

**TITLE: FINAL TEST PLAN FOR FY2013
BRINE MIGRATION EXPERIMENTS**

Fuel Cycle Research & Development

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**Appendix E
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Name/Title of Deliverable/Milestone Test Plan to Develop Hydrologic Laboratory Methods: Experiments of Brine Migration in Salt due to Thermal Gradient and /or Dehydration of Secondary Mineral Phases

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APPENDIX A

Review of Brines, Brine Chemistry, and Brine Migration in a Salt Repository for Spent Fuel or HLW..... 23

ACRONYMS

AEC	Atomic Energy Commission
ASTM	American Society for Testing and Materials
BRAGFLO	Brine and Gas Flow
BWIP	Basalt Waste Isolation Project
CCA	Compliance Certification Application
DOE	Department of Energy
DHLW	Defense High Level Waste
DTA	Differential Thermal Analysis
ENRESA	Empresa Nacional de Residuos Radioactivos
ERDA	Energy Research and Development Administration
ERDA-6	A synthetic brine representative of fluids in Castile brine reservoirs
FFT	Fast Fourier Transformed
Fm	Formation
FZK	Forschungszentrum Karlsruhe
GSF	Gesellschaft für Strahlen
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado brines
HLW	High-level Radioactive Waste
IFT	Institut für Tieflagerung
ILW	Intermediate Level Waste
IR	Infrared Spectroscopy
LLW	Low-Level Waste
LWA	Land Withdrawal Act
NNWSI	Nevada Nuclear Waste Storage Investigations
NRC	National Research Council
NWPA	Nuclear Waste Policy Act
NWTS	National Waste Terminal Storage Program
ONWI	Office of Nuclear Waste Isolation
ORNL	Oak Ridge National Laboratory
PA	Performance Assessment
PNNL	Pacific Northwest National Laboratory
RAMAN	RAMAN Spectroscopy
R&D	Research and Development
SAED	Selected Area Electron Diffraction
SNL	Sandia National Laboratory
SRP	Salt Repository Project
TEM	Transmission Electron Microscopy
TGA	Thermal Gravimetric Analysis
TG-DSC	Thermogravimetric Analyzer
TRU	Transuranic
USGS	United States Geologic Survey
WAESD	Westinghouse – Advanced Energy Systems
WIPP	Waste Isolation Pilot Plant
XRD	X-ray Diffraction

YMP Yucca Mountain Project

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Used Fuel Disposition Campaign

Final Test Plan for FY2013 Brine Migration Experiments

1. Preface

The text of this document was submitted on September 21, 2012, fulfilling the completion criteria for the SDI THM test plan (FCRD-UFD-2012-000346). This Salt R&D test plan incorporates an appendix (Review of Brines, Brine Chemistry, and Brine Migration in a Salt Repository for Spent Fuel or HLW) and minor text changes but the proposed experimental tests remain the same.

2. Objectives, goals and rationale

The research objectives proposed here are to advance our understanding of brine/water vapor migration in “intact” salt under thermal gradients created by point heat sources and radial and axial stress applied to the intact salt. Specifically, we will focus on the behavior of brine movement in both the intracrystalline region and at the grain boundaries and how minor associated hydrous mineral phases (clay or sulfates) affect brine migration. The experiments will be performed under high heat loads of up to 300 °C with temperature gradients of up to 10 °C/cm and confining pressures of up to 6000 psi. We will perform the experiments at a small scale (few cm) and intermediate scale (10’s of cm) and at times scales varying from few seconds to months. The planned experiments will make significant advances to address the following questions:

1. How does brine inclusions size impact their behavior under thermal load gradients?
2. How do brine inclusions behave at crystal defects, grain boundaries, and fractures? Does the size of the inclusions affect their behavior at grain boundaries?
3. What happens to water inclusions under high temperature when situated near secondary mineral phases?
4. How does axial stress and confining pressures affect brine migration in salt?
5. How does the knowledge gained at a single crystal and small core scale translate to the behavior of water inclusions under repository conditions (scaling)?
6. What is the behavior of water derived from mineral dehydration?
7. Under what temperature conditions do clays undergo phase transition? How do phase transitions affect porosity? Are the structural changes and dehydration processes reversible?
8. What are the effects of gypsum hydration/dehydration on water release and salt porosity?
9. Are the sulfate mineral hydration / dehydration processes reversible? What are the implications for the porosity of the secondary mineral phases and the salt?

3. Background and Significance

3.1 Water content of rock salt

3.1.1 Total water content. Water content in salt varies depending on the location and nature of the salt deposit. It is usually in the range of thousandths to tenths of wt. % in domal salt and up to several percent in bedded salt. Salt containing mainly halite has low water content of

usually 0.5 wt. % but increases in samples with increased content of clays and polyhalite. The water (brine) associated with salt occur as inter-crystalline inclusions (which are brine pockets present in the boundaries between salt crystals and fractures), intra-crystalline (which are brine inclusions of few microns to several millimeters in size present within the crystal structure), and water within minor hydrous mineral phases present in the salt such as carnallite, kieserite, gypsum, polyhalite and clay (Roedder, 1980; Roedder, 1981; Popielak, 1983). The total water content in salt and its attribution among the three components listed above is difficult to determine and the data provided in the literature vary considerably because of the difficulty of accurately measuring water content in each category and sample heterogeneity (Roedder, 1981; Shefelbine, 1982). The quantity of each of the major forms of water can vary significantly within samples from the same location. For example: analysis of salt specimens from a potash mine in the southwest New Mexico near the WIPP facility in which the major constituents were 90% halite, 5% sylvite, and 5 % polyhalite indicate that water associated to connected pores and low temperature hydrated minerals is in the range of 0.05 to 0.1 wt. % of the salt, intra-crystalline brine inclusions represent 0.11 to 0.3 wt.% of the water content, and high temperature hydrated minerals (up to 370 °C) represent 0.3 to 0.4 wt.% of the water content (Hohlfelder, 1979; Hohlfelder, 1981; Hohlfelder, 1982; Shefelbine, 1982).

3.1.2 Inter-crystalline water. Inter-crystalline water occupies pores and grain boundaries and can range in size from micron size inclusions to brine pockets of many cubic meters. They can be seen when separating adjacent crystals and rapidly evaporate when exposed to dry air leaving fine white efflorescences on the face of the salt crystal. Their distribution in the salt is extremely variable and can be easily identified by optical microscopy examination of the salt specimens. Inter-crystalline water is usually released by heating of salt solid samples to temperatures of less than 225 °C. However, the water released under these conditions will also include adsorbed water and structural water associated with low temperature hydrated minerals (Roedder, 1981, Shefelbine, 1982).

3.1.3 Intra-crystalline water. Intra-crystalline water occurs as fluid inclusions that are encapsulated within single crystals. Their size can range from micron to several millimeters. They are widespread in salt and can be visible to the naked eye. Smaller inclusions are easily identified by optical microscopy.

