

REVIEW OF DOE WASTE PACKAGE PROGRAM
Subtask 1.1 - National Waste Package Program
October 1983 - March 1984

P. Soo, Editor

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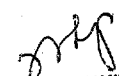
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Manuscript Completed: May 1984
Date Published: March 1985

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Prepared for the Division of Waste Management
Office of Nuclear Material Safety and Safeguards
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555
NRC FIN A3164


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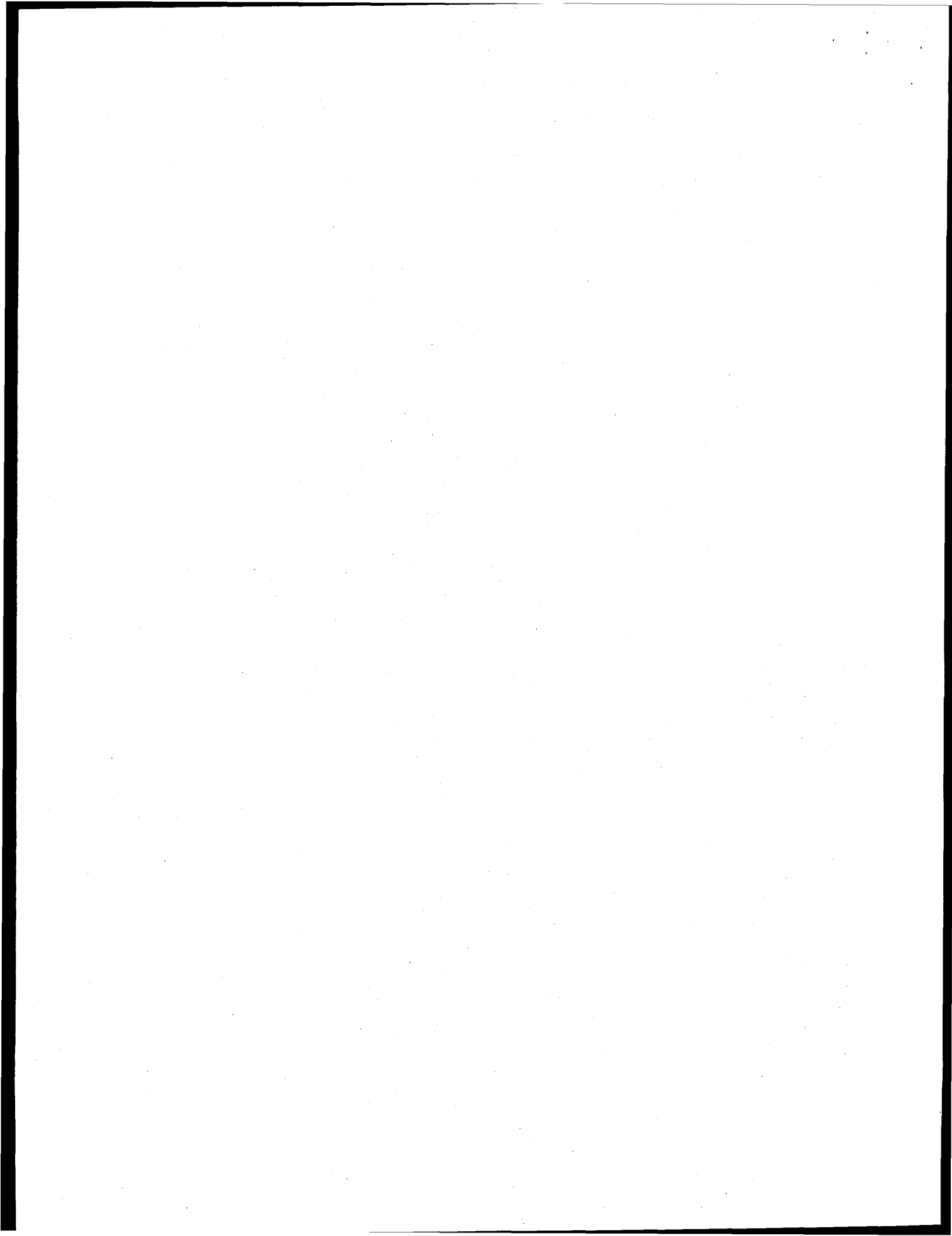
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ABSTRACT

The present 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, tuff, and granite repositories. In the current Biannual Report a review of progress in the new crystalline repository (granite) program is described. Other foreign data for this host rock have also been outlined where relevant. The use of crushed salt, and bentonite- and zeolite-containing packing materials is discussed. The effects of temperature and gamma irradiation are shown to be important with respect to defining the localized environmental conditions around a waste package and the long-term integrity of the packing.



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ACKNOWLEDGEMENT

The authors gratefully acknowledge the skills and patience of Ms. G. Searles and Ms. M. McGrath in the typing and preparation of this report.

EXECUTIVE SUMMARY

A review has been conducted of information currently available on the status of crystalline repository developments. The present work is concerned with an assessment of data and current efforts pertaining to a granite repository. Data are presented on the range of expected repository conditions and additional information needs, with respect to the crystalline rock evaluation process, are identified.

Current DOE efforts in the area of crystalline repository development have focused on site-selection criteria, initial regional screening and, predominantly, thermomechanical investigations of granite formations. Granitic formations exhibit considerable variation in hydraulic conductivity, permeability and porosity as a result of variation in the fracture system. Water flow and groundwater composition tend to vary considerably with depth and from locality to locality. Thermal and radiation fields are known to weaken the ultimate strength of the rock and alter the fracture/flow system. Currently, no conceptual designs for waste packages to be emplaced in tuff appear to have been specified.

A review was also conducted on the use of crushed salt and alternate packing material under salt repository conditions. Current conceptual designs for a waste package in a salt repository do not specifically include the use of a tailored packing material component. The use of packing material was, however, taken under consideration in Westinghouse work as an alternate solution to the need for long-term waste isolation in the event the container was shown not to meet the containment requirements. Crushed salt, bentonite, zeolite and sand packing materials were considered.

With respect to crushed salt, brine may be present as water of hydration, intergranular water or brine inclusions. Brine inclusions have been shown to migrate up the thermal gradient to the waste container but accurate estimates of anticipated inflow rates need to be established for prototypic conditions. Procedures for minimizing brine migration to the waste include selection of drier salt formations for repository use, avoiding salt that contains a large portion of hydrated minerals and including desiccants in the salt packing to absorb liberated water. Both CaO and MgO may be effective additives for this purpose.

Brine present at an early period after repository closure is likely to be acidic due to interaction with thermally released gases, such as HCl, CO₂ and SO₂. However, thermal annealing and gamma irradiation of salt will probably cause subsequent intruding brine to be basic. The main reason lies in the formation of sodium colloids which interact with the migrating brine to form NaOH and hydrogen. Thus, container materials need to be evaluated with respect to a wide range of pH's to quantify aqueous corrosion failure times. Some container materials may also be susceptible to hydrogen-induced failure because of hydrogen liberation from the colloidal sodium interaction, and because of the generation of this gas by gamma radiolysis of the brine.

Crushed salt packing material will be consolidated under the action of compressive stresses, temperature, and the presence of brine. Under long-term compressive creep conditions almost complete consolidation will occur if brine being released is allowed to escape.

Alternate packing materials for use in a salt repository include bentonite- and zeolite-containing mixtures. Bentonite clays, however, may be thermally altered to illite and smectite at temperatures well within anticipated repository conditions. Since these alteration products are more dense than bentonite, and have limited swelling potential from water absorption, bentonite packing may be subjected to increased permeability. In addition, bentonite may release water under high temperature conditions. A detailed assessment of this effect needs to be undertaken to quantify the effects of such water releases on container corrosion and waste form leaching.

Zeolites possess excellent radionuclide sorption behavior and will be useful for limiting the rate of radionuclide release. Nevertheless, they also may be subject to high-temperature alteration. Mordenite and clinoptilolite are two of the most important with respect to waste isolation. Under low water vapor pressures some workers have shown that at high temperature they will suffer irreversible dehydration reactions. One study shows that use of zeolite-containing rocks should only be employed for radionuclide retardation purposes at temperatures below 85°C in water-saturated conditions. This may not be a strictly valid argument for a salt repository but the limitations of zeolites as a packing are evident and need to be fully addressed.

With respect to the role of crushed salt packing material in meeting the radionuclide containment and controlled release criteria, the fact that brine migrates towards the waste form indicates that loss of containment, and control of radionuclide release, will not be governed by brine flow behavior. Compliance or non-compliance with regulatory criteria will, therefore, depend on establishing the rates of diffusion of radionuclides to the outer boundary of the packing material and beyond.

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 release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 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.

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 data on the use of crushed salt as a packing material (discrete backfill), and progress in the DOE program on crystalline repository development. 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.

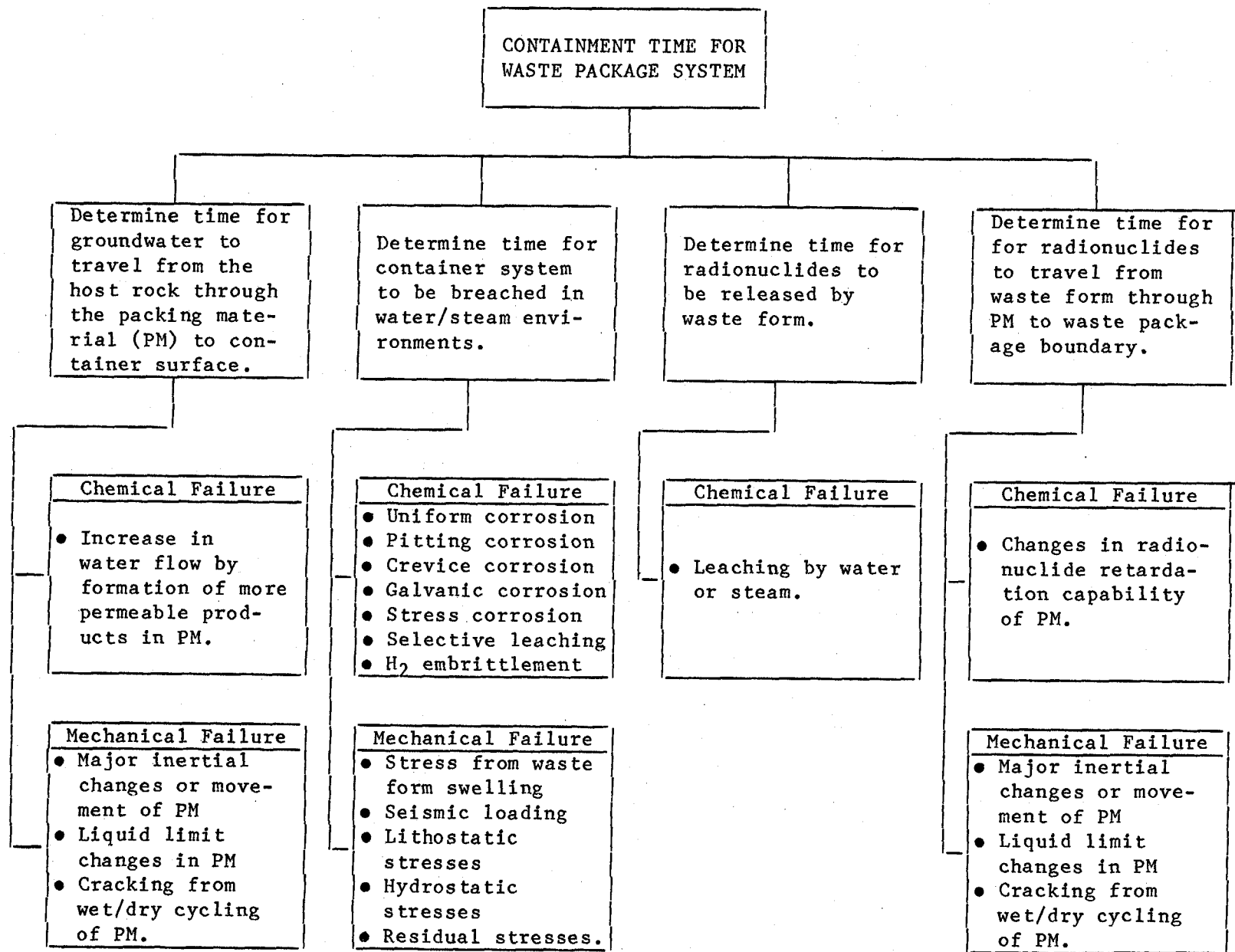


Figure 1.1 Chemical and mechanical failure/degradation modes affecting containment of radionuclides by the waste package system.

