Review of DOE Waste Package Program

Subtask 1.1 - National Waste Package Program
April 1983 - September 1983

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REVIEW OF DOE WASTE PACKAGE PROGRAM
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ABSTRACT

The current effort is part of an ongoing task to review the national high level waste package effort. It includes evaluations of reference waste form, container, and packing material components with respect to determining how they may contribute to the containment and controlled release of radionuclides after waste packages have been emplaced in salt, basalt, and tuff repositories. In the current Biannual Report a section on carbon steel container corrosion has been included to complement prior work on TiCode-12 and Type 304 stainless steel. The use of crushed tuff as a packing material is discussed and waste package component interaction test data are included. Licensing data requirements to estimate the degree of compliance with NRC performance objectives are specified.

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EXECUTIVE SUMMARY

This Biannual Progress Report is one in a series which describes a study to evaluate the national high level waste package program. The objective of the work is to define those features of the engineered barrier system which must be understood if a repository is to be characterized. Current effort is focused on defining the chemical and mechanical failure or degradation modes in the engineered system which influence its ability to meet NRC's two main performance objectives, viz. (a) the 300- to 1000-year radionuclide containment criterion for the waste package, and (b) the maximum annual radionuclide release rate from the engineered barrier system of one part in 10^5 of the inventory present 1000 years after repository closure.

Corrosion Failure Modes for Low-Carbon Steel

In this part of the program the data available on low carbon steel were evaluated to specify the failure modes which could compromise the ability of the container to meet the radionuclide containment criterion. Potential failure modes include uniform and pitting corrosion, galvanic corrosion, stress corrosion cracking, crevice corrosion, and hydrogen embrittlement. Current DOE efforts have focused primarily on uniform corrosion mechanisms and rates under conditions which do not reflect the changing environmental factors expected during the period of repository operation. Additional data requirements necessary for an adequate assessment and licensing are specified in the report and include long term testing and the development of predictive equations.

In assessing the susceptibility of carbon steel to pitting and crevice corrosion information is needed on the effects of groundwater composition, pH, temperature, steel heat treatment, and structure of the oxide film on the metal. The effects of radiolysis on the propagation of pits and crevices requires that testing programs be undertaken that would involve realistic conditions and extended test periods.

A review of available data indicates that there is considerable uncertainty regarding the susceptibility of carbon steel containers to stress corrosion cracking under expected repository conditions. There are indications that stress corrosion is likely to be accelerated by high repository temperatures, high stresses and high oxygen levels. Long term and accelerated testing should be undertaken involving various repository water chemistries, container stresses, and temperatures, in order to adequately assess the magnitude of this problem. High stress levels which would initiate cracking could arise from thermal gradients within the container caused by contact with cooler water, from local high loads at the contact points between the container and support posts (BWIP design), from weld stresses, and from hydrostatic/lithostatic stress components.

The most likely hydrogen assisted failure problem for carbon steel is associated with decreased ductility and delayed failure. There is insufficient information available to characterize the susceptibility of carbon steel with respect to hydrogen assisted failure under repository conditions. The

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mechanisms of hydrogen embrittlement should be identified and mathematically modeled to permit long term predictions. This effort will require an assessment of the range of repository conditions over which hydrogen assisted failure can be considered a potential failure mode.

Chemical Failure Modes for Tuff Waste Package Packing Materials

At present, the main packing material being discussed for use in a tuff waste repository is crushed tuff, designed to have 80% of the original density of the host rock. The most likely chemical degradation modes for tuff are mineralogical alteration and loss of sorptive capacity. Since these failure modes have been relatively little studied, such research may represent a high priority need for the NRC. Other materials which have been discussed as possible components of the packing are: bentonite, Mg and/or CaO, or charcoal. The arguments against introducing bentonite into a tuff repository are the following: (1) bentonite may lack the necessary hydrothermal stability at expected waste loadings, (2) bentonite might introduce water (sorbed or structural) into a relatively dry repository, (3) crushed tuff may possess less sorptive capability than the host rock itself.

The properties of tuff of most interest to its performance as packing material are: hydrothermal stability, permeability, thermal conductivity and sorption for various radionuclides under both oxidizing and reducing conditions. Such properties are site specific and depend on the mineralogy of the tuff and on the degree of porosity. Available sorption data are summarized but are preliminary in nature with few replicates, and do not cover the full range of possible conditions in a tuff repository.

The most likely degradation modes, mineralogical alteration and loss of sorptive capacity, have hardly been studied for tuff under repository conditions. Preliminary investigations indicate that limited alteration might actually improve the sorptive properties of crushed tuff due to the formation of zeolites while more extensive alteration would produce minerals with probably less favorable sorptive properties than the original tuff.

Evaluation of Interactive Effects Among Components of the Waste Package

This study evaluates interactive testing for components of the waste package and, also, whole package testing. It outlines the importance of packing material or crushed host rock with respect to their effects on the corrosion or leaching of the other components of the waste package.

Data on interactive testing of components of the waste package are fragmentary and not covering the full range of repository conditions. Although research on simpler systems may be useful to indicate trends, in such complex systems it is desirable to conduct engineering studies replicating the whole waste package and surrounding repository conditions as closely as possible (proof testing).

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Preliminary tests indicate that the packing material may be beneficial, marginal or even detrimental to the release rates depending on the choice of material, its ability to withstand the thermal period and its compatibility with other components of the waste package and with the host rock. Moist or wet bentonite in contact with the container may accelerate corrosion. Also, bentonite may accelerate the leaching of the waste form by ion depletion by preventing saturation of groundwater immediately surrounding the waste package.

Other components of the packing material such as basalt might reduce the corrosion of the low carbon steel by performing a protective silicate film. Under some circumstances, basalt can also reduce leaching of the borosilicate glass waste form.

Of the metals being considered for a HLW container, iron or low carbon steel appears to be inferior since iron in several groundwaters has been found to accelerate leaching of borosilicate glass.

From such preliminary data the need becomes apparent for more bicomponent and whole package testing covering the full range of repository conditions.

1. INTRODUCTION (P. Soo)

In the licensing procedure for a high level waste geologic repository two NRC criteria are of major importance with respect to the performance objectives for the engineered system. These are detailed in Final Rule 10 CFR 60 (Disposal of High Level Waste in Geologic Repositories) dated June 1983. The first objective specifies that:

"Containment of HLW within the waste packages will be substantially complete for a period to be determined by the Commission taking into account the factors specified in subsection 60.113(b) (of 10 CFR 60) provided, that such period shall be not less than 300 years nor more than 1,000 years after permanent closure of the geologic repository; and

"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, or such other fraction of the inventory as may be approved or specified by the Commission; provided, 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 relese 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 1,000 years of radioactive decay."

To meaningfully address these performance objectives it will be necessary for the license applicant to consider:

a. How and when groundwater enters the engineered repository system
b. How and when groundwater penetrates the geologic packing material (discrete backfill)
c. How and when groundwater penetrates the container system and causes corrosion failure
d. How and when groundwater leaches radionuclides from the waste form
e. How and when the radionuclides are transported through the failed container system, packing material and disturbed host rock to the near field environment.

For these scenarios, in which the individual engineered barriers are breached, probable chemical (corrosion) failure/degradation modes and mechanical failure/degradation modes need to be identified and quantified. These will depend on the specific design of the engineered system including selection of materials, local temperatures, local repository water conditions, radiation effects, water flow rates, and lithostatic/hydrostatic pressures, etc. It is only through a comprehensive knowledge of these factors that the performance of the individual engineered barriers can be determined and compliance with the above-mentioned NRC criteria demonstrated.

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The purpose of the current study is to outline in logical sequence the important performance assessments for barrier components which may need to be addressed for licensing with respect to demonstrating compliance with the containment and controlled radionuclide release performance objectives. Figures 1.1 and 1.2 are schematics outlining the logic for performance assessment. They specify those failure/degradation modes which are considered to be important for the materials and host rocks currently being considered in the national high level waste terminal storage program. By accumulating a comprehensive data base on these failure modes, those which will ultimately be controlling can be identified.

Although Figure 1.1 describes a plan for the comprehensive performance assessment of the individual engineered barrier components it is not mandatory for each component to be fully characterized. If the license applicant can demonstrate that one component alone can meet an NRC performance objective then a detailed characterization of the other engineered barriers is unnecessary. It would suffice to show that the other barriers are redundant and do not compromise the ability of the primary barrier to meet the objective. For example, if it can be shown that a container system alone can remain unbreached for 300-1000 years under anticipated waste package conditions, then a comprehensive data base on the performance of the secondary barriers would not be needed to address the containment time. Similarly, if the waste form has a radionuclide release rate which will meet the controlled release criterion under anticipated repository conditions a detailed knowledge of the radionuclide retardation capabilities of packing materials is also not needed. Thus, a licensing strategy based on full compliance with an NRC performance objective by a single barrier would be a cost saving endeavor. On the other hand, if compliance requires the conjoint action of more than one barrier, so that each barrier contributes partial compliance, the data base to characterize performance will necessarily involve single-component and multi-component tests to quantify interaction effects. Strategies which may be used to demonstrate compliance are discussed in a separate report (NUREG/CR-2951, 1982).

In the following sections of the current report are described corrosion failure modes for carbon steel containers, the use of crushed tuff as a packing material (discrete backfill), and whole package test data. This work complements work reported in prior Biannual Reports in this program.

1.1 Reference

NUREG/CR-2951, BNL-NUREG-51588, "Draft Staff Technical Position, Subtask 1.1: Waste Package Performance After Repository Closure," M. S. Davis and D. G. Schweitzer, Brookhaven National Laboratory, September 1982.

CONTAINMENT TIME FOR
WASTE PACKAGE SYSTEM

Determine time for groundwater to travel from the host rock through the packing material (PM) to container surface.

Determine time for container system to be breached.

Determine time for radionuclides to be released by waste form.

Determine time for for radionuclides to travel from waste form through failed containment and PM to waste package boundary.

Chemical Failure
- Increase in water flow by formation of more permeable products in PM.

Chemical Failure
- Uniform corrosion
- Pitting corrosion
- Crevice corrosion
- Galvanic corrosion
- Stress corrosion
- Selective leaching
- H_2 embrittlement

Chemical Failure
- Leaching.

Chemical Failure
- Changes in radionuclide retardation capability of PM.

Mechanical Failure
- Major inertial changes or movement of PM
- Liquid limit changes in PM
- Cracking from wet/dry cycling of PM.

Mechanical Failure
- Stress from waste form swelling
- Seismic loading
- Lithostatic stresses
- Hydrostatic stresses
- Residual stresses.

Mechanical Failure
- Major inertial changes or movement of PM
- Liquid limit changes in PM
- Cracking from wet/dry cycling of PM.

Figure 1.1 Chemical and mechanical failure/degradation modes affecting containment of radionuclides by the waste package system.

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                    ┌─────────────────────────┐
                    │  RADIONUCLIDE RELEASE   │
                    │  FROM ENGINEERED SYSTEM │
                    └─────────────────────────┘
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| Determine release rate from waste form. | Determine release rate through breached container system. | Determine release rate through packing material (PM). | Determine release rate through boundary of engineered system. |

Chemical Factors	Chemical Factors	Chemical Factors	Chemical Factors
• Temperature • Local water chemistry • Water flow rate • Eh/pH conditions • Solubility constraints.	• Not applicable.	• Changes in sorptive capability of PM.	• Sorptive capabilities of host rock. • Presence of alteration products.

Mechanical Factors	Mechanical Factors	Mechanical Factors	Mechanical Factors
• Presence of cracks in waste form.	• Local thermal/hydraulic conditions • Size and distribution of container penetrations.	• Major internal changes or movement of PM • Liquid limit changes in PM • Cracking from wet/dry cycling of PM.	• Cracking of host rock • Local thermal/hydraulic conditions in host rock.

Figure 1.2 Factors affecting radionuclide release from the engineered repository system.

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2. NEAR FIELD REPOSITORY CONDITIONS (B. Siskind, D. Hsieh, S. V. Panno)

Detailed assessments have been completed on anticipated near field conditions for salt, basalt and tuff repository systems. The salt and basalt work may be found in NUREG/CR-2482, Vol. 3, "Review of DOE Waste Package Program," dated March 1983. The section on tuff repository conditions is contained in NUREG/CR-2482, Vol. 4, "Review of DOE Waste Package Program," dated September 1983.

3. WASTE FORM FAILURE AND DEGRADATION MODES (J. Shao)

This section of the study has been completed and describes waste glass properties and environmental conditions which may affect the leachability of the glass. The work is presented in the last Biannual Report, NUREG/CR-2482, Vol. 4, "Review of DOE Waste Package Program," dated September 1983.

4. CONTAINER SYSTEM FAILURE AND DEGRADATION MODES (E. Veakis, J. Shao)

4.1 Chemical Failure Modes for TiCode-12

A comprehensive literature survey on the chemical (corrosion) failure modes for TiCode-12 was completed in a prior Biannual Report (NUREG/CR-2492, Vol. 3), "Review of DOE Waste Package Program," dated March 1983.

4.2 Chemical Failure Modes for Type 304L Stainless Steel

This study was also completed and may also be found in the Biannual Report referenced in Section 4.1.

4.3 Chemical Failure Modes for Carbon Steel

Current efforts by DOE in the selection of metallic containers for use in high level waste disposal are mainly directed at carbon steel. In the sections that follow, information is presented on the various degradation modes relevant to the corrosion of carbon steels based on theoretical and experimental considerations. Recommendations are made to address existing gaps in the data base crucial for metallic barrier evaluation and long term prediction of corrosion performance. An assessment of corrosion resistance of these steels requires an estimate of long term corrosion behavior under expected repository conditions. This work is a significant expansion of that presented in the last Biannual Report.

4.3.1 Uniform Corrosion

The electrochemical theory of uniform aqueous corrosion is concerned with the galvanic interaction that takes place between the anodic and cathodic areas of the metal surface. Uniform corrosion involves a reaction that proceeds over the entire exposed surface, or over a large area, of the metal. Investigations

of corrosion processes attempt to determine the nature of the corrosion products and the influence these have on the rate of reaction (Shrier, L., 1976). Dissolution of the metal at the anode and reduction at the cathode, in the case of steel, is often represented as:

$$Fe \longrightarrow Fe^{+2} + 2e^- \quad \text{and} \quad Fe + H_2O + 1/2 \; O_2 \longrightarrow Fe(OH)_2.$$
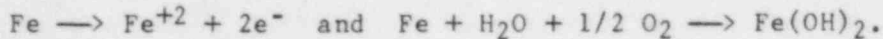
In the corrosion process, the driving force is provided by the differences in electrochemical potential between the anodic and cathodic areas. Some of the factors responsible for these differences include local variation in oxygen concentration of the solution, variation in dissolved metal ion concentration, and compositional variation of the metal along the exposed surface.

The acidity of the solution is a key factor affecting corrosion rate. In alkaline or neutral solutions the kinetics are dependent on oxygen availability. For a pH range of 4-10, in low velocity ambient temperature water, a layer of ferrous hydroxide forms acting as a diffusion barrier to oxygen. The metal surface environment is alkaline, resulting in low uniform corrosion rates (Uhlig, H., 1971). Increase in oxygen concentration results in hydrous ferric oxide and is evident as "rust." Typical corrosion rates of carbon steel in the pH range of 5-10 (air saturation, ambient temperature) is ~12 mpy. An increase in dissolved oxygen content in low velocity, ambient temperature water is accompanied by a linear increase in the corrosion rate (Uhlig, H., 1971).

Higher temperatures may increase the diffusion of oxygen through the hydrated iron oxide to increase corrosion. From ambient to ~80°C, the corrosion rate doubles for every 15°-30°C rise in temperature. Uhlig notes that in an open system, corrosion rates decrease at temperatures above 80°C as a result of a decrease in oxygen solubility (Uhlig, H., 1971). In closed systems, corrosion rates increase with temperature until oxygen consumption is completed. Effects of pH and temperature on the corrosion rate of carbon steel in water are summarized in Table 4.1.

Table 4.1. Summary of pH and temperature effects on corrosion rates for carbon steel in water (Kirby, G. N., 1979).

Effect of pH

2-6 mL O_2/L; 20°C
    pH 5-10: 4-12 mpy
    pH $\leq$ 2: >50 mpy

Effect of temperature

pH 5-10; oxygen saturation
    20°C: 12 mpy
    50°C: 20-50 mpy
    80°C: 40-50 mpy (and higher)

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The presence of dissolved salts (acid or neutral) may act to increase the conductivity of the solution and affect the solubility of the corrosion products leading to increased corrosion rates. Concentrations of up to 3% NaCl in aerated waters will increase corrosion rates. Other alkali metal salts (e.g., KCl, LiCl, Na_2SO_4) will exhibit similar effects (Uhlig, H., 1948). The presence of alkaline salts (e.g., Na_3PO_4, $Na_2B_4O_7$, Na_2SiO_3) may act to inhibit corrosion as a result of basic pH's resulting from hydrolysis.

Small amounts of oxygen can greatly accelerate corrosion of mild steel. With oxygen present, the reduction of O_2 becomes an important cathodic reaction. The formation of oxygen differential cells results in the intensification of nucleation and growth or acceleration of existing pits (DOE/ET/28317-TI, 1980). The effects of dissolved oxygen on the corrosion rate of carbon steel are illustrated in Figure 4.1(a) and 4.1(b) (Kirby, G., 1979). The decrease in corrosion rate indicated in Figure 4.1(b) results from the passivation of the iron exposed to near-neutral solutions and is not expected to occur in the presence of high chloride concentrations. In an unsealed repository (operating period), the availability of oxygen and the possibility of differential aeration may lead to increased corrosion of the metal (PNL-4474, 1982). Data on the effects of oxygen required to predict metallic barrier integrity under repository conditions, including the presence of radiation, are lacking at this time.

(a)   (b)
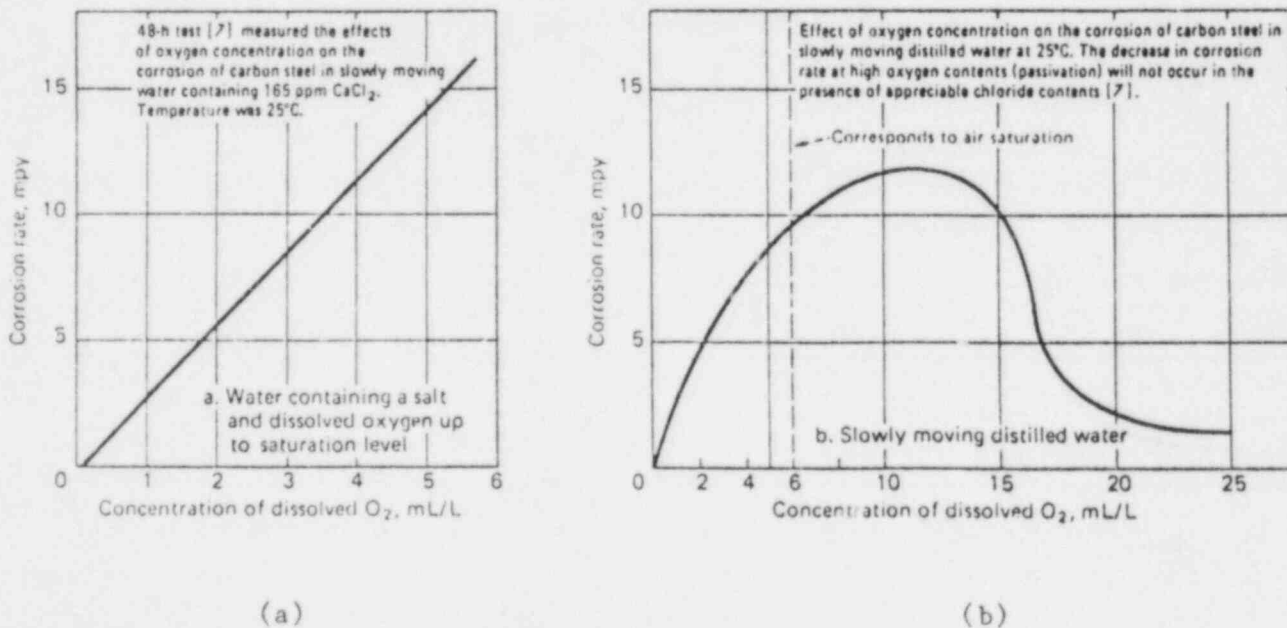
Figure 4.1. (a) Effects of oxygen concentration on the corrosion of carbon steel in water containing 165 ppm CaO_2 (25°C); (b) effect of oxygen concentration on the corrosion of carbon steel in water (Kirby, G. N., 1979).

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The relative corrosion resistance of metals, expressed as mils penetration per year (mpy) for typical ferrous and nickel based alloys, was ranked by Fontana and Greene as follows (Fontana, M., 1978): "outstanding": <1 mpy; "excellent": 1-5 mpy; "good": 5-20 mpy; "fair": 20-50 mpy; "poor": 50-200 mpy; "unacceptable": >200 mpy. The higher corrosion rates may be acceptable for materials with thick cross-sections.

Potential-pH (Pourbaix) diagrams, based on the application of thermodynamics to corrosion phenomena, have been used to predict the direction of reactions and to provide an estimate of the corrosion product composition. Since Pourbaix diagrams represent equilibrium conditions they are incapable of addressing rates of corrosion. Figure 4.2 shows a Pourbaix diagram for $Fe-H_2O$ at 25°C. For comparative purposes, Pourbaix diagrams are presented (Figures 4.3 and 4.4) for 200°C and 300°C (PNL-3569, 1981; R. Garnsey, 1979). The diagrams illustrate immunity-susceptibility corrosion characteristics as well as conditions favorable to the formation and stability of a passivating oxide film. A comparison of the diagrams indicates that low pH's enhance corrosion but there is also an increase in alkaline corrosion susceptibility with increased temperature for the $Fe-H_2O$ system. It should be noted, however, that the Pourbaix diagram is based on a pure $Fe-H_2O$ system so that minor additions of dissolved constituents to the water may considerably alter the diagram.

Under actual repository conditions, changes in the composition, Eh, and pH of groundwaters, including changes effected by radiolysis such as O_2 production, are of particular interest since these parameters will act to complicate systemic interactions.

Corrosion studies undertaken by Westerman, and others (PNL-4364, 1982) on cast irons and steels in basaltic groundwater (one- to six-month duration; 150°-250°C) are presented in Table 4.2. Cast iron showed a maximum corrosion rate of 0.30 mpy over a six-month period at 250°C. The data predict lower corrosion rates at lower temperatures. No pitting corrosion or other non-uniform corrosion modes were observed for the duration of these experiments. These workers caution, however, that the six-month period may have been insufficient for the development of pitting corrosion. Uniform corrosion data on the ferrous materials tested in basaltic groundwater at 250°C are shown in Figure 4.5. Results obtained do not address possible effects induced by radiation or mechanical stress interactions likely to occur under repository conditions. The principle corrosion products formed on the surface of ductile iron specimens were analcime $(NaAlSi_2O_6 \cdot H_2O)$ and nontronite $[(Fe,Al)Si_2O_5(OH) \cdot nH_2O]$.

Uniform corrosion studies involving tuffaceous groundwater at 250°C are shown in comparison to basaltic groundwater exposure in Figure 4.6. The data presented suggest that tuffaceous groundwater is less aggressive towards carbon steel in instigating corrosion than basaltic groundwater. Corrosion products determined were nontronite and magnetite (Fe_3O_4). No indication of pitting or other non-uniform corrosion modes were observed. It should be noted, however, that these tests employed synthetic groundwaters which are not fully representative of groundwater compositions likely to contact the waste package during resaturation.

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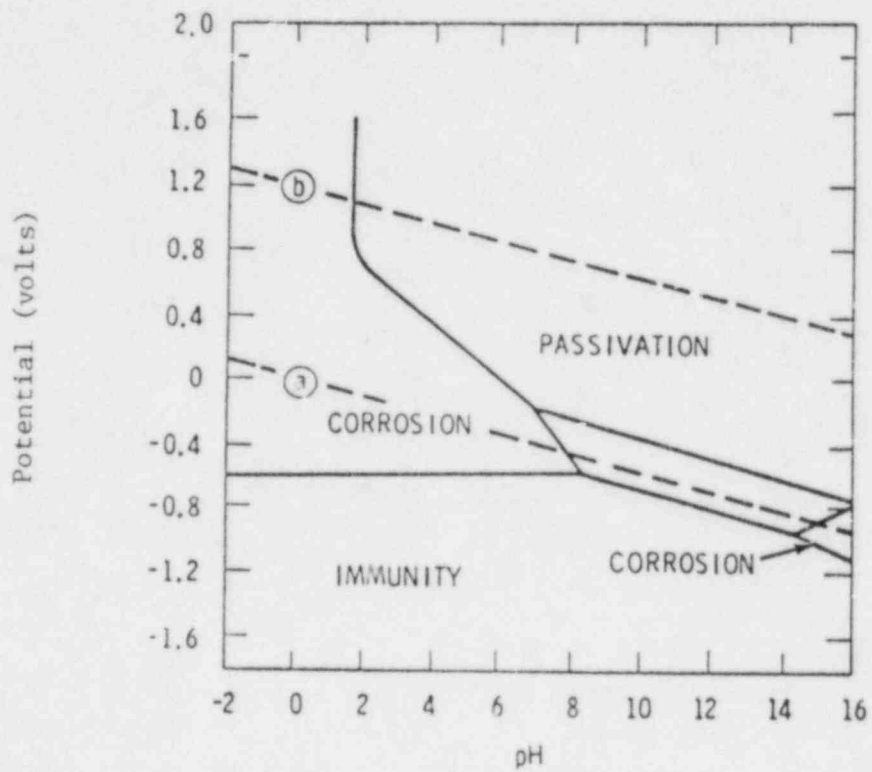
Figure 4.2. Potential-pH diagram at 25°C for Fe-H_2O showing areas of passivation (PNL-3569, 1981). Line (a) is the reduction to hydrogen; line (b) is the oxidation to oxygen.