Figure 1A illustrates the high density and variability of size and shapes of brine inclusions in a salt crystal obtained from WIPP. The water inclusions can be completely filled with brine or contain gas pockets along with brine. When heated to moderate temperatures (< 150 °C), the brine inclusions located deeper in the salt crystals change their regular shape and

adopt more rounded forms and many of the smaller inclusions coalesce to create larger inclusions (Figure 1B). Intra-crystalline brine is not readily released from salt even when heated to temperatures above 250 °C (Shefelbine, 1982). Brine contained in intra-crystalline inclusions

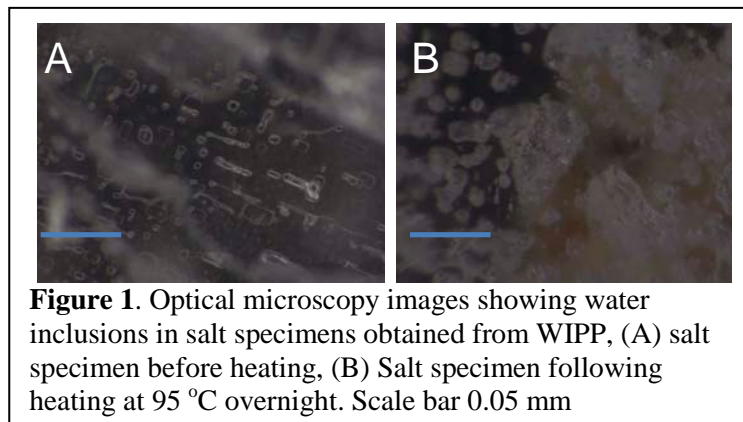


Figure 1. Optical microscopy images showing water inclusions in salt specimens obtained from WIPP, (A) salt specimen before heating, (B) Salt specimen following heating at 95 °C overnight. Scale bar 0.05 mm

is usually released by heating the salt to such high temperatures that the vapor pressure created fractures the salt crystal. It can also be released by crushing the salt crystal before heating, or by applying a heat gradient that causes the inclusions to move to grain boundaries. However, quantification of the water released via these processes has large uncertainties due to the size variability of the brine inclusions.

3.1.4 Water incorporated in hydrous minerals. Salt rocks contain a significant amount of water associated with hydrated minerals contained in the salt. Minerals most commonly associated with salt include oxyhydroxide minerals, carnallite ($\text{KMgCl}_3 \cdot 6(\text{H}_2\text{O})$), bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), polyhalite ($\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$) and various clay minerals. The distribution of these various hydrated minerals and the water associated with them is highly variable and varies significantly within samples from the same location (Braitsch, 1971; Stewart, 1963; Kopp and Fallis, 1973). The amount of water associated with each mineral component can be determined theoretically from their chemical formula. In a mixture of minerals, an accurate determination of the mineralogy of the sample and quantitative measurement of weight loss under thermal treatment using techniques such as differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) or a combination of the two methods could in theory assign water releases to specific mineral phases. The amount of water contained in each mineral phase, its ease of release, and the potential for rehydration vary significantly between and among mineral phases. Polyhalite contains up to 6 wt. % water, clay minerals can contain between 5 and 18 wt. % water and gypsum contains up to 20.9 wt. % water. The first and second dehydration temperature domains for polyhalite are 150-160 °C and 340 – 360 °C respectively. Clay minerals undergo dehydration between 100 and 800 °C. Gypsum undergoes dehydration between 75 to 175 °C. Carnallite, a minor hydrous mineral phase often associated with salt and which contains up to 38.9 wt. % water undergoes dehydration between 180 and 224 °C. These examples show the extent of water contained in mineral phases and the temperature domains at which many of these phases undergo dehydration. These temperature domains overlap, increasing the difficulty of assigning thermal gravimetric analysis (TGA) data to the various minerals and highlighting the importance of accurate quantification of water content and dehydration reaction conditions using site-specific minerals.

3.1.5 Brine composition. The constituents found in brine were extensively examined in the literature and a number of synthetic analogues have been proposed as model brines from the different brines that might come in contact with nuclear waste (Brush, 1990; Snider, 2003). Compositions of natural brines were determined by analysis of seeps collected in the Duval potash mine, N.M. and by analysis of microliter samples extracted from fluid inclusions (Dosch, 1976; Molecke, 1983). Synthetic analogs of this composition labeled Brine A (Table 1) was utilized in numerous studies that were intended to mimic the Duval mine brine. The composition of Brine A is different from the composition of brine obtained by dissolving WIPP salt in distilled water (Brine B, Table 1). These model brine solutions were later replaced by ERDA-6 (replaced Brine B) (Brush, 1990) and GWB (replaced Brine A) (Snider, 2003) in laboratory and modeling studies used for WIPP performance assessment. The synthetic ERDA-6 is designed to represent fluids in brine reservoirs in the underlying Castile Fm. (Popielak, 1983) and GWB is designed to represent the average composition of inter-granular brine fluids obtained through numerous analyses of inter-granular fluids obtained from WIPP salt specimens.

Table 1. Constituents of brine samples from the Duval mine and synthetic WIPP brines. Concentrations are in g/L for all constituents (Brush, 1990, Snider, 2003).

Constituent	Duval mine	Brine inclusions	WIPP Brine A	WIPP Brine B	GWB	ERDA-6
Na ⁺	49	33	42	115	81	112
K ⁺	52.5	26	30	0.015	18	3.8
Mg ²⁺	38.5	43	35	0.01	24.8	0.46
Ca ²⁺	1.26	5.5	0.6	0.9	0.56	0.48
Sr ²⁺	-	-	0.005	0.015	-	-
Cl ⁻	241.5	241	190	175	208	170
SO ₄ ²⁻	3.6	-	3.5	3.5	-	-
I	-	--	0.01	0.01	-	-
HCO ₃ ⁻	0.7	-	0.7	0.01	-	-
Br ⁻	0.385	-	0.4	0.4	2.12	0.88
HO ₃ ⁻	1.16	-	1.2	0.01	-	-
TDS	388	350	306	297	-	-

Brine inclusions are typically enriched in potassium and magnesium and relatively poor in calcium (Table 1). The origin of these fluids inclusions trapped within the halite crystals is the original brine in which the ionic ratios between Ca²⁺, Mg²⁺ and SO₄²⁻ were influenced by the reaction of brine with carbonates adjacent to the halite beds and the dissolution of efflorescent evaporate crusts that were not in equilibrium with precipitated evaporates (Bein, 1991). A more comprehensive discussion of brine compositions can be found in Appendix A.

3.2 Brine migration in salt.

3.2.1 General considerations. The migration of water trapped in the rock salt under the influence of a thermal load was investigated extensively in relation to the disposal of heat producing radioactive waste. It is postulated that brine contained in the rock salt will move toward the heat generating radioactive waste under repository conditions and that contact between brine and nuclear waste packages could result in the corrosion of the waste packages and possibly result in the mobilization of radionuclides. Most previous studies concerning brine migration in salt focused on the behavior of brine inclusions and moisture release from polycrystalline salt rock samples under temperature gradients. Their conclusions are summarized below. However, these studies addressed mainly brine migration in pure salt and did not address the potential effect of minor mineral phases such as clay seams commonly found in salt. These minor mineral phases could play a significant role in brine migration through hydration/dehydration processes which could affect rock salt porosity, and migration of brine. The research proposed here will specifically focus on addressing knowledge gaps related to the effect of minor mineral phases associated with salt (e.g., clay, gypsum) on brine migration and transformation of minor mineral phases under repository conditions applicable for the disposal of heat-producing radioactive nuclear waste.