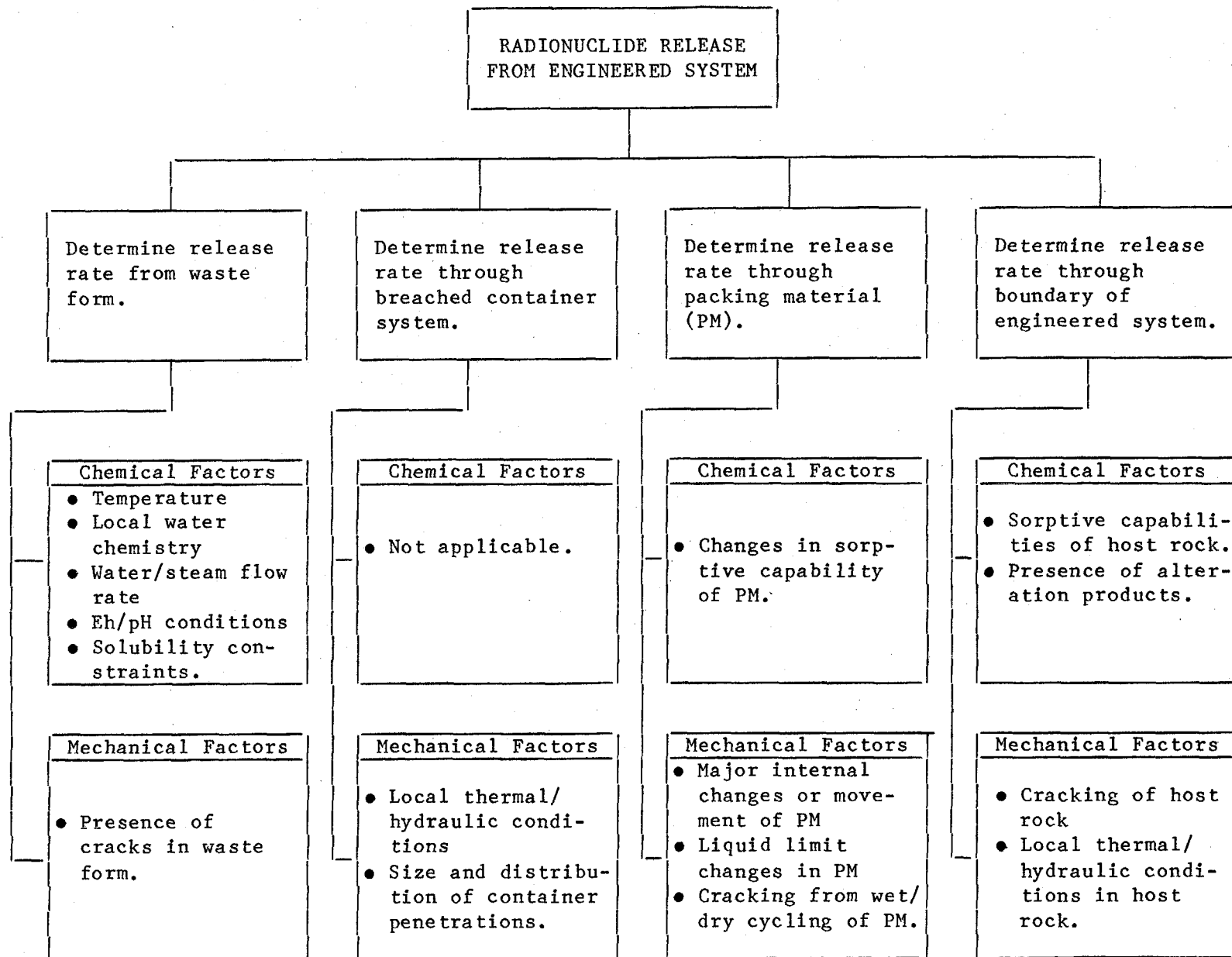


Figure 1.2 Factors affecting radionuclide release from the engineered barrier system.

2. NEAR-FIELD REPOSITORY CONDITIONS

2.1 Basalt

This section of the program has been completed and is reported in a previous Biannual Report (NUREG/CR-2482, Vol. 3, 1983).

2.2 Salt

This section of the program has been completed and is reported in a previous Biannual Report (NUREG/CR-2482, Vol. 3, 1983).

2.3 Tuff

This section of the program has been completed and is reported in a previous Biannual Report (NUREG/CR-2482, Vol. 4, 1983).

2.4 Granite (E. Veakis)

2.4.1 DOE Program on Crystalline Repository Development

As part of the effort to continue and expand the assessment of the national waste package program, BNL is identifying information needs from national and international efforts in the area of crystalline repository development for the NRC. In order to facilitate the review of data pertinent to NRC's licensing actions with regard to a high level radioactive waste package performance assessment, the near-field repository environment for the particular host rock requires characterization. The present work is concerned with an assessment of data and current efforts pertaining to a granite repository. Data are presented on the range of expected repository conditions and additional information needs, with respect to the crystalline rock evaluation process, are identified.

A national reconnaissance and evaluation program conducted by the Office of Crystalline Repository Development (OCD), in response to DOE's increased emphasis on crystalline rock as a potential future host for repository siting, focused on exposed masses of crystalline rock -- as opposed to deeply buried rock masses -- for initial regional screening.

The reasons for limiting the initial screening on exposed masses were as follows (OCD-1, 1983):

1. The amount of information currently available for exposed crystalline rocks far surpasses that available for deeper formations.
2. Exposed formations are easier to map and sample whereas deep formations can only be evaluated by extensive drilling and geophysical surveys.
3. Exposed crystalline rock formations occur over a wide range of geographic locations which may be suitable for locating a repository.

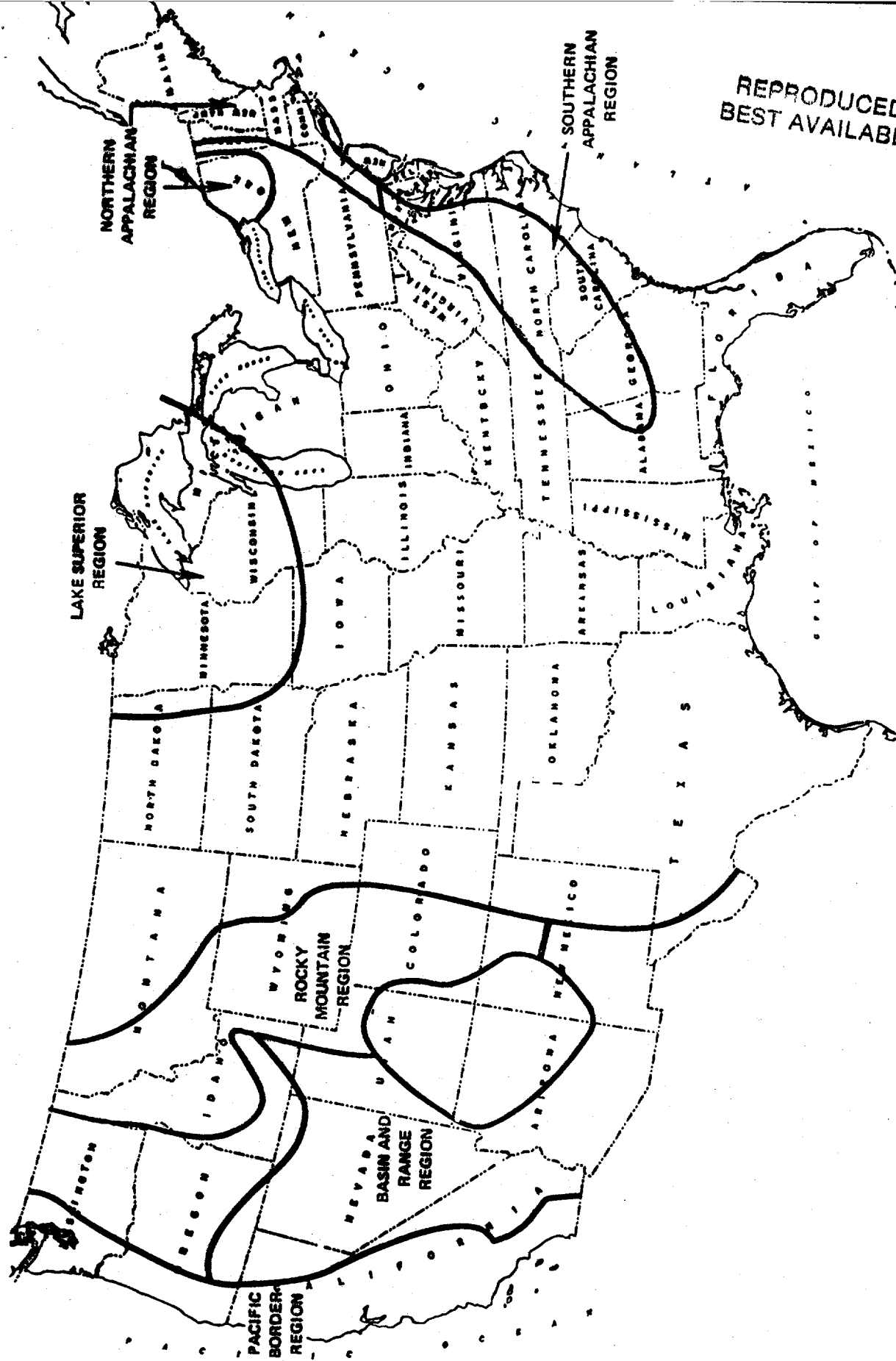
In attempting to narrow the field of candidate localities suitable for repository siting, OCRD excluded from further consideration areas exhibiting:

- Greater than 1000 m of vertical movement in the crust over the last 10-million years
- Evidence of young faults (~15-million years old or younger)
- Evidence of known epicenters of earthquakes of intensity V or greater on the Modified Mercalli Scale
- Evidence of horizontal acceleration of the ground surface of ~10 percent g or greater over the next 50 years
- Evidence of quaternary volcanic rocks and deposits
- Known major mineral deposits
- Known high temperature convective groundwater systems
- Extreme erosion
- Potentially high regional hydraulic gradients judged on the basis of topographic relief.

Areas exhibiting favorable conditions based on these preliminary, qualitative criteria are presented in Table 2.1. Figure 2.1 illustrates the geographic position of each of the major regions under investigation by OCRD.

Table 2.1. Comparison of regions of crystalline rocks and physiographic provinces (OCRD-1, 1983).

Major Regions of Exposed Crystalline Rocks	Physiographic Provinces Included
Pacific Border Region	Pacific Border Province Sierra Nevada Province Cascade Province
Basin and Range Region	Basin and Range Province
Rocky Mountain Region	Northern Rocky Mountains Province Middle Rocky Mountains Province Southern Rocky Mountains Province Wyoming Basin Province
Lake Superior Region	Central Lowland Province Superior Highland Province
Northern Appalachian and Adirondack Region	New England Province Adirondack Province
Southern Appalachian Region	Valley and Ridge Province Piedmont Province Blue Ridge Province



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Figure 2.1. Major regions under investigation by the OCRD (OCD-1, 1983).

From the geotechnical standpoint, Witherspoon and Watkins (LBL-14082, 1982) identified three basic areas in need of investigation: (1) characterization of the rock mass fracture system, (2) thermomechanical effects, and (3) characterization of the fracture hydrology -- including permeability, effective porosity, and sorptive capacity of the host rock.

2.4.2 Crystalline Rock Compositions

The term "crystalline rock" is an inexact designation for referring to igneous or metamorphic rock, although the term has also been used in reference to sedimentary rocks composed of coarsely crystalline grains. The texture of crystalline rock is characterized by closely fitting particles consisting of crystals or crystal fragments. Granitic rock is a term applied to coarse-grained plutonic rock having quartz as an essential component in addition to feldspar and mafic minerals (Bates, R. L., 1980). The term "granitic rock" encompasses three major rock types: granites, monzonites, and granodiorites - igneous rocks in which the alkali feldspars constitute important components (Frye, K., 1981). Average chemical compositions for granitic rocks are shown in Table 2.2.

Site-specific host rock compositional characterization is important in the determination of petrogenetic processes that have taken place, including mineral alterations and host rock influence on groundwater composition. Table 2.3 presents the major and accessory minerals and weathering products of granite. The actual proportions of these minerals will vary with each particular site. Included in this table are some probable chemical effects associated with a particular mineral or weathering product.

Earlier studies undertaken by Dames and Moore for the Office of Waste Isolation were concerned with detailed reviews of available information on rock properties in order to arrive at a generic base for a "typical" granitic formation (Y/OWI/TM-36/5, 1978). Rock mass properties derived by Dames and Moore for a typical granite are presented in Table 2.4.

2.4.3 Hydrology and Groundwater Compositions

Hydraulic parameters, including hydraulic conductivity, permeability or porosity, vary considerably from site to site as a result of variations in the occurrence and extent of fractures. Concentration of fractures and their physical configurations are key parameters in determining groundwater velocity. Table 2.5 shows hydraulic properties of different hydrologic structures in granite to illustrate the point.

Permeability testing of fractures conducted by Lawrence Livermore Laboratory (LLL) in the Climax stock granite indicate that permeability can be highly variable depending on the nature and extent of the fracture zones present (UCRL-85231, 1980). Intact rock or healed fractures exhibited a permeability of $<10^{-9}$ darcies whereas moderately to highly fractured zones encountered exhibited a permeability in the range of 10^{-4} to 10^{-1} darcies. At high temperatures permeability of granitic rocks may increase as a result of

Table 2.2. Compositional averages of granitic rocks (number of analyses used for average in parentheses; weight percent)

	Alkali Granites ^a (48)	Granites-A ^a (72)	Granites-B ^b	Quartz Monzonites ^a (121)	Grano- diorites ^a (137)
SiO ₂	73.86	72.08	77.0	69.15(69.1) ^c	66.88(67.6) ^c
TiO ₂	0.20	0.37	----	0.56(0.4)	0.57(0.4)
Al ₂ O ₃	13.75	13.86	12.0	14.63(15.8)	15.66(15.8)
Fe ₂ O ₃	0.78	0.86	0.8	1.22(1.5)	1.33(1.8)
FeO	1.13	1.67	0.9	2.27(1.3)	2.59(1.6)
MnO	0.05	0.06	----	0.06(<0.05)	0.07(0.1)
MgO	0.26	0.52	----	0.99(0.6)	1.57(0.8)
CaO	0.72	1.33	0.8	2.45(3.2)	3.56(3.7)
Na ₂ O	3.51	3.08	3.2	3.35(3.0)	3.84(3.1)
K ₂ O	5.13	5.46	4.9	4.58(3.9)	3.07(3.5)
H ₂ O ⁺	0.47	0.53	0.3	0.54(0.9)	0.65(1.0)
P ₂ O ₅	0.14	0.18		0.20(0.2)	0.21(0.2)
qz*	32.2	29.2		24.8 (28)	21.9 (28)
ov	30.0	32.2		27.2	18.3
ab	29.3	26.2		28.3	32.5
an	2.8	5.6		11.1	16.4
c	1.4	0.8		----	----
CaSiO ₃	----	----		----	----
MgSiO ₃	0.6	1.3		2.5	3.9
FeSiO ₃	1.1	1.7		2.2	2.9
ac	----	----		----	----
mt	1.2	1.4		1.9	1.9
il	0.5	0.8		1.1	1.1
ap	0.3	0.4		0.5	0.5

^aAverage compositions based on Wedepohl, 1969.

^bDOE/ET-0028, 1979.