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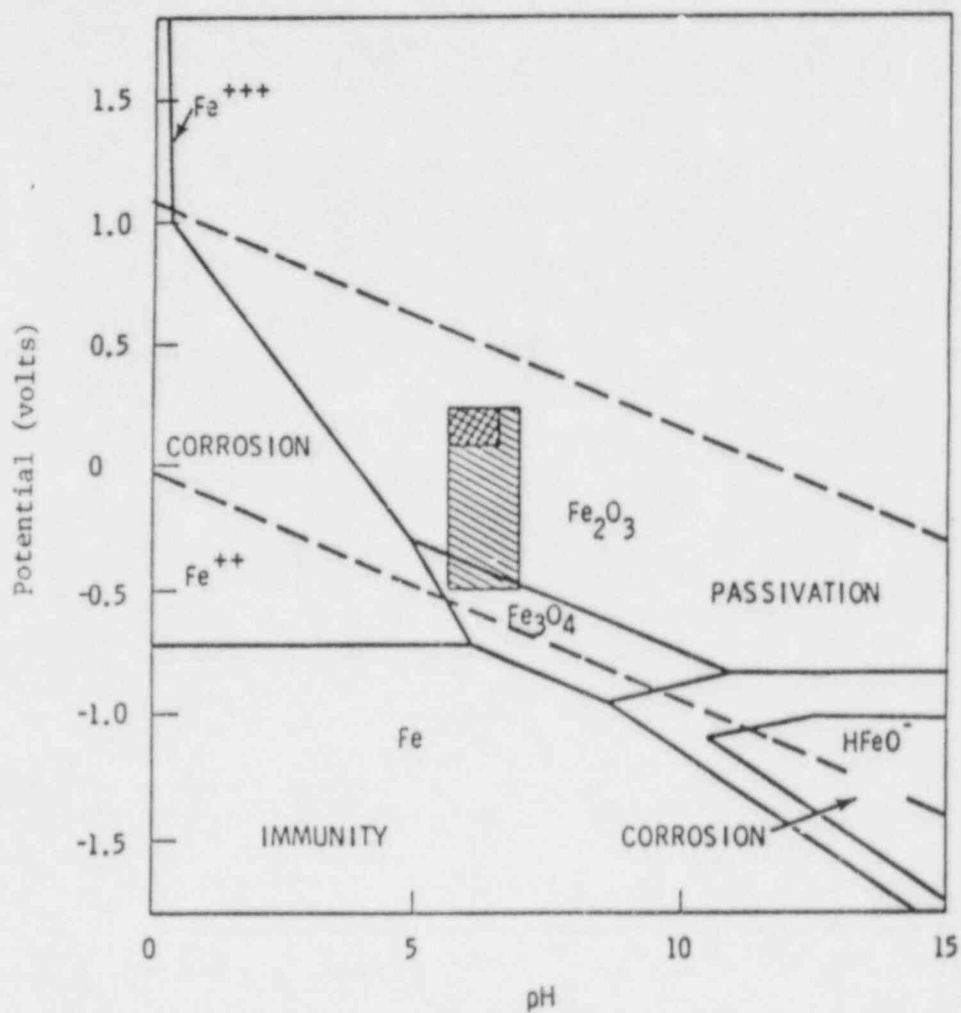
Figure 4.3. Potential-pH diagram at 200°C for Fe-H_2O; shaded area is potential region for oxygenated neutral water; cross-hatched area is potential region for hydrogen peroxide addition to neutral waters (PNL-3569, 1981).

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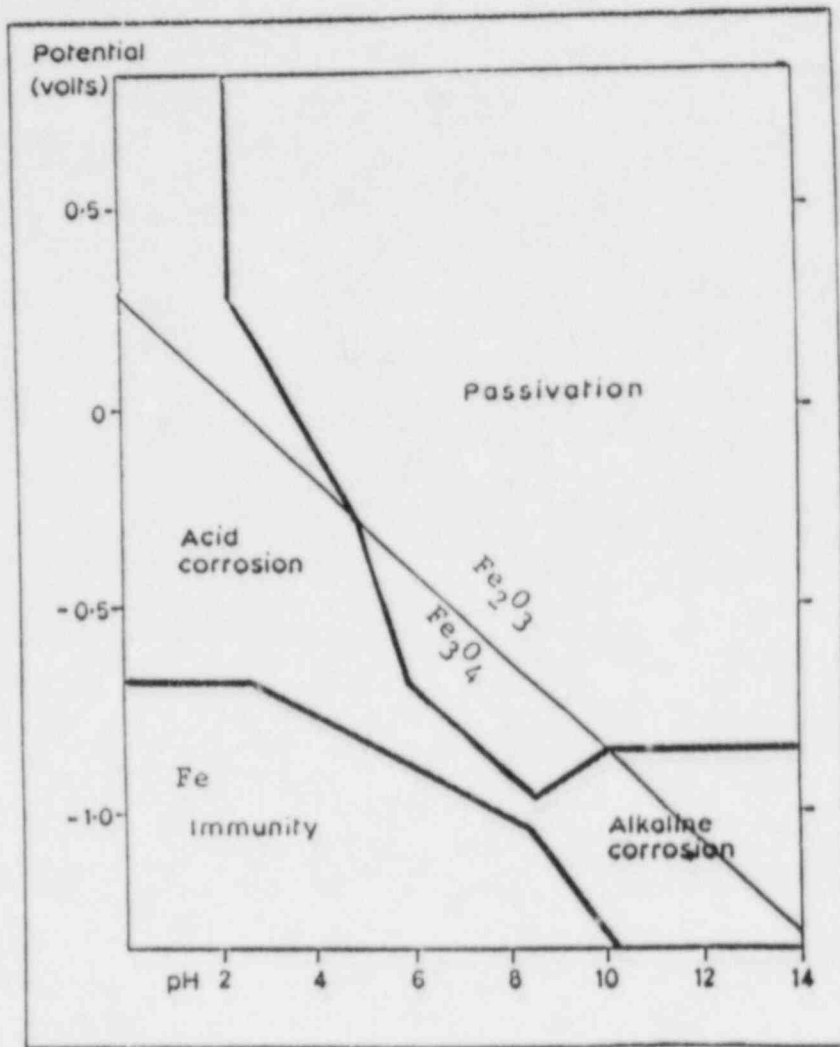
Figure 4.4. Potential-pH diagram at 300°C for Fe-H_2O (Garnsey, R., 1979)*.

*Based on normal boiler operations. As shown, slightly alkaline water indicates that corrosion will be inhibited by a passivating film of magnetite (Fe_3O_4). Does not take into account oxidizing or reducing agents. Dissolved oxygen can increase potential in nearly pure water so that hematite (Fe_2O_3) replaces magnetite as the protective surface film.

Table 4.2. Corrosion rates of cast iron and cast steels in groundwaters in flowing autoclave tests (PNL-4474, 1982).

Material	Solution	Temperature (^{o}C)	Test Duration (month)	Rate (mpy)
Ductile Cast Iron	Basaltic Groundwater[a]	150	1	0.35, 0.28
		150	3	0.15
		150	6	0.14
		250	1	1.02, 0.91
		250	3	0.31
		250	6	0.27, 0.19
Cast Steel 2-1/2 Cr 1 Mo	Basaltic Groundwater[a]	150	1	0.13
		150	3	0.079
		150	6	0.10, 0.047
		250	1	0.55, 0.59
		250	3	0.16
		250	6	0.11, 0.059
Cast Steel 1-1/4 Cr 1/2 Mo	Basaltic Groundwater[a]	150	1	0.080
		150	3	0.098
		150	6	0.095, 0.12
		250	1	0.55, 0.98
		250	3	0.17
		250	6	0.23, 0.071
Ductile Cast Iron	Tuffaceous Groundwater[b]	250	1	0.18, 0.27
Cast Steel 2-1/2 Cr 1 Mo	Tuffaceous Groundwater	250	1	0.21, 0.25

[a]Synthetic Grande Ronde groundwater passed through crushed basalt; pH 9.8 to 10, inlet oxygen 6-8 ppm, outlet ~0.3 ppm.
[b]J-13 Well water from Nevada Test Site flowed through Bullfrog Horizon tuff rock; inlet oxygen 6-8 ppm.
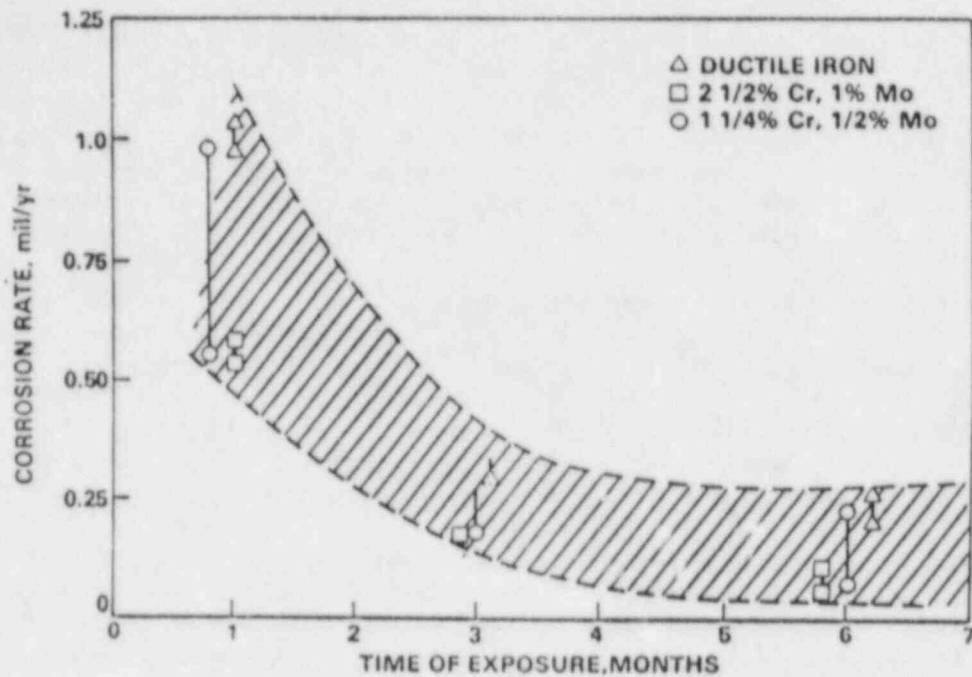
Figure 4.5. General corrosion of cast ferrous materials in Harford basalt groundwater at 250°C. Based on linear corrosion kinetics (PNL-4364, 1982).
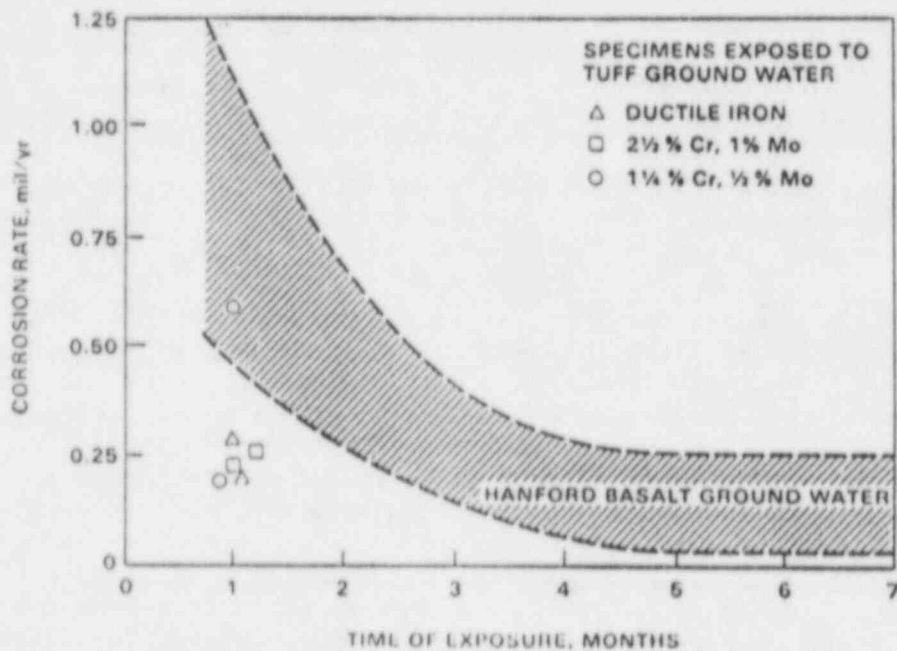
Figure 4.6. General corrosion of cast ferrous materials in tuff groundwater at 250°C compared with rates found in Hanford basalt groundwater. Based on linear corrosion kinetics (PNL-4364, 1982).

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Carbon steel corrosion results from the Avery Island Salt Mine, based on a three-year test, indicated a maximum localized penetration depth of 120 mpy. Average corrosion rates, over the three years, ranged from 0.079 mpy to 5.35 mpy. Results in the high end of the range suggest that in this test the corrosion of carbon steel was temperature-dependent (ORNL/TM-8351, 1982). The test conditions were relatively dry. Although brine was present at the bottom of the emplacement hole it was not in direct contact with the specimens.

Results of studies conducted on the corrosion of mild steel in deoxygenated brines (250°C; P = 5 MPa) indicated somewhat higher rates of attack: 67 mpy (Brine A) and 2.76 mpy (Brine B). No pitting or crevice corrosion was observed (SAND 78-2111, 1978). The corrosion rate of mild steel in oxygenated brine (600 ppm O_2; Brine A) was determined to be 275.6 mpy. The duration of these experiments was from 2-8 weeks; no pitting or other non-uniform corrosion modes were observed.

Results of corrosion tests conducted in support of geothermal energy development are based on extremely severe conditions of high temperatures, solution strength, and flow rates. Data based on geothermal brine studies may be useful in screening materials but are not directly applicable to an assessment of metallic barrier performance under expected repository conditions.

Uniform corrosion rates of 1020 steel in MESA G-1 liquid and steam brine exposed for 22 days were 11.4 mpy (liquid, 152°C; 11,000 ppm Cl^-; brine pH = 5.2) and 16.6 mpy (steam, 140°C; 3000-5000 ppm Cl^-; pH = 5.2) (BUMINES-RI-8504, 1981). 1020 steel showed no evidence of pitting or crevice corrosion under optical microscopy. All alloys tested, including 1020 carbon steel, exhibited scale formation. Corrosion rates of carbon steel exposed to liquid brines have been shown (Figure 4.7) by Shannon to increase with salinity (PNL-2456, 1977).

Chloride concentration in KGRA fluids is in the region of 3-15% (as NaCl). Chloride concentration of <3% (NaCl) was found to have little effect on the uniform corrosion rate of mild steel (DOE/ET/28317-TI, 1980).

The estimated uniform penetration in the absence of a radiation field, of cast iron and carbon steel for varying environments is presented in Table 4.3.

The effects of radiation on the corrosion rates of carbon steel will tend to influence considerably any predictive assessments of long term durability of metallic barriers. Radiolysis effects, involving a shift in the chemical potential of the groundwater contacting the metal, require extensive characterization.

Tests of iron based alloys in an irradiated basalt groundwater environment indicated higher corrosion rates than in non-irradiated conditions (PNL-4364, 1982). Figure 4.8 illustrates corrosion rates obtained for irradiated and non-irradiated regimes. Surface corrosion products for the irradiated specimens included nontronite, analcime, and hematite. These tests were preliminary in nature and have yet to address the complex interactions occurring in the irradiated system.
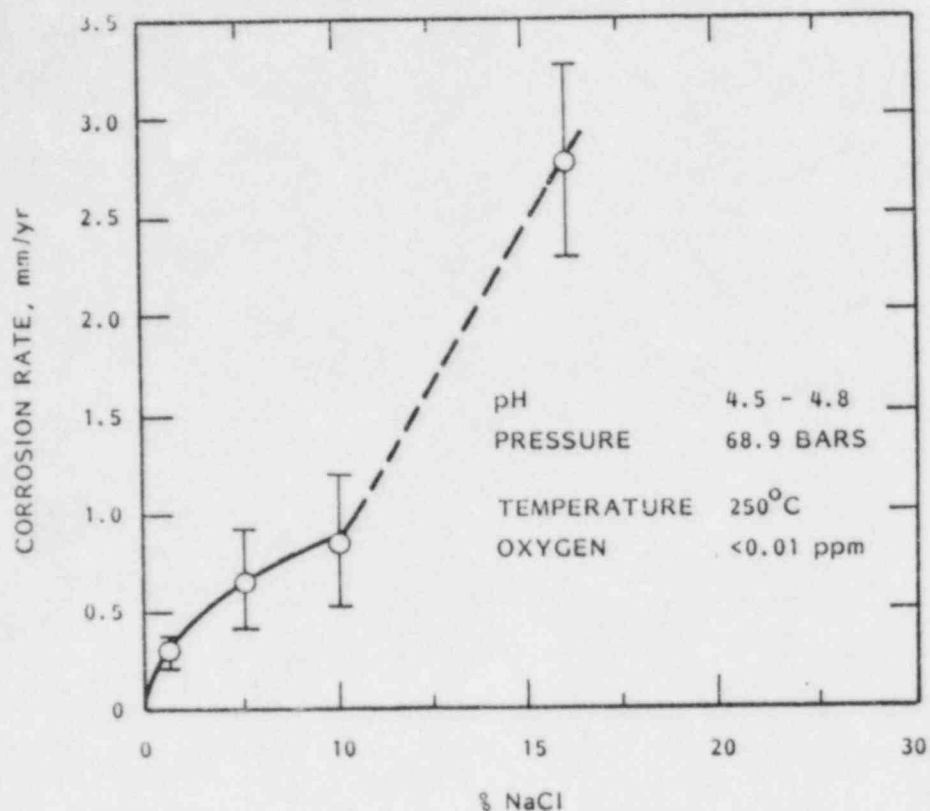
Figure 4.7. Average corrosion rate of carbon steel vs salinity (PNL-2456, 1977).

Table 4.3. Estimated uniform metal penetration in cast iron and carbon steel (PNL-4474, 1982).

Rate Law	Temperature, $^\circ$C	Environment	Penetration, mm 500 yr	1000 yr
Parabolic[a]	250	pH 7 to 8 H_2O	28	38
Linear[b]	250	13% NaOH	20	38
Linear[b]	250	Neutral H_2O	33	66
Linear[c]	Ambient	Soil	25	51

[a]The weight change used in determining this rate expression comprises both the iron lost to the environment and iron left on the metal as corrosion product.
[b]The corrosion rate based on weight gain (corrosion product growth) after the initial rapid corrosion. The data do not consider metal lost to the system due to the solubility of the corrosion film.
[c]Descaled weight loss data after 10 years underground.
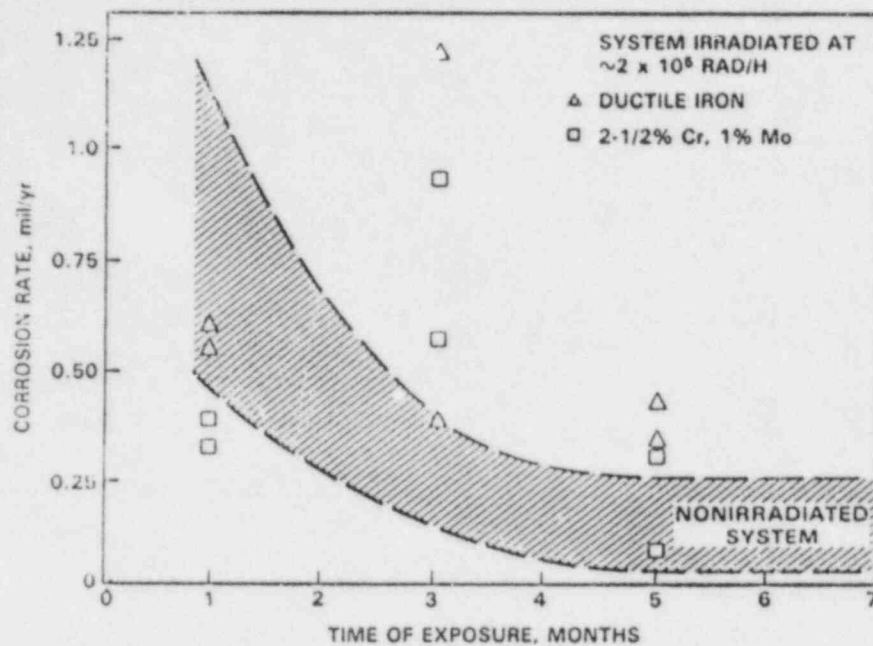
Figure 4.8. General corrosion of two cast ferrous materials in basalt groundwater at 250°C, with and without radiation. Based on linear corrosion kinetics (PNL-4364, 1982).

Earlier work by Jenks (ORNL-TM-3717, 1972) noted that radiolysis products expected by the irradiation of brine would include H_2, O_2, and possibly ClO_3^- and BrO_3^-. The presence of a high thermal field may involve decomposition of the ClO_3^- and BrO_3^- to O_2 and halides. The presence of gas bubbles within brine fluid inclusions could result in additional O_2 and H_2 availability (NUREG/CR-3219, 1983). The presence of $MgCl_2$ in the brine was postulated to produce HCl by hydrolysis. Depending on the rate of H_2 produced by radiolysis, the rate of H_2 produced by the corrosion process, and the availability of cathodic depolarizers, the local environment may shift from one of reducing to one of oxidizing conditions. Molecke and his co-workers have reported a factor of ten increase in the corrosion rate for 1018 steel in brine in going from 10^5 to 10^7 R/h ^{60}Co radiation (SAND81-1585, 1981). Table 4.4 is a presentation of the test conditions and findings.

4.3.1.1 Conclusions and Recommendations

Evidence outlined above suggests that the presence of a radiation field will result in increased corrosion rates. Molecke (SAND81-1585, 1981) gives a factor of ten increase in corrosion rates in the presence of radiation while Byalobzhesky (1966) mentions a 10- to 100-fold increase in iron corrosion rates. Data are needed to determine the effects of radiolysis on the corrosion rate of carbon steel for the purpose of developing predictive equations. These include characterization of radiolysis products and changes in the electrochemical potential of the system.

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Table 4.4. Corrosion rates of 1018 steel in ^{60}Co radiation in Brine A, Brine B, and seawater at 90°C (SAND81-1585, 1981).

Dose Rate (R/h)	Solution	Test Duration (Days)	Corrosion Rate (mpy)
10^7	Brine B	79	39.4
10^7	Brine A	79	39.4
10^5	Brine A	49	3.9
10^5	Seawater	49	1.2

Attention needs to be focused on the changing groundwater chemistry as a result of repository operations and during early post-closure periods when boiling and concentration of groundwater may occur. DOE efforts have mainly focused on determining corrosion behavior in pristine groundwater and do not address in detail conditions causing changes in groundwater chemistry.

The relatively small number of samples used in determining corrosion susceptibility and rates are not sufficient for any statistical treatment of barrier performance and need to be increased.

Future efforts in corrosion research pertaining to HLW metallic barriers should involve tests of longer duration (up to 10 years) as suggested by the work of Westerman (PNL-4364, 1982). Long term testing should involve expected repository conditions and site-specific groundwater chemistries in the presence of radiation and surrounding packing materials.

4.3.2 Pitting and Crevice Corrosion

Pitting corrosion is a specific form of localized attack resulting in rapid dissolution and penetration of a metal at isolated points. This form of corrosion is typically associated with metallurgical heterogeneities, acting as pit initiation sites, and with the breakdown of a passive film on the metal surface (Fontana, M., 1978; Baboian, R., 1976). Pitting corrosion for non-passivated mild steel involves three phases: pit initiation, pit coalescence, and pit propagation. In the case of passivated mild steel, the corrosion mechanisms are similar to those for non-passivated steel, with the exception of pit coalescence (Gainer, L., 1977). The presence of Cl^- ions tends to act as the primary initiator of localized attack. Estimates of a metal's tendency toward pitting involve:

- Determination of critical potentials for pitting initiation
- Determination of the minimum concentration of Cl^- ions necessary for the initiation of pitting corrosion (Szklarska-Smialowska, Z., 1971)
- Determination of the critical temperature for localized corrosion in a standard solution

- Determination of the number of pits and their geometry in a standard solution
- With respect to HLW containment environments, determination of the above-mentioned parameters under repository conditions expected during times of repository operations, thermal, and geologic control periods.