3.2.2 Intra- vs. inter-granular water migration in salt. Extensive studies examined brine migration in salt at scales ranging from cm to meters in the laboratory and under real mine settings (Machiels, 1981; Yagnik, 1982; Yagnik, 1983; Bradshaw, 1971; Krause, 1983; Nowak,

1986; Nowak, 1987; Rothfuchs, 1988). Under the influence of temperature gradients, water/brine contained in the grain boundaries (inter-granular) is released by a vapor transport process. This process is facilitated by the opening of the grain boundaries in polycrystalline natural salt due to the thermal stresses which accompany the thermal gradients applied to the salt (Machiels, 1981). The intra-granular water migration in a temperature gradient depends on the nature of the brine inclusion. All-liquid brine inclusions within the salt crystals migrate in the temperature gradient according to a mechanism controlled by the rate of salt dissolution at the hot face of the inclusions and to a lesser extent on the rate of crystallization at the cold face of the inclusion (Olander, 1980; Olander, 1981a; Olander, 1981b). Inclusions are predicted to move towards the heat source because of the temperature effect on the solubility of salt. Salt will dissolve at the interface closest to the heat source and precipitate at the interface furthest from the heat source because salt solubility increases with increasing temperature (Machiels, 1981, Yagnik, 1982, Yagnik, 1983). This process is highly dependent on the presence of imperfections and impurities in the crystal structure. A dissolution front with imperfections in which the atoms of the solid salt are less tightly bound than in a perfect atomic plane will dissolve faster (Machiels, 1981). The rate of inclusion transport is highly dependent on the nature of the salt and the presence of impurities, and to a lesser extent? on the rate of ion diffusion through the brine droplet, and the precipitation of salt at the cold side of the salt.

Brine inclusions containing a gas phase will move away from the heat source because water will evaporate at the hot side of the gas bubble and move to the colder side of the inclusion and condense. This mechanism will create an internal flow that continually brings dissolved salt from the cooler side of the inclusion to the hot side of the inclusion and water vapors from the hot side of the inclusion to the cooler side of the inclusion. This flow and evaporation mechanisms will induce the gas-liquid inclusions to move away from the heat source (Anthony, 1972; Olander, 1981a; Olander, 1981b).

The behavior of all liquid and gas-liquid inclusions becomes complicated when the inclusions reach grain boundaries, or deposits of secondary minerals associated with salt. In some studies, the migration of the inclusions was reported to continue within the adjacent grain and in other cases it ceases and the fluid spreads into micro-cracks at the boundary between grains (Shelfbine, 1982). The behaviors of brine in inclusions that accumulate at grain boundaries and inter-crystalline brine are basically unknown. It is also unknown how the presence of minor hydrous mineral phase such as gypsum, polyhalite and clay affect brine migration. Multi-scale laboratory and field studies are essential to investigate knowledge gaps in individual processes and integrate the knowledge gained at a small scale (0.1 to 10 cm) to interpret larger scale *in situ* testing studies.

3.2.3 In situ field investigations of brine migration in salt. There have been four major *in situ* examinations of thermal driven brine migration in salt. These are: 1) the cavity-migration test in Project Salt Vault (Bradshaw and McClain, 1971); 2) the Avery Island, LA, brine-migration test (Krause, 1983); 3) the WIPP brine-migration study (Nowak, 1986; Nowak and McTigue, 1987); and 4) the German-American brine-migration test in the Asse salt mine in Lower Saxony, Germany (Rothfuchs, 1988). These studies were performed by emplacement of electrically powered heat sources into boreholes drilled in the salt bed and focused on measurement of the amount of brine that migrated towards the heat source.

The temperature in the Project Salt Vault increased to a maximum of 200 °C. The *in situ* studies and modeling efforts determined that between 2 to 10 liters of brine inflow could come in contact with each waste package over a period of 20 to 30 years following initial burial. The *in situ* examination of brine migration at the Avery Island salt mine examined brine migration under heated and unheated conditions in three boreholes. The maximum temperature in the salt adjacent to the midplanes of the boreholes was only 51 °C. They observed brine migration rates at heated sites that were twice those of ambient temperatures. Their modeling calculations determined a rate of 0.0173 ml/day at steady state temperature conditions and a temperature gradient of 1.44 °C/cm.

The WIPP brine-migration study used four boreholes each equipped with an electrical heat source. The maximum temperatures in the salt adjacent to the midplanes of the boreholes increased exponentially to 55 °C in two boreholes (at 441 days), and to 120 °C in the third borehole and 130 °C in the fourth (at 600 days). The water collected after application of the thermal treatment increased to a peak, then decreased, and then stabilized at a constant flow for the duration of the experiment (Nowak, 1986; Nowak and McTigue, 1987). The total mass of water collected in the first two boreholes was 4.3 kg at 441 days. The total masses collected in the remaining two boreholes were 36 and 38 kg at 600 days. The rate of water transfer was about 8 g/day at steady state for boreholes 1 and 2, and over 30 g/day for boreholes 3 and 4.

The Asse brine-migration test was conducted in four boreholes spaced 15 m apart. Two boreholes contained electrical heaters and the other two contained two ⁶⁰Co (Half-life = 5.3 years) heat sources with eight “guard heaters” (peripheral heaters) arranged in an octagonal array of boreholes 1.5 m from the centerline of the central borehole. Power was applied to the heaters in the first two boreholes to obtain a maximum temperature of ~210 °C in the salt adjacent to the midplanes of the central boreholes. In boreholes 3 and 4 the maximum temperatures in the salt was close to 210 °C. The total volumes of brine that flowed into the different boreholes were 125, 125, 100, and 137 mL for boreholes 1, 2, 3, and 4, respectively (Rothfuchs, 1988). These volumes were in the range predicted by the fluid-inclusion model, which predicted that about 400 mL of brine would flow into the central borehole after about 2 years. However, they were lower than the volumes predicted by vapor-phase transport models which predicted about 2 to 4 L assuming a permeability of 0.1 and 1 μ Darcy respectively (Rothfuchs, 1988).

The amount of brine released by the salt rock under thermal gradient varied considerably between experiments. The WIPP salt released the highest water content among all four experiments performed. It also had the highest rate of water release. These data are consistent with the higher water content in the WIPP salt relative to the other mines tested. The data also highlight the high variability in water migration between different sites and points to the necessity of performing site specific tests if a salt site is to be used for the disposal of thermally active waste. A more comprehensive discussion of brine migration can be found in Appendix A.

3.3 Dehydration of secondary minerals associated with salt.

3.3.1 Clay stability. Clay minerals present as minor mineral phases in salt rocks can play a critical role in the performance of the repository. They can influence the performance of the repository through their chemical interaction with radionuclides, retention and release of water, and influence mechanical behavior of the salt (porosity). Clays can undergo dehydration

processes and change physical structure and chemical composition under heat and pressure loads. These changes in turn can influence their capacity to retain water, and their sorption/desorption capacity and concomitant retention of radionuclides.

A number of previous studies examined changes in smectite clay at elevated temperatures and/or pressures. Altaner and Ylagan (1997) provide a good introduction to the concepts of smectite alteration. Smectite illitization is considered to proceed through mixed-layer illite/smectite (I/S) intermediates as the percentage of illite interlayer increases. Important factors for the changes include increasing temperature, potassium (K) concentration, time, and water/rock ratio. Possible reaction mechanisms for smectite illitization include solid-state transformation, dissolution and crystallization, and Ostwald ripening. Wu and colleagues (Wu et al. 1997) examined partial dehydrated Ca- and Mg-exchanged montmorillonite by heating samples at pressures from the H₂O liquid-vapor boundary to about 10 kbars. Progressive dehydration caused shrinkage of the crystal lattice from the 19 Å hydration state to the 15 Å at 260-350 °C with further dehydration to the 12.5 Å state at higher temperature. Mg-montmorillonite dehydrates to the 15 Å state at 200-250 °C, with further dehydration to the 12.5 Å state at 590-605 °C. Similar experiments with Na-exchanged montmorillonite (Huang, 1994) identified shrinkage from the 19 Å hydration state to the 15 Å hydration state at 330-385 °C and from 15 Å to 12.5 Å at 485-500 °C. The 19 Å fully hydrated montmorillonite therefore, is stable up to 200-380 °C under pressures in the absence of potassium.