^cClimax (NTS) granites (UCRL-53309, 1982).

*qz-quartz, ov-K-feldspar, ab-albite, an-anorthite, c-corundum, ac-acmite, mt-magnetite, il-ilmenite, ap-apatite.

Table 2.3. Chemical effect of main minerals of granite and some important accessory minerals and weathering products (UCRL-53155, 1981).

Mineral or Weathering Product	Chemical Effect
Main minerals:	
Quartz 25-30%	Source of colloid SiO_2 ?
Feldspar 50-75%	
e.g., orthoclase KAlSi_3O_8	Interstitial K, Na, Ca-exchangeable?
e.g., plagioclase $(\text{Na}, \text{Ca})(\text{Al}, \text{Si})_4\text{O}_8$	Easily weathered
Amphiboles <20%	
e.g., hornblende	
$\text{Ca}_2\text{Na}(\text{Mg}, \text{Fe})_4(\text{Al}, \text{Fe}, \text{Ti})_3\text{Si}_8\text{O}_{22}(\text{O}, \text{OH})_2$	
Micas <20%	Cation exchangers?
e.g., biotite $\text{K}(\text{Fe}, \text{Mg})_3(\text{AlSi}_3\text{O}_{10}\text{VOH})_2$	
Accessory minerals:	
Magnetite Fe_3O_4	Eh-effect
Pyrite FeS_2	Eh-effect; SO_4^{2-} source
Ilmenite FeTiO_3	
Zircon ZrSiO_4	
Fluorite CaF_2	F^- source
Calcite CaCO_3	CO_3^{2-} source
Apatite $\text{Ca}_5(\text{F}, \text{Cl}, \text{OH})(\text{PO}_4)_3$	PO_4^{3-} source
Monazite $(\text{Ce}, \text{La}, \text{Th})\text{PO}_4$	Sorption of Ln and An?
Weathering products:	
Kaolinite $\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8$	From feldspars; cation exchanger
Chlorite $(\text{Mg}, \text{Fe}, \text{Al})_4(\text{Si}_4\text{O}_{10})(\text{OH})_8$	From amphiboles and micas; cation exchanger

Table 2.4. Estimated rock mass properties for generic granite
(based on Y/OWI/TM-36/5, 1978).

Type of Property	Parameter	Value
Index	Unit weight	2640 kg/m ³ (165 lb/ft ³)
	Natural moisture content	---
	Porosity (effective)	0.4%
Stress-strain	Young's modulus	1.7 x 10 ⁴ MPa (2.5 x 10 ⁶ lb/in ²)
	Poisson's ratio	0.18
Strength	Unconfined compressive strength	131 MPa (19,000 lb/in ²)
	Tensile strength	6.9 MPa (1,000 lb/in ²)
Thermal	Coefficient of linear thermal expansion	8.1 x 10 ⁻⁶ °C ⁻¹ (4.5 x 10 ⁻⁶ °F ⁻¹)
	Heat capacity:	
	<u>Temperature, °C</u>	<u>Heat Capacity, W·sec/kg·°C</u>
	0 (32°F)	880 (0.21 BTU/lb-°F)
	100 (212)	920 (0.22)
	200 (392)	960 (0.23)
	Thermal conductivity:	
	<u>Temperature, °C</u>	<u>Conductivity, W/m °C</u>
	0 (32°F)	2.85 (1.65 BTU/h-ft °F)
	50 (122)	2.70 (1.56)
	100 (212)	2.56 (1.48)
	150 (302)	2.44 (1.41)
	200 (392)	2.34 (1.35)
	300 (572)	2.15 (1.24)
	400 (752)	1.99 (1.15)

Table 2.5. Hydraulic properties of different hydrogeologic structures for the reference repository site area in granite at depths of 1 m and 500 m (National Research Council, 1983).

Description	Width (m)	Conduc- tivity (m/s)	Porosity	Velocity (Unit Gradient) (m/s)	Water Travel Time for 1 km Under 0.001 Gradient (yr)
Rock mass					
1 m depth		10^{-7}	3×10^{-3}	3.33×10^{-5}	951
500 m depth		10^{-10}	10^{-5}	1×10^{-5}	3170
First-order fracture zones (tension)					
1 m depth	50	10^{-5}	3×10^{-2}	3.33×10^{-4}	95
500 m depth		10^{-8}	10^{-4}	10^{-4}	317
Second-order fracture zones (tension)					
1 m depth	10	10^{-5}	3×10^{-2}	3.33×10^{-4}	95
500 m depth		10^{-8}	10^{-4}	10^{-4}	317
Second-order fracture zones (shear)					
1 m depth	20	5×10^{-7}	5×10^{-3}	1×10^{-4}	317
500 m depth		5×10^{-10}	1.7×10^{-5}	3×10^{-5}	1057
Second-order fracture zones (compression)					
1 m depth	5	10^{-6}	5×10^{-3}	2×10^{-4}	159
500 m depth		10^{-9}	1.7×10^{-5}	6×10^{-5}	529

anisotropic thermal expansion leading to grain boundary cracking. The variability and extent of natural fracture systems precludes obtaining any reliable values of permeability based on laboratory experiments. Fracture permeability will vary, and not necessarily decrease with depth, in any predictable manner. Brace found that in situ permeability values at specific localities are not predictable within a factor of 10^5 (Brace, W. F., 1980; also National Research Council, 1983).

Recent sampling and characterization of Climax granite groundwater indicate that chemical composition varies considerably among samples and with depth. The major differences occur with chloride, sodium, calcium, sulfate, bicarbonate, and magnesium (UCRL-53309, 1982). Table 2.6 shows results from chemical analyses of Climax groundwater samples. Included in the table are reported ranges for Stripa granitic groundwater constituents for comparison. Figure 2.2 shows chemical variation of groundwater with depth at Stripa.

The deep granitic groundwaters at Climax were found to be neither dilute nor in equilibrium with the granite. As indicated, Climax groundwaters are high in total dissolved solids (1110-1910 mg/L) and high in sodium (72-250 mg/L). The difference in composition between samples from Climax suggests that the variation results from different fracture systems present in the area from which the samples were obtained. Since granite is essentially impermeable, the groundwaters flowing into the area via fractures are chemically "tailored" by the fracture fill materials present, such as quartz, calcite and pyrite. The heterogeneity present in the chemical composition of Climax groundwater suggests that site characterization will require extensive groundwater sampling. With regard to the assessment and testing of waste package components, selection of synthetic granitic groundwaters and test procedures need to take into account the possibility of compositional variation that may result from complex fracture flow systems.

2.4.4 Effects of Temperature on Rock Stability

Recent efforts on the part of OCRD were concerned with establishing expected repository environments in a generic granite repository for commercial high level waste (CHLW), defense high level waste (DHLW), and spent fuel (SF). Thermoelastic analysis was undertaken for the purposes of predicting stresses and displacements in response to the elevated temperatures induced by the waste package as well as stresses resulting from excavation of the borehole (BMI/OCRD-9, 1983). The model used in the OCRD study assumed a two-row configuration of waste containers, a repository depth of 1000 m and initial temperature of 20°C. Figure 2.3 shows the thermal model used; Table 2.7 presents the basic parameters pertaining to the room and drillhole. Table 2.8 gives the generic granite properties used (BMI/OCRD-7, 1983). For the purposes of the model, during the first 25 years after emplacement the disposal room remained open; at 25 years the room was backfilled with crushed granite. Results of the study indicate that the effect of temperature on the vertical stresses exceeds that induced by excavation and may result in an unstable drillhole. Instability takes place with elevated temperatures with the upper part of the borehole becoming more unstable than the lower portion. After ten years the analysis

Table 2.6. Chemical analyses of Climax and Stripa groundwater samples (concentrations in mg/L except as noted). Taken from UCRL-53154, 1981; UCRL-53309, 1982.

Parameter	CGW-1 (10) ^a	NH-01 (1)	UG-02 (3)	C-30 (2)	C-36 (2)	Stripa (Ranges)
Na	250	229	214	72	56	43-125
Ca	283	240	114	161	126	10-59
K	3.4	3.8	4.7	6.5	4.8	0.2-5.4
Mg	0.9	4.8	1.5	118	63	0.5
Sr	5.6	7.9	4.2	0.8	1.8	
Cs	0.002	ND ^b	ND	ND	ND	
Al	0.03	0.05	0.02	<0.05	<0.05	
SiO ₂	15.8	22.5	23.9	29.3	33.8	11.0-12.8
U	1.8	18.5	<0.1	<0.1	<0.1	
Fe	0.006	0.5 ^e	0.8 ^d	0.003	<0.004	0.02-0.24
Zn	0.005	0.03 ^e	0.03 ^d	0.008	0.004	
Mn	0.05	0.008	0.05	0.002	0.03	
Li	0.25	0.17	0.17	0.14	0.07	
W	0.15	ND	ND	ND	ND	
Mo	0.72	0.22	0.09	0.20	0.18	
As	0.03	ND	ND	ND	ND	
PO ₄	<0.5	0.5	<0.3	1.9	1.2	
Ti	0.004	0.02	<0.002	0.003	<0.001	
Cl	77	160	70	77	52	52-283
SO ₄	1060	850	480	750	325	2.7-19
S	<0.01	ND	3.0	ND	ND	
HCO ₃	163	65	165	167	316	15.4-78.7
NO ₃	<0.02	ND	ND	ND	ND	
F	0.9	ND	1.4	ND	ND	
TDS ^c	1900	1770	1110	1910	1150	
Conductivity (μS)	2160	2050	1340	1700	1200	
Dissolved O ₂ (mg/L)	<0.01	ND	<0.15	ND	ND	
Eh (mV)	+410	ND	+86	ND	ND	
pH	7.3	8.2	7.5	8.1	7.8	8.85-9.75
Sample depth (m)	420	420	565	64	73	

^aNumbers in parentheses are number of samples analyzed.

^bND = Not determined.

^cTDS = Total dissolved solids (mg/L).

^dSample contaminated with Fe and Zn from drill bit.

^eSample contaminated by wire mesh covering collection site.

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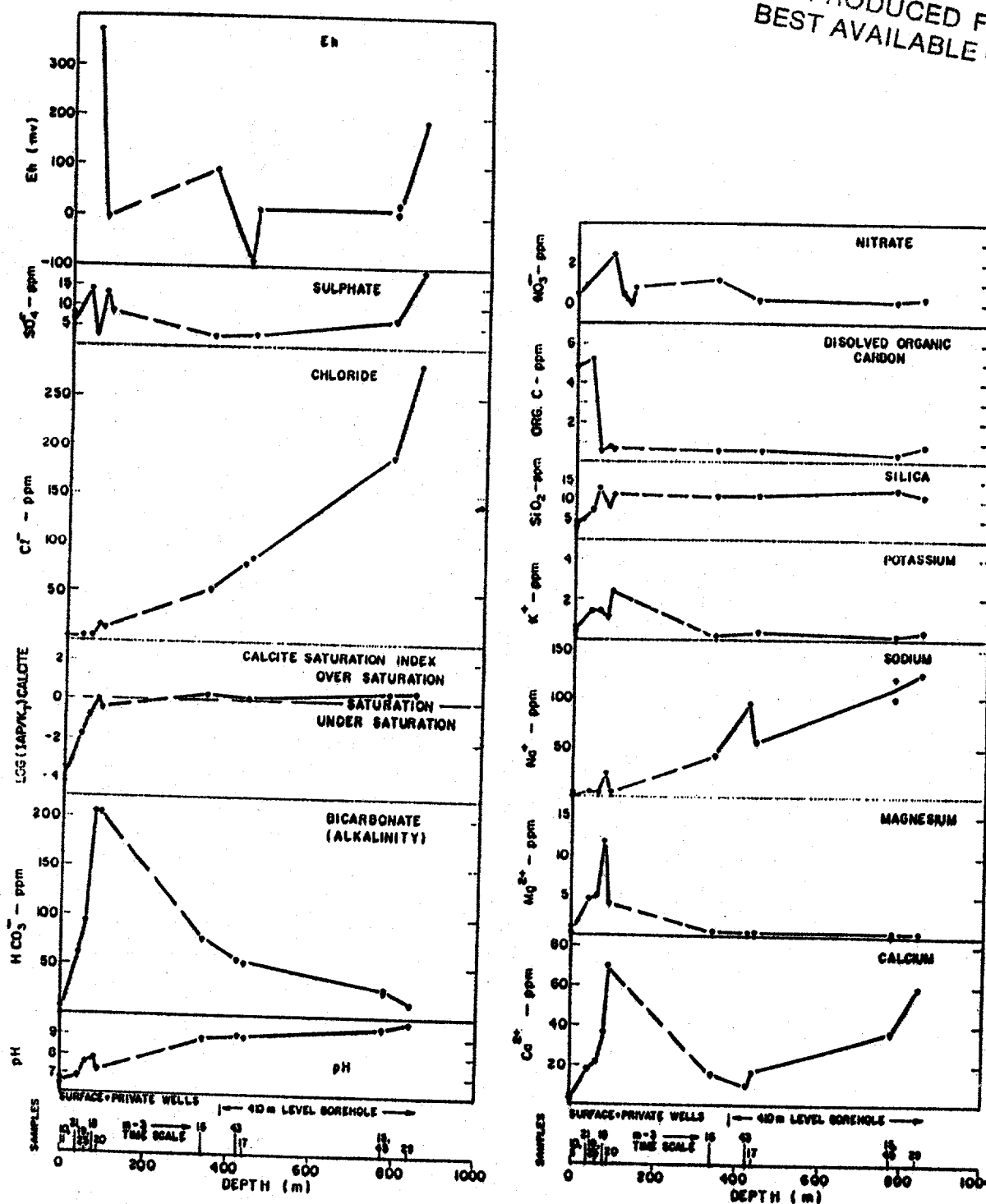
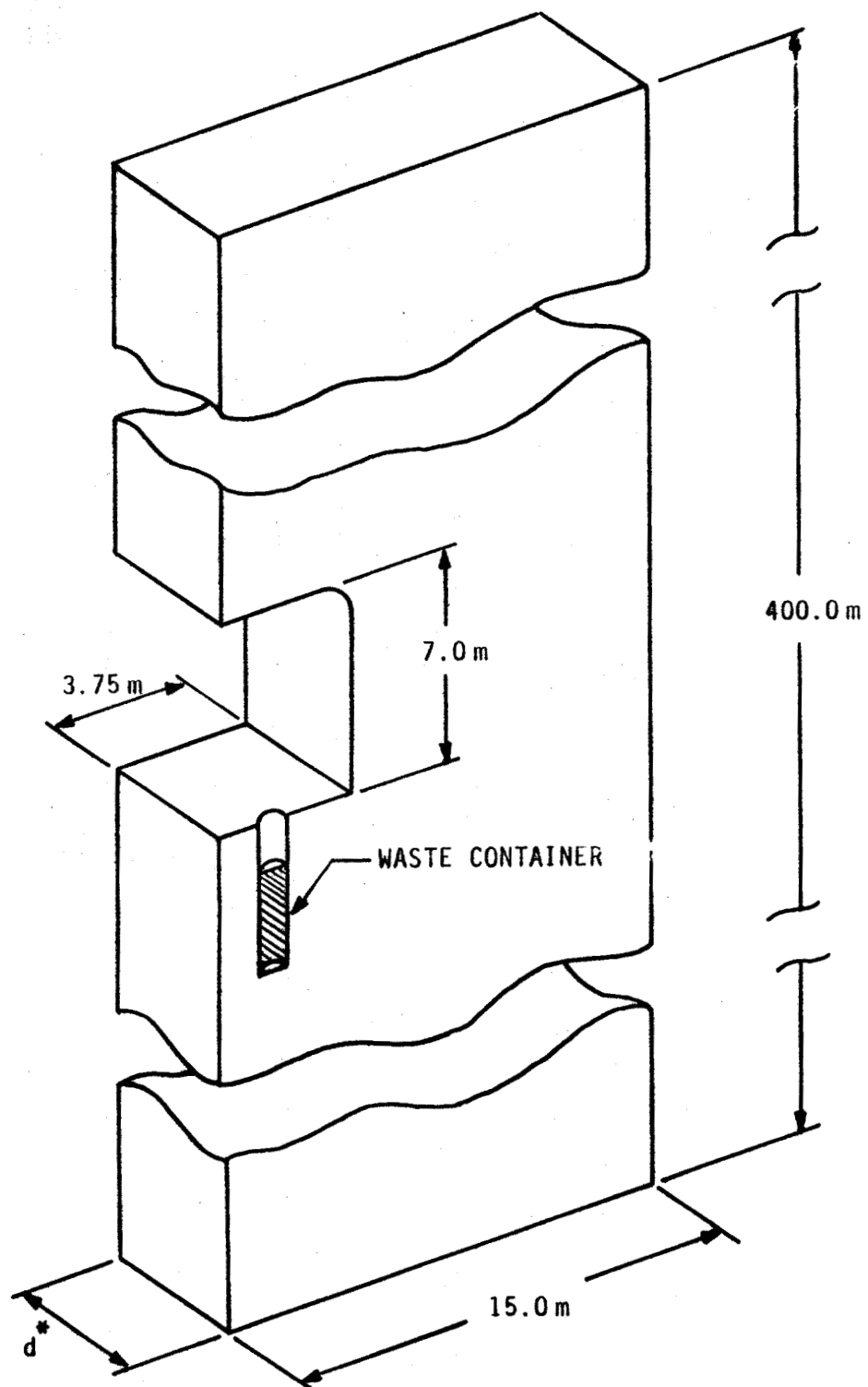