Potential differences between an anodic pit and cathodic bulk metal results in a self-sustaining (autocatalytic) corrosion process where pit propagation rates may be very fast. Figure 4.9 illustrates the autocatalytic pit growth process. In this process, the aerated sodium chloride solution in contact with the metal is causing metal dissolution to take place within the pit and oxygen reduction to occur at the surface surrounding the pit. This autocatalytic process is driven by the positive charge produced by metal dissolution and the flow of chloride ions to the pit.
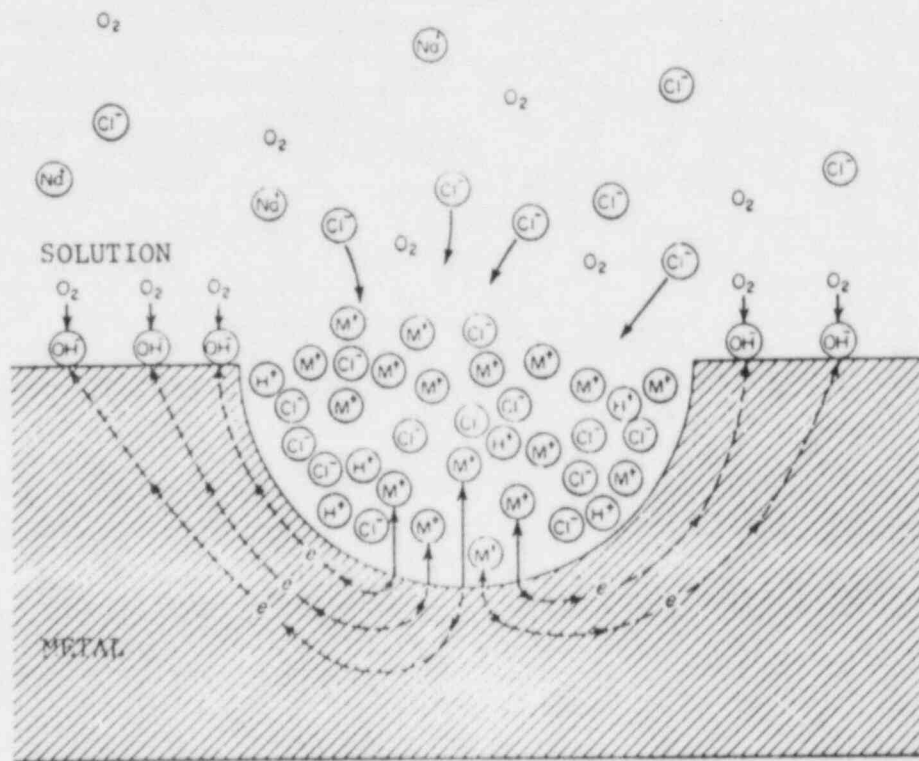
Figure 4.9. Autocatalytic pit growth process (Fontana, M., 1978).

Chao and his co-workers developed a point defect model to account for the kinetics of growth of passive films on metal surfaces (Chao, C. Y., 1981). This model addresses the following generalizations: (a) the migration of oxygen anions or oxide ion vacancies are required for passive film growth, (b) metal cation diffusion or cation vacancies result only in metal dissolution, and (c) provides for an integrated rate law for film growth. The model is shown to account for experimental data on the growth of anodic films on iron.

The point defect model has also been extended to account for the chemical breakdown of the film (Lin, L. F., 1981). The model focuses on halide induced passive film breakdown and is in quantitative agreement with experimental data derived for the pitting of iron and nickel in halide containing aqueous solutions. Although emphasizing Cl^- containing solutions, the model can be extended to other halide ions (Br^- or I^- containing systems). The critical potential, V_c, above which film breakdown occurs is a function of halide activity of the form $V_c = A - B \log a_x^-$ where A and B are constants and a_x^- is the activity of the halogen anion. The constant A tends to increase with the energy of incorporation of an anion into an oxygen vacancy and B is independent of the identity of the anion. Values for A are expected in the order of $I^- > Br^- > Cl^-$. Experimentally derived data on the critical pitting potential for iron in iodide, bromide, and chloride containing solutions, as shown in Figure 4.10, are in agreement with the theoretical predictions of the model.
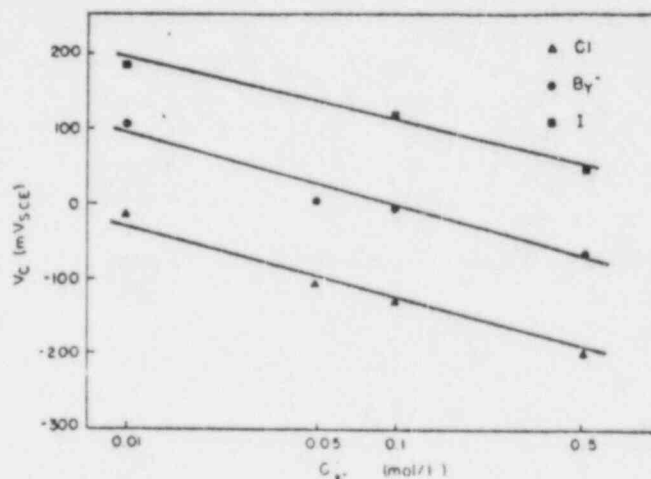
Figure 4.10. Critical pitting potential, V_c, vs halide concentration (Lin, L. F., 1981).

Although emphasis in pitting corrosion studies has focused on chloride containing solutions, the model presented by Lin, Chao, and Macdonald clearly illustrates the possibility of pitting initiation in the presence of other halide ions.

Crevice corrosion is promoted in a small volume of stagnant electrolyte in contact with metal surfaces and shielded from the bulk electrolyte. Transport of reactants and products in the crevice region are restricted due to the occluded cell geometry. Crevice corrosion is related to a depletion of oxygen in the crevice which tends to lower the electrode potential, creating an anodic region. Metal ion hydrolysis and migration of anions results in dissolution of the passive film within the crevice. Crevice corrosion often causes pitting and deep penetration over a relatively small, localized area of the crevice surface. The mechanisms of pit and crevice corrosion are similar and metals susceptible to pitting are also susceptible to crevice corrosion, although the

reverse is not always true (Fontana, M., 1978). Crevice corrosion is associated with shielded areas, surface deposits, welds, joints and sites narrow enough to maintain a stagnant zone. Pitting corrosion, on the other hand, initiates its own microcrevice. With regard to the induction and growth periods, pitting corrosion relies on damage to the passivating film allowing for pit nucleation while crevice corrosion is dependent on the time required to attain a sufficient difference in the oxygen concentration within the crevice and that of the bulk electrolyte (Szklarska-Smialowska, Z., 1975).

Corrosion occuring under restricted diffusion conditions is termed "occluded cell corrosion" or OCC. Pitting, as well as crevice corrosion and stress corrosion cracking are manifestations of the OCC phenomenon. Solutions within the pit or crevice tend to be acidic as a result of the hydrolysis of metallic ions.

In cases where the solution contains oxygen, the metal surface outside the occluded cell is typically passivated, acting as an aerated cathode. The surface inside the occluded cell is active, acting as a non-aerated anode. The transfer of anions from the cathodic area to the anodic will, in the case of corroding solutions containing chloride, involve the formation of hydrochloric acid inside the pits or crevices.

Characterization of the electrochemical problems associated with OCC require data and interpretation of electrode potential values for the cathodic sites, the anodic sites, and the potential difference of the two electrodes with additional consideration given for the initiation and progression of the corrosion process.

4.3.2.1 Environmental Factors Affecting Localized Corrosion

Corrosion research conducted by the Bureau of Mines involving high salinity geobrines in high temperature autoclave tests ($232^{\circ}C$; 15-day exposure; pH 6.1), reported that 1020 carbon steel did not exhibit any crevice corrosion in deaerated brine. In brine containing 100 ppm dissolved oxygen, the detection of crevice effects was hampered by the severe general corrosion rates (1060 mpy). The pitting corrosion rate for 1020 carbon steel in deaerated brine was 67 mpy (deepest pit measured) while rates in brine containing oxygen were detected but not quantified (BUMINES-RI-8415, 1980).

The presence of chloride in the solutions likely to contact the low carbon steel may initiate pitting due to the concentrations exceeding some critical value (Kononova, M. D., 1974; Khedv, M. G. A., 1982). M. D. Kononova and his co-workers (1974) used a neutral borate buffer solution (0.2 M H_3BO_3 + 0.05 M $Na_2B_4O_7 \cdot 10H_2O$; pH 7.35) containing additions of NaCl and Na_2SO_4 at $50^{\circ}C$. The critical concentration of chlorine ions in aerated solutions was 20 mg/liter. At certain potentials for a given system, exceeding the critical concentration will result in the initiation of pitting corrosion. Szauer and Jakobs (1976) have shown that the potential of pit nucleation (potential for stable pit formation), E_p, is dependent on chloride concentration. Potentiokinetic polarization of carbon steel specimens in a borate buffered

(pH 8.4) solution, indicated that as the concentration of Cl⁻ in the solution increased from 0.005 to 0.1 N KCl, E_p shifted in the active direction by more than one order of magnitude. The critical chloride-ion concentrations need to be determined under actual repository conditions if they are to be used as an indicator of metal susceptibility to pitting corrosion.

Figure 4.11 shows the Pourbaix diagram for iron in chloride solution and illustrates the anodic potential required for pitting and crevice attack. Clearly, pitting may occur over a wide range of potentials and pH's.
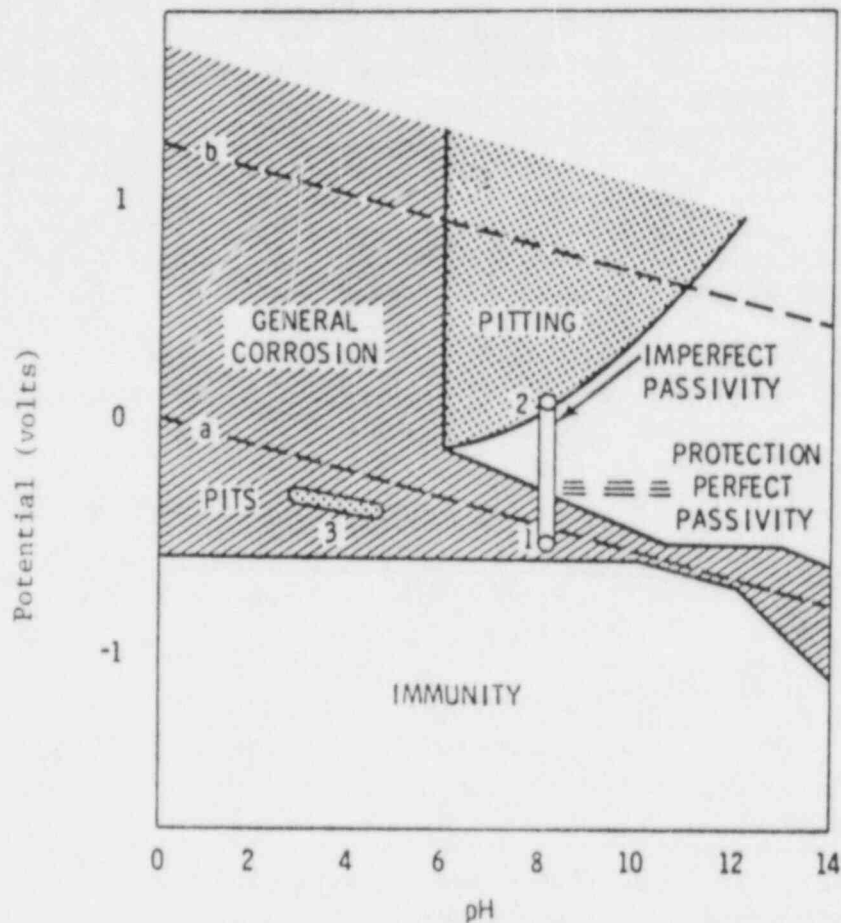
Figure 4.11.   Electrode potentials of iron in a solution of pH 8, 355 ppm Cl⁻. Region 1: oxygen-free solution and general corrosion; region 2: oxygen, nonpolarized and pitting; region 3: active pitting and crevice attack (PNL-3569, 1981).

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The effects of temperature on localized corrosion and, in particular, pitting corrosion have not been adequately determined. There are indications of a decrease in the critical pitting potential associated with increases in temperature; however, typical investigations have been limited, for the most part, to low temperatures (ambient to ~90°C). Increasing temperature may tend to increase the pit density resulting in a decrease in pit growth (Szklarska-Smialowska, Z., 1975). Other work by Tait (1979) addressed the effects of temperature on the pitting corrosion of mild steel under non-passivating conditions. Neutral, oxygen saturated waters, whose composition is shown in Table 4.5, were used in these experiments. Figure 4.12 presents the pitting corrosion rate data for this system. The results of this experiment indicate that temperature is a dominant factor governing pitting rates. The results also indicate that the pitting rate was only slightly affected by total dissolved solids (TDS) in the range of deionized water to 1800 ppm and suggested a slight decrease in pitting rates at higher TDS levels.

Several studies concerned with localized corrosion behavior of ferrous metals have utilized the extensive data base developed by the National Bureau of Standards (NBS) (PNL-3569, 1981; AESD-TME-3113, 1981; NUREG-0960, 1983). An expression of maximum pit depth (P) in mils for ferrous metals in soils of varying resistivity and pH was given as:

$$P = K_n K_a \ (10-pH)^n \ (\theta/\rho)^n \ A^a$$

where

ρ = soil resistivity, ohm-cm

θ = time, years

A = exposed surface area, ft^2

K_a, a = material-dependent factors

n = 1/6, 1/3, 1/2, or 2/3 for soils that are well aerated, fairly well aerated, poorly aerated, or poorly aerated with soluble corrosion products, respectively

K_n = 170, 222, or 355 for soils that are well aerated, fairly well aerated, or poorly aerated, respectively.

Charlot and Westerman (PNL-3569, 1981) warn, however, that the determination of the material-dependent factors is subject to variation and, therefore, not amenable to generalizations. Because of this, data derived from soil corrosion studies are inconclusive with respect to probable corrosion rates likely to occur under repository conditions. Chemical equilibria in soils represent inter-actions of sufficiently different parameters (acidity, organic content, aeration, groundwater velocity, temperature, etc.; see Bohn, H., 1979; Lindsay, W., 1979) as to negate their usefulness as indicators of probable corrosion rates likely to occur in deep geologic formations.

Table 4.5. Composition of test solutions used by Tait (1979).

	OX			3X	
Na^+	0	ppm	Na^+	63.6	ppm
HCO_3^-	0	ppm	HCO_3^-	33.0	ppm
Cl^-	0	ppm	Cl^-	54.3	ppm
Mg^{+2}	0	ppm	Mg^{+2}	18.0	ppm
Ca^{+2}	0	ppm	Ca^{+2}	60.0	ppm
SO_4^{-2}	0	ppm	SO_4^{-2}	250.8	ppm
	7X			12X	
Na^+	148.4	ppm	Na^+	254.4	ppm
HCO_3^-	77.0	ppm	HCO_3^-	132.0	ppm
Cl^-	126.1	ppm	Cl^-	217.2	ppm
Mg^{+2}	42.0	ppm	Mg^{+2}	72.0	ppm
Ca^{+2}	140.0	ppm	Ca^{+2}	240.0	ppm
SO_4^{-2}	585.2	ppm	SO_4^{-2}	1003.2	ppm
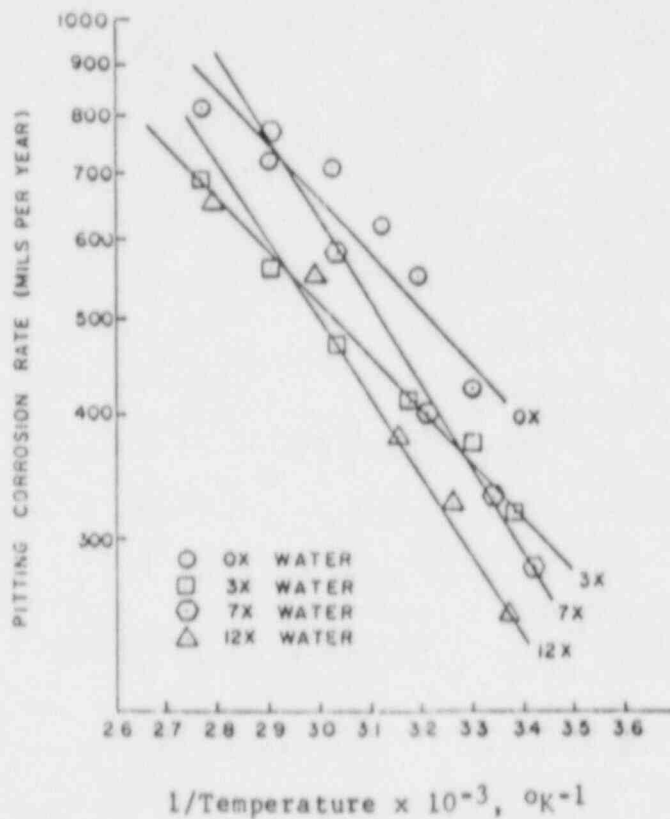
Figure 4.12. Pitting corrosion rates as a function of temperature (Tait, 1979).

In summary, the soils reported by Romanoff (1957) represent environments in which moisture, oxygen and temperature were either not controlled or not known by the investigators. The effects of these parameters on the corrosion process are addressed elsewhere in this report. The soil studies also do not address the adverse effects of radiation on the corrosion rate of the metallic barrier. Justification for the use of this data base is generally stated to be the long term duration of these studies (>30 years) and the large number of specimens involved in the tests. Unlike current efforts, the large data base presented by NBS is amenable to statistical analysis and offers the potential for constructing predictive equations, but is limited in application to soil systems.

4.3.2.2 Conclusions and Recommendations

Information on the initiation and growth of pits is difficult to obtain under experimental conditions. Direct observation may be hampered by the formation of corrosion products and by the fact that the attack is anisotropic. Attempts to characterize the resistance of metals to pitting require the determination of the breakdown potential and the potential for repassivation (Szklarska-Smialowska, Z., 1971). Factors to be considered in assessing the susceptibility of low carbon steels include effects of electrolyte composition, pH, temperature, heat treatment, and structure of oxide film on passivated metals. In the case of crevice corrosion, the approach may entail initiation of crevices in order to evaluate the susceptibility of a particular metal to crevice corrosion for the purpose of extrapolating short term tests to long term predictive equations. Current DOE efforts have focused primarily on uniform corrosion mechanisms and rates under conditions which do not reflect the changing environmental factors expected during the period of repository operation, particularly with respect to groundwater chemistry (PNL-3569, 1981). Although the assumption is often made that environments inducing pitting will also induce rapid overall corrosion (Kirby, G., 1979), the presence of pitting/crevice corrosion associated with stagnant or low-flow aqueous solutions, requires further investigation. The effects of radiolysis on the propagation of localized corrosion also require that testing programs be undertaken that would involve realistic repository conditions.

Specific recommendations with respect to additional information needs for localized corrosion of carbon steel include:

• Determination of changes occurring in groundwater chemistry and, particularly, in chemical potential due to radiolysis.

• Determination of radiolysis products, rates of production, and effects on corrosion rate.

• Determination of critical potentials for pitting initiation in candidate repository groundwater regimes.

• Past emphasis by DOE has been on uniform corrosion phenomena. Assumptions such as those made by Charlot and Westerman (PNL-3569, 1981) that

if pitting should occur, it would be expected to be no worse than that reported in soils, require verification. Wood and his co-workers reported decreased pitting and crevice corrosion in tests involving low-carbon steel in basalt groundwater (DOE/NWTS-30, 1982). It is evident that carbon steel susceptibility to pitting and crevice corrosion under expected repository conditions has not been adequately addressed. The effects of radiolysis on the propagation of pits and crevices also require that testing programs be undertaken that would involve realistic repository conditions and very extended test times.

- In the case of pitting, a statistical approach to pit formation and a definition of "failure" may be established as suggested by current MCC efforts (PNL-4474, 1982). This approach requires the determination of pit depth, frequency of formation, and areal extent; in the case of crevice corrosion, the approach may entail initiation of crevices in order to evaluate the susceptibility of a particular metal to this type of attack.

4.3.3 Stress Corrosion Cracking

Stress corrosion cracking (SCC) is a failure mode which occurs as a result of the conjoint action of a tensile stress and a specific corrosive medium (Fontana, M. G., 1978). Hydrogen assisted failures will be classified and addressed elsewhere as a separate phenomenon since the mechanisms may be quite different. For example, an effective method for preventing SCC is cathodic protection which would tend to accelerate hydrogen embrittlement effects.

4.3.3.1 Environmental Factors Which Affect SCC

There are many different mechanisms of SCC which can occur for a specific environment. Tensile stresses are required and usually are present as either residual or applied stresses. Compressive stresses are not damaging. During SCC, the metal does not necessarily experience severe uniform corrosion but fine cracks initiate and propagate through the bulk metal. The time to failure is usually dependent upon the severity of the stress and environment and can vary from minutes to years.

A recent survey on the susceptibility of carbon steel to stress-corrosion cracking (SCC) revealed that three types of environment are of major concern. These are aqueous solutions containing carbonate/bicarbonate, nitrate, and alkali (Parkins, R. N., 1972). A more detailed list is given in Table 4.6. It should be noted that the type of SCC being discussed is intergranular.

The first cases of carbonate/bicarbonate SCC were found in buried steel pipes for which groundwater solutions adjacent to the cracks contained 0.5-1.4 percent CO_3^{2-} and 0.5-0.8 percent HCO_3^-. The pH of the solutions was in the range 9.7 to 12.3. Laboratory confirmation that CO_3^{2-}/HCO_3^- solutions can give rise to SCC in carbon steel has been obtained by Sutcliffe and others (1972). These workers carried out slow-strain-rate tests at 22, 50, 70 and 90°C and showed that the ductility, measured as a reduction in

cross-sectional area of the failed samples, was greatly reduced as the temperature was increased. The worst case detected was at 90°C under a controlled potential of about -670 mV (s.c.e.) for which the reduction in area decreased from 60 percent to 15 percent.

Table 4.6 Reagents known to cause stress-corrosion cracking in carbon steels (Kirby, G. N., 1979).

Ammonia, anhydrous	Magnesium choride
Ammonium nitrate	Monoethanolamine
Barium nitrate	Nickel nitrate
Calcium nitrate	Nitric acid
Chromic acid	Potassium hydroxide
Cresol	Silver nitrate
Cresylic acid vapors	Sodium aluminate
Cyanogen	Sodium fluoride
Ethylamine	Sodium hydroxide
Ferric chloride	Sodium-lead molten metal
Hydrogen cyanide solutions	Sodium nitrate
Hydrogen chloride	Strontium nitrate
Hydrogen sulfide acidic	Sulfate liquor
solutions	Sulfuric acid
Lithium metal	Sulfuric acid + nitric acid

With respect to solutions containing 0.05 percent nitrate, Wenk (1972) has shown that X-52 carbon steel stressed to 80 percent of the notched tensile strength will suffer from SCC at 93°C after only three-four weeks. For a 10 percent solution, failure occurred after eight hours. Fractographic analysis of carbon steel exposed to boiling nitrate solutions showed that SCC could occur over a wide potential range between -600 and 1200 (s.c.e.)

Caustic cracking in carbon steel was prevalent for many years in riveted locomotive boilers (Reinoehl, J. E., 1972). Alkali would accumulate in highly-stressed rivet holes and lead to SCC. Reinoehl and Berry (1972) have compiled a list of SCC failures for NaOH and have shown that under free corrosion potentials the ranges of susceptibility are 4-85 percent NaOH and 35-85°C. However, they state that these ranges may be extended or contracted depending on a number of environmental and metallurgical factors.

The greatest potential for NaOH buildup in a repository would occur in rock salt. Gamma radiation produces colloidal sodium which will interact with migrating brine bubbles to form NaOH and H_2 (NUREG/CR-2482, Vol. 3, BNL-NUREG-51494, 1982). Since the brine migrates towards the hot containers, a high concentration of caustic is likely to attack the metal.

In seawater environments, the yield strength of the steel appears to determine to some extent the susceptibility to SCC. The results of Phelps (1969) suggest that at yield strengths above 1380 MPa (200 ksi), all of the

steels tested were susceptible to stress corrosion but that below 1034 MPa
(150 ksi) the problem was much less severe. The review of SCC by Carter
(1977) has also shown that for low alloy and carbon steels having yield
strengths below ~690 MPa (~100 ksi), stress corrosion cracking has not been
identified as a cause of failure in applications involving exposure to marine
atmospheres and seawater. However, it should be expected that this trend
would be dependent upon the environment and therefore, low strength steels
would still require SCC evaluation before use under repository conditions.
Also, there usually does not exist a clear-cut threshold strength level below
which stress corrosion would not occur with increasingly longer time periods
to failure at lower stress levels.

For commercial mild steels, in the annealed or normalized conditions in
which they are most often used, the carbon content is a major factor in
determining SCC susceptibility. As shown in Figure 4.13, the threshold stress
in boiling 4N NH_4NO_3 increases with increasing carbon content. However,
if the carbon content is below about 0.001%, then susceptibility again is
decreased. This effect can be explained in terms of the carbon distribution
in the steel. At intermediate carbon contents, the carbon segregates to the
ferrite grain boundaries resulting in susceptibility. At low carbon content,
there is less carbon at the boundaries. At high carbon contents, the pearlite
phase in the steel increases and the number of carbide particles in the
boundaries decreases (Parkins, R. N., 1972).
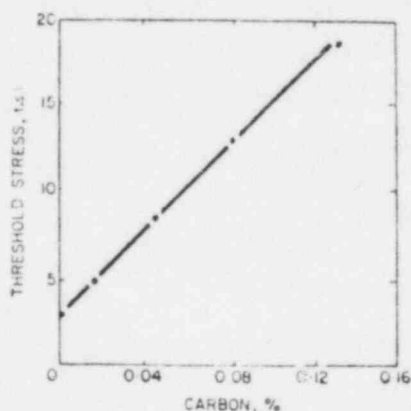
Figure 4.13. Effect of carbon content of annealed mild steels upon
threshold stress for cracking in boiling 4N NH_4NO_3
(Parkins, R. N., 1972).

Grain size is also a factor in determining susceptibility, as shown in
Figure 4.14. Coarse-grained materials are found to be more susceptible to
cracking than those with small grain size.