Ferrage et al. (2011) presented some of the best evidence for the mechanism of S to I/S transformation. They studied the hydrothermal reactivity of K-exchanged low-charge montmorillonite (SWy-2) at 250-400 °C and 1 kbar, with reaction times of 5 to 120 days. The authors provide experimental evidence for a dissolution-crystallization mechanism following the Ostwald step rule in which metastable smectite transforms into illite through a series of metastable illite-smectite phases. Dehydration and lattice shrinkage that occurs in this temperature range is fully or almost fully reversible. However, at higher pressures, the rehydration initially follows a lower-temperature path relative to the thermal path of dehydration.

3.3.2 Clay minerals at WIPP. The WIPP repository is located within the Salado Formation, which consists primarily of halite, with minor amounts of anhydrate, polyhalite, gypsum, manganosite, quartz, clays, and trace amounts of K-feldspar. The total content of minor mineral phases in the WIPP salt is approximately 5 wt. % (Stein, 1985). Clays occur either as discrete layers with thicknesses ranging from a few to several cm, or as finely dispersed material throughout the halite (Figure 2). Characterization by X-ray diffraction identified three main clay minerals (mixed-layer saponite-chlorite, chlorite, and illite) as the bulk of the argillaceous material comprised in the salt. This is consistent with clay minerals common to many other salt bed formations typically consisting of illite and an assortment of Mg-rich poorly-ordered, randomly-

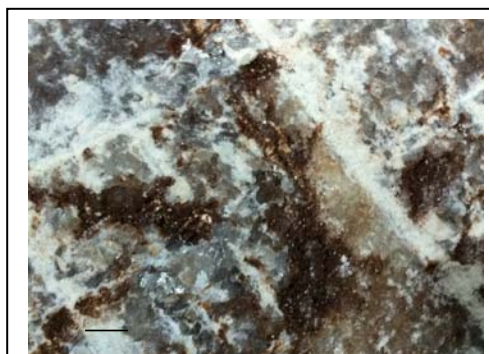


Figure 2. Photograph of a salt specimen obtained from WIPP showing discrete layers of clay within the halite deposit. The scale bar represents 1.0 cm

interstratified clays (Braitsch, 1971). The X-ray spectra vary significantly between samples suggesting either variation in the relative proportions of the trioctahedral chlorite and trioctahedral smectite layers or the lack of ordering between the chlorite and smectite layers.

The clay-bearing strata do not show any significant systematic mineralogical variations. Within any given layer the proportions of the three clays appear to vary randomly from place to place except the apparent enrichment of mixed-layer in the upper clay compared to the lower clay. The mixed-layer/illite and mixed-layer/chlorite ratios appear to be higher in the upper clay, while the illite/chlorite ratio shows no trend.

The effect of dehydration was examined at 250, 500, and 650 °C by treating the samples for 1 hour at the designated temperatures (Krumhansl, 1990). The results show significant structural alterations as a result of the heat treatment. The peaks characterizing the chlorite and corrensite are significantly reduced by the heating process. However, the illite peak remains prominent throughout the various heat treatments examined (Krumhansl, 1990).

3.3.3 Sulfate minerals occurrence in salt and their dehydration properties.

Sulfate minerals associated with salt have been examined to determine their ability to retain and release significant amounts of water through hydration/dehydration processes as a function of heat and pressure loads. The gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to anhydrite transformation creates a large water release (up to 21% wt. loss) and volume reduction (of up to 40%) (Smyth and Bish, 1988). Volume loss results in contraction, which can affect salt porosity by creation of fractures. In addition to gypsum, hydrated minerals most commonly associated with salt (other than clays) include carnallite ($\text{KMgCl}_3 \cdot 6(\text{H}_2\text{O})$), bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), and polyhalite ($\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$). Calcium sulfates are classified in three different mineral forms based on their degree of hydration. The phase changes of the calcium sulfates are: gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), and anhydrite (CaSO_4). The phase transformations occur naturally through dehydration processes but are accelerated following heat treatments. Phase transformations are influenced by the amount of water present, the temperature, pressure, and amount of dissolved electrolytes or organics (Freyer and Voigt, 2003).

At low temperature gypsum is the most stable phase and at high temperature anhydrate is the most stable mineral form. Hemihydrate is metastable at all temperatures. Hydration/dehydration of calcium sulfates have been studied extensively in relation to their utilization as binders in building materials (Freyer and Voigt, 2003). Gypsum/anhydrite transition temperatures are in the range of 25 to 52 °C (Freyer and Voigt, 2003). However, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) also converts to anhydrite (CaSO_4) in evaporite beds between the temperatures of 100 and 140 °C. In that 40 °C gap is hemihydrate, a metastable but kinetically favored phase (Shcherban and Shirokikh, 1971). These transition temperatures are strongly influenced by electrolytes. Increased electrolyte influences the solubility domains of each mineral phase and their transition temperatures. In a solution saturated with NaCl the transition temperature for the gypsum/anhydrite is estimated to 18 °C (Hardie, 1967, D'Ans, et al 1955), and the transition of gypsum/hemihydrate estimated to 76 °C (Freyer, 2000). Increased pressure increases the solubility of all calcium phases and also influences the transition between the different phases. Solubility increases as a function of pressure for the different phases and shifts the phase transition temperatures of gypsum/anhydrate and gypsum/hemihydrate. However, only a few

reports based on thermodynamics exist on calcium sulfate phase transition as a function of pressure (Monnin, 1990, Monnin, 1999, Krumgalz et al 1999).

Dehydration of carnallite occurs in the 80 °C to 170 °C and results in the release of 3 to 8 wt. % water. A second dehydration stage occurs at much higher temperatures to produce a mixture of magnesium chloride and magnesium oxide. The dehydration of bischofite occurs between 155 to 220 °C. Recent examinations of bischofite dehydration in the temperature range 25 °C to 600 °C using high-quality *in situ* synchrotron powder diffraction data identified at least eight phases including: $MgCl_2 \cdot nH_2O$ ($n = 1, 2, 4$ and 6), $MgOHCl \cdot nH_2O$ ($0 \leq n \leq 1.0$), $MgCl_2$ and MgO (Sugimoto, 2007). Polyhalite minerals, which possibly formed as a result of the reaction of brine with gypsum or anhydrite, are described as a tippie salt and are represented by the formula $(K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O)$. It is the most wide spread sulfate mineral in evaporitic rock salt formations and can be present in WIPP salt up to 5% wt. The formation of polyhalite minerals may be the result of the reaction of brine with gypsum or anhydrite. The hydrate water is coordinated to the magnesium ion and therefore is only released at temperatures above 250 °C. The loss of water from salt between 280 °C and 360 °C is typically attributed to the dehydration of polyhalite.