Figure 2.2. Geochemical variation of groundwaters with depth (UCRL-53154, 1981).



*d = f (WASTE TYPE AND THERMAL LOADING)

Figure 2.3. Thermal model -- adiabatic boundaries (BMI/OCRD-9, 1983).

Table 2.7. Description of disposal room and container drillhole
(BMI/OCRD-9, 1983).

Characteristics	CHLW	DHLW	SF
Room Description:			
Room width (m)	7.50	7.50	7.50
Room height (m)	7.00	7.00	7.00
Adjacent pillar thickness (m)	22.50	22.50	22.50
Container Emplacement Holes:			
Rows per room	2	2	2
Row separation (m)	2.50	2.50	2.50
Hole pitch (along row) (m)	2.67	1.86	1.83
Hole depth (m)	5.00	5.00	6.70
Hole diameter (m)	0.524	0.810	0.556
Containers per hole	1	1	1
Container length (m)	3.00	3.00	4.70
Container diameter (m)	0.324	0.610	0.356
Container power (W)*	1000	256	550
Areal thermal loading (W/m ²)	25	9.2	20
*At time of emplacement.			

Table 2.8. Material and strength properties (BMI/OCRD-9, 1983).

Property	Granite	Crushed Granite	Air	SF	CHLW	DHLW
Thermal conductivity (W/m-K)	2.52	0.266	75 ^a	1.21 ^b	1.21	1.35
Specific heat (J/kg-K)	809.3	809.3	314	837.4 ^b	837.4	1047
Coefficient of thermal expansion (°C ⁻¹)	7.8x10 ⁻⁶	8.0x10 ⁻⁷	---	---	---	---
Density (kg/m ³)	2650	1828	1.2	2995 ^b no density	2995	2800
Elastic modulus (GPa)	49.9	10	0.001	---	---	---
Poisson's ratio	0.21	0.40	0.40	---	---	---
Cohesion (MPa)	19	---	---	---	---	---
Angle of internal friction (Deg)	45	---	---	---	---	---

^aEquivalent conductivity to simulate radiative, convective and conductive heat transfer.

^bInternal details of the containers were ignored. The container was modeled as a heat generating solid which does not affect the accuracy of the temperature predicted on the container's surface and in the granite.

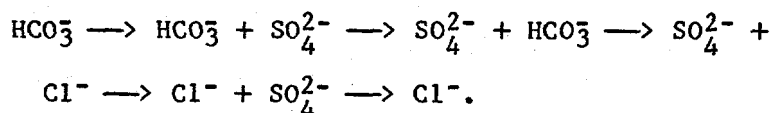
indicates that in the case of both the CHLW and SF, the drillhole is experiencing instability along its entire length. Evidence of tensile stresses along the drillhole were highest for CHLW. It should be noted that the magnitude of these tensile stresses will depend on the initial condition of the rock (i.e., prior to excavation) and that the presence of fissures and joints will result in lower stress levels required to induce failure (BMI/OCRD-9, 1983).

A laboratory investigation of the mechanical strength of Climax stock quartz monzonite, Nevada Test Site, was undertaken in order to determine the effects of radiation on the host rock (UCRL-87475, 1982). Gamma irradiation was conducted on samples obtained from a section of 22-inch diameter core. The samples were exposed to a total dose of 1.3×10^9 rads. The samples (25.4-mm diameter) were taken from the core for uniaxial compression and tensile testing. Tensile tests indicated no difference in strengths between the irradiated and control samples; a mean of $11.9 \text{ MPa} \pm 1.5 \text{ MPa}$ for the former (15 samples) and a mean of $11.4 \text{ MPa} \pm 1.8 \text{ MPa}$ for the latter (14 samples). Compression tests indicated that the effects of gamma irradiation may have contributed to the reduction of the ultimate strength of the rock. The 14 irradiated samples exhibited a mean strength of $163.7 \text{ MPa} \pm 35.2 \text{ MPa}$ while the control samples had a strength of $204.4 \text{ MPa} \pm 33.4 \text{ MPa}$. The samples were not subjected to any increase in temperature during the testing.

Conclusions based on the LLL work indicate that gamma irradiation has a degrading effect on the unconfined compressive strength of the rock and there is a possibility, based on SEM examination of the samples, that irradiated rock will tend to suffer microfracturing at lower stress levels.

2.4.5 Waste Package Considerations for a Granite Repository

Granite rocks typically exhibit low solubilities in water (commonly <300 mg/L total dissolved solids). These rocks contribute a relatively low silica content and alkali concentrations (typically <2 meq/L) with sodium dominance over potassium (Matthess, G., 1982). Shallow granitic groundwater is typically in the neutral pH range, and slightly oxidizing. Deeper groundwater is also in the neutral pH range and slightly reducing. In some localities, particularly in the lower zones of slow groundwater flow, high Cl^- concentrations may be encountered. Chebotarev (in Freeze, R., 1979) has determined that as these groundwaters flow from the upper zones of well leached rocks, where the dominant anion is HCO_3^- , to the lower zones of sluggish flow, over geologic times, the groundwater tends to evolve chemically toward the composition of seawater. The dominant anion species evolve as follows with each dominant constituent given first:



Deep granitic water may, therefore, be characterized by old and extremely slow moving saline brines.

In Sweden, an early waste package design is composed of a 10-cm thick lead vessel that is sheathed with 6 mm of titanium alloy. The maximum rock temperature expected is $\sim 50^{\circ}\text{C}$ (wastes are to be stored at surface facilities for 40 years prior to emplacement). A bentonite-sand mixture will be used as packing material. Spent fuel will be placed in copper containers and bentonite will serve as packing material for the SF design as well (Ahlstrom, P., 1979; UCRL-53154, 1981). At the present time a U.S. waste package design for use in a granite repository has not been formally proposed.

The monitoring of current Swedish KBS efforts are of interest to the Waste Package Program in providing important information on multicomponent waste package material testing in advance of a U.S. waste package design.

In a joint project between the University of Florida, Savannah River Laboratory (SRL), and KBS, attempts are under way to evaluate the corrosion behavior of waste glass that includes SRL defense waste glasses and Swedish glass compositions. Table 1 shows the waste glass compositions used in these ongoing evaluations (Hench, L., 1982; DP-MS-83-66, 1983).

Table 2.9 KBS-SRL waste glass compositions (weight percent).

Oxide	ABS 39	ABS 41	SRL-A	SRL-B	SRL-C
SiO ₂	48.5	52.0	40.6	47.7	37.6
B ₂ O ₃	19.1	15.9	10.3	7.0	9.6
Al ₂ O ₃	3.1	2.5	2.7	2.7	3.2
Na ₂ O	12.9	9.9	12.4	9.1	11.5
Fe ₂ O ₃	5.7	3.0	13.4	13.4	15.8
ZnO	0	3.0	0	0	0
Li ₂ O	0	3.0	4.0	4.9	3.7
Waste	9	9	29.8	29.8	35

The experimental conditions were as follows: Assemblies of glass samples (5-mm-thick slices taken from a 51-mm diameter x 80-mm long casting) were prepared by stacking them together with other materials that included metals and compacted bentonite. These assemblies were placed in boreholes located at the 350-m level of the Stripa mine. The glasses were analyzed prior to burial and after one- and three-month storage at 90°C (pH ~ 8.1).

Although, at present, only a limited amount of data are available surface analysis has shown that the most extensive surface degradation occurred on glasses interfaced with bentonite. Results are only available on the one-month samples.

An assessment of material requirements and container and waste form behavior will require extensive and detailed information on groundwater composition and rock mineral composition for the specific site under

consideration. As stated by Rydberg (UCRL-53155, 1981), the behavior of the container and waste form will be dependent on the maximum solubilities of the chemical elements in groundwater and on the kinetics of the dissolution process. Until such site-specific information becomes available, one can only estimate the behavior of waste package components based on assumed environmental conditions.

Chemical failure modes for TiCode-12, Type 304L stainless steel, and carbon steel in basalt have been summarized in prior BNL reports (NUREG/CR-2492, Vol. 3, 1983; NUREG/CR-2482, Vol. 5, 1983) and are also applicable to the type of repository conditions likely to be encountered in granitic formations.

2.4.6 Conclusions

Current DOE efforts in the area of crystalline repository development have focused on site-selection criteria, initial regional screening and, predominantly, thermomechanical investigations of granite formations (NTS). Investigations have also been conducted on the chemical characterization of NTS groundwaters. To date, there has been no formal presentation of a waste package design for use in a granite repository.

Granitic formations were shown to exhibit considerable variation in hydraulic conductivity, permeability and porosity as a result of variation in the fracture system. With respect to waste package performance, these parameters become important not only with respect to flow or water availability but also with respect to the age and chemical composition of the groundwater. As indicated by recent testing at NTS, Climax granite groundwater composition tends to vary with depth. This finding was confirmed by the Stripa investigations. This heterogeneity in chemical composition makes it difficult to estimate the maximum solubilities of the chemical elements in groundwater and the kinetics of the dissolution process. The age of the groundwater and the fracture system of the granite for the particular locality under investigation will also determine the dominant ion species present and whether the metallic components of the waste package are likely to encounter a high Cl^- environment. The presence of thermal and radiation fields, as a consequence of waste emplacement, may act to weaken the ultimate strength of the rock and alter the fracture/flow system.