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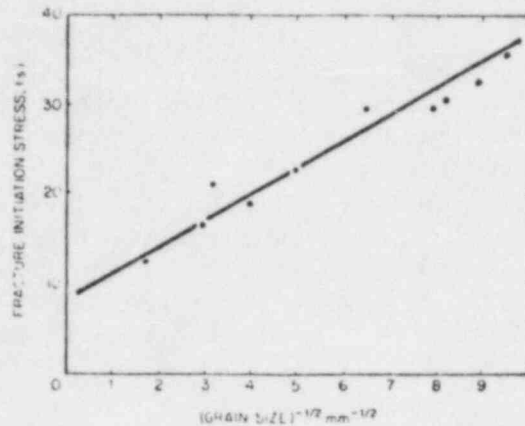
Figure 4.14. Grain size dependence of stress corrosion cracking
parameter for mild steel in boiling nitrate solution
(Parkins, R. N., 1972).

The chloride concentration in the solution environment does not signifi-
cantly affect the threshold stress intensity value but can affect the crack
growth rate. Changing the environment from distilled water to 3% sodium
chloride solution decreased the failure time by about two orders of magnitude
for an AISI 4120 steel. Most of this reduction in life occurred in the weaker
solutions containing 0.5% sodium chloride. At much higher concentrations of
chlorides, the effect on SCC may be reduced due to rapid corrosion and crack
blunting (Yamamoto, 3., 1969, cited by Carter, C. S., 1977).

Generally, there is little effect of pH on SCC susceptibility in the pH
range of 3 to 10. However, very low pH solutions will promote cracking and
highly basic solutions restrict crack initiation and propagation as shown in
Figure 4.15.

Studies on the effect of temperature on cracking of low carbon steels in
nitrate solutions yield Arrhenius plots as shown in Figure 4.16. Typical
activation energies range from 10 to 30 kcal/mol (Parkins, R. N., 1977).

Although increasing temperature tends to increase the incidence or sever-
ity of SCC in other solutions such as hydroxides and carbonates, the interde-
pendence of temperature and solution concentration must also be considered in
determining whether SCC will occur. Figure 4.17 illustrates this point.

4.3.3.2 Stress Corrosion Cracking Mechanisms

The initiation sites for SCC can be divided into three categories
(Parkins, R. N., 1972):

1. Pre-existing active paths.
2. Strain-generated active paths.
3. Specific adsorption at subcritically stressed sites.

STRESS INTENSITY, ksi-in.$^{1/2}$

- ● 3.5% NaCl
- ■ BUFFER
- ○ BUFFER + NaCl
- • H_2SO_4
- △ HCl
- □ NaOH

STEEL: 0.27 C, 0.5 Mn, 9 Ni, 11 Cr, and 0.14 Mo

TYS: 1310 MN/m^2 (190 ksi)

K_{IC}: 80 ksi-in.$^{1/2}$

pH
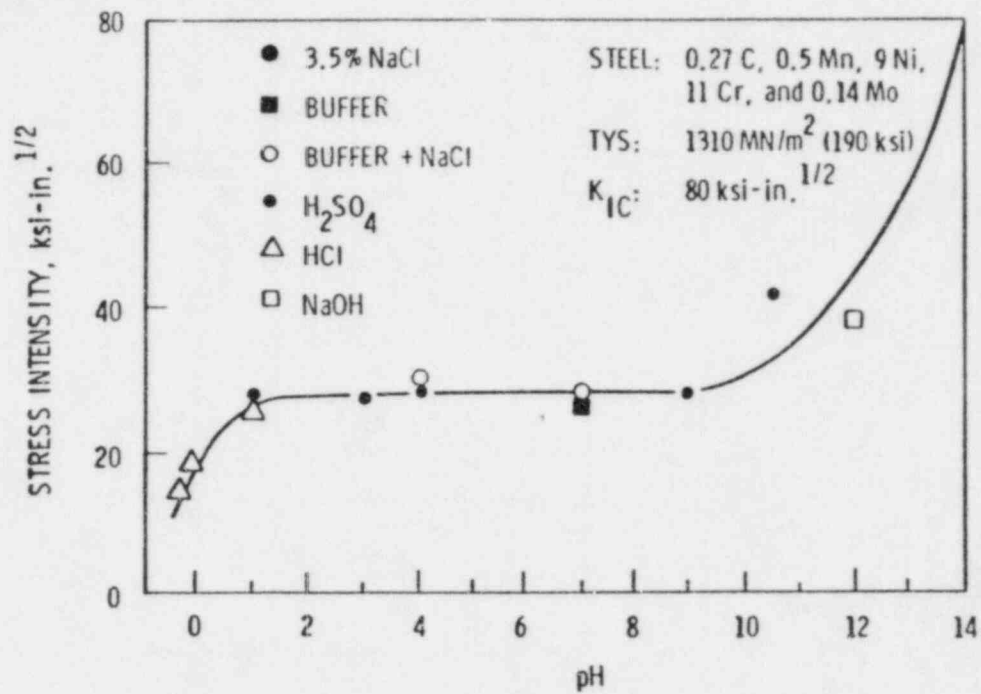
ENVIRONMENT	pH
2 N HCl	0.3
N HCl	0
N/10 HCl	1
N/10 H_2SO_4	1
BDH BUFFER	3.1
BDH BUFFER	4.0
BDH BUFFER + 3.5% NaCl	4.0
BDH BUFFER	7.0
BDH BUFFER + 3.5% NaCl	7.0
3.5% NaCl	7.0
BDH BUFFER	9.2
BDH BUFFER	11.4
N/10 NaOH	13.0
1 N NaOH	14.0

Figure 4.15. Effect of pH on the threshold stress intensity (M. J. May, 1968, as cited in PNL-3569, 1981).
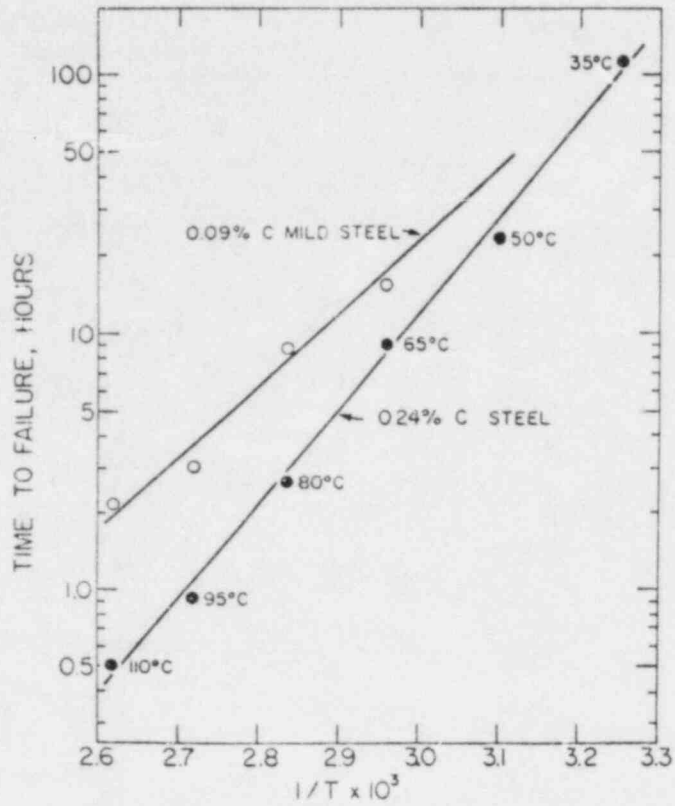
Figure 4.16. Effect of temperature on time to failure in 60% calcium
nitrate, 3% ammonium nitrate solution (each point an
an average of 3 to 5 tests) (Mazille, H., 1972).
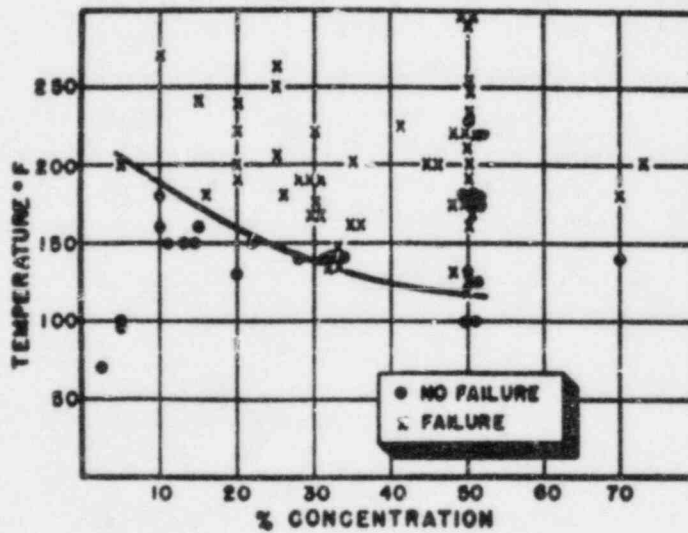
Figure 4.17. Relation of temperature and concentration of NaOH to cause
cracking (Schmidt, H. W., 1951).

When SCC is associated with pre-existing active paths, the alloy will probably show structural features, such as segregates or precipitates at grain boundaries, which create local galvanic cells. The cracking of mild steel in nitrate solutions discussed previously is an example of where the carbon distribution determined the likely sites of the active path.

The strain generated active path mechanism usually occurs in metals which possess a protective film. Stress or plastic strain in the underlying metal can rupture the protective film thereby exposing active metal until the film can reform. Crack propagation is cyclic as the film ruptures and repairs itself. In the slip dissolution model, slip steps can act as the initiation sites for strain generated active paths (Scully, J. C., 1980).

In the mechanism for specific adsorption at subcritically stressed sites, adsorbed species decrease the surface energy, thereby reducing the stress required to enlarge surface cracks. The adsorbing species can act at the crack tip or diffuse into the metal and cause embrittlement. Hydrogen embrittlement, with the hydrogen generated from corrosion reactions can be considered a form of stress corrosion (Vasilenko, I. I., 1978).

Some U-bend testing of ductile cast iron and cast steel was conducted at 150 and 250°C in simulated Hanford groundwater. No evidence of SCC was found (Westerman, R. E., 1982).

It is clear from the above review that there is a lack of SCC data for low carbon steel under repository conditions. The types of data which are needed for licensing include long term static tests and enviromechanical studies such as a slow-strain-rate and fatigue crack growth rate testing under appropriate conditions. Some of this work is presently being carried out at Pacific Northwest Laboratory; e.g., enviromechanical tests in WIPP Brine A for 1025 steel (Jain, H., 1983). The effects of solution radiolysis should also be evaluated since it will be a source of H_2 and O_2, etc.

The SCC behavior of welded specimens should be studied as stresses and active paths can be introduced by the welding process. Testing should also be performed in concentrated basaltic and tuffaceous groundwaters which may be produced by evaporation effects (Pescatore, C., 1983) particularly since carbon steels are susceptible to SCC in carbonate solutions (Sutcliffe, J. M., 1972).

4.3.3.3 Conclusions and Recommendations

Based on the above review of SCC it is clear that there is great uncertainty regarding the susceptibility of carbon steel containers to SCC when exposed to HLW repository conditions. In Grande Ronde basalt the carbonate and bicarbonate levels in pristine groundwater at ambient temperatures range up to 88 and 70 mg/L, respectively (RHO-BWI-ST-7, 1980). In other Hanford basaltic waters the carbonate value may be as high as 314 mg/L (RHO-BWI-ST-7, 1980). In tuffaceous rock bicarbonate values of 120 mg/L have been recorded (AESD-TME-3138, 1980). In repositories where gamma radiolysis of groundwater

can occur nitric acid may be generated due to dissolved N_2/O_2 mixtures. This could result in nitrate-assisted SCC of carbon steel. The problems with carbonate/bicarbonate and nitrate SCC are magnified by the concentration of these ions when groundwater contacts the hot container. Boiling of the water will occur during the repository operations period and after closure until the hydrostatic pressure becomes sufficiently high to prevent it. At this time it is almost certain that after repository closure high concentrations of dissolved salts will be present in the repository water in contact with the containers. For salt repositories containing non-shielded waste packages, gamma irradiation of the surrounding rock salt may lead to very high concentrations of NaOH.

High stress levels which would initiate cracking could arise from thermal gradients within the container caused by contact with cooler water, from local high loads at the contact points between the container and support posts (BWIP design), from weld stresses, and from hydrostatic/lithostatic stress components.

At this time there are apparently no studies being conducted to evaluate the possibility of SCC in carbon steel containers exposed to repository waters that have been consideraly enriched in bicarbonate/carbonate, nitrate, and NaOH due to boiling of the water during the repository operations period and during the time following closure when the pressure within the repository is too low to prevent boiling. Based on available data stress-corrosion is likely to be accelerated by high repository temperatures, high stresses and high oxygen levels. Work is needed to scope the magnitude of this problem and should include the following types of research:

- Long term and accelerated testing should be performed under various repository solution chemistries, stresses, temperatures, etc.

- The effects of solution radiolysis on SCC need to be determined.

- Enviromechanical testing which include slow-strain-rate and corrosion fatigue tests would be useful in determining SCC susceptibility.

- SCC testing should be performed on both base metal and weld structures.

- It is important to test under concentrated groundwater solutions which would be formed by evaporation at the container surface.

- Any detailed changes in fracture mode or loss in ductility should be investigated further.

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4.3.4 Hydrogen Assisted Failure

The potential for hydrogen embrittlement in carbon steels has been recognized for many decades in industry (Spiedel, M. O., 1977, Spahn, H., 1977). In certain cases, failure in steels may appear to be caused by stress-corrosion cracking, when, in fact, hydrogen effects at the tips of propagating cracks are the source of failure. In many aqueous environments, however, stress-corrosion cracking and hydrogen embrittlement effects may be closely connected.

There are many potential sources for the presence of hydrogen in a repository environment. Hydrogen may be present in the metal before service exposure; it can be produced during metallic corrosion; or it can be generated by the radiolysis of water. A particularly important source of hydrogen in a basalt repository was recently reported (DOE/RL 82-3, 1982) and concerns the equilibrium conditions attained in basalt/water mixtures. Under the reducing conditions present hydrogen pressures between 0.25 and 0.90 MPa were predicted.

In general, it is acknowledged that most carbon steel hydrogen embrittlement problems in industry occur for materials heat treated to high strength (Spiedel, M. O., 1977). Steels with yield strengths below about 500 MPa (70 ksi) are generally considered to be immune to hydrogen assisted failure (Spiedel, M. O., 1977). However, it has been stated that under laboratory conditions, failure may occur for steels with yield strengths as low as 350 MPa (50 ksi) (Spiedel, M. O., 1977).

Spahn and others (1977) report a case in which a carbon steel pipeline failed in the weld zone. The pipe was in contact with a pool of slightly acidic water containing H_2S and CO_2. They also describe a hydrogen embrittlement failure in a 0.17 percent soft carbon steel compressor cone at ambient temperature. The crack also formed in the welded area, which was in the presence of a $CO/CO_2/H_2S/H_2O$ gas mixture at 10 atmospheres pressure. Failure occurred by slow crack propagation after five years of service. Spahn concluded that soft carbon steels (yield strength <500 MPa, 70 ksi) can fail by hydrogen embrittlement but it may take several years to occur.

Fractographic studies by Poulson (1975) on unnotched cathodically-charged carbon steel (0.09 percent C) gave clear evidence for embrittlement after slow-strain-rate studies at room temperature. He observed regions in which hydrogen caused quasi-cleavage effects.

4.3.4.1 Effects of Hydrogen on Mechanical Properties and Delayed Failure of Low Carbon Steel

The effect of hydrogen on the yield strength of low strength steels has been shown to be a competition between softening and hardening mechanisms (Hirth, J. P., 1980). Seabrook and others (1950) reported a hardening of SAE 1020 steel with increasing charging current as shown in Figure 4.18.
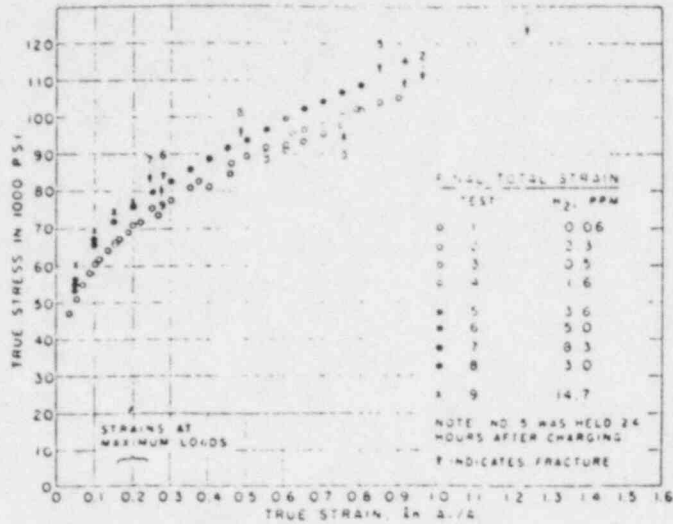
Figure 4.18. True stress-true strain tensile curves for various hydrogen contents (Seabrook, J. B., 1950).

Beachem (1972), however, observed a lower torsional flow stress for 1020 steel when a cathodic charging current was applied as shown in Figure 4.19.

It has been suggested that when deformation is by single slip mechanisms such as in creep and low strain flow, hydrogen can produce softening. Hardening occurs when deformation occurs by multiple slip as in grain boundary regions in polycrystals and large strain regions of single crystals (Hirth, J. P., 1980).

The predominant concern of the effect of hydrogen on low carbon steel is the loss of ductility and delayed cracking at stresses below the yield stress. Toh and Baldwin (1956) measured the ductility of SAE 1020 steel charged with different quantities of hydrogen. Figure 4.20 shows the decreased strain at fracture with increasing hydrogen content.

In addition to the effect of hydrogen itself, the measured tensile properties are affected by the temperature, strain rate, stress concentration, strength of the steel and prior cold work (Interrante, C. G., 1982). Grant and Lunsford (1955) studied the effect of cold work on the embrittlement of mild steel SAE 1020 as a function of hydrogen absorption by cathodic charging. Figure 4.21 illustrates the percent reduction of area versus hydrogen content and shows increased embrittlement due to prior cold work.

Fractography is a technique often used to study hydrogen assisted failure. In high strength steels, hydrogen embrittlement usually produces a transition from ductile type failure to that of quasi cleavage or brittle cleavage. In low strength steel, however, hydrogen does not result in an obvious change in fracture mode though there can be a significant decrease in the reduction of area at fracture.

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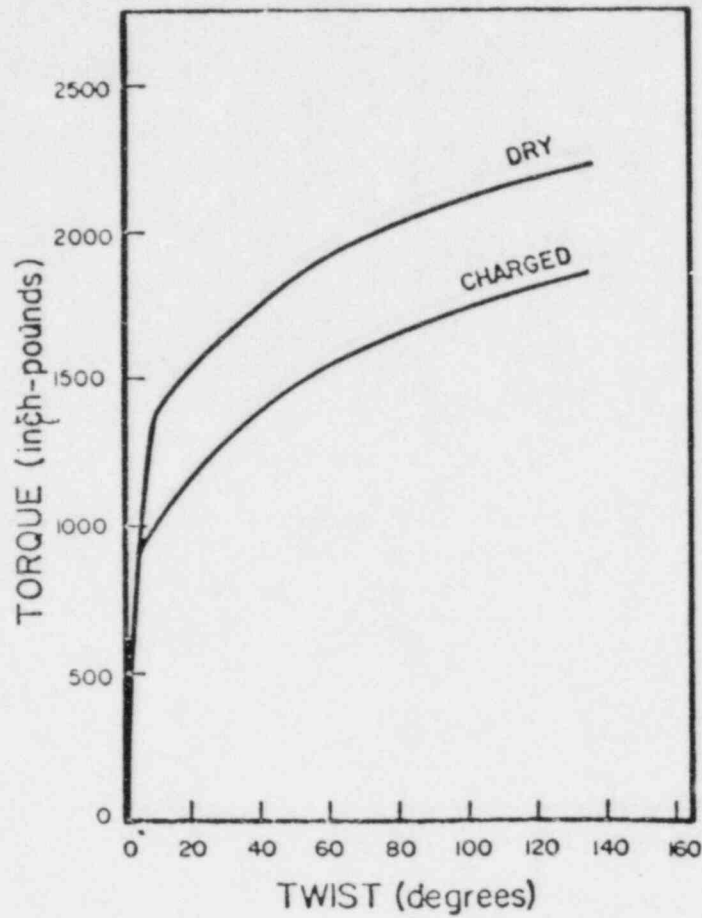
Figure 4.19. Comparison of flow curves from torsion tests of mild steel tubes tested dry (uncharged) and while being electrolytically charged (Beachem, C. D., 1972).
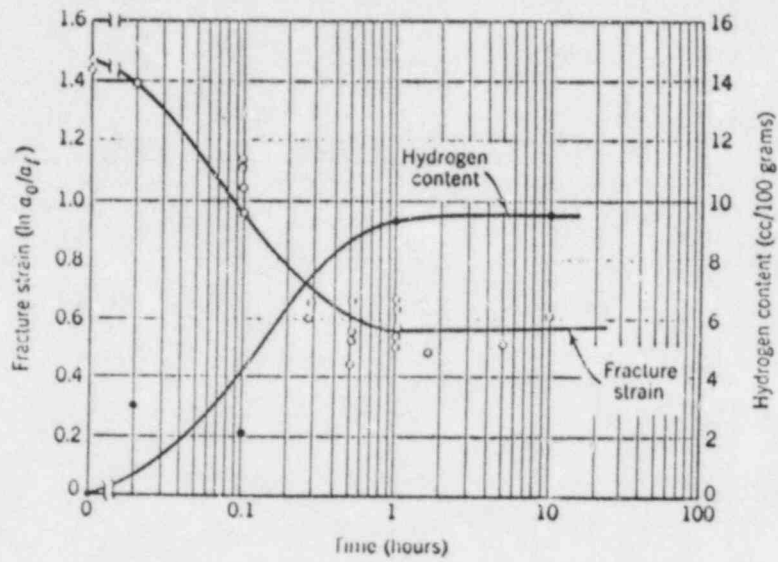
Figure 4.20.   Fracture (at room temperature and 0.005-in./in./min strain rate) and hydrogen content of an SAE 1020 steel as a function of charging time (Toh, T., 1956).
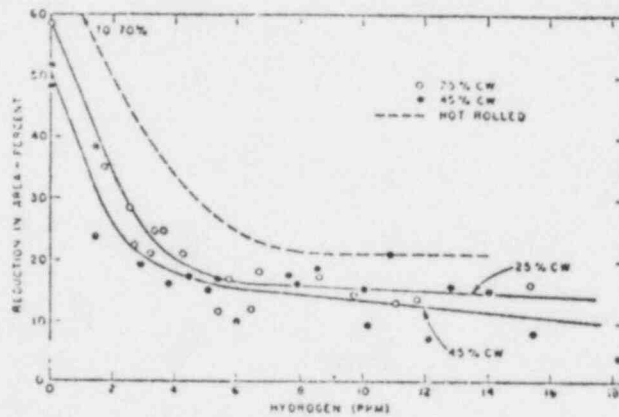
Figure 4.21   Reduction in area, per cent, as a function of hydrogen content in 1020 steel (Grant, N. J., 1955).

Lee and others (1979), bend tested specimens of spheroidized AISI 1095 steel with yield strengths less than 400 MPa (<58 ksi). Hydrogen was found to reduce ductility by enhancing void nucleation and growth and by promoting plastic instability along characteristic slip lines.

Cialone and Asaro (1981) studied hydrogen assisted fracture of several spheroidized plain carbon steels with yield strengths ranging between 250 to 350 MPa (~36 to 51 ksi). They also reported void growth and coalescence accelerated by hydrogen. However, specimens with significant inclusion contents were observed to undergo a partial transition in fracture mode to quasi cleavage. It was suggested that the inclusions acted as hydrogen sinks during charging which was then released in large amounts during deformation to cause quasi cleavage fracture to occur.

Recently, an investigation of the internal methane pressure in hydrogen attack on two carbon steels and pure iron was conducted which derived an average methane pressure based on methane content and total bubble volume (Natan, M., 1983) The test temperatures (>370°C) are higher than those anticipated in a repository, but the formation of methane could possibly occur in steel containers at their maximum temperatures given sufficient time. The chemical compositions of the metals used in this study are presented in Table 4.7. The methane content, N (c.c. gas/g material), in the attacked specimens was measured using a vacuum extraction technique. The total void volume, V (c.c.), was determined from density measurements before and after hydrogen attack. The average methane pressure, P, was then calculated for density loss (d.l.) greater than 0.05%. The 1020 steels exhibited higher levels of methane than the Ferrovac E as a consequence of higher carbon content in the former materials. Figure 4.22 shows methane content increases with decreasing temperature. The highest methane content measured was 2.80 cm^3 CH_4/g steel at 400°C and 6.77% d.l., equivalent to ~75% of the carbon content of the steel.

Methane formation differed between the two carbon steels as shown in Figure 4.23. The authors point out that SAE 1020 B, as indicated in Table 4.7, was considered to be more "alloyed" than 1020 A. The higher Cr content in SAE 1020 B would tend to increase resistance to hydrogen attack by contributing to the formation of stable carbides.

Since pressure and methane formation are a function of environmental conditions, carbon content of steels, bubble volume, and are dependent on the behavior of carbon forming elements, such parameters should be investigated under prototypic conditions likely to be encountered in a repository.

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Table 4.7. Compositions of materials used by Natan and Johnson (Natan, M., 1983).