4. Task Implementation

4.1 Tasks outline

Our experimental plan for the laboratory analysis of brine migration in salt will focus on the following three research tasks: **1) Brine transport within salt crystals and crystal aggregates** (e.g., behavior of water at grain boundaries, effect minor mineral phases on brine migration); **2) Brine transport within salt core** (e.g., brine behavior under isothermperature conditions, effect of variable temperature gradients, importance of minor mineral phases; impact of radial and axial stress; **3) Hydrous mineral phase transformations** under high heat and pressure loads (e.g., clay transformation under high temperature and pressure, clays and sulfate hydration/dehydration under variable pressure and temperature loads; behavior of water released from dehydrated minerals encapsulated within salt). Proposed experiments will be performed with salt samples collected from WIPP and preserved on site to retain their moisture content. The detailed outline of the proposed tasks is as follows:

Task 1. Brine transport within salt crystals and crystal aggregates

- 1.1 Brine transport within salt crystals with **no mineral impurities**
 - i. Transport within a single crystals
 - ii. Transport at grain boundaries and between grains
- 1.2 Brine transport within aggregates of salt crystals **with mineral impurities**
 - i. Brine transport in salt aggregates containing mineral impurities away from grain boundaries
 - ii. Transport within salt aggregates containing mineral impurities at grain boundaries

Task 2. Brine transport within salt core

- 2.1 Brine transport in salt core under **isothermperature** conditions
 - i. Rate of water release from **pure salt core**
 - ii. Profile of brine transport within “intact” pure salt core

- iii. Effect of mineral impurities (e.g., **Clay seams** distributed through the intact core, **Clays seams** as a barrier between two salt cores)
- 2.2 Brine transport in “intact” salt core under **variable temperature gradients**
 - i. Rate of water release
 - ii. Profile of water transport as a function of time and temperature gradient
 - iii. Effect of hydrous mineral impurities
- 2.3 Brine transport within “intact” salt core subjected to **radial and axial stress and temperature gradient created by a point heat source**
 - i. Transport as function of radial and axial stress loads
 - ii. Transport as a function of the temperature gradient
 - iii. Effect of extensive fracturing (e.g., fracturing of a fraction of the salt core)

Task 3. Hydrous mineral phase transformation under high heat and pressure loads

- 3.1 **Clay dehydration** under different temperature and pressure loads
- 3.2 **Clay phase transformation** under high heat under variable water contents
- 3.3 **Gypsum** phase transformation under **high heat/pressure conditions**
- 3.4 Hydrothermal reactivity of **other sulfates** under elevated temperature and pressure conditions

4.2 Detailed task implementation

Task 1. Brine transport within salt crystals and crystal aggregates

Task 1.1 Brine transport within aggregates of salt crystals with no mineral impurities. The mechanisms for brine migration in salt due to a temperature gradient depend on the nature of the brine fluids and their location within the salt. The mechanism for intra-crystalline brine transport is probably the most understood. Under a heat gradient intra-crystalline liquid inclusions will migrate towards the heat source because of the temperature effect on the solubility of salt and the difference between the heat conductivity of salt and the brine solution (see background section and related references for more details). Intra-crystalline water inclusions containing a gas phase will move away from the heat source because water will evaporate at the hot side of the gas bubble and move to the colder side of the inclusion and condense.

However, this behavior becomes complicated when the inclusions reach grain boundaries. In some cases the inclusions migrate across the grain boundary into the adjacent grain and in other cases the inclusions spread into microcracks at the boundary between grains. We will examine inter-crystalline brine migration within a single crystal and at the grain boundaries between two adjacent grains under the influence of a point source temperature. We will examine the influence of the inclusion size, the presence of gas and how it behaves at the grain boundaries. We will attempt to answer the following questions: 1) how do brine inclusions behave under isothermal temperature conditions and under thermal gradients? 2) How do brine inclusions behave at grain boundaries and fractures? 3) Does the size of the inclusion affect its behavior at grain boundaries? 4) What is the effect of brine inclusion size on their rate of transport and behavior under a temperature gradient? 5) How does self-healing/sealing at grain

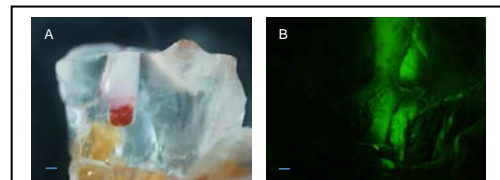


Figure 3. Artificial brine inclusions created in single salt crystals using a natural dye (A) and a fluorescent dye dissolved in brine (B). Scale bar represents 1.0 mm (Exploratory LANL experiment).

boundaries and fractures affect brine migration?

Individual pure salt crystals and aggregates of pure salt crystals obtained from WIPP will be utilized in these examinations. We will use both unaltered and altered salt samples in different temperature settings to gain an in-depth knowledge of brine transport. Full halite crystals and crystal aggregates with macroscopic fluid inclusions are common at WIPP and will be easily obtainable for these experiments. Unaltered salt samples will be separated from large salt samples, characterized for their water content and used without any modifications. Altered samples will be manipulated by precise drilling in the salt crystal to create water inclusions of specific sizes/compositions at the desired locations (Figure 3). Following drilling, a specific volume of brine will be deposited in the drilled cavity and sealed using a heat resistant epoxy resin with thermal conductivity properties similar to that of salt (i.e. $7 \text{ Wm}^{-1}\text{K}^{-1}$) will be used to insulate the inclusion. Initial tests have already been performed in our laboratory, as seen in Figure 3.

We will begin our examinations by subjecting the pure halite crystals containing water inclusions to different desired temperatures using a point heat source. We will examine both intact and slightly fractured salt crystals and aggregates. The salt crystals will be mounted on a microscope stage and continually monitored using a digital camera mounted on a microscope that can capture up to 20 frames per second but can also be adjusted to capture slow events (see equipment section for more details). The salt crystals will be subjected to a desired temperature (i.e., 50, 90, 200 and 300 °C) different time scales to determine the effect of temperature on the behavior of water inclusions. We will analyze the digital images captured at different times scales and sizes (μ to cm) to determine the parameters that affect water inclusion transport, the effect of inclusion size on their transport, and more importantly the parameters that affect water inclusions behavior at the grain boundaries/micro-fractures. The data will allow an in-depth knowledge of the mechanisms of water inclusions transport, and determination of the parameters that affect rate of inclusions transport at small scale in a pure halite crystal.

Complementary pore-scale modeling will be performed based on the lattice Boltzmann method. The dissolution/precipitation of salt at the brine-salt interface, the evaporation/condensation of water, the brine-water vapor two-phase flow, heat transfer, as well as transport of dissolved salt in the brine will be simulated to predict the behavior of brine inclusions. A series of numerical experiments will be performed to investigate the effect of the temperature gradient, size and shape of the brine inclusion, and the salt self-sealing/healing at the grain boundaries and fractures, on the behavior of brine inclusions. The modeling results will not only help interpret experimental results, but also guide the design of new experiments. Both experimental and simulation results at this scale will be upscaled to provide input parameters for the core-scale modeling.

Task 1.2 Brine transport within aggregates of salt crystals with mineral impurities. Natural and artificially altered salt aggregates will be used to examine the effect of minor mineral phases (i.e., clay) present within salt on brine migration. Aggregates of salt containing minor mineral phases (which are often present at the grain boundaries) and natural brine inclusions will be separated from salt samples obtained from WIPP. Alternatively, we will modify salt aggregates containing minor mineral phases to introduce artificial brine inclusions at the desired locations (see figure 3

for illustration of artificial inclusions). Figure 3 shows examples of artificial water inclusions created in salt crystals using brine solution amended with artificial dyes. Our goal is to examine how the presences of minor mineral phases influence the transport of brine. We will attempt to answer the following questions: 1) What happens to water inclusions under high temperature when situated near secondary mineral phases? 2) How do secondary mineral phases affect water movement under different temperature regimes? 3) How do minor mineral phases affect water movement when present away from grain boundaries versus what happens when they are at the grain boundaries? 4) What is the behavior of water released from dehydrated minerals encapsulated in salt? Does it transform to separate water inclusions and migrate away from the secondary mineral phases?

