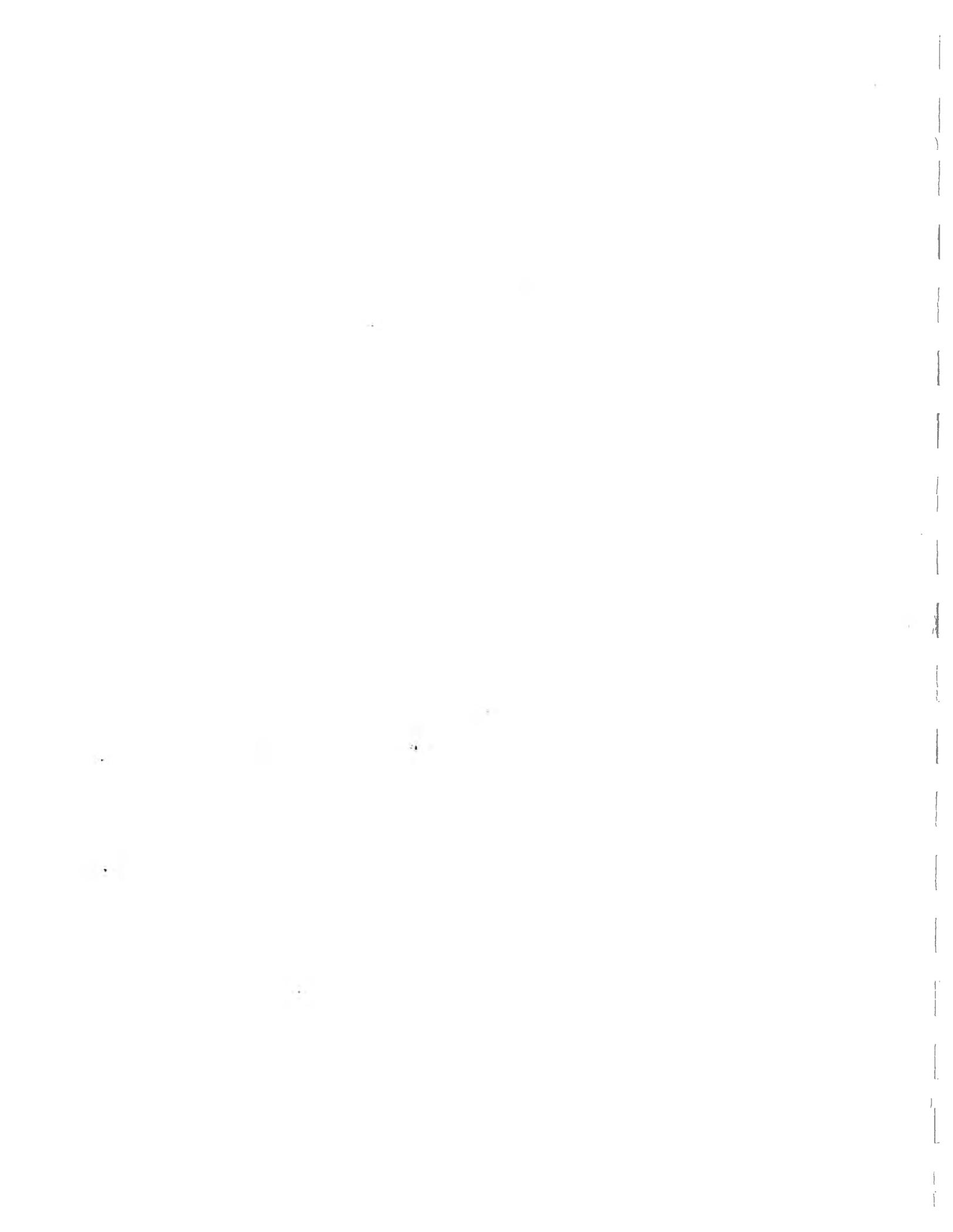
A final consideration is the potential for modifying the waste package designs. A design for the safe disposal of spent fuel in a geologic repository has been successfully demonstrated by the Swedish KBS-3 approach. The adequacy of spent fuel as a waste form must be demonstrated in the context of a given waste package design and under repository conditions. Indeed, performance assessment entails design assessment. If a performance assessment showed that radionuclide release from spent fuel did not comply with regulatory criteria, several divergent conclusions could be drawn. The first conclusion might be that spent fuel was universally inadequate as a waste form. A second might be that spent fuel could be an adequate waste form if it were modified or treated. Yet a third conclusion might be that spent fuel would be an adequate waste form if the waste package design were modified. A fourth conclusion might be that spent fuel would be an adequate waste form if a reasonable reinterpretation of the regulatory criteria were made. Evaluation of the relative programmatic merits, perhaps including cost and scheduling, of these different conclusions obviously lies well beyond the scope of this technical survey of the literature relating to the performance of spent fuel as a waste form.

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