2.4.7 References

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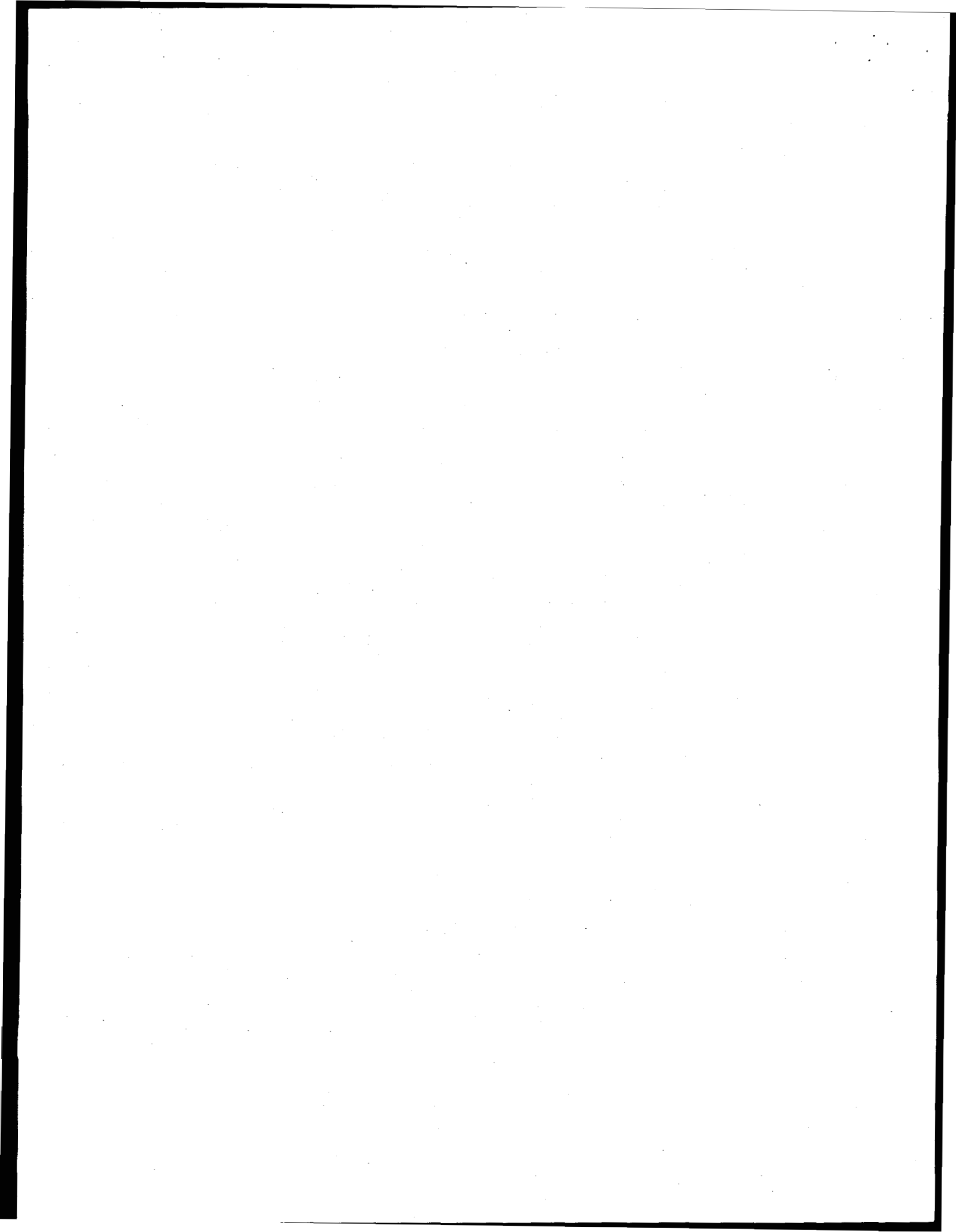
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3. WASTE FORM FAILURE AND DEGRADATION MODES

Prior BNL Biannual Reports have summarized borosilicate glass failure/degradation modes for basaltic and salt repository conditions (NUREG/CR-2482, Vol. 1, 1982; NUREG/CR-2482, Vol. 4, 1983). Comparatively little work has been performed on the behavior of glass under anticipated tuff and granitic repository conditions. Such studies will be reviewed, however, when data become available.

4. CONTAINER SYSTEM FAILURE AND DEGRADATION MODES

Prior BNL Biannual Reports have addressed container failure/degradation modes for basaltic and salt repository conditions. Materials evaluated include carbon steel, stainless steel and titanium-based alloys (NUREG/CR-2482, Vol. 2, 1983; NUREG/CR-2482, Vol. 3, 1983; NUREG/CR-2482, Vol. 4, 1983; NUREG/CR-2482, Vol. 5, 1984).

5. PACKING MATERIAL FAILURE AND DEGRADATION MODES

5.1 Basalt-, Zeolite- and Bentonite-Containing Packing Materials

Earlier BNL Biannual Reports have addressed the subject materials mainly with respect to the basalt repository program (NUREG/CR-2482, Vol. 3, 1983; NUREG/CR-2482, Vol. 4, 1983).

5.2 Crushed Tuff Packing Materials

This part of the program has been completed and is reported in a prior BNL Biannual Report (NUREG/CR-2482, Vol. 5, 1984).

5.3 Crushed Salt Packing Material (E. Veakis)

Current conceptual designs for a waste package in a salt repository do not specifically include the use of a tailored packing material component (ONWI-438, 1983). Justifications cited for the omission of tailored packing material in the Westinghouse designs are (1) that the candidate waste containers can be shown to meet the containment requirements and (2) given the expected limited amounts of brine present, tailored packing material will not be required to control fluid flow. The use of packing material was only taken into consideration in the Westinghouse report as a means for long-term waste isolation in the event the container was shown not to meet the containment requirements.

Previous efforts reported in an earlier Biannual Report addressed the status of data presently available on bentonite and zeolite packing materials under conditions expected in a salt and basalt repository (NUREG/CR-2482, Vol. 4, 1983). These efforts will not be comprehensively repeated here; rather the main emphasis will be on data pertinent to an assessment of crushed salt as packing material. Alternate packing materials that have been reported in the literature for a salt waste package will only be briefly discussed.

The principal near-field conditions anticipated in a salt repository have been addressed at length in an earlier Biannual Report (NUREG/CR-2482, Vol. 2, 1983), and will not be repeated here. Maximum temperature expected, based on thermal loading per unit area are, however, presented in Table 5.1 for purposes of continuity and clarity. It should be noted that the report of Claiborne, Rickertsen and Graham (ORNL/TM-7201) is used by the Reference Repository Conditions-Interface Working Group (RRC-IWG) as the basic reference on expected repository conditions (ONWI-483, 1983). Although the reference repository configuration does not address thermal loadings higher than 25 W/m^2 , the 37 W/m^2 loading was specified in the Westinghouse design (ONWI-438, 1983) and is included for comparative purposes to illustrate the effects of higher thermal loads. The maximum salt temperature and temperature gradient are given in Figure 5.1 for the 25 W/m^2 areal loading.

5.3.1 Brine Migration Effects

It is well established that water in rock salt may be present as water of hydration in minerals, as intergranular water, and as fluid inclusions. The behavior of such water must, therefore, be assessed with respect to the behavior of crushed salt packing material, as well as other waste package components. Currently, a joint effort by the U.S.A. and the Federal Republic of Germany (FRG) is underway to measure brine migration rates at the Asse salt mine in Germany (ONWI-242, 1983). The two types of brine migration under consideration in this study include liquid inclusion migration through salt crystals and along grain boundaries and, also, vapor migration along pressure gradients. Since laboratory and field tests have shown that water present in rock salt will migrate up a thermal gradient to the waste package, it is important to assess the rate of brine accumulation as a function of temperature, thermal and pressure gradients, and salt characteristics.

Jockwer (1981) conducted tests on 202 salt samples from the Asse salt mine in order to determine the water content of the salt and any variations with depth and at different stratigraphic levels. His findings confirmed that water content is dependent on the amount of minor minerals present containing water of hydration and that water content varied by a factor of 10 within a distance of 1 m in various stratigraphic layers. The liberation of water from the hydrated minerals was also found to be dependent on humidity. This relationship is shown in Figure 5.2 for carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$). The "release velocity," given as

$$g = \frac{G}{t \cdot E}$$

where G is weight loss resulting from the liberation of hydration water, t is time, and E is total sample weight, is shown for polyhalite and kieserite in Figures 5.3 and 5.4 on a log scale as a function of the reciprocal absolute temperature at varying humidity levels. The data are shown schematically so that estimates of reproducibility cannot be made.

Table 5.1 Maximum temperatures in the salt rock formation, container surface, and waste centerline.^a

	Salt			Container Surface			Waste Centerline (or Center Pin)		
	Maximum Temperature ^b		Years After Emplacement	Maximum Temperature		Years After Emplacement	Maximum Temperature		Years After Emplacement
	°F	°C		°F	°C		°F	°C	
HLW, 150 kW/acre (37.1 W/m ²)	412	211	15	587	308	10	670	354	3
HLW, 100 kW/acre (24.7 W/m ²)	312	156	15	508	264	3	603	317	1.5
HLW, 50 kW/acre (12.4 W/m ²)	228	109	5	459	237	0.67	580	304	0.5
SF, 60 kW/acre (14.8 W/m ²)	211	99	50	237	113	25	280	138	~5
SF, 40 kW/acre (9.88 W/m ²)	171	77	50	202	94	15	270	132	~3

^aAssumes that waste is 10 years old on emplacement. The HLW decay rates were based on fuel that is a 3:1 mix of fresh UO₂ and MOX fuels. The HLW container thermal loading was 2.16 kW, and the SF was 0.55 kW (one PWR fuel element) Adapted from ORNL/TM-7201, 1980.

^bThe difference between salt (host rock) temperature and container temperature is due to the presence of an air gap; an annulus between the container and the overpack.

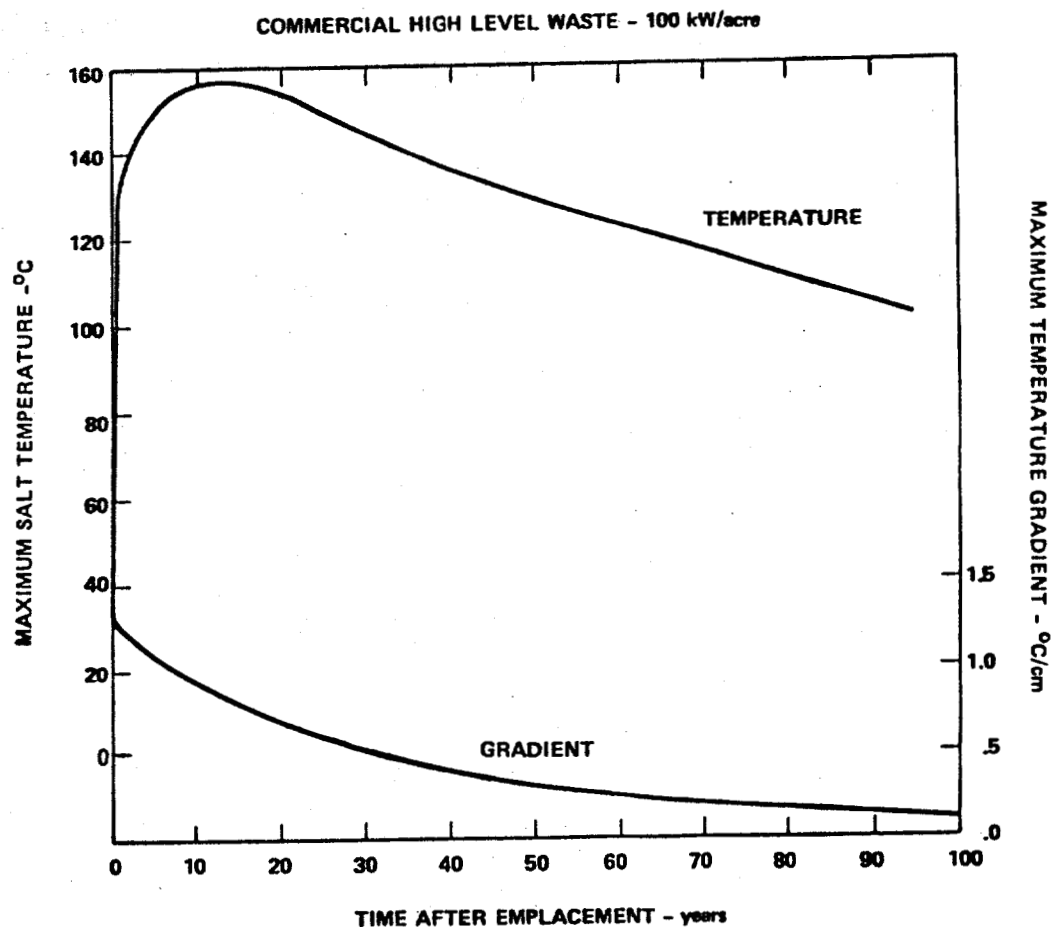


Figure 5.1. Temperature/temperature gradient for HLW (ONWI-242, 1983).

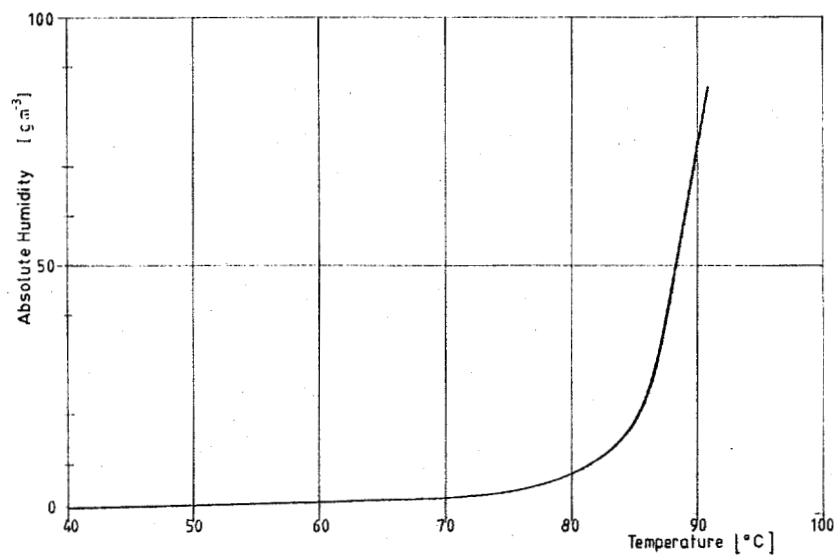


Figure 5.2. Temperature at which the liberation of the hydration water of carnallite begins versus the absolute humidity (Jockwer, N., 1981).