We propose to investigate the behavior of water inclusions at small scale (cm scale) in solid halite (NaCl) crystals as a function of the location of the minor mineral phases /fractures and exposure time. We will use the video microscopy system shown in the instrumentation and equipment section and examine behavior of brine at different time scales and different temperature regimes. Halite crystals with minor mineral impurities (mainly clay, but with other trace phases) will be subjected to heat conditions selected on the basis of the most relevant heat treatments determined from the previous experiments (pure salt). Continuous imaging of the salt specimens at different scales (μ to cm) will allow the determination of the brine behavior in proximity to minor mineral impurities as function of their location and the heat treatment. Following the heat treatment, the samples will be characterized using microscopy techniques, Infrared spectroscopy (IR), RAMAN spectroscopy (RAMAN), and X-ray diffraction (XRD) to determine the transformations of the mineral phases and their implications for hydration/dehydration processes that might occur at a small scale. These examinations will determine the effect of mineral impurities on brine inclusions as function of the heat treatment. The characterizations at the small scale will produce the data that will be utilized to interpret the results from experiments performed at a core scale. It will also produce data that can be used to formulate empirical equations to quantify the rate of water migration in salt.

Task 2. Brine transport within salt core

Task 2.1 Brine transport in salt core under isothermperature conditions. With the knowledge gained on brine migration at a small scale (from the experiments detailed in the previous task) we can focus on examining transport in salt core samples of intermediate scale (10's of cm). Our examinations of brine/water transport in salt core will utilize core samples collected from WIPP and will include intact core samples and core samples modified experimentally to introduce water inclusions and layers of minor minerals at specific locations of the core samples. Artificial water inclusions in the salt core will be created by creating small voids within the salt core, deposition of the desired brine quantity, and resealing of the intrusions using heat resistant epoxy resins. Artificial secondary mineral seams within the salt core will be created inside the core by creating small voids within the salt, deposition of the desired quantity of secondary minerals, or by inclusion of secondary mineral layers between two salt cores.

Our goal is to examine brine behavior in intact salt core subjected to isothermperature conditions and how brine migration is affected by minor mineral phases under isothermperature conditions. We will answer the following relevant questions: 1) How does the knowledge gained on brine transport at a single crystal and crystal aggregates translate to the behavior of brine inclusions at intermediate scales (10s of cm), 2) How do brine inclusions behave at grain boundaries and fractures in an intact core subjected to a constant heat load, 3) How do secondary mineral

barriers affect brine transport in intact salt core? 4) How do minor mineral phases in intact salt core react (dehydration) under isothermal conditions?

The first set of experiments will be performed by applying a constant heat load to a salt core encapsulated (jacketed by metal foil). The heat load will be applied to the entire salt core by inserting the jacketed salt core into an autoclave. We will conduct these experiments at different temperatures and for different durations (1 month and 6 months). The first set of experiments will be performed under ambient pressure. Three salt core samples will be set up simultaneously and the temperature increased slowly until it reaches the desired temperatures (100, 200 or 300 °C). At the completion of the heating stage the salt core will be left under isothermal conditions for the duration of the experiment. The release of moisture from the core sample will be monitored continually by capturing the moisture released using desiccants. At the completion of the experiment the salt core will be allowed to cool to ambient temperature. Moisture release during the cooling process will also be monitored. Following the cooling process the salt samples will be sectioned into 1 cm sections and each section will be analyzed for moisture content and mineralogical composition, and by optical microscopy to determine the mechanisms of brine behavior. Mineral transformations will be characterized (contraction level) by X-ray diffraction (XRD) analysis. These experiments will allow us to determine how moisture/brine behavior at a small scale (μ to cm) compare to its behavior under intermediate scales (10s cm), and will also determine the effect of secondary mineral impurities on moisture movement and most importantly determine the behavior of brine at grain boundaries and in the presence of clay seams. These experiments will also determine the rate of water release during the initial heating stages, the prolonged steady state of the temperature conditions and during the cooling period. These data will help improve our understanding of brine inclusions behavior under isothermal conditions and help improve prediction of the rate of water release from intact salt core under different temperature regimes.

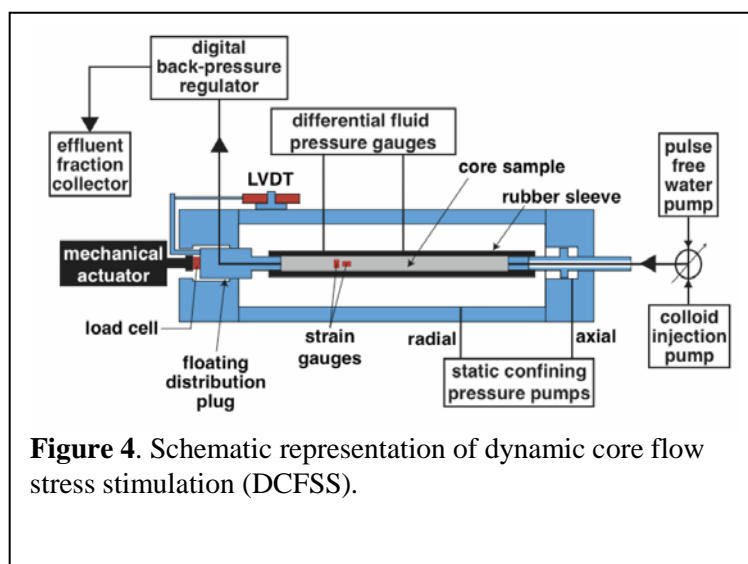
Task 2.2 Brine/water transport in salt core under variable temperature gradients. Research proposed in this section will focus on studying the effect temperature gradients have on brine migration in an intact salt core. Temperature gradients of different amplitudes will be created within intact salt cores by subjecting one end of the salt core to a point source temperature and the other end to a cooling source to evacuate heat from the core. By varying the temperature of the hot source we will create different heat gradients between the two extremities of the salt core which will affect moisture migration. The goal of these experiments is to answer the following questions: 1) How does the extent of the temperature gradient affect the rate of moisture release from the salt core, 2) How does the temperature gradient affect water migration at grain boundaries, and 3) How do mineral impurities affect brine movement under different temperature gradients? We will use intact and experimentally modified core samples with artificial brine inclusions and inclusions of layers of clays and variable temperature gradients from few °C per cm to 10's of °C per cm. The temperature of heating point source will be varied from (50, 90, and 200 and 300 °C) to create temperature gradients of up to 10 °C/cm (the gradient expected initially in the repository near the heat source). Moisture released from the core samples will be captured by continually flowing dry nitrogen through the core samples and capturing the released moisture using desiccants. At the completion of the experiment the salt core will be sectioned into small discs and analyzed using microscopy techniques to determine the behavior of brine at the grain boundaries and the effect of mineral impurities present in salt.

Addition of fluorescent tracers to the brine will facilitate mapping of water/brine distribution in the core. Reconstruction of the 3D image of the water migration profile for each of the artificially created water inclusions would be possible by microscopic analysis of thin sections of the areas marked by the fluorescent dyes. The information gained from these studies will help determine how variable temperature gradients affect water migration in an intact salt core at intermediate scales.

Core-scale experiments will be simulated using FEHM or PFLOTRAN. FEHM is a finite-volume-based code which simulates the multiphase fluxes of water, gas, and heat in porous media, subject to the effects of reactive chemistry and mechanical stresses. PFLOTRAN, developed in a DOE Scientific Discoveries Through Advanced Computing (SciDAC-2) project at LANL, is a next-generation reactive flow and transport code for modeling subsurface processes at the continuum scale. It has been run on up to 204,000 processor cores on the Cray XT5 supercomputer Jaguar at ORNL, achieving petascale performance. Using the upscaled results of experiments and numerical simulations at the smaller scale, continuum-scale simulation will be used to interpret the core-scale experimental data, as well as design new experiments.