Material Element	SAE 1020 A Pct	SAE 1020 B Pct	Ferrovac E Pct
C	0.20	0.17	0.0204
H	----	not given	6×10^{-5}
P	0.005	0.009	----
S	0.019	0.005	0.002
Co	0.001	0.002	0.002
Cr	0.007	0.05	0.001
Cu	0.02	0.19	0.001
Mn	0.44	0.65	0.001
Mo	----	----	0.001
Ni	0.04	0.04	0.11
Va	0.001	----	----
Fe	balance	balance	balance
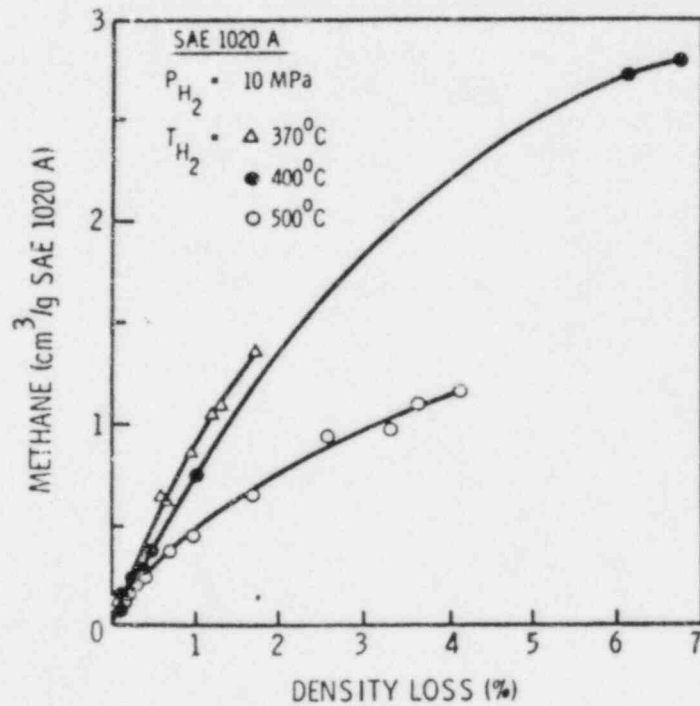
Figure 4.22. Dependence of methane content on temperature in the Natan-Johnson study (Natan, M., 1983).

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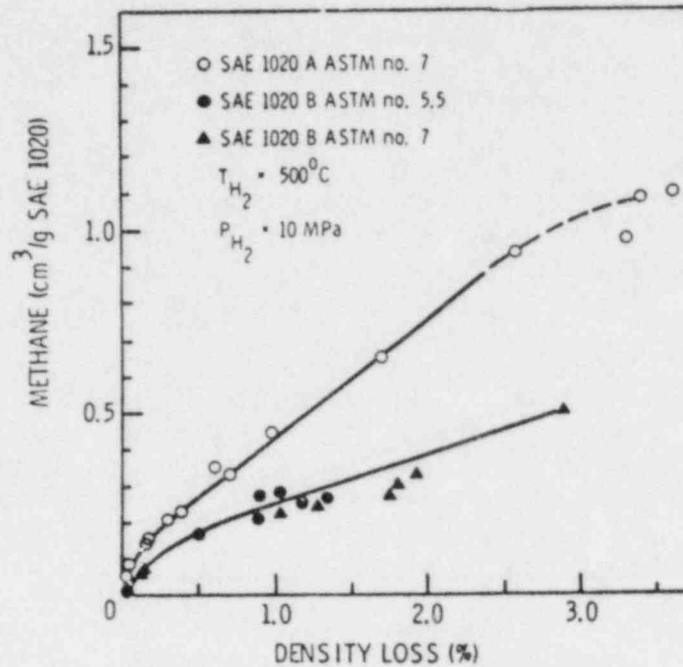
Figure 4.23. Effect of SAE 1020 compositions on methane formation in the Natan-Johnson study (Natan, M., 1983).

4.3.4.2 Mechanisms for Hydrogen Assisted Failure

The various proposed mechanisms to explain hydrogen embrittlement phenomena have been briefly described by Interrante (1982) and Hirth (1980) as follows:

- In the internal pressure mechanism, precipitation of hydrogen gas at internal defects assists the growth of voids or internal cracks by the buildup of large internal pressures. This acts to lower the apparent fracture stress (Zapffe, C. A., 1941).

- The model proposed by Petch and Stables (1952, 1956) suggests that hydrogen adsorption lowers the surface energy of the surfaces created during cracking. This promotes cracking due to the lowering of the work required for fracture.

- Beachem (1972) proposed a hydrogen assisted cracking theory in which the role of hydrogen was to ease dislocation motion or generation or both. The presence of sufficiently concentrated hydrogen dissolved in the lattice just ahead of the crack tip aids whatever deformation process that the microstructure allows. This model is different from the previous models in that instead of embrittling the lattice, hydrogen enhances local plasticity.

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- In the decohesion model proposed by Troiano (1960) and modified by Oriani (1977, 1978) it is postulated that dissolved hydrogen at high concentrations lowers the maximum cohesive force between the atoms of the alloy in the lattice at grain boundaries and at interfaces.

- Bastien and Azou (1951) suggested that dissolved hydrogen can be carried along by moving dislocations and precipitated elsewhere. This may explain or relate the transport of hydrogen to the kinetics of hydrogen assisted crack propagation but does not address the problem of the mechanism by which hydrogen causes embrittlement.

At this time there are insufficient data to determine which of the above mechanisms is likely to apply to HLW containers. Possibly, more than one could be jointly responsible for embrittlement effects. An elucidation of the mechanisms would be necessary if long term prediction of hydrogen-assisted failure behavior is to be achieved.

4.3.4.3 Conclusions and Recommendations

It is unlikely that low carbon steel will experience classical high temperature "hydrogen attack" during repository service due to the high temperatures required (300-500°C). In this temperature range hydrogen entering the steel reacts with carbon to form high pressure methane bubbles (Weiner, L. C., 1961). However, if temperatures are to exceed 200°C (Rioja, R. J., 1982) then investigation into other forms of hydrogen assisted failure will be needed.

The most likely hydrogen assisted failure problem is "hydrogen embrittlement" which can result in decreased ductility and true stress at fracture and also delayed failure. The factors involved can include the hydrogen content, strength of the steel, strain rate, temperature, microstructure and amount of previous cold working. Even low strength steels are not immune to the effects of hydrogen. Though the fracture mode may remain predominately ductile, severe decreases in macroscopic ductility (reduction in area) can result.

There exists little or no data on the effects of hydrogen on low carbon steel in a repository environment. To assess the range of repository conditions over which hydrogen assisted failure can be a potential failure mode, the following areas of study are recommended.

- Mechanical properties of low carbon steel such as yield strength, ultimate tensile strength, elongation, reduction in area, hardness and impact strength should be determined as a function of temperature, hydrogen concentration, microstructural variations and strain rates.

- Fracture mechanics methods should be used to determine delayed failure potential. Threshold stress intensity, crack growth rates and times to failure should be measured in terms of the various test parameters mentioned above.

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- The influence of repository environmental parameters such as various groundwaters (brine, basaltic and tuffaceous groundwaters) and appropriate gamma radiation levels should be assessed.

- Determination of the quantity of hydrogen expected should be made and the hydrogen uptake efficiency should be measured.

- The mechanism of hydrogen embrittlement should be identified and mathematically modelled to permit long term predictions.

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5.   PACKING MATERIAL FAILURE AND DEGRADATION MODES* (D. Eastwood)

The objective of this section on packing materials (discrete backfill) is to review the currently available data on candidate packing for the DOE repository programs and to determine additional data needs for the NRC licensing process. In particular, the possible types of chemical failure modes which could degrade performance have been addressed.

5.1   Chemical Failure Modes for Packing Material in a Basalt Repository

This section of the program has been completed and reported in the last Biannual Report, "Review of DOE Waste Package Program," (NUREG/CR-2482, Vol. 4, Section 5.1, BNL-NUREG-51494, 1983).

5.2   Chemical Failure Modes for Packing Material in a Tuff Repository

In this section possible packing materials for use in a tuff repository, with most of the emphasis on crushed tuff, will be discussed with respect to their performance with special emphasis on sorptive properties. At present, the only packing material being discussed for use in a tuff waste repository is crushed·tuff, designed to have 80% of the original density of the host rock (private communication with V. M. Oversby, April 1983). Since the properties of tuff necessary for understanding the performance of crushed tuff as packing material have not been discussed in previous BNL reports, it is necessary to first address these properties before discussing degradation modes. The most likely chemical degradation modes for tuff are mineraological alteration and loss of sorptive capacity. Since these failure modes have been relatively little studied, such research may represent a high priority need for the NRC. Other materials which have been discussed as possible components of the packing are: bentonite, MgO and/or CaO, or charcoal. The advantages and disadvantages of bentonite as a component of packing material for basalt repositories have been already discussed in a previous BNL report (NUREG/2482, Vol. 3, 1983). The arguments against introducing bentonite into a tuff repository are the following: (1) bentonite may lack the necessary hydrothermal stability at the waste loadings presently under consideration as discussed in a previous BNL report (NUREG/CR-2482, Vol. 3, 1983); (2) bentonite might introduce water (sorbed or structural) into a relatively dry repository; (3) crushed tuff itself may inherently possess the necessary sorptivity and has as secondary mineralization products, clays and zeolites, so that its sorptive capacities might be improved if limited alteration were to take place during the thermal period.

The use of bentonite in tuffaceous rocks with groundwater containing potassium requires low waste loading per package or substantial aging of the waste to prevent development of high temperature in the packing material and waste form. Otherwise the presence of K^+ would cause the bentonite to convert to illite as discussed in the previous BNL Biannual Report (NUREG/CR-2482, Vol. 4, 1983).

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*A glossary of geological terms is given in Appendix A.

Before the chemical failure/degradation modes can be discussed, the performance of the possible packing materials under conditions in a tuff repository must be understood. As for bentonite and zeolites (Section 5.1), the most important degradation modes will be expected to be mineralogical alteration and change in sorptive properties. This information is only partially available.

5.2.1 Crushed Tuff as Packing Material

This section will address the properties of crushed tuff itself as a packing material. Properties of tuff as a host rock under near field repository conditions have been discussed in a previous BNL report (BNL-NUREG-51494, Vol. 4, 1983). The properties of tuff of most interest to its performance as packing material are: hydrothermal stability, permeability, thermal conductivity, and sorption for various radionuclides under both oxidizing and reducing conditions. Such properties as permeability, thermal conductivity, and sorption are site-specific, depending critically on the mineralogy of the tuff and on the degree of porosity as well as on other factors. Welded tuff has thermomechanical properties such as thermal conductivity, heat capacity, thermal expansion and strength which are similar to other igneous rocks such as granite and basalt (SAND-79-0402C, 1979). The tuff presently being considered for the host rock (and presumably also as packing material) is the Topopah Springs member of the Paintbrush Tuff formation which is vitrophyric, i.e., densely welded and devitrified (private communication from V. M. Oversby, 1983). Relevant properties of tuff are summarized in Tables 5.50 and 5.51* and in Section 2 of a previous BNL report (NUREG/CR-2482, Vol. 4, 1983). Figure 5.14** also shows the thermal conductivity of various tuffs as a function of grain density. Permeability and thermal conductivity will also depend on the degree of compaction and method of preparing the crushed tuff. Since the likely site for the repository is in the unsaturated zone above the water table, a low permeability for the tuff as packing material is probably less critical for a tuff repository then is the case for a crushed basalt-bentonite packing material in a basalt repository where the rate of water flow is predicted to be much higher.

5.2.1.1 Alteration in Crushed Tuff Packing Material

Crushed tuff is likely to be subjected to mineralogical alteration during the thermal period in the repository. According to Wolfsberg and Erdal (LA-8739-PR, 1981), the reaction of clinoptilolite to yield analcime, silica and water may begin in these rocks at temperatures as low as 95°C. These reactions will probably cause rock fracture because of a net volume loss and will also release water. To minimize this problem the recommended maximum temperature for a clinoptilolite-rich tuff is 85°C.

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* The table numbers follow the sequence established in Section 5.1 of the last Biannual Report.
**The figure numbers follow the sequence established in Section 5.1 of the last Biannual Report.

Table 5.50. Comparison of material properties data for six rock types
being studied as potential repository media
(adapted from SAND-79-0402C, 1979).

	Welded Tuff	Nonwelded Tuff	Basalt	Granite	Salt	Argillite	Units
Bulk Density	2.2	1.9	2.9	2.6	2.2	2.6	Mg/m^3
Porosity	10	35	0.5-13	0.5-2	0.5-1.7	9	Vol %
Water Content	6	18	1.8	0.8	0.25	3.5	Wt %
Thermal Conductivity	1.6	0.6	1.5	4	7	2.5	W/m K
Specific Heat	0.85	1.4	1	1	1	1	kJ/kg K
Linear Thermal Expansion Coefficient	12.5	---	5.4	7	40	12	$X10^{-6}/K$
Young's Modulus	30	8	70	70	7	7	GPa
Poisson's Ratio	---	0.15	0.26	0.25	0.4	0.35	---
Uniaxial Compressive Strength	117	25	200	200	30	40	MPa
Tensile Strength	---	0.7	14	14	NA	1.9	MPa

Table 5.51. Comparison of tuff properties data (adapted from SAND79-0402C, 1979).

Property	Nonwelded Tuff		Welded Tuff		Units
	Range	Typical	Range	Typical	
Bulk Density	1.5-2.1	1.9	2.0-2.4	2.2	Mg/m^3
Porosity	25-55	35	2.0-25	10	Vol. %
Water Content	10-25	18	2-10	6	Wt %
Thermal Conductivity	0.8-0.4	0.6	1.2-1.9	1.6	W/m K
Specific Heat	0.8-1.7	1.4	0.8-0.9	0.85	kJ/kg K
Linear Thermal Expansion Coefficient	+2 to -1.5	---[a]	6-18	12.5	$X10^{-6}/K$
Young's Modulus	7-9	8^b	23-41	30	GPa
Poisson's Ratio	<0.1-0.25	0.15	----	----	----
Uniaxial Compressive Strength	7-30	25	----	117	MPa
Tensile Strength	0.1-1.4	0.7	----	----	MPa
In Situ Permeability	$10^{-6}-10^{-3}$	10^{-4}	$\leq 1.4 \times 10^{-3}$	10^{-5}	darcys

[a]Thermal expansion behavior of nonwelded tuff is extremely rate-dependent and highly variable with temperature.
[b]Range given for nonwelded is for 0 to 200°C.

Figure 5.14. Theoretical grain density-conductivity relationship and calculated K_o values for silicic tuffs (adapted from SAND 81-1873, March 1982).

In heating tests on tuff, with variable alteration mineral assemblages (primarily zeolites), the results showed behavior correlating with mineralogy (LA-8612, 1981). On heating in dry air, clinoptilolite-rich samples (10-90%) showed the greatest weight and volume loss; an analcime-rich sample (60-90%) had an intermediate weight loss and a near-zero volume change and a glassy specimen exhibited a volume decrease and a small weight loss. These changes in weight, volume and density for temperatures up to 500°C are illustrated in Figures 5.15 through 5.17. Only part of the water loss due to dehydration is reversible on rewetting.

As pointed out by Dibble and Tiller (1981), chemical equilibrium between fluids and mineral phases is not likely to be attained in sedimentary rocks containing volcanic glass. Metastable reactions occur because the formation of less stable phases such as clays and disordered zeolites lower the total free energy of the glass bearing system faster than the growth of the stable mineral assemblages including ordered feldspars, quartz and micas. Since these intermediate metastable states can delay the attainment of true equilibrium by millions of years, mineral reactions involving zeolites and clays in tuffaceous sedimentary rocks can be explained by growth and dissolution reaction kinetics. Since the systems are very complex and the kinetics are often slow, they are best investigated empirically using long term testing and/or accelerated conditions.

As discussed by Tyler (SAND-79-0402C, 1979), the effects of heat and radiation on a medium which may contain as much as 10% water by weight are unknown. Hydrothermal alteration of the minerals could release water or change mechanical, thermal and hydraulic properties of the crushed tuff used as packing material. Combined with the effects of radiolysis, this alteration could release non-condensible volatiles. These changes in the packing material may or may not be compensated for by the host rock, but nevertheless represent important licensing data requirements.

5.2.1.2 Sorption Properties of Tuff Packing Material

As discussed in previous BNL reports (NUREG/CR-2482, 1983 Vol. 3; NUREG/CR-2755, 1982) distribution coefficients or ratios determined statically and retardation factors measured in dynamic or flow-through experiments depend on a number of factors including mineralogy of the material, particle size and distribution, temperature, pressure, groundwater parameters including pH, Eh, composition and ionic strength, etc. In general, distribution ratio is a more correct term than distribution coefficient since it is an empirical term not suggesting that equilibrium has been attained. This is a particularly important distinction for tuff since equilibrium in sorption experiments was apparently not attained in experiments lasting weeks or months. Also, distribution ratios for sorption and desorption experiments often gave different values.
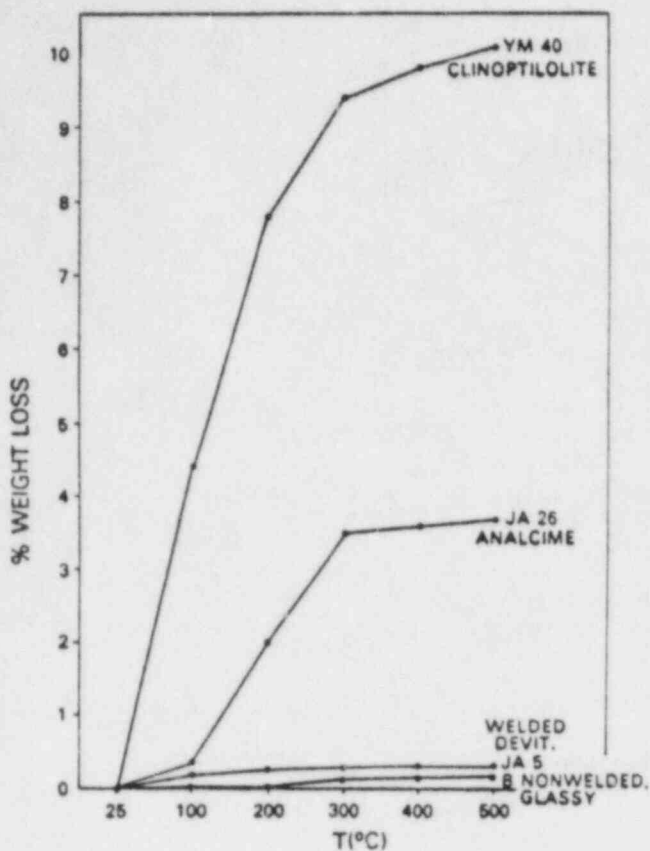
Figure 5.15. Cumulative percent weight loss for tuff samples of various mineralogies.
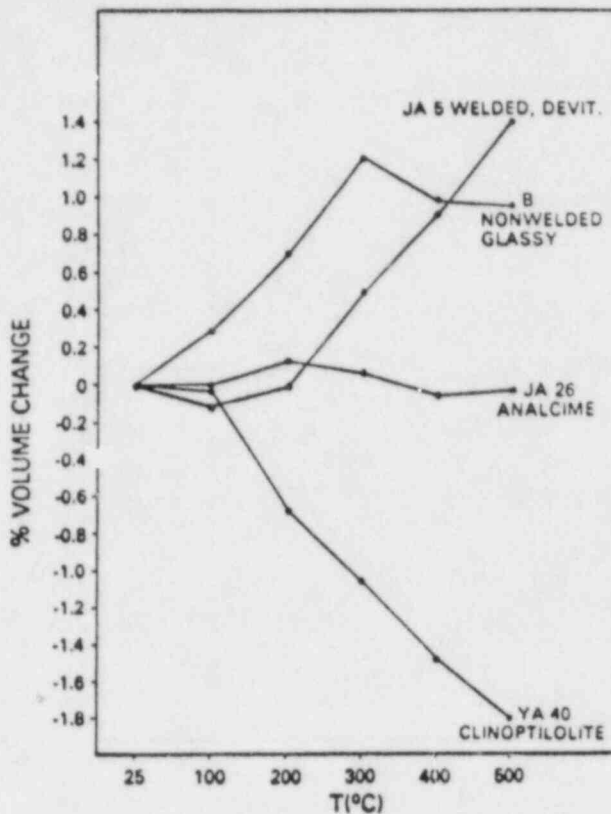
Figure 5.16. Cumulative percent volume change on heating for tuff samples.

(LA-8612-PR, 1980)

Sample Description

JA-5   Tiva Canyon Member, Paintbrush tuff. Welded, vitric tuff. Phenocrysts are primarily quartz and sanidine.

JA-26   Prow Pass Member, Crater Flat tuff. Nonwelded, zeolitized (analcime) ash-flow tuff. Phenocrysts are quartz, plagioclase, and K-spar.

YM-40   Bedded tuff of Calico Hills. Altered, nonwelded vitric tuff. Zeolitized with Na + K-rich clinoptilolite. Phenocrysts are quartz, sanidine, and plagioclase.

B   Central portion of Bandelier tuff. Nonwelded, nonzeolitized, ash-flow tuff with large pumice fragments and moderate amount of lithic fragments.

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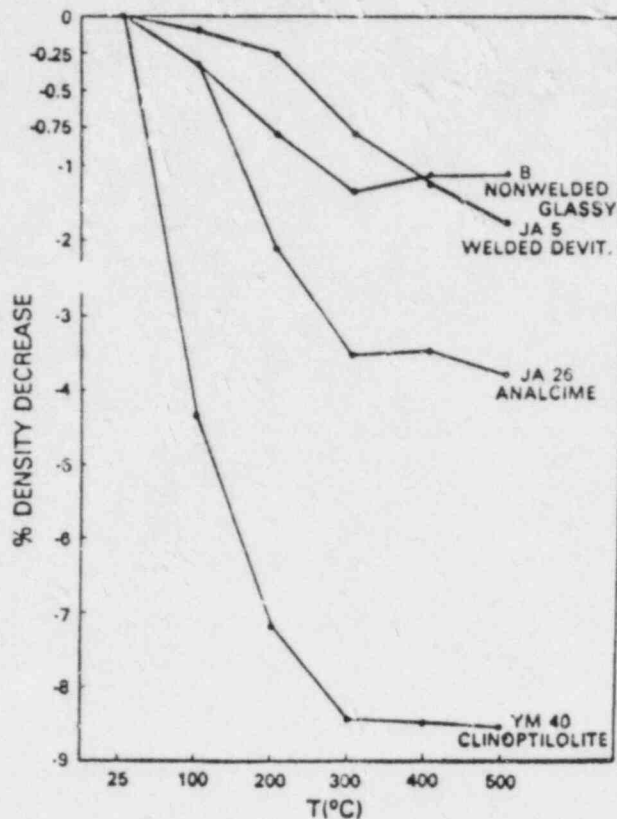
Figure 5.17. Cumulative percent density change on heating for tuff
samples (adapted from LA-8612-PR, 1980).

Sorption properties for tuff were found to be especially dependent on
site-specific mineralogical composition. For specific radionuclides, distri-
bution ratios may vary for oxidizing and reducing conditions with sorption
generally being higher under reducing conditions; however, tuff groundwaters
in the unsaturated zone are expected to be somewhat oxidizing. Sorption
properties for tuff are summarized in Tables 5.52 through 5.60. It should be
emphasized that many of these measurements are preliminary in nature with few
replicates and do not include all of the radionuclides of interest or cover
the full range of possible conditions for a tuff repository.

Sorption of tuff samples is strongly related to the zeolite content.
Tuff samples range from those with significant zeolite concentration (often
clinoptilolite) to other devitrified samples containing mainly feldspar and
silica with little zeolite. The following is a summary of the sorption
properties of different forms of tuff for some of the more important
radionuclides (SAND80-1464, 1980):

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- Cs, Sr, and Ba sorb better on zeolitized tuff (2000 to 130,000 mL/g) than on devitrified tuff (50 to 1500 mL/g).

- Pu sorbs moderately well (50 to 150 mL/g) in air on zeolitized, devitrified, or clayey tuff. Sorption ratios in a nitrogen atmosphere are high > 600 mL/g for zeolitized tuff and moderately high (100-600 mL/g) for devitrified tuff.

- Sorption ratios for americium and the rare earths cover a wide range, but are highest for tuff containing clay.

- Sorption of anionic species such as iodine, Tc, or U complexed as carbonate is low (<25 mL/g). Sorption of Tc and U are higher in a N_2 atmosphere.

- Simple equilibria cannot explain the results. Sorption and desorption values may vary by a factor of 10 or more for lanthanides, actinides, Tc or U. Irreversible sorption or slow desorption may be due to speciation changes, diffusion into minerals, crystallization reactions, or non-ionic sorption of colloids and precipitates.

Table 5.52. Approximate sorption ratios for several geologic media (mL/g) (adapted from SAND-79-0402C, 1979).

Element	Zeolitized Tuff	Tuffaceous Alluvium	Climax Granite	Eleana Argillite	Basalt	Rock Salt	Bentonite
Sr	300	200	15(5)[a]	100(200)	100(200)	0.1	2,000
Cs	600	7,000	400(700)	1,000(1,000)	700(300)	0.1	2,000
Ba	700	5,000	100	1,000	700(300)	0.1	5,000
Eu	6,000	>20,000	300	20,000	700(300)	0.1	>10,000
Pu	10,000	>1,000	(5,000)	(300)	(20)	0.1	>10,000
Am	7,000	>1,000	(60,000)	(3,000)	(200)	0.1	>10,000

[a]Values in parentheses are in non-pre-equilibrated water.

Table 5.53. Approximate sorption ratios at 20°C for various welded tuffs (mL/g) (adapted from SAND-79-0402C, 1979).