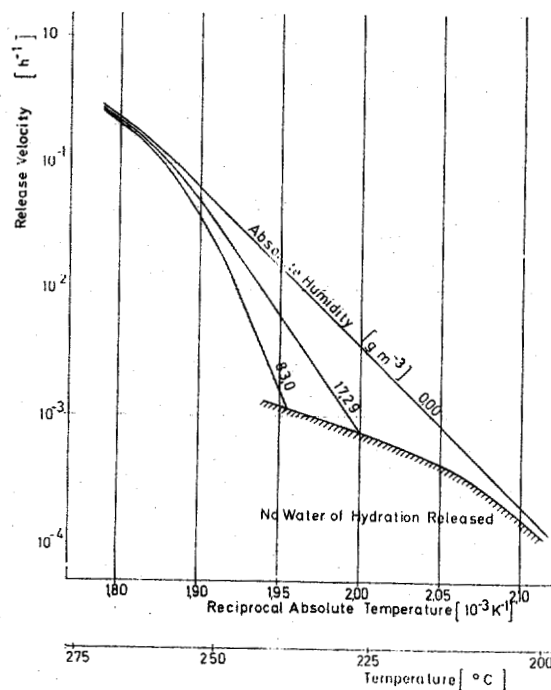


Figure 5.3. Release velocity of the hydration water from polyhalite at absolute humidities between 0 and 83.0 g/m³ versus the reciprocal absolute temperature (Jockwer, N., 1981).

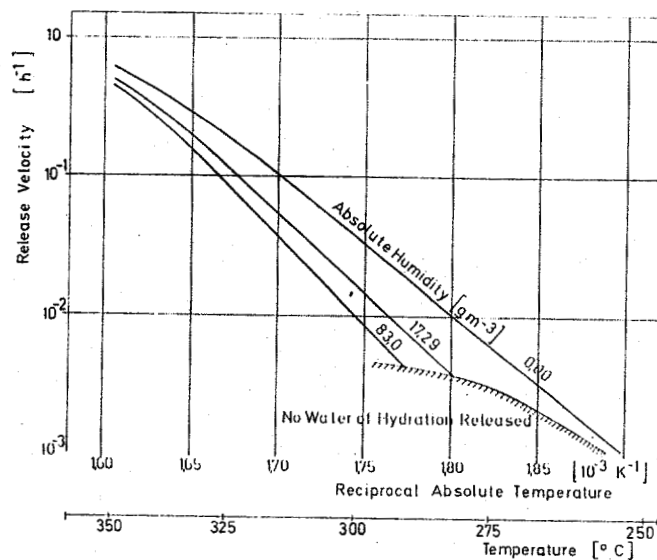


Figure 5.4. Release velocity of the hydration water from kieserite at absolute humidities between 0 and 83.0 g/m³ versus the reciprocal absolute temperature (Jockwer, N., 1981).

Jenks and Claiborne's (ORNL-5818, 1981) estimates of brine accumulation are approximately 25 liters for CHLW, 8 liters for spent fuel and 1 liter for DHLW in bedded salt (over a 100-year time period). In domal salt with 0.03 weight percent inclusions, the estimated brine accumulation for CHLW is ~2.5 liters with correspondingly lesser amounts for spent fuel and DHLW. The uncertainty in these estimates is based to a large extent on the effective permeability of the rock salt adjacent to the emplacement hole.

Brine migration experiments conducted at the Avery Island salt mine included measurement of temperature, moisture collection, and pre- and post-test permeability [ONWI-190(4), 1983]. Electrical heaters emplaced on the floor of the mine, at a depth of 169 m, were used to heat the salt over a period of ~325 days at which point heating was gradually reduced (20% per day over five days). The maximum temperature at the midheight of the heater borehole wall was ~51°C. During power reduction, moisture was collected from the borehole to determine moisture inflow at two localities. Moisture collection over the 325 days was in the range of 5-8 g; however, one site experienced a moisture surge during power reduction and the moisture inflow rate increased to ~2.8 g per day. During power reduction the magnitude of measured salt permeability increased by approximately four orders of magnitude. Table 5.2 presents a summary of results. Follow-up experiments and a more reliable moisture collection system were recommended in future efforts.

In order to avoid excessive brine accumulation at the emplacement hole, Jenks and Claiborne (ORNL-5818, 1981) offered the following recommendations:

1. Locate the emplacement holes within the salt formation where there is a minimum amount of brine that could conceivably migrate from the salt into the emplacement hole.
2. Employ designs and practices such that the walls of the emplacement hole are maintained under compressive stresses. In order to accomplish this it may be necessary to employ container dimensions and packing material that will minimize post-closure movement of the salt walls.
3. Avoid impurities in the rock salt that could yield water upon thermal or radiolytic decomposition and thus contribute to the amount of water that might migrate into the emplacement hole. Design the emplacement procedure so that the maximum temperature of the salt walls does not exceed about 250°C in order to avoid possible decrepitation of salt, and the release of trapped water.
4. Design so that the maximum pressure within the emplacement hole remains less than the compressive stresses on the salt walls, to reduce the development of microcracks within the salt.
5. Consider the use of a desiccant-barrier material as part of a back-fill, with the objective of absorbing water, shielding the metallic components from brine and corrosive vapors, and possibly sorbing

Table 5.2. Site SB -- heater borehole accumulated total moisture gain compared to approximate permeability and pressure decay rate during heater power reduction [ONWI-190(4), 1983].

Date	Percent Full Heater Power ^a	Measurement in Brine Borehole	Heater Borehole Accumulated Total Moisture (g)	Approximate Permeability (m ²)	Pressure Decay Rate (kPa/h)
7/27/79 ^b	--	B4	-----	2 x 10 ⁻²¹	<0.690
		B8		3 x 10 ⁻²¹	<0.690
		B2		Not Tested	Not Tested
8/25/80	80	B2		2 x 10 ⁻²¹	<0.690
		B4	17.51 ^c	2 x 10 ⁻²¹	<0.690
		B8		2 x 10 ⁻²¹	<0.690
8/26/80	60	B2		7 x 10 ⁻²¹	<0.690
		B4	18.02	9 x 10 ⁻²¹	1.380
		B8		2 x 10 ⁻²¹	<0.690
8/27/80	40	B2		6 x 10 ⁻¹⁹	21.0
		B4	18.80	1 x 10 ⁻²⁰	8.3
		B8		6 x 10 ⁻²⁰	4.1
8/28/80	20	B2		9 x 10 ⁻¹⁹	34.0
		B4	19.85	9 x 10 ⁻¹⁹	32.0
		B8		6 x 10 ⁻¹⁹	24.0
8/29/80	00	B2		4 x 10 ⁻¹⁸	131.0
		B4	23.23	2 x 10 ⁻¹⁸	94.0
		B8		7 x 10 ⁻¹⁹	52.0
9/2/80	00	B2		5 x 10 ⁻¹⁷	1080.0
		B4	33.78	4 x 10 ⁻¹⁷	1186.0
		B8		4 x 10 ⁻¹⁷	896.0
9/3/80	00	B2		2 x 10 ⁻¹⁶	919.0
		B4	34.65 ^d	7 x 10 ⁻¹⁷	758.0
		B8		9 x 10 ⁻¹⁷	805.0
9/10/80	00	B2		2 x 10 ⁻¹⁷	514.0
		B4	-----	3 x 10 ⁻¹⁷	655.0
		B8		3 x 10 ⁻¹⁷	557.0

^aPower level: 3 KW; heat flux: 888.6 W/m²; canister and heater dimensions: 406-mm diameter, 2.4-m length.

^bPre-test conditions.

^cTotal amount of moisture previously collected from the heater borehole at the initiation of power reduction.

^dFinal amount of total moisture collected prior to decommissioning of Site SB on 9/4/80.

radionuclides. Dessicants such as CaO or MgO in combination with sand or crushed salt are estimated to absorb more than the predicted accumulation of brine.

5.3.2 Temperature and Radiation Effects

In bedded salt, data available indicate that brines are rich in MgCl_2 ($\sim 2.4 \text{ M}$), saturated in CaSO_4 ($\sim 0.03 \text{ M}$) and NaCl ($< 2.0 \text{ M}$), and contain appreciable amounts of Br^- ($\sim 0.05 \text{ M}$). The MgCl_2 present in bedded salt brines would result in a more corrosive environment than domal salt brines which contain a much lower concentration of solutes other than NaCl (ORNL-5818, 1981).

Recent work at BNL shows that preannealing Carlsbad, New Mexico, rock salt has a strong influence on the pH and total base of solutions made by dissolving 3 gms of salt in 25 mL of deionized water. The data shown in Figure 5.5 are for salt preheated for 24 h at temperatures in the range of 30 to 167°C. Total base increased from $\sim 0.13 \text{ } \mu\text{eq/g}$ for unannealed rock salt solutions to $1.5 \text{ } \mu\text{eq/g}$ for solutions from rock salt annealed at 125°C. The pH ranged from 6.4 (unannealed) to 9.5 (annealed at 125°C). These effects are dependent on site-specific chemical composition (impurities) of the rock salt and may differ from locality to locality. The increased alkalinity is probably associated with the thermal decomposition of bicarbonates to carbonates, as well as the release of acidic gases prior to dissolution of the salt. Table 5.3 gives supporting data obtained from analyses of gases released from heated unirradiated salt and also samples of salt that were heated during gamma irradiation in dry and wet conditions. For unirradiated salt, significant quantities of CO_2 and SO_2 were released during the initial 30-minute heating period at 180°C, together with H_2 , O_2 and water vapor. In the following 15-minute heating period, similar quantities of these gases were released. During the irradiation of "dry" salt, much larger quantities of H_2 and CO_2 are released. For salt irradiated in the presence of saturated brine even more hydrogen is released but the CO_2 appears to have dissolved in the brine to a major extent. The BNL study shows that this brine becomes acidic during irradiation (pH ~ 3.7) and seems to be associated with the dissolution of acidic gases released during heating and irradiation.

Other studies on gas released from heated Asse mine salt were carried out in a German program (Uerpmann, P., 1982, Jockwer, N., 1982, 1983). They detected H_2S , HCl , CO_2 , SO_2 , CH_4 , H_2 and O_2 . The gas components varied depending on salt mineralogy. They believe that the HCl is generated by thermal decomposition of trace minerals. Figure 5.6 shows some of the data obtained for salt which was gamma irradiated up to $5 \times 10^7 \text{ rad}$ at $\sim 60^\circ\text{C}$ for $\sim 60 \text{ h}$. Gas release rates were measured as the irradiated salt was slowly heated in a vacuum. They show that gas generation is at a maximum at 230 and 330°C for unirradiated salt. The maxima for irradiated material are shifted to higher temperatures. Irradiation is also found to increase the yields of H_2S , HCl , CO_2 and CH_4 .

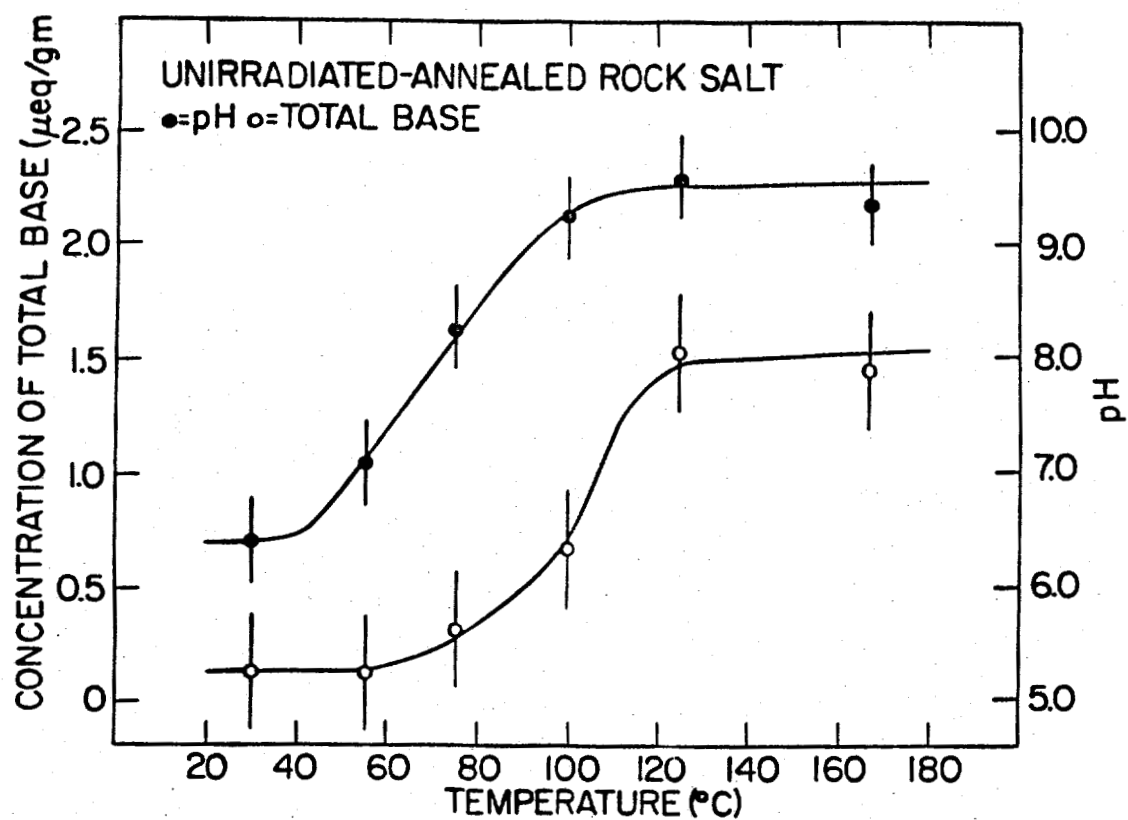


Figure 5.5. Plot of pH and total base of brine versus temperature of annealing of parent rock salt showing the temperature sensitivity of the rock salt used in this study.

Table 5.3 Experimental results of gas analyses of samples irradiated wet and dry at a dose rate of 8×10^6 rad/h at a temperature of $125^\circ \pm 5^\circ\text{C}^a$ (NUREG/CR-3091, Vol. 3, 1984).