Task 2.3 Brine transport within salt core subjected to radial and axial stress and temperature gradient created by a point heat source. In addition to heat gradients, confining pressures and radial stresses can also affect brine/water vapor transport in salt. We will approach the studies of the effect of axial and confining pressures on brine transport in two ways. First, a salt core sample (2.5 cm x 50 cm) will be loaded in our in-house-built dynamic core flow stress stimulator (DCFSS, Figure 4) (see detailed description in equipment section) and subjected to confining pressures of up to 10000 psi and radial stress at ambient temperature. The radial pressure will be controlled by high precision high pressure pumps and can vary from ambient pressure to up to 10000 psi. Moisture release from the salt core will be measured by continually circulating dried nitrogen through the salt core and collecting the released water using desiccators.

This experimental design would mimic an *in situ* moisture release of moisture from salt rock before emplacement of the hot waste sources. In a second set of experiments, a salt core (2.5 cm x 50 cm) will be loaded into the DCFSS equipped with a heating source at one end. The use of a core with a length of 50 cm is optimal to create the large temperature gradient that is expected to vary from up to 300 °C at the contact with the heat source to ambient temperature at the other end away from the heat source. The temperature profile will be monitored continually using monitoring ports installed every 4.5 cm of the salt core. The temperature and pressure conditions can be maintained at the steady state conditions for extended times (months). The salt



core will be subjected to confining pressures of up to 10000 psi and radial stress at ambient temperature. The confining pressure will be fixed at the start of the experiment and different temperature gradients will be applied at constant pressure by varying the temperature of the heating source applied at one end of the salt core.

We will use intact salt core samples from the WIPP repository and as necessary create water inclusions amended with fluorescent dyes to facilitate monitoring of brine migration within the intact salt core. At the completion of the heating and cooling stages of the experiment designated sections of the salt core (amended with fluorescent tracers) will be sectioned for analysis using optical microscopy to determine the behavior of water inclusions under the applied P,T conditions. The brine inclusions leave visible tracks during migration in salt, which provide critical data on transport phenomena. The experiments performed under this section will determine how confining pressures and varying temperature gradients affect the rate of water release from intact salt core. Post experiment microscopy examination of salt fragments and thin sections of the salt will establish an in-depth knowledge on the mechanisms involved in brine transport under confining pressures. Having established the behavior of brine at a small scale and intermediate scales without confining pressures in the previous sections, the data obtained here will allow comparison between the different sets of conditions and establish how confining pressures affect brine migration. We will specifically focus on the behavior at grain boundaries and the effect secondary mineral phases present in salt.

Task 3. Hydrous mineral phase transformation under high heat and pressure loads

Task 3.1 and 3.2 Clay hydration/dehydration under different temperature and pressure loads.

Clay minerals present as minor minerals associated with salt have been recognized for their potential to significantly influence brine migration in salt repositories. In addition of their critical role in brine migration, clays can affect radionuclide retention and the overall physical and mechanical performance of the salt. The fundamental research proposed in this section will focus on studies of clay hydration/dehydration and crystal structure changes at elevated temperatures and pressure conditions similar the conditions expected under repository conditions.

Our goal is to examine how high temperature/pressure conditions, time, the moisture content and the presence of cations (i.e. K^+) affect the structure of clays associated with salt. We will attempt to answer the following questions: 1) Under what temperature/pressure conditions will clays associated with salt undergo phase transformation, 2) What is the effect of clay structural changes on clay porosity, and 3) Are the hydration/dehydration processes reversible? And what are the implications for the porosity of the clay phases and salt? We will specifically focus on clays separated from clay seams from the WIPP site. We will examine how elevated temperature and pressure conditions affect the chemical structure of clays, the behavior of the water release from the clays, and reversibility of the hydration/dehydration processes. We will approach these studies in two ways that will simulate repository conditions.

The first set of experiments will simulate the continual heating of the clays to 300 °C and relative humidity of up to 90 %. The behavior of the clays under variable temperature and humidity conditions will be examined *in situ* using a Bruker D8 X-ray diffractometer and an environmental cell surrounding the sample stage that allows control of relative humidity from 10% to 90% and temperatures of up to 400 °C (Figure 5) (See equipment description for more details). Powdered clay specimens will be equilibrated under the desired humidity in the cavity mount. Measurement of diffracted X-rays from the specimens will be recorded *in situ* as a function of the temperature treatment, the relative humidity and the presence of cations potentially present in brine (i.e. K^+ , Mg^{2+} , Ca^{2+}). The data obtained from these measurements will be compared to the data obtained from the mineral characterization obtained from in task 2.1 with intact salt core subjected to isothermal temperature conditions and will allow accurate determination of mineral transformation as a function of the applied temperature and relative humidity.

The second type of experiments will examine the hydrothermal reactivity of clays under elevated temperature (300 °C) and pressure (up to 200 bar) conditions. We will determine the temperature and pressure regimes of clays transformation (and potential reversibility) of the dehydration processes. Experimental variables will include the clay water ratio, the temperature (300 °C) /pressure (up to 200 bar) regimes, the presence of exchangeable cations (i.e. K^+ , Mg^{2+} , Ca^{2+}), and the reaction times (5 to 120 days). We will perform these experiments in our hydrothermal laboratory at LANL using both Dickson cell and cold seal vessels (Figure 6) and will utilize clay specimens from WIPP. Clays samples will be equilibrated with brine solution in a hydration chamber at room temperature until they reach the desired water content. The samples will be loaded in a gold reaction vessel (Figure 6). The vessel will then be mounted in an autoclave furnace (depicted in Figures 8 and 9 in equipment section) and heated under the desired P, T conditions for the desired reaction time (up to several months). Following the reaction, the samples will be cooled and an accurate determination of the mineral abundance in the samples performed along with characterization of the crystal lattice of the transformed minerals (shrinkage level) by X-ray diffraction (XRD) analysis. Transmission electron

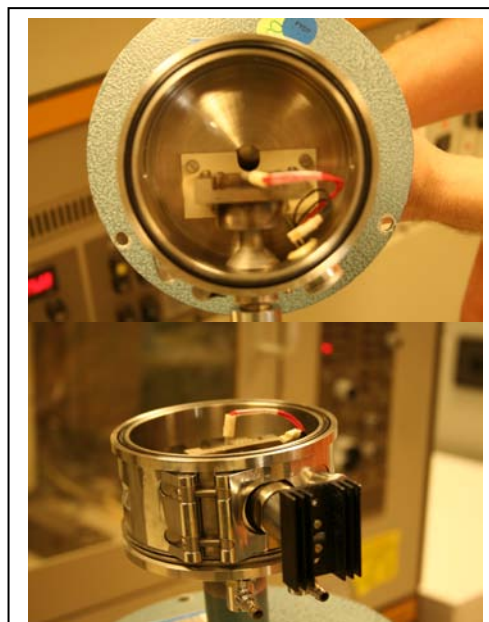


Figure 5. Figures showing the top and side views of the XRD cell that will be used for *in situ* XRD examination under controlled temperature and relative humidity. The temperature of the heating element can reach 400 °C and the relative humidity can of range from 10 to 90 %.