	Densely Welded (Glass, Moderate Zeolitization)	Partially Welded (Devitrified, Low Zeolitization, Microgranite)	Partially Welded (No Glass, High Zeolitization)
Sr	10,000	50	300
Cs	20,000	200	600
Ba	4,000	400	700
Eu	30	200	6,000
Pu	200	2,000	10,000
Am	200	1,000	7,000
Cation Exchange Capacity (MEQ/100 g)	75	2	17
Surface Area (m^2/g)	7.5	3.3	10

Table 5.54. Representative sorption ratios for tuff[a] (adapted from Erdal, B. R. and others, 1980).

Element	Vitric 22°C	Vitric 70°C	Devitrified 22°C	Devitrified 70°C	Zeolitized 22°C	Zeolitized 70°C
Sr[b]	13 000	20 000	55	106	300	1 200
Cs[b]	6 000	19 000	150	103	740	2 100
Ba	4 800	50 000	440[b]	1 100[b]	850[b]	5 000[b]
	30 000	110 000				
Ce(III)	40	43	80	80		
	180	320	400	600		
Eu(III)	30	43	90	190	6 000	4 200
	150	270	800	1 800	13 000	14 000
U(VI)	4		2		4	
	15		8		8	
Pu	140		~110		~280	
Am	190	220	120	110	600	910

[a]The second value listed for each element is that obtained from the desorption measurements.
[b]Average of all the sorption and desorption measurements since all values were within the estimated uncertainties.

Table 5.55. Comparison of sorption ratios (R_d) measured under atmospheric and controlled atmosphere (CA) conditions[a] (adapted from LA-8747-MS, 1981).

Element	Effect
Cs	No effect
Sr	No effect
Ba	No effect
Ce	No effect
Eu	No effect
Tc	Higher in CA (factor of >10)
U	Higher in CA[b] (factor of 2-3)
Pu	Higher in CA (factor of 2)
Am	No effect[c]

[a]Nitrogen, <0.2 ppm oxygen and <20 ppm carbon dioxide.
[b]YM-38 (zeolitized) tuff only; otherwise no effect.
[c]May depend on mineralogy.

Table 5.56. Freundlich isotherm parameters[a] (adapted from LA-8747-MS, 1981).

Rock Type	Fraction (μM)	Element	n	-log k
YM-22	<75	Sr	0.83	2.23
		Cs	0.80	2.17
		Ba	0.83	1.34
		Eu	1.1	-1.20
	75-500	Sr	0.71	2.85
		Cs	0.79	2.34
		Ba	0.82	1.57
		Eu	0.92	0.46
YM-38	<75	Sr	0.85	0.38
		Cs	1.0	-0.66
		Ba	1.0	-2.41
		Eu	1.1	-1.0
	75-500	Sr	0.87	0.41
		Cs	1.0	-0.65
		Ba	1.1	-2.50
		Eu	0.98	-0.29

[a]Freundlich isotherm $y = kc^n$, where y is the concentration on the solid in moles/g and c is the concentration in solution in moles/L.

Table 5.57. Average[a] sorption ratios (mL/g) for Am and Pu under atmospheric and controlled atmosphere[b] conditions for three different tuff samples (adapted from LA-8747-MS, 1981).

		Sorption		Desorption	
Tracer	Core	Atmospheric	Controlled	Atmospheric	Controlled
Pu-237	YM-22	140(38)[c]	220(46)	1 400(95)	1 600(330)
	YM-38	250(88)	800(87)	2 000(490)	>2 200
	YM-54	84(17)	120(29)	670(35)	1 300(190)
Am-241	YM-22	4 000(1 200)	1 400(210)	4 600(990)	3 700(830)
	YM-38	5 500(1 100)	5 600(950)	9 500(1 300)	14 000(2 100)
	YM-54	590(200)	1 000(210)	600(45)	2 500(380)

[a]Sorption ratios for unfiltered solution after contact have been averaged over two particle sizes and three contact times.
[b]Nitrogen, <0.2 ppm oxygen, <20 ppm carbon dioxide.
[c]Standard deviations (absolute) of the means for six measurements are given in parentheses.

Table 5.58. Average sorption ratios[a] for Am and ^{237}Pu data (adapted from LA-8110-MS, 1980).

			R_d (mL/g)	
Element	Core	Temp. (°C)	Sorption	Desorption
Am	JA-18	22	435 (6)	960 (15)
	JA-32	22	1 400 (110)	2 700 (420)
	JA-37	22	12 000 (500)	14 000 (2100)
		70	34 000 (6000)	5 300 (720)
^{237}Pu	JA-37	22	700 (210)	4 600 (1000)

[a]Sorption ratios are given for the "pH adjusted" method of preparing the traced feed solutions. They are averaged over 1-, 2-, 4-, and 8-week contact times and 106- to 150- and 355- to 500-μm particle sizes. Values in parentheses are the standard deviations of the means (absolute value).

Table 5.59. Freundlich isotherm parameters for plutonium (adapted from LA-8739-PR, 1981).

Core	Fraction (µM)	n	k
YM-22	<75	0.94	0.012
	75-500	0.84	0.001
YM-49	<75	1.05	0.633
	75-500	1.09	1.480

Table 5.60. Recommended K_d values (adapted from LA-7216-MS, 1978).

	Tuffaceous Alluvium	Bentonite
Sb	215 + 30[a]	35 + 20[a,b]
Sr	217 + 45	2000 + 700
I	640 + 300[a]	
Ru	2500 + 1200[a]	
Nb	~2600[a]	1800 + 700[a]
Ba	5200 + 2000	5400 + 600[a]
Cs	7000 + 1600	2100 + 200[a]
Co	20000 + 9000[a]	5000 + 3000[a]
Y	>20000	>2000
Ce	>20000	>2000
Eu	>20000	>10000

[a]Value taken from desorption experiments.
[b]Value from commercial tracer experiments

Wolfsberg and others (LA-7480-MS, 1979) performed sorption measurements in air at 22 and 70°C and also found that sorption ratios varied greatly with the lithologic variety of tuff. A tuff high in zeolite minerals was found to have high sorption ratios for Eu, Ba, Cs, and Am and intermediate values for Sr and Pu. A tuff high in glass showed very high ratios for Ba, Sr, and Cs, intermediate values for Am and Pu and low values for Ce and Eu. A devitrified tuff similar to a microgranite exhibited intermediate values for Ba, Cs, Am, and Pu and low values for Eu, Ce, and Sr. Sorption values for Ru were low and those for Mo, Sb, and I were very low or zero for the three types.

Vine and others (LA-8110-MS, 1980) found that sorption ratios of Sr, Cs, and Ba were higher in less concentrated solutions rather than in more concentrated solutions probably because of less competition for available sorption sites. The opposite effect of concentration changes were found for Ce and Eu perhaps because of a greater tendency of Ce and Eu to form radiocolloids.

Experiments by Wolfsberg (LA-7216-MS, April 1978) indicated that sorption of radionuclides by tuffaceous alluvium (which is a weathering product of tuff) was greater in general than for bentonite under the same conditions (see Table 5.60). This perhaps indicates that limited alteration might actually improve the sorptive properties of crushed tuff, assuming that zeolites such as clinoptilolite were produced. More extensive alteration would produce products such as analcime (with sorptive properties similar to devitrified tuff) and feldspar with probably less favorable sorptive properties than the original tuff.

5.2.2 Mixed Packing Material Systems in a Tuff Repository or Alternate

CaO and/or MgO have been proposed as additives to improve the sorptive capacity of the tuff and provide some swelling capability by volume expansion on formation of their hydroxides [70% for $Mg(OH)_2$] without introducing moisture into the repository (private communication with V. M. Oversby, 1982). Charcoal also has been suggested as a means of improving the capability of the packing material to adsorb radionuclides such as Tc and I which tend to form anionic species and which are not readily sorbed by bentonite or rock (also see Table 5.61).

If crushed tuff, combined with bentonite or some alternate sorptive material, is used as a composite packing material, possible synergistic interactions between tuff and other components must be considered. For bentonite, such interactive effects would be expected to be minimal (except for the possible introduction of additional water and perhaps more sodium into the groundwater since clays are likely secondary mineralization products of tuff.

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Table 5.61. Dependence of sorption of ^{95m}Tc on percentage charcoal in tuff[a] (adapted from LA-7216-MS, April 1978).

Percent Charcoal	Percent Tuff	Average R_d (mL/g)
0	100	0.17
1.0	99.0	36.9
4.3	95.7	485
10.0	90.0	1960
10.0[b]	90.0[b]	1600
50.4	49.6	35100

[a]Four-week contact time. Technetium initially present as TcO_4^-.
[b]These samples were opened daily and stirred.

5.2.3 Conclusions and Recommendations

The previous discussion has indicated that the properties of tuff which could affect its performance as packing material during the thermal period in a waste repository have been studied to a limited extent. Many of these measurements were preliminary in nature with few replicates and did not cover the full range of possible conditions for a tuff repository.

The most likely chemical degradation modes, mineralogical alteration under hydrothermal conditions and loss of sorption capability, have hardly been studied for tuff under repository conditions. Preliminary investigations indicate that limited alteration might actually improve the sorptive properties of crushed tuff due to the formation of zeolites while more extensive alteration would produce minerals with probably less favorable sorptive properties than the original tuff. More extensive investigation is required for the ranges of anticipated conditions specified in a prior BNL report (NUREG/CR-2482, Vol. 4, Section 2, May 1983).

Moreover, the sorptive properties of tuff are extremely site-specific and must be studied more thoroughly for each site for all of the radionuclides of interest over the full range of conditions to be expected in the repository with special emphasis on effects of T, Eh, pH, secondary transformation products and effects of groundwater (including changes in groundwater under thermal conditions, see Table 5.62). Although the sorptive properties of tuff as a geological medium appear favorable, the sorptive properties of tuff under near-field conditions and possible effects of chemical degradation modes on those sorptive properties for tuff used as packing material, need to be better characterized than they have been to date. These considerations may present critical research needs for the NRC in its licensing process.

Table 5.62. Interaction of tuff with groundwater to determine change in
groundwater after reaction with hot rock (150°C, 4+ days)
(adapted from DOE/NWTS-30, A. J. Rothman, 1982).

Element	Water	After Reaction Results to Date, µg/mL
Si	31	140
Na	48	100
Ca	12	5
K	5	6-14
Al	0.01	0.2
pH	7.0	8.5

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6. RESULTS OF TESTING FOR INTERACTIVE EFFECTS AMONG COMPONENTS OF THE
   WASTE PACKAGE (D. Eastwood)

In other BNL work testing techniques for evaluating interactive effects
among components of the waste package and whole package testing were discussed
(Siskind, B., 1983). The work in this section will describe the results of such
testing in detail and, in particular, outline the importance of packing material
or crushed host rock (basalt, tuff, salt) on the corrosion or leaching of the
other components of the waste package.

6.1 Interactions of Packing Material with Other Components of the Waste Package

Packing material as defined here will be either bentonite (Na-montmoril-
lonite) clay and/or crushed host rock (basalt, tuff, rock salt) with possible
additions of other components as buffering or conditioning agents. According to
Wicks (1982), based on preliminary systems tests, the packing material may have
more influence than any other component of the waste package on the release rate
of radionuclides. The packing material may be beneficial, marginal, or even
detrimental to the release rates depending on the choice of material, its
ability to withstand the thermal period and its compatibility with other
components of the waste package and with the host rock. Conditioning of the
groundwater by the packing material will also alter its effect on other com-
ponents of the waste package. Some of the results reported here, especially
based on work by Hench (1982) and Lanza (1982), contradict assumptions made
previously by some researchers that clay packing materials are usually
beneficial to waste package integrity.

Clark (1982 a,b) found that the influence of adjacent barrier materials on
glass leaching appeared to be minimal although he did not explore high surface
areas relevant to crushed rocks or pre-equilibration of the distilled water with
the rocks before adding glass to the system which might have provided greater
buffer protection and higher concentrations of passivating species. When the
solution pH is altered by external sources the protective film on the surface of
the glass may become unstable for pH <3 or >11.

6.1.1 Bentonite Clay-Glass Interactions

Van Iseghem and others (1982) studied the corrosion resistance of five
borosilicate glass HLW waste forms in contact with wet clay, clay-water mix-
tures or distilled water for periods up to 80 days and at a surface area to
solution volume ratio of 1 cm^{-1} under aerated conditions for temperatures
between 40 and 200°C. They found that wet clay corroded the waste form faster
than the clay-water mixture or distilled water. In distilled water, corrosion
was limited by saturation effects for Si, Ca, Mg, Sr, Fe and U.

Experiments involving static leach tests for PNL waste glass in the presence of Na bentonite yielded enhanced leach rates from glass because of bentonite sorption properties as well as reactions between bentonite and dissolved silica (PNL-SA-10773, 1983). Also, colloidal bentonite particles apparently were formed which, in low ionic strength solutions, could remain stable as sols over a w de pH range and these could be transported by groundwater flow. Such colloids were also found to exist in high ionic strength solutions and to retain a sorptive capacity for actinides in the presence of high concentrations of competing cations. Flocculation would prevent groundwater transport but was not observed. If such colloidal transport is likely, sorption of radionuclides on colloidal particles may represent an important data need for the NRC in their evaluation of radionuclide release. At least for dilute solutions sorption phenomena can be explained by speciation and surface particle charge. Figures 6.1 through 6.4 illustrate sorption phenomena as a function of oxidizing conditions. These figures show the sorption of various radionuclides including Pu-237, U-233, Tc-95, Np-235, Cs-137 and Sr-85 on Na bentonite colloids as a function of pH at 25°C. As will be seen from these figures sorption of radionuclides was relatively high especially for Pu-237, U-233 and Sr-85 at intermediate pH. (Information on iron silicate colloids, also shown on these figures, will be discussed separately in Section 6.2.)

When a dry pressed clay is immersed in water the affinity of water and clay produces potential gradients which facilitate water diffusion and permit homogeneous distribution of water in the clay within a relatively short period of time (few weeks or months). Consequently, clay may prevent high water flow rates due to its low permeability but does not appreciably delay water from coming into contact with the container and, after container failure, with the waste form (Lanza, F., 1982).

The sorbent nature of the clay around the glass initially tends to eliminate the saturation conditions expected in aqueous solutions. At least in the beginning, a model of dissolution in large amounts of water tended to fit the experimental leaching data for a simulated compacted clay-glass waste form system better than a model based on saturation effects (Lanza, F., 1982).

Bentonite was found to accelerate leaching for nuclear waste glasses tested by burial in a granite repository. The effect of bentonite increased as the bentonite/H_2O ratio decreases. Moist or wet bentonite in contact with the glass apparently accelerated the rate of ion depletion from surface layers of the glass (Hench, L. L., 1982). (See Figures 6.5 and 6.6 and Table 6.1.)

Montmorillonite and clinoptilolite did not seem to alter under simulated wet and semi-wet repository conditions (300°C and 30 MPa) based on short term tests (28 days) by Sasaki and others (1982). However, both materials altered to feldspar (oligoclase) in the presence of borosilicate glass under the same conditions. Reactions of these packing materials with simulated wastes immobilized waste elements such as Cs, Mo, etc. by forming new phases such as analcime, oligoclase and powellite. Sasaki's analysis indicated that the presence of packing materials during the alteration of waste solids served to
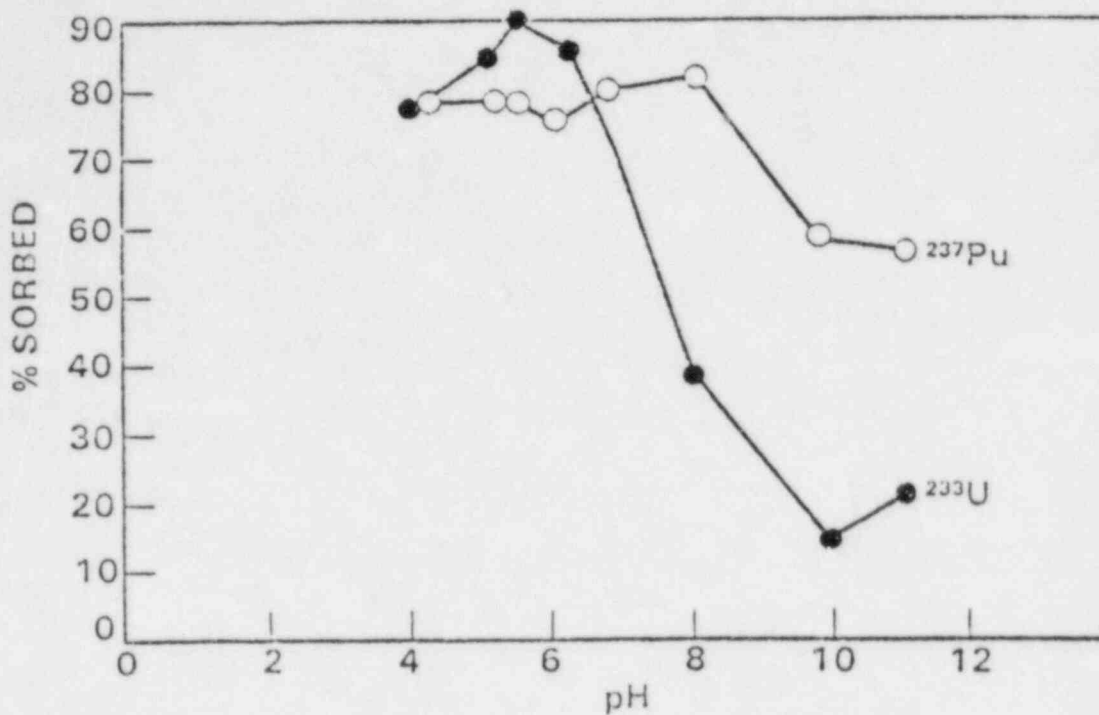
Figure 6.1. Sorption of ^{237}Pu and ^{233}U on Na bentonite colloids as a function of pH in deionized water at 25°C. (Adapted from PNL-SA-10773, 1983.)
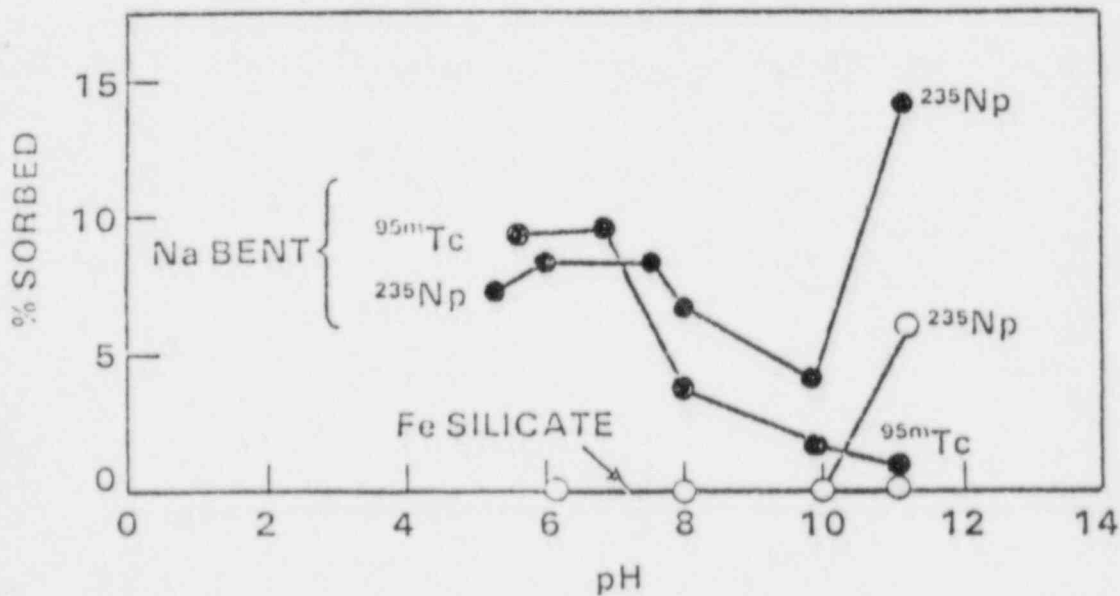
Figure 6.2. Adsorption of ^{95}Tc and ^{235}Np on Na bentonite and Fe silicate colloids as a function of pH at 25°C. (Adapted from PNL-SA-10773, 1983.)
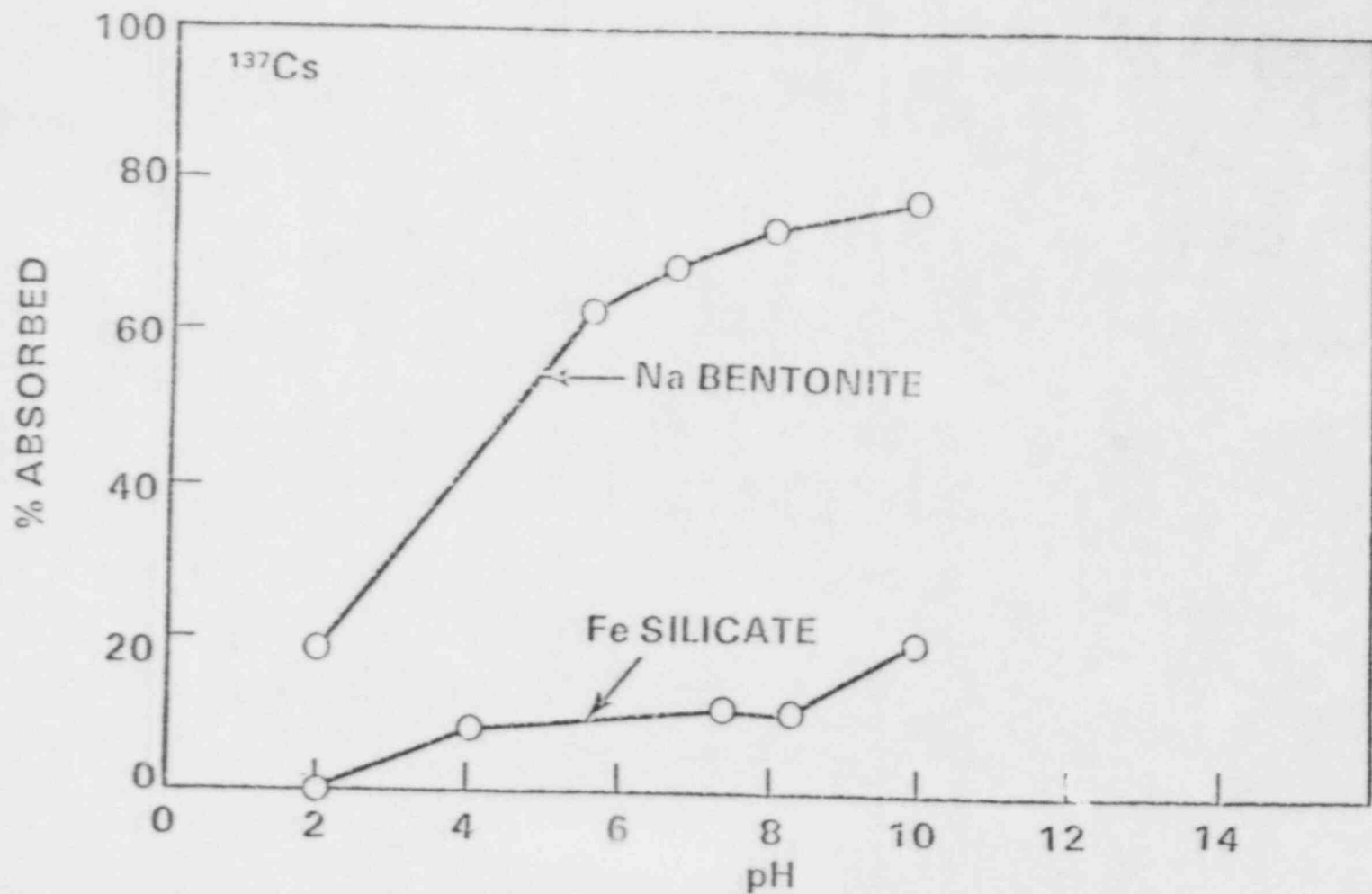
Figure 6.3. Adsorption of ^{137}Cs on Na bentonite and Fe silicate colloids as a function of pH at 25°C. (Adapted from PNL-SA-10773, 1983.)
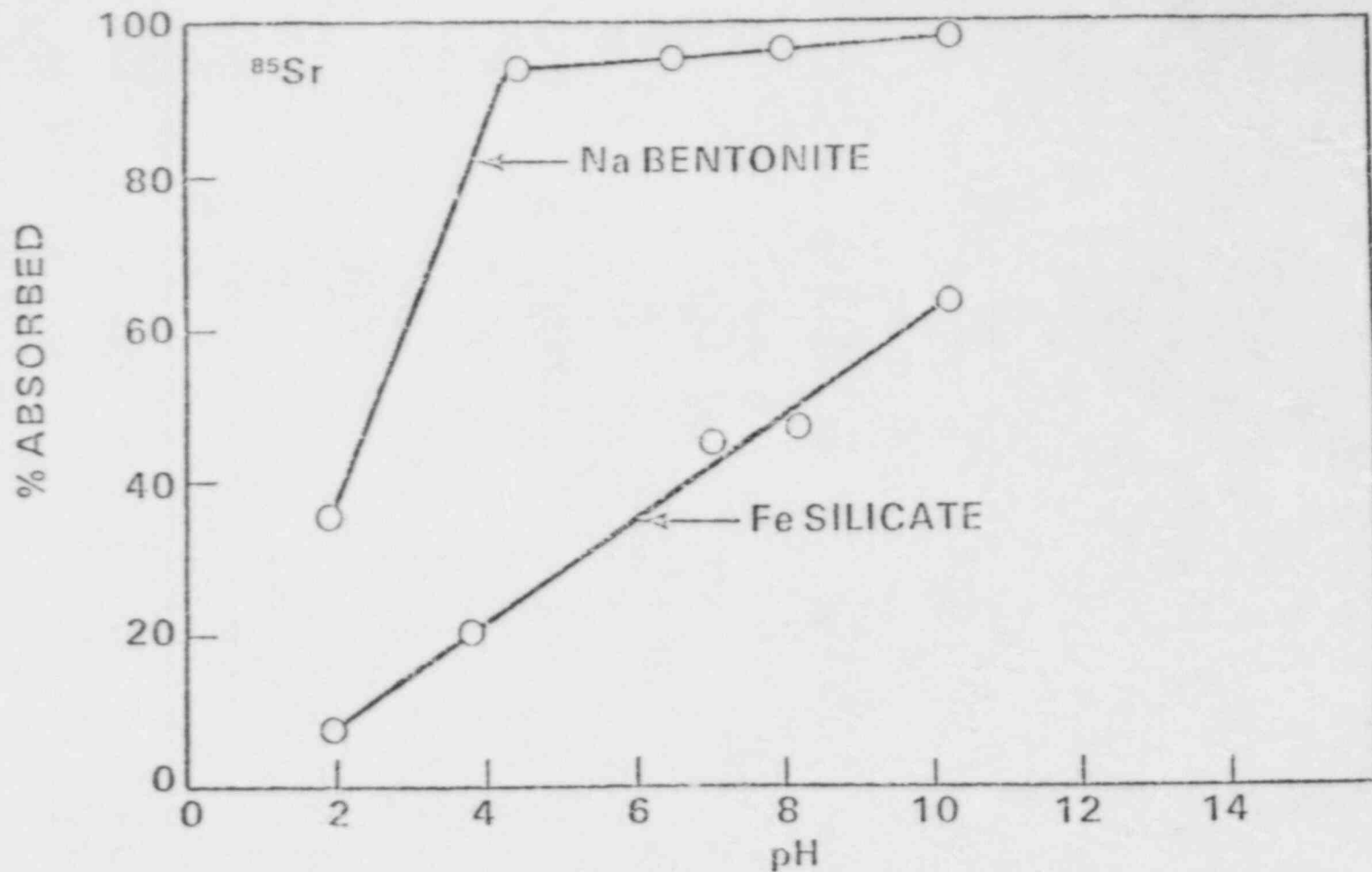
Figure 6.4. Absorption of [85]Sr on Na bentonite and Fe silicate colloids as a function of pH at 25°C. (Adapted from PNL-SA-10773, 1983.)
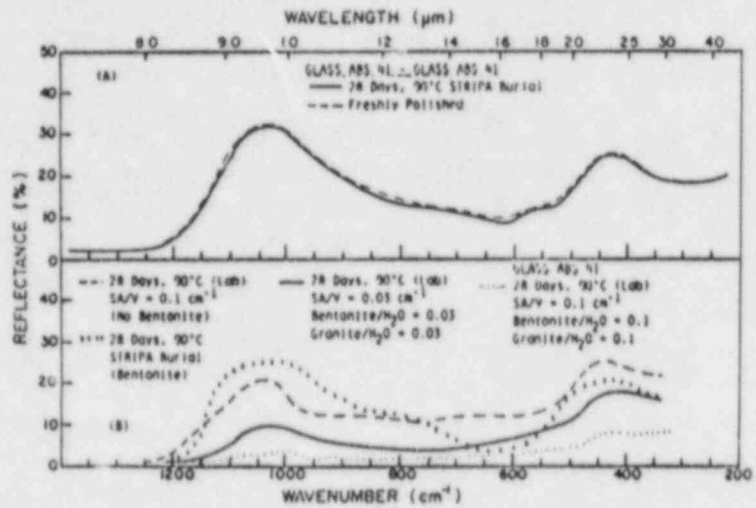
Figure 6.5.   Infrared reflection spectra of glass ABS 41 before and after
              28 days, 90°C STRIPA burial and various 90°C laboratory
              simulations. (This illustrates the effect of exposure of the
              glass waste form to bentonite and granite.) (Adapted from
              Hench, L. L., 1982.)
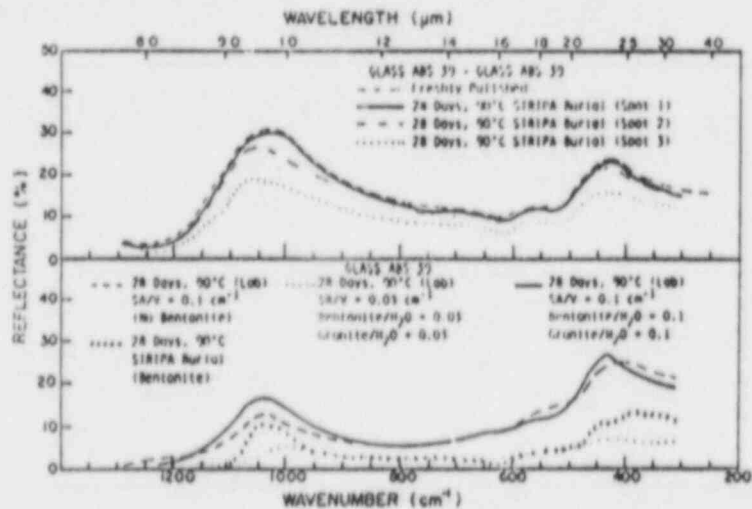
Figure 6.6.   IRRS spectra of glass ABS 39 before and after 28 days, 90°C
              STRIPA burial and various 90°C laboratory simulations.
              (This illustrates the effect of exposure of the glass waste
              form to bentonite and granite.) (Adapted from Hench, L. L.,
              1982.)