Sample Number	Radiation Dose (rad)	<u>Volume Percent of Gas</u>				
		H ₂	O ₂	CO ₂	SO ₂	H ₂ O
<u>No Irradiation, Heated at 180°C</u>						
30 minutes after heating		0.38	3.1	2.9	0.02	77
45 minutes after heating		0.59	2.5	3.7	0.02	79
<u>Dry Irradiations^b</u>						
RS4D	7.2 x 10 ⁸	72	--- ^d	22.2	BDL	5.6
RS8D	1.3 x 10 ⁹	64	BDL	9.0	3.6	23.2
RS5D	2.6 x 10 ⁹	65	BDL	29.4	BDL	5.9
<u>Wet Irradiations^c</u>						
RS29T	7.1 x 10 ⁸	94	2.78	3.3	ND	ND
RS14T	4.8 x 10 ⁹	99	0.43	0.12	BDL	ND

^aData normalized to Ar (assuming all Ar present is due to atmospheric contamination) in order to quantify any N₂/O₂ contamination from air ingress. Data expressed in mole percent. Accuracy of analyses is $\pm 10\%$.
BDL = Below Detection Limits.

ND = Not Determined.

^bSystem backfilled with 10 psig N₂. Gas generated = 0.33% of total in capsule.

^cSystem backfilled with 5 psig He. Gas Generated = 63% of total in capsule.

^dContamination, possibly by sealing torch, consists of a large quantity of O₂ has been eliminated from these data. This sample may yield data that are representative of different experimental conditions.

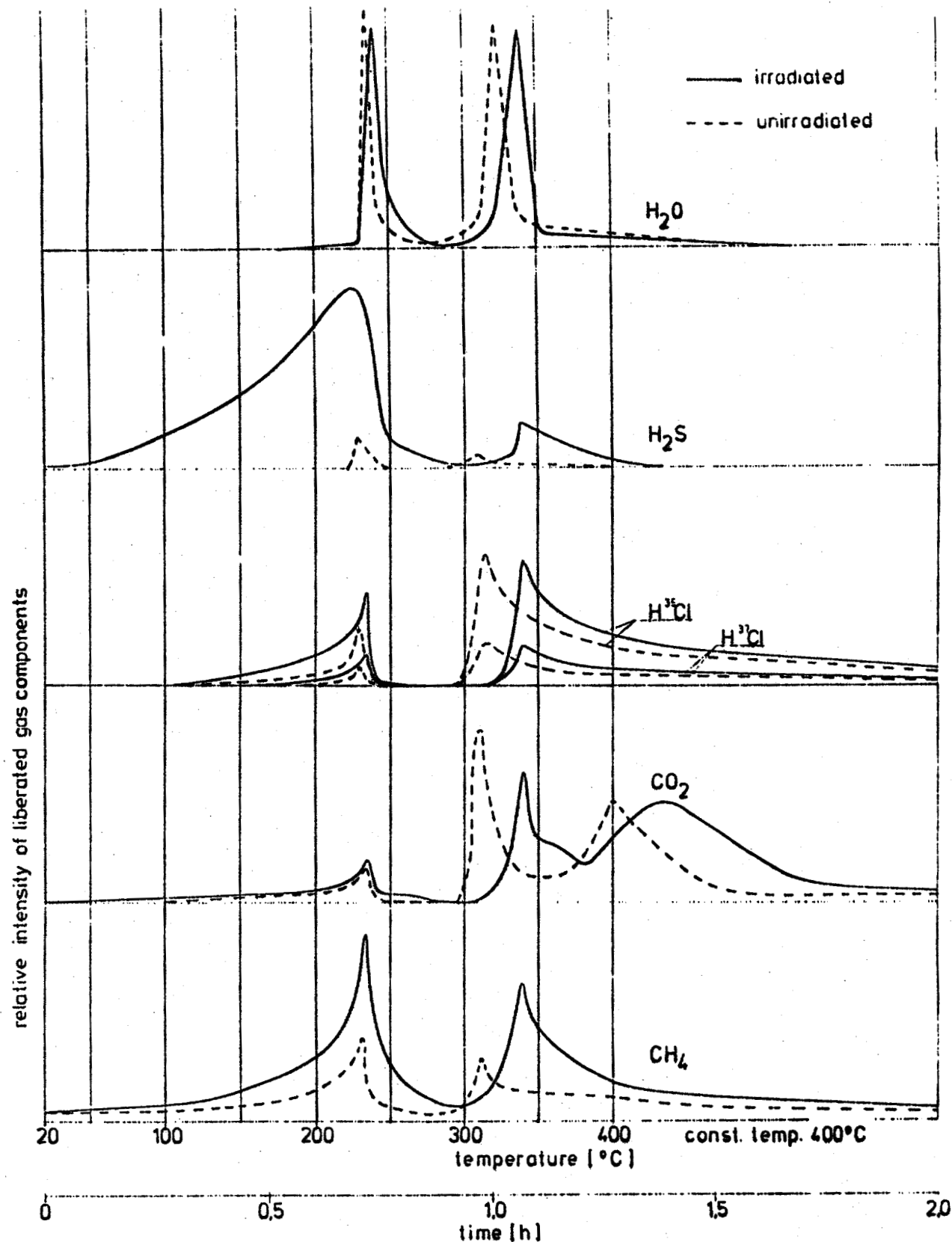


Figure 5.6. Liberation of the gas components H₂O, H₂S, HCl, CO₂ and CH₄ versus the temperature of an irradiated and unirradiated sample. Mineralogical composition: 95 weight percent halite, 5 weight percent anhydrite, polyhalite and kieserite. (Jockwer, N, 1983).

The above-mentioned BNL study also evaluated the alkalinity of brines made by dissolving gamma irradiated salt in deionized water. Colloidal sodium produced during irradiation interacted with the water to yield NaOH and H₂, causing the pH to rise to a stable value of about 9.5. This finding has important implications with respect to waste package performance since brine migrating through irradiated salt would tend to become increasingly alkaline. Earlier work in the current program has addressed the effects of pH and H₂ absorption on the corrosion of a range of candidate high level waste container and waste form materials (NUREG/CR-2482, Vol. 3, 1983, and NUREG/CR-2482, Vol. 5, 1984).

Apart from compositional and pH effects caused by the dissolution of heated and heated/irradiated salt, it is important to understand how brine itself is affected by irradiation and how this may influence waste package integrity. Preliminary PNL experiments, involving gamma irradiation of Permian Basin brine, showed radiolytic gas formation which may result in pressurization [ONWI-9(83-1), 1981]. The gases formed consisted of ~70% hydrogen with the remainder primarily oxygen. Gas generation in Permian Basin brine was greater than that expected for saturated NaCl solutions and was attributed to the presence of Br⁻ or other trace impurities which tend to hinder recombination of radiolytic products (PNL-SA-10928, 1983).

Studies on the irradiation of WIPP Brine A showed that the pH of acidic brine will increase, as shown in Table 5.4 (BNL-NUREG-33012, 1983). Based on the above discussion it seems likely that brine initially reaching a waste container will be acidic because of interactions with gases, such as HCl. As increasing quantities of colloidal sodium are formed in the rock salt from gamma irradiation, brine which later reaches the container will be alkaline. An alkaline brine environment is potentially beneficial to the localized aqueous corrosion of Grade-12 titanium containers, since the potential for pitting and crevice attack is decreased (BNL-NUREG-33012, 1983). However, hydrogen generated by brine radiolysis, and from colloidal sodium interactions with brine, may present a significant problem in terms of hydrogen-assisted failure in this alloy.

In the case of low-carbon steel exposed to anoxic (~0.5 ppm dissolved O₂) simulated Permian Basin brine at 150°C (one-month test duration; refreshed autoclave system) conducted at PNL, corrosion rates ranged from 0.48 to 0.74 mils/yr [ONWI-9 (83-1), 1982]. A tenfold increase in corrosion rates was reported when the steel was exposed to a 1×10^5 rad/h gamma field under identical experimental conditions. The major corrosion product was magnetite (Fe₃O₄). PNL reported the formation of an anhydrite phase (CaSO₄), in addition to magnetite in the irradiated samples.

5.3.3 Salt Consolidation Effects

The consolidation of a crushed salt packing during service must be estimated since it will affect thermal properties, brine migration rates and radionuclide release. Such investigations were undertaken by Sandia National Laboratories on salt fragments measuring up to about one centimeter in size

Table 5.4. Results of radiolysis of Brine A at room temperature.
Total dose $\sim 1.0 \times 10^9$ rads at 2.4×10^6 rad/h.

	Run 11	Run 12	Run 13
Starting pH	1.0	7.4	0.3
Final pH	5.8	7.1	5.3
Final pressure (MPa)	0.9	1.2	0.7
Gas composition (mol/percent)			
H ₂	64.0	62.7	78.0
O ₂	27.4	29.4	19.1
N ₂	7.6	6.3	1.6
CO ₂	0.8	0.1	0.2
H ₂ /O ₂	2.3	2.1	4.1
Overall G	0.42	0.52	0.35
G(H ₂)	0.32	0.38	0.32

(SAND-82-0630, 1982). They included quasistatic tests at temperatures ranging from 21°C to 100°C, at pressures up to 21 MPa. A series of twelve creep tests was also conducted over the same temperature range at pressures ranging from 1.72 MPa to 10.1 MPa.

Results from 5 quasistatic tests conducted at a compaction pressure of about 21 MPa showed that the average density of the compacted salt increased by approximately 30 percent over the temperature range 20-100°C. At the higher test temperatures the density was about 5 percent greater. Creep effects on compaction were small since the test time was limited to 2.2 hours.

Compaction of dry salt was also detected in compressive creep tests lasting 55.6 hours. The maximum density achieved was 80 percent of that for intact salt, i.e. the void space between salt fragments was 20 percent.

In earlier experiments, data obtained indicated that the primary factors affecting the rate of consolidation of salt in the presence of brine were applied stress and particle size. It was concluded that when crushed salt in brine is subjected to a constant stress, consolidation occurs in an approximately linear fashion with the logarithm of time (ORNL-5774, 1981). It should be noted, however, that some experiments show that rock salt being gamma irradiated in the presence of brine at 125°C will consolidate in the absence of an applied stress (NUREG/CR-3091, Vol. 3, 1983).

Studies on the migration of brine within stressed salt specimens suggests that the flow of brine is influenced by consolidation (ORNL-5950, 1983) since the expulsion of brine during consolidation was found to match the decrease in specimen volume. These results using 250- to 420- μ m salt crystals in a column 9.54 cm in diameter are shown in Table 5.5 and plotted in Figure 5.7. Conclusions drawn from the study show that under stress, salt consolidated readily in the presence of brine and that consolidation proceeds more rapidly with increasing temperature (to 85°C). Reasonably complete consolidation occurs if brine is allowed to escape from the compressed salt. In a repository, however, such a situation may not exist, and brine may remain trapped between salt particles or it may form discrete volumes of water close to the container.

Table 5.5. Salt consolidation test results (ORNL-5950, 1983).

Run	Applied Stress (bar)	Temperature (°C)		Elapsed Time ^a (min)	Void Fraction	Brine Expelled (g)	
		Ram End	Anvil End			Ram End	Anvil End
Run 201 - NaCl crystals: ^b 1540 g in 9.537-cm-diam column							
				0	0.251		
	155	20	20	9685[1]	0.071	[0]	[0]
	155	50	50	12565[2]	0.065		
	155	80	80	14505	0.041		
	310	84	85	15705	0.015		
	155	76	95	28507	0.013	0.548	18.325
Run 202 - NaCl crystal: ^b 1556 g in 9.537-cm-diam column							
				85	0.159		
	155	20	20	3940[1]	0.104		
	155	50	50	13690	0.0367	[0]	[0]
	155	50	50	17810[2]	0.0315	0.256	4.080
	155	57	48	18140	0.0278	22.618	6.624
	155	85	67	35225	0.0024	4.961	18.295
		85	67	48903		15.190	20.625

^aNumbers in brackets refer to points in Figure 5.7.

^bInitial particle size, 250-420 μ m.

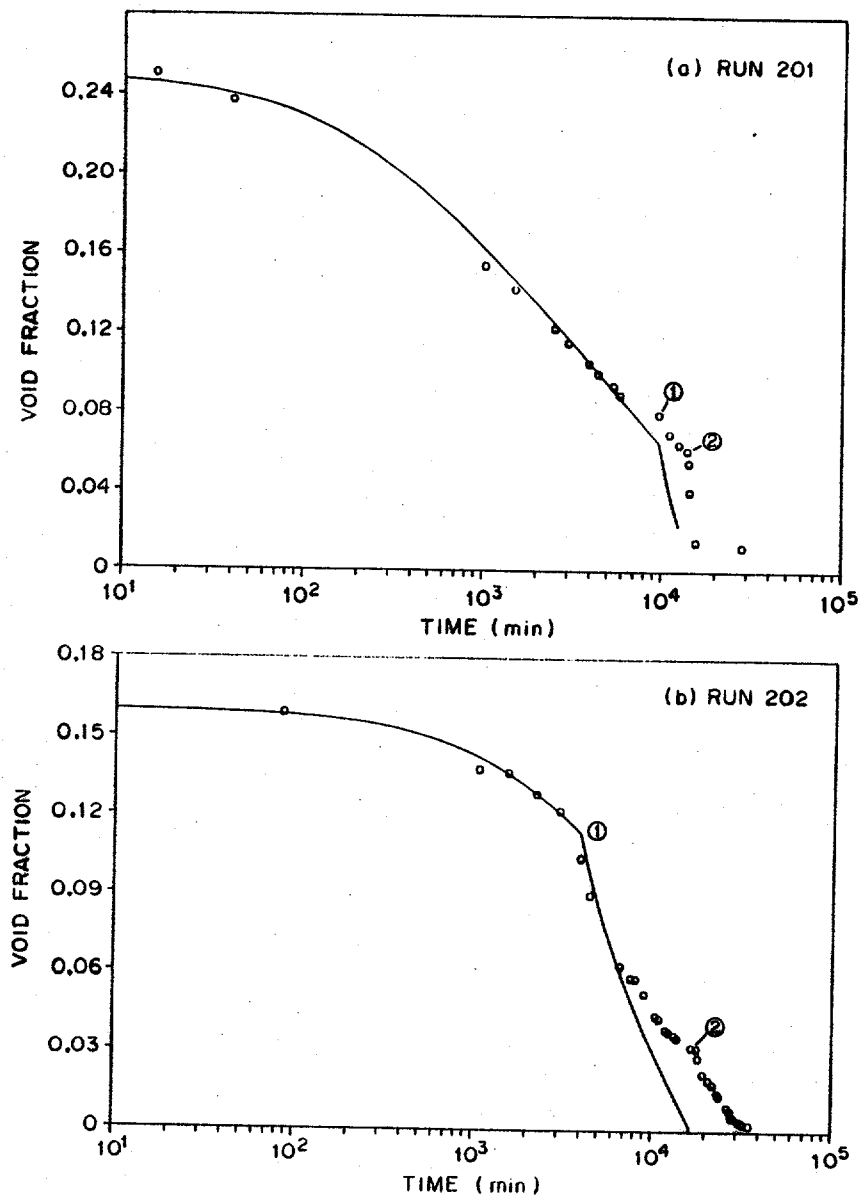


Figure 5.7. Consolidation of salt crystals (250-420 μm) in brine (numbered points indicate a change in conditions)(ORNL-5950, 1983).