drastically reduce the concentrations of some radionuclides in solutions.
See Table 6.2 for the percent of radionuclides in solution as affected by
montmorillonite.

Table 6.1. Concentrations (atom-% of cations) in different parts of
            leached profiles of borosilicate glass waste form [after bur-
            ial in Stripa (granite) repository for three months] (ABS 39).
            Symbols: gl - glass against glass; bt -against bentonite.
            (Adapted from Hench, L. L., 1982.)

| | Surface | | Plateau | | |
	gl	bt	gl	bt	Bulk
Na	5.3	20.3	5.3	7.9	19
Li	0.5	1.5	0.05	0.07	0.1
Cs	0.4	0.3	0.4	0.05	0.3
Ca	0.3	0.3	1.2	1.7	0.01
Sr	0.06	0.01	0.1	0.06	0.1
La	0.09	0.005	0.2	0.3	0.1
U	0.1	0.006	0.02	0.1	0.1
Fe	3.9	12.5	2.5	8.6	3.6
B	1.7	0.2	1.9	0.8	31
Al	6.5	21.2	6.7	19.8	3.2
Si	78	65	78	67	40

Table 6.2 Percent* of waste element in solution as affected by
           montmorillonite. (Adapted from Sasaki, N., 1982.)

| Element	BG**	BG+M
B	91	87
Ba	0.3	<0.3
Ce	0.8	0.9
Cs	9.9	0.2
Mo	95	17
Nd	0.2	0.1
Ni	--	--
Rb	8.1	<1.5
Sr	0.9	<0.6
U	--	--

* Percentage of the amount of the element originally
  present in the waste form.
**BG = borosilicate glass; M = montmorillonite

6.1.2 Basalt-Glass Interactions

Scheetz and others (1978) found that basalt added to deionized water and borosilicate glass increased the amount of Cs released into solution at 100°C or 300°C for times up to four months by a factor of two or four while other elements such as Sr, Ba, Ca, Na and Si were decreased. Basalt had an effect on the hydrothermal alteration behavior of the glass waste form both by causing new solid phases and by modifying the solution chemistry significantly.

Experiments carried out by Myers and others (DOE/NWTS-30, 1982) indicate that under hydrothermal conditions (200 or 300°C) basalt reacts with borosilicate glass waste forms or spent fuel to form secondary minerals such as silica, illite, potassium feldspar and smectite. This alteration assemblage acts to control the steady-state solution composition of elements such as Al, K, Ca, Mg and Fe. Initially, the dissolution of the borosilicate glass has the effect of increasing the pH relative to the steady-state pH values for the basalt-water system. At first, reaction of water with silicates results in the release of hydroxyl ions and dissolved silica; for example:

$$MSiO_3 + 3H_2O \longrightarrow M^{2+} + 2OH^- + H_4SiO_4$$
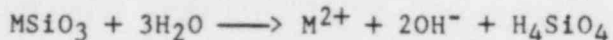
The solution pH rises until the dissolved silica buffers pH by the reaction:

$$H_4SiO_4 + OH^- \longrightarrow H_3SiO_4^- + H_2O$$
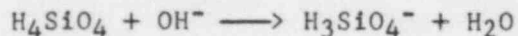
As stated by Coons and Patera (ONWI-212, 1980), the leach resistance of glass in the presence of basalt is not yet understood. Different laboratories obtained greatly different results when using different water-to-rock ratios (see Table 6.3). Leaching of glass is also very sensitive to pH, Eh and temperature variations.

On the other hand, leached radionuclides from spent fuel were found to react at high temperatures with basalt to form new mineral phases. Also, basalt was found to suppress uranium solubility due to precipitation of uranium dioxide (UO_2) under reducing conditions.

Wood and Coons (1982) conducted preliminary experiments with Umtanum basalt, water and waste forms including borosilicate glass and simulated spent fuel over a temperature range of 100-300°C. In the presence of basalt, Cs, Rb, Sr and Mo were almost completely removed from solution by reacting with the glassy component of basalt to form new stable solid phases which immobilize these elements. Mineral products included pollucite $(Cs,Rb,Na)AlSi_2O_3 \cdot H_2O$ and powellite $(CaMoO_4)$ with the Ru likely to follow Cs into plagioclase. Strontium was found in both plagioclase and powellite.

Table 6.3. Leachability[a] of simulated PNL 76-68 glass using distilled water and in the presence of basalt (near 300°C)[b]. (Taken from Coons and Patera in ONWI-212, 1980, p. 124.)

	The Pennsylvania State University[b]			Pacific Northwest Laboratory[c]		
	Glass	Glass and Basalt	Net Change	Glass	Glass and Basalt	Net Change
Rb	12	17	+ 5%	16	0.06	-15.4
Cs	14	20	+ 6%	6	0.04	- 5.96
Sr	ND[d]	0.4	+ 4%	0.2	0.05	- 0.15
B	80	88	+ 8%	100	5.9	-94.1
Mo	68	59	- 9%	49	0.05	-48.95
U	--	--	--	0.1	0.002	- 0.998
Si	2.3	1.3	- 1%	2.2	0.07	- 2.13

[a]Experiments 1 month in duration; concentrations reported as relative percent oxide (grams in liquid/grams in original solid).
[b]Water:rock = 20:1.
[c]Water:rock = 1:1.
[d]Not determined.

6.1.3 Salt-Glass Interactions

Since crushed salt may be used as a packing material in a rock salt repository, the interaction of salt and brine with other components at the waste package is also of interest. In a report by Komarneni and others (ONWI-305, 1982), a prototype waste glass, PNL 76-68, was reacted under hydrothermal conditions (at 100, 200 and 300°C) with a brine (Ca-Mg-K-Na-Cl). Reaction products included talc (hydrated magnesium silicate), powellite ($CaMoO_4$), hematite (Fe_2O_3) and, sometimes, an unidentified uranium-containing phase. Although most elements were extracted, the silicate framework remained intact as a hydrated gel. The concentration of silica in brine solutions was an order of magnitude lower than that in deionized water, while other elements were 10-100 times higher than in deionized water. These results are shown in Figures 6.7, 6.8 and 6.9, and Table 6.4.

|←——— 300 to 400 μm ————————→|

DISSOLVED LAYER   ←→ 10-20 μm   30-50 μm ←→   "BULK"
                        REACTION RIND   GLASS

Corrosion   ·Mg Front ↗   ↖Na-K Front
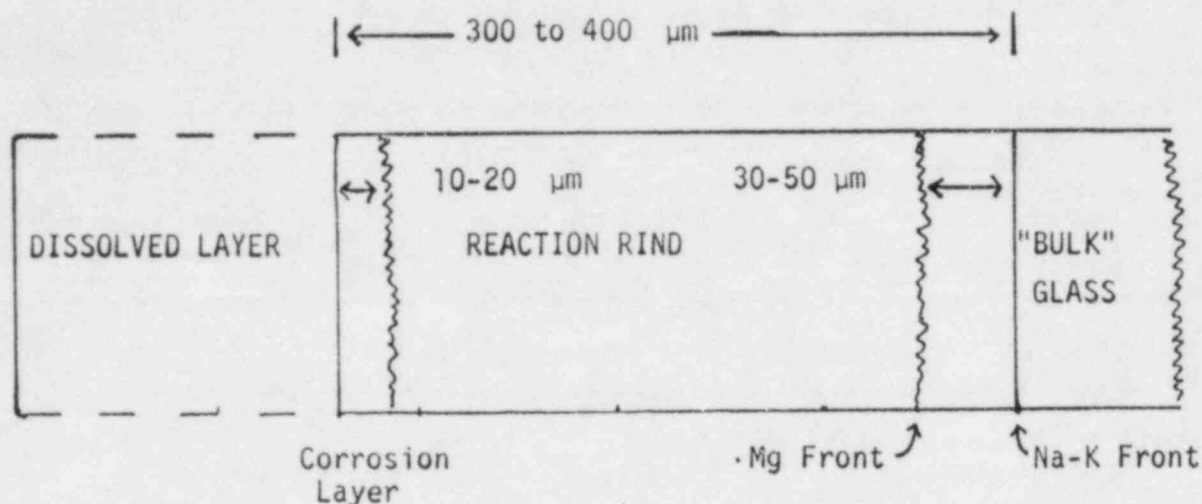Layer

Figure 6.7.   Schematic drawing of main reaction layers in PNL 76-68 glass
              reacted hydrothermally with Ca-Mg brine. (Adapted from
              ONWI-305, 1982.)

6.1.4 Bentonite Clay-Metal Interactions

According to Casteels (1978), in a clay environment carbon steel was found
to possess only limited resistance to humid atmospheres. The carbon steel was
attacked in an air stream passing over clay with the formation of FeO and FeS.
The unprotective nature of the corrosive layers resulted in rapid attack and
destruction of the steel. At higher temperatures, it was found that sulfur-
containing compounds were the main cause of atmospheric corrosion in a geolog-
ical clay formation. Sulfur dioxide was present in the gases escaping from the
clay due to the pyrite in the clay and the chemical reaction between the pyrite
component of the clay and water. Carbon steel has long been known to have high
corrosion rates in acid environments.

Titanium and titanium alloys were found to have excellent corrosion re-
sistance in the same atmospheres, but a small amount of a compound containing
sulfur did appear on the surface of the titanium.

6.1.5 Basalt-Metal Interactions

Anderson (RHO-BWI-ST-15, 1981) conducted corrosion tests of metal con-
tainer materials (Ti, Fe, Ni and Cu) in a simulated basalt environment at
250°C, pH 5 and reducing conditions. Preliminary results indicated that the
basalt environment is not highly corrosive to the materials tested. Variations
in oxygen fugacity had only a minor effect on corrosion of Ti, Ni and Zr; how-
ever, the corrosion of a cupronickel alloy was drastically reduced at a lower
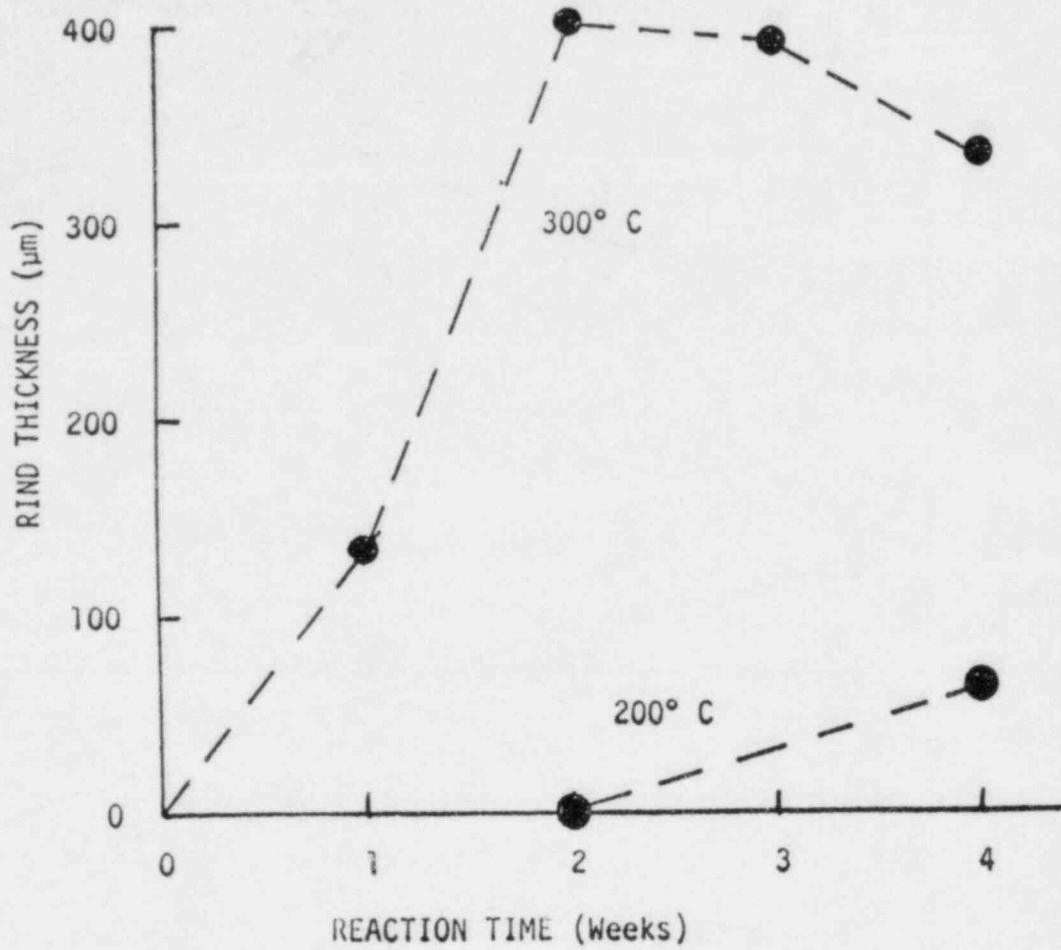oxygen fugacity.

Figure 6.8. Thickness of reaction rind as function of reaction time.
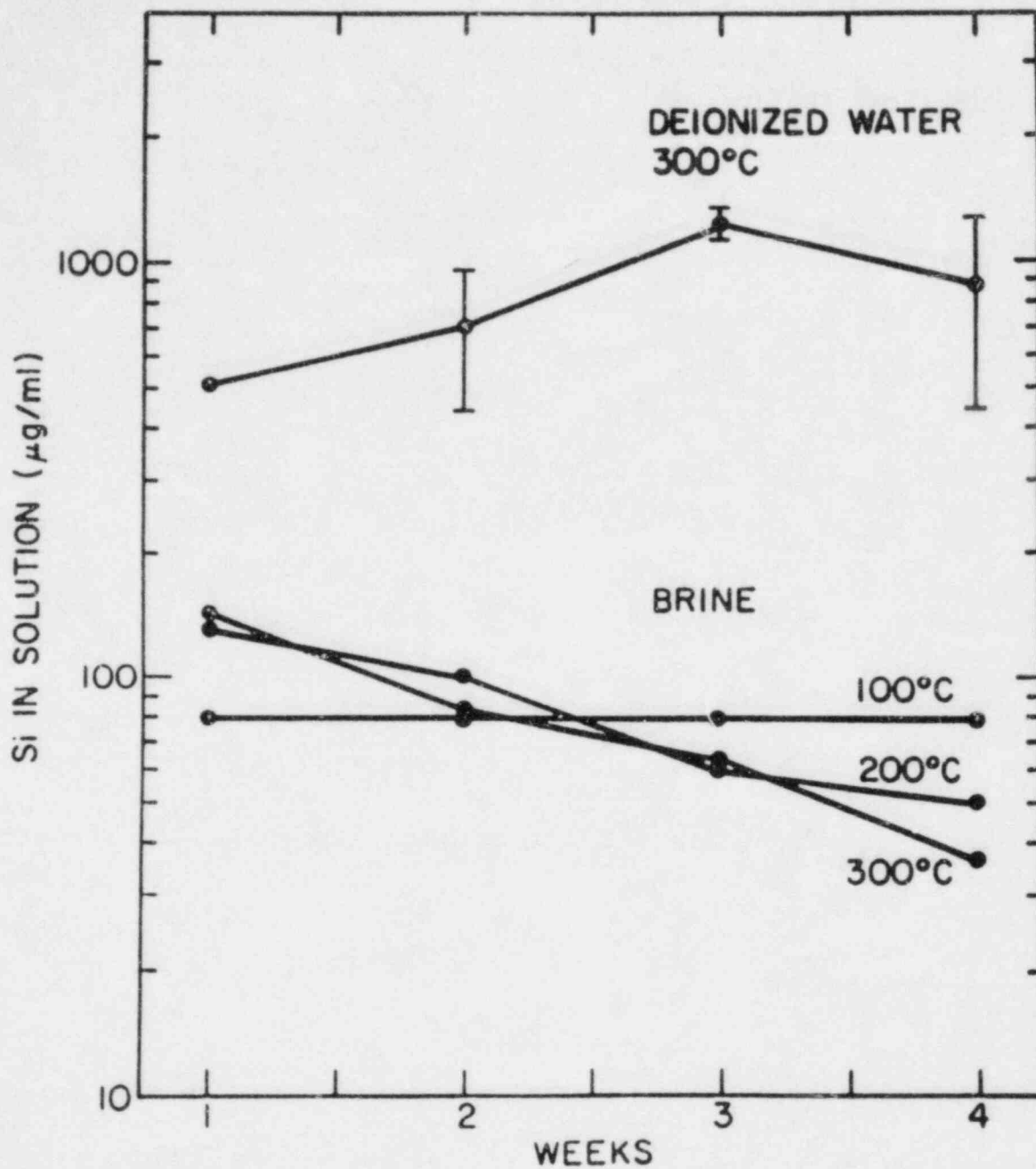(Adapted from ONWI-305, 1982.)

Figure 6.9. The concentration of silica, expressed as elemental Si, in solution at various run times. (Adapted from ONWI-305, 1982.)

Table 6.4. Percentage of initial inventory detected in solution brine extraction from PNL 76-68 glass. (Four weeks; 30 MPa; glass:solution = 1:12.5 brine, 1:10 water) (Adapted from ONWI-305, 1982.)

Element	Bittern Brine (USGS NBT-6a)			Deionized Water		Hanford Groundwater
	100°C	200°C	300°C	200°C	300°C	300°C
Cs	3.2	13	52	0.1	5.0	4.5
Sr	0.9	22	49	<0.1	0.2	<0.1
Ln[a]	<2.5	8.0	37	<2.5	0.5	<2.5
U	<0.1	0.23	18	0.11	0.03	<0.1
Na	--	--	--	3.8	45	47
B	0.2	12	48	6.7	93	89
Si	0.4	0.3	0.2	3.2	4.6	1.0
Mo	1.0	1.6	3.3	5.2	72	79

[a]Ln = La + Nd.

The presence of basalt decreased pitting and crevice corrosion and enhanced the formation of an adherent surface film on the low carbon steel. Preliminary data suggest that a protective silicate film may form on steel in a basalt repository (DOE/NWTS-30, 1982).

Basalt may also inhibit corrosion by scavenging O_2. It is important, therefore, to identify the role played by basalt in the corrosion protection of low carbon steel.

6.2 Metal-Glass Interactions

The direct interaction of metal and metal corrosion products from the container with the borosilicate glass waste form must also be considered. Lanza reported that, for clay-glass systems, the addition of Fe_2O_3, to simulate container corrosion products, seemed to increase leaching and waste glass loss.

McVay (PNL-4382, 1982) discussed the effect of several metals (Fe, Cu, Sn, Al, Ti and Pb) on the leaching of borosilicate glass. Ductile iron was found to increase leaching regardless of groundwater (see Figure 6.10). The leach rates are the same as initial rates in deionized water; however, the leach rates do not decrease rapidly with time so that more leaching occurs and the depleted layer becomes deeper. Apparently, this is because iron silicate precipitates are formed as silicon is leached. (See Figures 6.11 and 6.12 from

PNL-SA-10773, 1983, and Figures 6.2, 6.3 and 6.4 included earlier.) These precipitates remove many of the other leached elements from solution so that leaching is not inhibited by saturation effects. The other more reactive metals retard leaching while the more inert metals have little effect. With lead present, the glass leaching was halted by a lead hydroxide film which rapidly covered the glass surface.
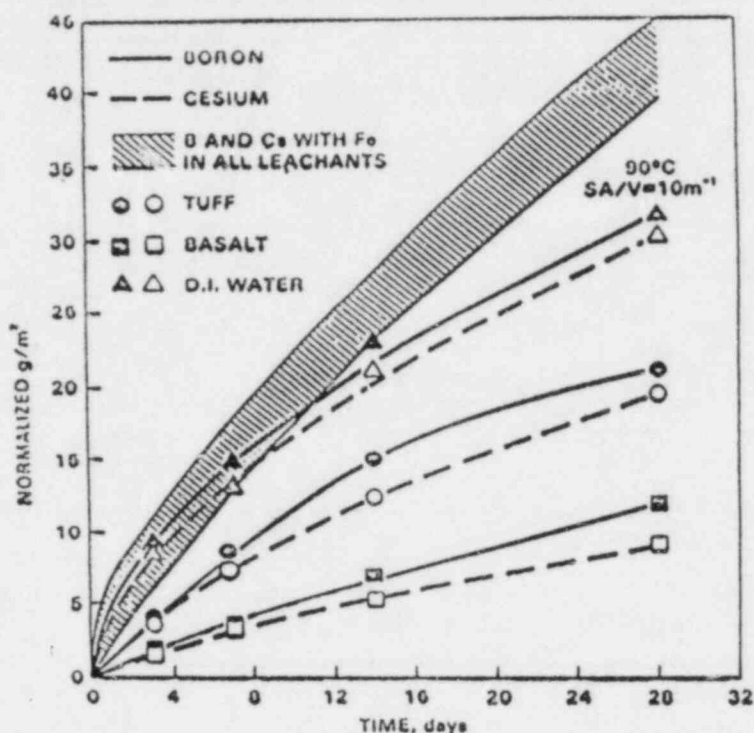
Figure 6.10. An illustration of two effects on the leaching character-
istics of PNL 76-68 glass: the effect of groundwater com-
position without iron present and the effect of having iron
present during leaching (PNL-4382, 1982).

According to Werme and others (1982), metal overpack materials (such as Pb, Cu and Ti) seem to have little effect on the corrosion of nuclear waste borosilicate glasses up to 90°C under burial conditions. Werme postulated that this was because there is room only for a very thin water film between the glass and the metal. The thin water film can become rapidly saturated with corrosion products and future corrosion is slower.

Mirschinka (1982) recommended that stainless steel and other alloys con-taining Cr not be used for in-can melting containers since Cr has been found to preferentially dissolve in the glass. Instead low carbon steel was recommended.

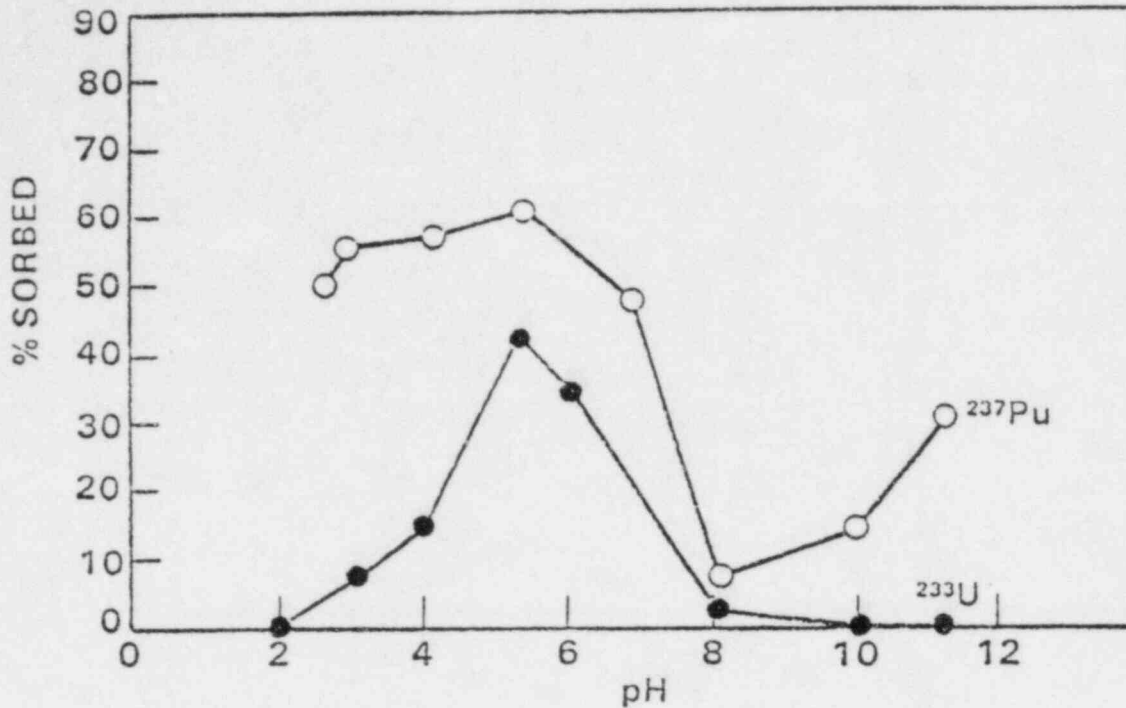Figure 6.11. Sorption of ^{237}Pu and ^{233}U on Fe-silicate colloids initially in 0.01 M NaOH at 25°C as a function of pH. (Adapted from PNL-SA-10773, 1983.)

6.3 Whole Package Testing

Relatively few experiments have been carried out on whole-package systems thus far.

Vandegrift and others (1983) conducted experiments with radioactive borosilicate glass, bentonite and mechanically fissured basalt rock in a flowing water system. Changes in the groundwater after passing through the fissure included a drop in pH from 10 to 8, loss of suspended particulates and loss of dissolved or suspended U, Np and Pu.

Molecke and others (1982) described a preliminary test on waste package interactions in a salt environment using borosilicate glass, a stainless steel waste container, TiCode 12 overpack, bentonite clay-sand packing material, excess brine leachant and bedded rock salt in an autoclave at 250°C for 95 days. The alteration of the packing material was minimal, the glass waste form showed some surface alteration and the TiCode 12 overpack showed minimal uniform corrosion. No major interactive effects were observed which would rule out the use of any of the components in a waste package. Obviously such tests need to be extended for longer periods and to cover the full range of repository conditions. Accelerated tests should be performed also to help identify any long term effects.
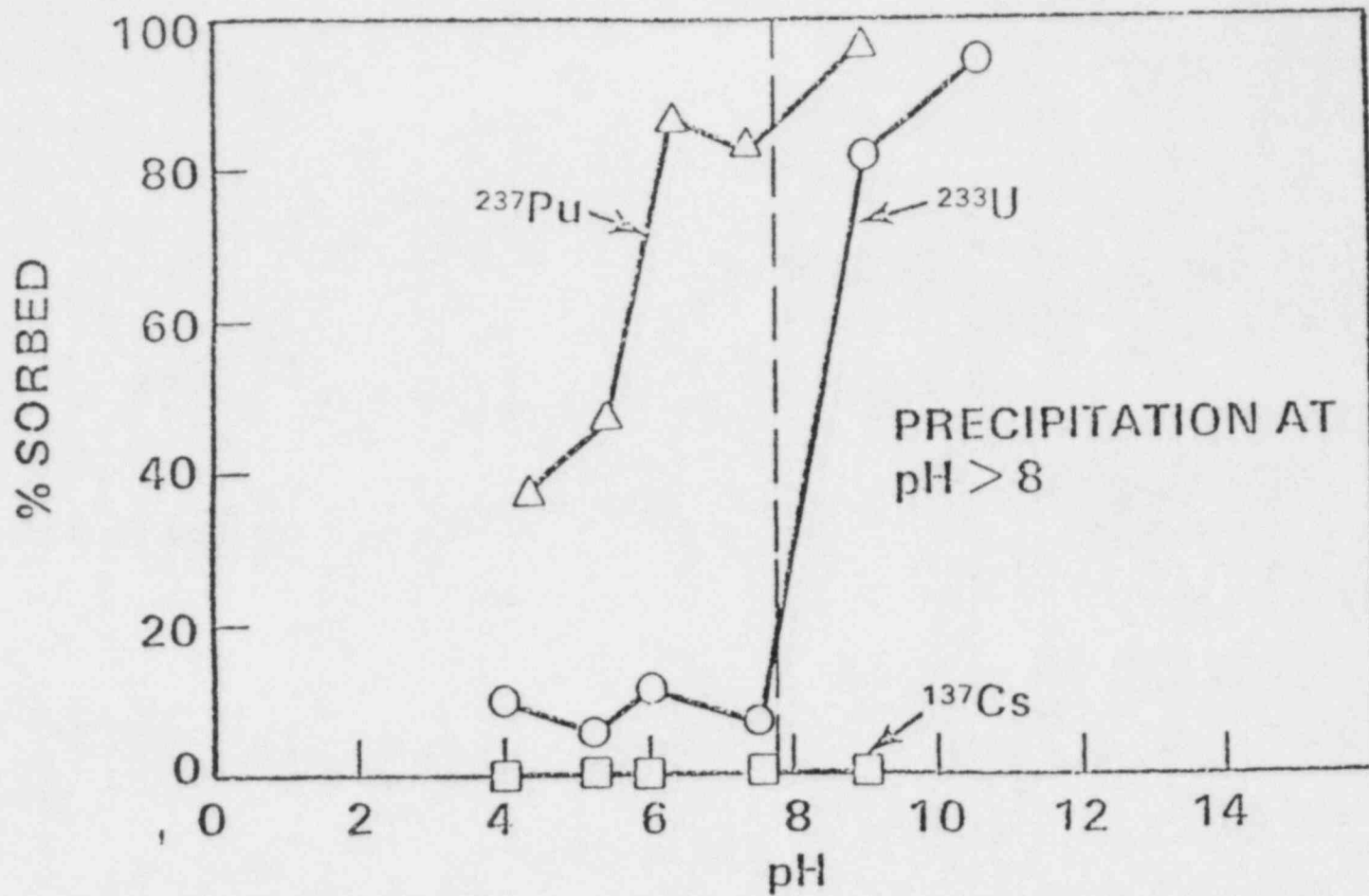
Figure 6.12. Adsorption of ^{237}Pu and ^{233}U on Fe silicate colloids in brine at 25°C as a function of pH. (Adapted from PNL-SA-10773, 1983.)

The state of whole package testing is in a very preliminary form and, like other interactive testing of waste package components, represents an urgent research need for the NRC licensing process.

6.4 Conclusions and Recommendations

The data on interactive testing of components of the waste package which has been presented in this section are preliminary, fragmentary and not covering the full range of conditions to be expected in various repositories. Obviously, this area of study represents a real and continuing research need. Although research on simpler systems (single and bicomponent testing) may be useful to indicate trends, in such complex systems it is desirable to conduct engineering studies replicating the whole waste package and surrounding repository conditions as closely as possible (proof testing).

Nevertheless, certain trends may be perceived even in the limited data now available. The packing material is an important component of the waste package. Although it serves a significant role in restricting and controlling the flow of groundwater to the waste package, and perhaps in buffering and conditioning the groundwater during an initial period, it can also be harmful to the container and/or the waste form under some conditions. It does not delay moisture reaching the container and moist or wet bentonite in contact with the container may accelerate corrosion. Also, bentonite may accelerate leaching of the glass waste form by ion depletion by preventing saturation of groundwater immediately surrounding the waste package. Bentonite clay may also form colloidal particles which could sorb and under some circumstances such as high water flow rates could transport radionuclides. Bentonite may later retard the movement of radionuclides if the packing material retains its mineral structure and does not crack or channel water during the thermal period. However, since sorption is a reversible process, radionuclides will not be permanently contained unless precipitation or some other mineralogical transformation takes place.

Other components of the packing material such as basalt might reduce the corrosion of the low-carbon steel by forming a protective silicate film. As has been discussed, basalt under some circumstances can also reduce leaching of the borosilicate glass waste form.

Of metals being considered for a HLW container, iron or low carbon steel appear to be inferior in that iron in several groundwaters has been found to accelerate leaching of borosilicate glass. In basaltic groundwater, iron tends to form iron silicate which readily forms colloidal particles and can capture radionuclides by coprecipitation or sorption and subsequently may transport them. Lead on the other hand tends to form a protective layer on the surface of the glass and thus may limit leaching.

From such preliminary data, the need for more bicomponent and whole package testing becomes apparent. Such testing should cover the full range of repository conditions such as those specified in prior BNL work (NUREG/CR-2482, Volumes 2 and 4, 1983). Also, accelerated testing is needed to identify effects which would not be revealed under prototypic repository conditions.

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APPENDIX

GLOSSARY OF CHEMICAL AND GEOLOGICAL TERMS*

aging
: The process by which metastable materials convert to their lowest energy states. Aging reactions might include: precipitation of new phases, crystallization of an amorphous material such as a glass, or recrystallization of an already crystalline material.

albite
: (a) A mineral of the feldspar group: $NaAlSi_3O_8$.

(b) A pure sodium feldspar.

alluvium
: A general term for unconsolidated detrital material deposited during comparatively recent geologic time as a sorted or semi-sorted sediment by running water.

analcime
: A mineral: $NaAlSi_2O_6 \cdot H_2O$. A zeolite commonly found in alkali-rich basalts. Synonym: analcite.

aphanitic [ign]
: Said of the feature of an igneous rock in which the crystalline components are not distinguishable by the unaided eye, both microcrystalline and cryptocrystalline features are included.

argillaceous
: Largely composed of or containing clay-sized particles or clay minerals.

basalt
: A general term for dark colored, ferromagnesian basic igneous rocks.

bentonite
: (a) A soft, plastic, porous, light-colored rock composed essentially of clay minerals of the montmorillonite (smectite) group plus colloidal silica and produced by devitrification and accompanying chemical alteration of a glassy igneous material, usually a tuff or volcanic ash. The rock commonly has the ability to absorb large quantities of water accompanied by an increase in volume of about eight times.

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*Geological terms are adapted from the Glossary of Geology (Bates, R. L., 1980). Chemical terms are adapted from the Merck Index (Windholz, M., 1976) or from a standard dictionary.

(b) A commercial term applying to any of the numerous variously colored clay deposits (especially bentonite) containing montmorillonite (smectite) as the essential mineral and presenting a very large total area, characterized by the ability to swell in water.

calcic [geochem]

Said of minerals and igneous rocks containing a relatively high portion of calcium.

cement [sed]

Mineral material, usually chemically precipitated, that occurs in the spaces among the individual grains of a consolidated sedimentary rock, thereby binding the grains together as a rigid, coherent mass; it may be derived from the sediment or its entrapped waters, or it may be brought in by solution from outside sources.

cementation [sed]

The diagenetic process by which coarse sediments become lithified or consolidated into hard, compact rocks, usually through deposition or precipitation of minerals in the spaces among the individual grains of the sediment.

chabazite

A zeolite mineral: $CaAl_2Si_4O_{12} \cdot 6H_2O$. It sometimes contains sodium and potassium. Also spelled chabasite.

chemical failure modes

Modes of chemical degradation by which the material may fail to perform its function or seriously decrease its ability to perform by chemical or mineralogical transformation or reaction.

chlorite

A group of minerals of the general formula: $(Mg, Fe^{2+}, Fe^{3+}) AlSi_3O_{10}(OH)_8$. It is characterized by prominent ferrous iron and by the absence of calcium and alkalis. Chlorites are associated with and resemble the micas; they may also be considered clay minerals.

clay

A loose, earthy, extremely fine grained, natural sediment or soft rock composed primarily of clay-size ($<4 \overset{\circ}{A}$) or colloidal particles and characterized by high plasticity and by a considerable content of clay minerals.

clay mineral

One of a complex and loosely defined group of finely crystalline, metacolloidal or amorphous hydrous silicates, essentially of aluminum (and sometimes of magnesium and iron). There may be exchangeable cations on the surfaces of the silicate layers, in amounts determined by the excess negative charge within the layer. They are characterized by small particle size and ability to adsorb substantial amounts of water and ions on the surfaces of the particles.

clinoptilolite

A zeolite mineral:
$(Na,K,Ca)_{2-3} Al_3(Al,Si)_2 Si_{13}O_{36} \cdot 12H_2O$.
It is a potassium-rich variety of heulandite.

diagenesis [sed]

All of the chemical and physical changes undergone by a sediment after its initial deposition, and during and after its lithification, exclusive of weathering and metamorphism. It embraces those processes (such as compaction, cementation, reworking, authigenesis, replacement, crystallization, leaching, hydration, bacterial action and formulation of concretions) that occur under conditions of pressure (up to 1 Kb) and temperature (maximum range of 100° to $300^\circ C$) that are normal to the outer part of the Earth's crust.

early diagenesis

The initial phase of diagenesis or post-sedimentary changes, occurring in the zone where the sediment is still unconsolidated, the prccess being complete when the sediment has been converted to a more or less compact sedimentary rock.

erionite

A zeolite mineral:
$(Ca,Na_2,K_2)_4 (Al_8Si_{28})O_{72} \cdot 27H_2O$.

facies

A distinctive rock type broadly corresponding to a certain environment or mode of origin.

feldspar

A group of abundant rock-forming minerals of the general formula: $MAl(Al,Si)_3O_8$ where M = K, Na, Ca, Ba, Rb, Sr and Fe.

fixation

The state of being fixated, i.e., made fixed, stationary or immobilized.

fulvic acid

That organic matter of indefinite composition which remains in solution when an aqueous alkaline extract of soil is acidified.

A-3

gel

A semisolid, apparently homogeneous substance in a colloidal state, generally elastic and jellylike, offering littl? resistance to liquid diffusion and containing a dispersion or network of fine particles which have coalesced to some degree.

greenschist facies

The set of metamorphic mineral assemblages of basic rocks including albite + chlorite. The facies includes the common products of low grade regional metamorphism in all parts of the world. It is believed to correspond to temperatures in the range of 300 to 500°C.

groundmass

The material between the phenocrysts of a porphyritic igneous rock. It is relatively finer grained than the phenocrysts and may be crystalline, glassy or both.

humic acids

A mixture of complex macromolecules having polymeric phenolic structures with the ability to chelate with metals, especially iron. They are usually found in soils, coals and peat, resulting from the decomposition of organic matter, particularly dead plants. Slightly soluble in water, usually with much swelling; soluble in alkali hydroxides and carbonates. Black acidic organic matter extracted from soils, low grade coals and other decayed plant substances by alkalis, insoluble in acids.

hydrothermal stability

Stability on exposure to liquid water whose temperature is high enough to make it geologically or hydrologically significant, usually ranging in temperature from 50 to 400°C and at high enough pressures to keep the water in a liquid state.

illite

A general name for a group of three-layer, mica-like clay minerals that are widely distributed in argillaceous sediments (especially in marine shales or derived soils). They are intermediate in composition and structure between muscovite and montmorillonite, have 10 $\overset{o}{A}$ c-axis spacings with substantially no expanding lattice characteristics and have the general formula:
$(H_3O,K)_y(Al_4 \cdot Mg_4 \cdot Mg_6) \cdot$
$(Si_{8-y} \cdot Al_y)O_{20}(OH)_4$ with y usually between 1 and 1.5. Illite contains less potassium and more water than true micas and more potassium than kaolite and montmorillonite; it appears intermediate between kaolin and montmorillonite clays in cation-exchange capacity, in ability to absorb and retain water, and in physical characteristics (such as plasticity index).

kaolin   A group of clay minerals characterized by a two-layer crystal structure having an approximate composition, $Al_2Si_2O_5(OH)_4$. They have lower base exchange capacities than montmorillonite and illite and they absorb less water and thus have lower plasticity indices, lower liquid limits and less shrinkage when drying from a wet state.

kaolinite   A common clay mineral of the kaolin group: $Al_2Si_2O_5(OH)_4$. It is a high-alumina clay mineral that does not appreciably expand under varying water content and does not exchange iron or magnesium.

kerogen   A complex bituminous material closely associated with the inorganic aggregates of oil shale, also found in bentonite.

lithification   The conversion of a newly deposited, unconsolidated sediment into a coherent, solid rock, involving processes such as cementation, compaction, desiccation and crystallization.

mesostasis   The last formed interstitial material, either glassy or aphanitic of an igneous rock.

metastable   Said of a phase that is stable with respect to small disturbances but that is capable of reaction with evolution of energy when sufficiently disturbed. In general, metastability is due to the reluctance of a system to initiate the formation of a new, stable phase.

montmorillonite clay   A group of expanding lattice clay minerals of formula $R_{0.33}Al_2Si_4O_{10}(OH)_2 \cdot nH_2O$ where R includes one or more of the cations Na^+, K^+, Mg^{2+}, Ca^{2+}. The minerals are characterized by a three-layer crystal lattice; by deficiencies in charge balanced by the presence of cations (usually Na^+ or Ca^{2+}) subject to base exchange and by swelling on wetting (and shrinking on drying) due to the introduction of considerable interlayer water in the c-axis direction.

mordenite   A zeolite mineral: $(Ca, Na_2K)_4Al_8 Si_{40}O_{96} \cdot 28H_2O$. It has a high Si/Al ratio and is the most hydrothermally stable of the common zeolites.

nontronite | A dioctahedral iron-rich clay mineral of the montmorillonite group: $Na_{0.33}Fe_2^{3+}(Al_{0.33}Si_{3.67})O_{10}(OH)_2 \cdot nH_2O$. It represents an end member in which the replacement of aluminum by ferric iron is essentially complete. Nontronite commonly occurs in weathered basaltic rocks, where it may occupy vesicles or veins or occur between lava flows.

oligoclase | A mineral of the plagioclase feldspar group. It is common in igneous rocks with intermediate to high silica content.

paragonite | A mineral of the mica group: $NaAl_2(AlSi_3)O_{10}(OH)_2$. It corresponds to muscovite but with sodium instead of potassium and it usually occurs in metamorphic rocks. Synonym: soda mica.

phenocryst | A term widely used for a relatively large, conspicuous crystal in a porphyritic rock.

phillipsite | A zeolite mineral: $(K_2,Na_2,Ca)\ Al_2Si_4O_{12} \cdot 4-5H_2O$. It sometimes contains sodium, but always contains considerable potassium. It is common in marine sediments.

plagioclase | A group of feldspar minerals of the general formula $(Na,Ca)Al(SiAl)Si_2O_8$. The Al/Si ratio ranges from 1:3 to 1:1. Synonym: sodium-calcium feldspar.

porphyritic | Said of the texture of an igneous rock in which the larger crystals (phenocrysts) are set in a finer grained groundmass which may be crystalline or glassy or both.

powellite | A mineral: $CaMoO_4$.

prehnite facies | A mineral: $Ca_2Al_2Si_3O_{10}(OH)_2$, commonly associated with zeolites but stable to a somewhat higher temperature.

pumice | A light colored vesicular glassy rock, often buoyant enough to float on water.

pyroclastic | Pertaining to rock composed of rock fragments formed by volcanic explosion or aerial expulsion from a volcanic vent.

radiolysis | Chemical decomposition caused by radiation.

rectorite	A white clay mineral mixture with a regular inter-stratification of two mica layers and one or more water layers.
sanidine	A high temperature mineral of the alkaline feldspar group, $KAlSi_3O_8$. It is a highly disordered monoclinic form occurring in clear glassy crystals embedded in unaltered acid volcanic rocks. It appears to be stable under equilibrium conditions above approximately 500°C. Some sodium is always present. Syn. glassy feldspar, ice spar.
sepiolite	A chain-lattice clay mineral: $Mg_4(Si_2O_5)_3 (OH)_2 \cdot 6H_2O$.
shale	A fine-grained detrital sedimentary rock, formed by the consolidation of clay, silt or mud.
smectite	A name for the montmorillonite group of clay minerals, dioctahedral (montmorillonite) and trioctahedral (saponite), that possess swelling properties and high ion exchange capacities.
tuff	A general term for consolidated rocks formed by fragments from a volcanic eruption.
vitric	Said of pyroclastic material which contains more than 75% glass.
vitric tuff	A tuff which consists predominantly of volcanic glass fragments.
vitrophyre	Any porphyritic igneous rock having a glassy groundmass.
vitrophyric	Said of a porphyritic igneous rock having large phenocrysts in a glassy groundmass.
welded tuff	A glass rich pyroclastic rock that has been indurated by the welding together of its glass shards under the combined action of the heat retained by particles, the weight of overlying material and hot gases. It is generally composed of silicic pyroclasts and appears banded.
zeolite	A generic term for a large group of hydrous alumino-silicates which are analogous in composition to the feldspars with sodium, calcium and potassium as their chief metals and are characterized by their easy and reversible loss of water of hydration and by their use as sorbents or cation exchange agents.

1. REPORT NUMBER (Assigned by TIDC, add Vol. No., if any)
NUREG/CR-2482, Vol. 5
BNL-NUREG-51494

2. TITLE AND SUBTITLE	3. LEAVE BLANK
Review of DOE Waste Package Program Subtask 1.1 - National Waste Package Program April 1983 - September 1983	

	4. DATE REPORT COMPLETED	
5. AUTHOR(S)	MONTH	YEAR
P. Soo, Editor	November	1983

	6. DATE REPORT ISSUED	
	MONTH	YEAR
	August	1984

7. PERFORMING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)	8. PROJECT/TASK/WORK UNIT NUMBER
Brookhaven National Laboratory Upton, NY 11973	Task 1
	9. FIN OR GRANT NUMBER
	A3164

10. SPONSORING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)	11a. TYPE OF REPORT
Division of Waste Management Office of Nuclear Material Safety and Safeguards U.S. Nuclear Regulatory Commission Washington, DC 20555	Final
	b. PERIOD COVERED (Inclusive dates)

12. SUPPLEMENTARY NOTES

13. ABSTRACT (200 words or less)

This report addresses part of an ongoing task to review the national high-level waste package effort. It includes evaluations of reference waste form, container and packing material components with respect to determining how they may contribute to the containment and controlled release of radionuclides after waste packages have been emplaced in salt, basalt, and tuff repositories. A section on carbon steel container corrosion is included to complement prior work on TiCode-12 and Type 34 stainless steel. Use of crushed tuff as a packing material is discussed, and waste package component interaction test data are included. Licensing data requirements are specified.

14. DOCUMENT ANALYSIS — a. KEYWORDS/DESCRIPTORS	15. AVAILABILITY STATEMENT
waste packages	Unlimited
	16. SECURITY CLASSIFICATION
	(This page)
	Unclassified
b. IDENTIFIERS/OPEN-ENDED TERMS	(This report)
	Unclassified
	17. NUMBER OF PAGES
	18. PRICE

UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D.C. 20555

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OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, $300