5.3.4 Alternate Packing Materials for Salt Repositories

Westinghouse, in its conceptual waste package design study, considered the potential use of non-salt packing materials (ONWI-438, 1983). These include combinations of bentonite clays, zeolites and quartz sand. However, a major concern with respect to bentonites and zeolites, which are hydrous aluminosilicates, is their stability under hydrothermal condition. They have been shown to suffer from early diagenesis which represents an important degradation mode (NUREG/CR-2482, Vol. 4, 1983).

Work by Weaver (ONWI-21, 1979) and Aoyagi and Kazama (1980), on the diagenesis of clay minerals shows that the following transformation takes place: bentonite transforms first to a mixed layer illite-smectite mineral (I/S) and then to illite, by removal of interlayer water and replacement of Ca^{2+} or Na^{+} by K^{+} , i.e.,

Bentonite \longrightarrow I/S \longrightarrow illite

Weaver claimed that montmorillonites (including bentonite) can be converted to illite eventually at temperatures between 90 and 160°C. Based on observed diagenetic alteration of clays in Gulf Coast sediments he reported that some alteration of montmorillonite to chlorites and illites occurred at temperatures as low as 40°C. This process under natural conditions in shales takes place with an increase in the Al content (perhaps by loss of Si) followed by the release of interlayer water to the pores, clay layer contraction, and the fixation of K (from K-feldspar) between the contracted layers. Calculations indicated that at 120°C, 80% of the smectite layers could be converted to illite in 5000 years (Howard, J. D., 1981). While these calculations indicate some potential for stability over extended periods of time, laboratory experiments at 250°C indicated that the same amount of contraction was obtained in 167 days (Howard, J. D., 1981). Illite has less exchange capacity and is somewhat more permeable than bentonite, but is relatively resistant to further change with temperature over the range 200-300°C. When Mg or Fe is readily available, chlorite may also be formed as a by-product when montmorillonite is converted to illite and this conversion can begin at temperatures as low as 70°C. Since these alteration products of bentonite are 5-10% more dense than bentonite, and have little swelling capacity, packing material cracking due to hydrothermal alteration is likely to lead to increased permeability of the packing material.

Concerns have also been expressed with respect to the use of bentonite packing given that their use will contribute more water than would otherwise be available from brine in-flow in a salt repository (ORNL-5818, 1981). Claiborne estimated that a 30.5 cm diameter container surrounded by a 30.5 cm thick packing of 20% bentonite-80% sand mixture and 10% water (approximate minimum amount required to produce a sufficiently plastic bentonite), will contain approximately 66 liters of water. If pure bentonite was used the water content would be ~330 liters (ORNL/TM-8372, 1982). The predictive techniques used by Jenks and Claiborne (ORNL-5818, 1981) appear to be

adequate for short-term estimates of brine migration (in-flow). Long-term in-situ experiments are required, however, in order to assess whether the transport mechanisms contributing to short-term brine release are adequately defined and applicable to long-term predictive modeling efforts.

The hydrothermal stability or early diagenetic processes for zeolites has been explored by researchers over the last ten years and, in the past two years, new research has been performed both with respect to natural geological analogs and to laboratory experiments (NUREG/CR-2482, Vol. 4, 1983). As Wheelwright (PNL-3873, 1981) stated, there is still not much information available on the hydrothermal stability of zeolites under conditions expected in basalt and salt repositories. According to Aoyagi (1980), the transformation of zeolites during diagenesis is faster than for clay minerals. The most important physical factor for the transformation of zeolites is temperature. The chemical composition of the pore water may also be relevant. The crystallochemical transformation of zeolites will be indicated by replacement of cations (K^+ , Na^+ , and Ca^{2+}), as well as SiO_2 and H_2O in the lattice structure; therefore, the activity of silica will also be relevant. Both geological analogs and short term laboratory studies have indicated that mordenite is the most hydrothermally stable zeolite with clinoptilolite the next most stable (NUREG/CR-2482, Vol. 4, 1983). Therefore, these two minerals have been most extensively considered for use as packing material components in high level radioactive waste repositories.

Recent research by Smyth (1982) on natural geological analogs of zeolite-containing tuffs and basalts indicates that even clinoptilolite and mordenite are unstable at elevated temperatures and low water vapor pressures breaking down either by reversible dehydration or irreversible mineralogical transformations with net volume reduction and evolution of fluids. These mineralogical changes would lead to mechanical failure by shrinkage fractures and perhaps would provide a driving force (fluid pressure) for the release of radionuclides to the biosphere. Smyth (1982) recommends the use of zeolite-containing rocks (and his arguments would also apply to use of zeolites as packing materials) only in radioactive waste repositories which can be kept below $\sim 85^\circ C$ and in water-saturated conditions.

Other packing materials have been specified to include desiccants, such as CaO and MgO combined with sand or crushed salt to maintain an anhydrous environment around a waste container (ONWI-214, 1980; ONWI-449, 1983).

Jenks and Claiborne (ORNL-5818, 1981) estimated that a CaO -sand or MgO -sand packing material mix with properties such as shown in Table 5.6 can react with and absorb 43 kg and 63 kg of water, respectively, under reference repository conditions that include a 5-cm-thick packing (see Table 5.7).

The desiccant-backfill materials used must exhibit adequate stability and appropriate thermal conductivity so as not to contribute to an adverse environment. Dicalcium silicate has been studied, to establish the hydration properties of this material, at $20^\circ C$ and one atmosphere (ONWI-449, 1983). Test procedures at this stage of screening are clearly not representative of

Table 5.6. Chemical and physical properties of oxides and hydroxides of Ca and Mg relevant to packing for reference repositories (ORNL-5818, 1981).

Molar volume ^a , mL/mol	
CaO	16.76
Ca(OH) ₂	31.63
MgO	11.26
Mg(OH) ₂	24.50
Ratio of molar volumes, Ca(OH) ₂ /CaO	1.89
Ratio of molar volumes, Mg(OH) ₂ /MgO	2.18
H ₂ O vapor pressure over hydroxide ^b , kPa	
Ca(OH) ₂	
301°C	0.35
401°C	2.2
Mg(OH) ₂	
85°C	17
100°C	31
171°C	84
Solubility in H ₂ O at 100°C ^a , mm	
Ca(OH) ₂	10
Mg(OH) ₂	0.69

^aHandbook values.

^bInternational Critical Tables, Vol. 7, pp. 291-294.

repository conditions. Preliminary indications suggest that the dicalcium silicate variant used in the screening tests is inferior to MgO with respect to the extent and rate of reaction with water and that it lacks moderate temperature stability. There is at present, no information pertaining to the behavior of these desiccant additives in the presence of a radiation field. The effects of radiolysis or the presence of corrosion products on the behavior of a desiccant-backfill system need to be addressed prior to any assessment as to the benefits of including such components as part of the waste package design.

Table 5.7. Packing material (backfill) desiccant-oxide capacities in reference salt repositories (ORNL-5818, 1981).

Backfill parameter	Type of Waste		
	CHLW	SF	DHLW
Volume of backfill space ^a , m ³	0.18	0.28	0.37
Volume of void space in sand or crushed salt backfill ^b , m ³	0.072	0.11	0.15
CaO capacity ^c , k mol	2.4	3.6	4.9
Total hydration, kg of H ₂ O ^d	43	65	88
MgO capacity ^c , k mol	3.5	5.4	7.3
Total hydration, kg of H ₂ O ^d	63	97	131

^aFor reference repositories; the height of annular space is assumed to equal the active length of the waste canister. Spaces above and below waste are not included here.

^bAssuming packing to 60% of theoretical density.

^cMoles of oxide powder required to fill void spaces to 55% of theoretical density, using handbook values for oxide densities at 25°C.

^dMass of H₂O required to completely hydrate the amounts of oxide given here.

5.3.5 Role of Packing Material With Respect to Regulatory Criteria

In Section 1 it was stated that the waste package must contain the radionuclides in the waste for a period of not less than 300 nor more than 1000 years after repository closure, and that the engineered barrier system must limit the release of radionuclides to less than 1 part in 10⁵ per year following loss of containment. A salt repository is unique in the sense that brine tends to migrate towards the hot waste so that any radionuclide migration will not usually be assisted by water flow.

If a packing material is not utilized then loss of containment will immediately follow breaching of the container/overpack system since this constitutes the boundary of the waste package. If a simple crushed salt packing is used as an integral part of a waste package, however, containment will be lost when radionuclides diffuse to the outer boundary of the packing. Desiccants in the packing will likely minimize the rate of inflow of brine to the container and retard general corrosion rates, but hydrogen embrittlement and stress-corrosion cracking may be viable failure mechanisms for some container materials, as described above. Bentonite clay packing materials may be beneficial in retarding water ingress to the container surface and also in

retarding radionuclide migration to the package boundary. However, more detailed assessments are required under appropriate conditions to establish the role of any packing material in meeting the waste package containment criterion.

With respect to the controlled release rate from the engineered barrier system, a packing material is likely to be beneficial since it can retard radionuclide release rates by sorption processes. A crushed salt packing may be less effective than a bentonite containing material since it is difficult to remove porosity during the consolidation process. In addition, bentonite- and zeolite-containing materials possess an ability to sorb a range of radionuclide species (NUREG/CR-2482, Vol. 4, 1983).

5.3.6 Conclusions

Temperature gradients surrounding the waste package can cause brine inclusions within the rock salt to migrate towards the heat source. The need to determine the amount of brine likely to accumulate around the waste container is important in assessing corrosion behavior of the container and waste form leaching. Adequate estimates of moisture inflow are not available at this time.

The near-field aqueous environment likely to exist around a nonshielded waste package may be composed of brines that will tend to vary in pH and chemical composition with time. Initially, brine reaching a waste container will be acidic because of the dissolution of thermally-released gases from the salt, such as HCl. As increasing amounts of colloidal sodium are formed in salt by gamma irradiation, brine migrating through the irradiated salt will become alkaline. Therefore, container candidate materials will need to be evaluated with respect to initial acidic brine conditions followed by longer term neutral to alkaline conditions.

Gas pressurization with a package borehole is possible after repository closure and occurs from thermally-released gases from the crushed salt packing material as well as brine radiolysis effects.

Indications are that consolidation can be rapid in bedded salt. Consolidation of crushed salt packing material may result in enhancing the liberation of brine in the vicinity of the waste package. Additional information is needed on the possibility of forming pockets of brine adjacent to the container due to these effects.

The predictive techniques used by Jenks and Claiborne appear adequate for short-term estimates of brine in-migration. More accurate predictions of long-term brine accumulation require in-situ testing for long durations and an assessment of the effects of radiation, consolidation, and temperature on the effective permeability of the salt.

There is insufficient information to adequately assess the behavior of desiccant material additives to packing material. There are no data available on the behavior of these materials under actual repository conditions. The effects of radiolysis or the presence of corrosion products on the hydration properties or stability of these desiccant-packing mixtures is not known.

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BIBLIOGRAPHIC DATA SHEET

1. REPORT NUMBER (Assigned by DDC)

NUREG/CR-2482, Vol. 6

BNL-NUREG-51494

4. TITLE AND SUBTITLE (Add Volume No., if appropriate)

Review of DOE Waste Package Program

Subtask 1.1 - National Waste Package Program

October 1983 - March 1984

2. (Leave blank)

3. RECIPIENT'S ACCESSION NO.

7. AUTHOR(S)

P. Soo, Editor

5. DATE REPORT COMPLETED

MONTH

May

YEAR

1984

9. PERFORMING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)

BROOKHAVEN NATIONAL LABORATORY

UPTON, NEW YORK 11973

DATE REPORT ISSUED

MONTH

March

YEAR

1985

6. (Leave blank)

8. (Leave blank)

Subtask 1.1

10. PROJECT/TASK/WORK UNIT NO.

11. FIN NO.

A-3164

12. SPONSORING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)

Division of Waste Management

Office of Nuclear Materials Safety and Safeguards

U.S. Nuclear Regulatory Commission

Washington, DC 20555

13. TYPE OF REPORT

Technical

PERIOD COVERED (Inclusive dates)

October 1983 - May 1984

15. SUPPLEMENTARY NOTES

14. (Leave blank)

16. ABSTRACT (200 words or less)

This report is part of an ongoing effort to review the national high level waste package program. The contributions of individual waste package components to containment and controlled release of radionuclides after emplacement in salt, basalt, tuff and granite repositories are evaluated. The U.S. crystalline (granite) repository program is reviewed and relevant foreign data are outlined. The use of crushed salt, bentonite and zeolite-containing packing materials is discussed. Temperatures and gamma irradiation are shown to be important environmental parameters in assessing waste package performance.

7. KEY WORDS AND DOCUMENT ANALYSIS

waste package

17a. DESCRIPTORS

7b. IDENTIFIERS/OPEN-ENDED TERMS

8. AVAILABILITY STATEMENT

Unlimited

19. SECURITY CLASS (This report)

UNCLASSIFIED

21. NO. OF PAGES

20. SECURITY CLASS (This page)

22. PRICE

S