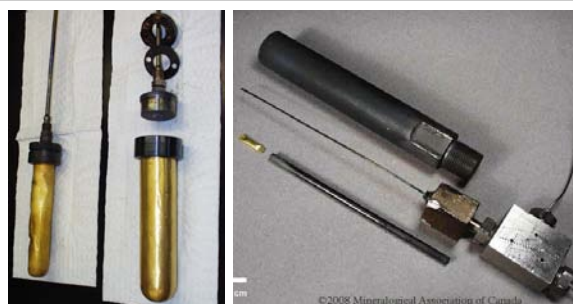


Figure 6. Gold reaction cells 120 ml cell (left), cold seal reaction vessel, disassembled (800°C, 2.5 kbar max.; right).

microscopy (TEM) will be performed on the different reacted clays and the rehydrated phases to document the transformation processes related to crystal structure changes potential rehydration of the reacted minerals will be examined to determine the degree of reversibility of the reacted minerals and their swelling levels. This will be performed by measurement of the levels of moisture uptake and by X-ray analysis of the crystal lattice. Hydrothermal reactivity in the presence of exchangeable cations will also be performed under similar conditions to determine their effect on the clays structural transformation under high heat and pressure loads.

Task 3.3 Gypsum transformation under high heat/pressure. Gypsum associated with salt has a theoretical water content of 20.9 wt % and undergoes its first dehydration between 75-175 °C. This first dehydration step is due to the phase transformation to hemihydrates. Little is known on the behavior of water released from gypsum under high heat loads. Our objective is to examine gypsum samples separated from salt samples obtained from WIPP and to answer the following questions relevant to brine migration in salt: 1) Are there different gypsum hydration/dehydration mechanisms in effect at higher heat loads? 2) What are the implications of gypsum dehydration on water release and salt porosity? 3) Are the dehydration/hydration processes reversible? 4) How does the water released from gypsum dehydration behave in the salt core?

We will approach these studies as follows: first, we will examine the dehydration of pure gypsum samples under different temperature and humidity conditions. The goal is to determine the temperature domains at which structural water molecules are released. Samples will be ground dry and will be mounted in heating stage on a Bruker D8 diffractometer. *In situ* XRD data will be collected rapidly to allow rapid (< 30 min), repetitive measurements. The temperature and relative humidity in the chamber will be controlled (Figure 5). Temperatures will be varied from ambient temperature (23.5 °C) to 400 °C in fixed increments. Humidity will be varied from 20 % to 80% RH. We will also evaluate water release from the samples using thermogravimetric analyzer (TGA). The X-ray analysis will allow an accurate determination of the purity of the sample and the presence of any impurities, which will help establish an accurate interpretation of the TGA data. The *in situ* XRD examinations will allow the determination of how the XRD patterns of the gypsum specimens change with temperature and relative humidity. Analysis of the data will allow identification of the different phases that form and their temperature stability domain. The patterns observed in the *in situ* XRD examinations will be used with the TGA data to phase transitions and dehydration processes associated with each temperature domain. Rehydration of the phases formed will be examined by re-equilibrating the phases formed at room temperature and controlled humidity. These examinations will determine the temperature domains at which water molecules that are integral to gypsum structure are released and their reversibility when re-equilibrated with air at ambient temperature.

We will examine the behavior of gypsum samples from obtained from WIPP and associated with other minerals (halite, clay) using the same procedure. The samples will be characterized using X-ray analysis to establish their exact mineralogical content and will be examined *in situ* under variable temperatures to examine how their patterns change as a function of temperature. The X-ray patterns will be compared to the TGA data obtained on the same samples to establish how mineralogical composition affects the behavior of structural gypsum transformation and its implications for water release. Second, gypsum will be incorporated into artificially created

water inclusions in salt crystals and will be subjected to temperature domains that were determined to induce its dehydration. Following the heat treatments the salt specimens will be examined to determine the behavior of the water released from the gypsum, if any. The gypsum specimens will be collected and analyzed by XRD to determine its structure and hydration level.

Task 3.4 Other sulfates transformation under high heat/pressure The final type of experiments will examine the hydrothermal reactivity of sulfates under elevated temperature (300 °C) and pressure (up to 200 bar) conditions. We will determine the temperature and pressure regimes of sulfate transformation (and potential reversibility) of the dehydration processes. Experimental variables will include the brine water content (up to 30%), the temperature (300 °C) and pressure (up to 200 bar) regimes, the presence of exchangeable cations (i.e. K^+ , Mg^{2+} , Ca^{2+}), and the reaction times (5 to 120 days). We will perform these experiments in our hydrothermal laboratory at LANL using both Dickson cell and cold seal vessels (Figure 6) and will utilize sulfate specimens from WIPP. Sulfate samples will be equilibrated with brine solution in a hydration chamber at room temperature until they reach the desired water content. The samples will be loaded in a gold reaction vessel. The vessel will then be mounted in an autoclave furnace and heated under the desired P, T conditions for the desired reaction time (up to several months). Following the reaction, the samples will be cooled and an accurate determination of the mineral abundance in the samples performed and to characterize the crystal lattice of the transformed minerals using X-ray diffraction analysis. Transmission electron microscopy (TEM) will be performed on the different reacted sulfate and the rehydrated phases to document the transformation processes. Potential rehydration of the reacted minerals will be examined to determine the degree of reversibility of the reacted minerals and their swelling levels. This will be performed by measurement of the levels of moisture uptake and by X-ray analysis of the crystal lattice.

The combination of experimental dehydration of discrete phases at elevated P,T conditions and subsequent characterization by TEM, and the in-situ characterization of hydrous phases at elevated T and atmospheric P (with variable water content) with the XRD environmental cell will be used to constrain sulfate dehydration and metastable phase fields in high heat load repository settings. Both dehydration experiments will provide data to answer questions 3 and 4 posed in Task 1.2.

4.3 List of equipment

The list of equipment that will be used to perform the activities described in the different tasks and a brief description of their performed uses are as follows:

1. *Real-time microscopic visualization system.*

The equipment consists of a state of the art microscopy system equipped with a digital camera, a high pressure cell and a microscopic heating stage. It can be used to monitor microscopic events at a rate of up to

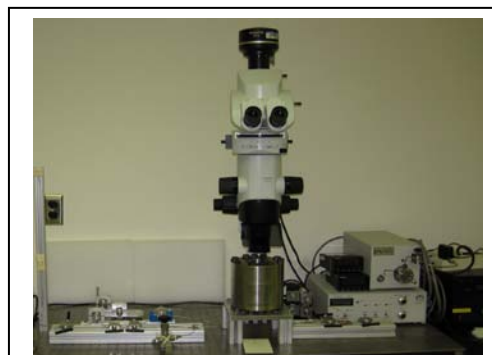


Figure 7 . DP72 microscope and digital camera system with a high pressure cell allowing direct visualization of specimens under high pressure and temperature conditions.

20 frames per second but can also be adjusted to monitor events for longer observation times (days) (Figure 7).

- 2. *Transmission electron Microscopy (TEM).*** TEM analysis will be performed in collaboration with Dr. Longzhu Ma from the University of Nevada, Las Vegas (Las Vegas, NV). All TEM analysis will be performed on a TECNAI-G2-F30 transmission electron microscope with a 300 keV field emission gun. The samples will be analyzed using the conventional bright-field (BF) mode and HRTEM mode. Localized fast Fourier transformed (FFT) micrographs will be also used in the analysis of the selected area electron diffraction (SAED) patterns and HRTEM images. The elemental distribution will be determined using the corresponding X-ray energy dispersive spectrometry (EDX) of the scanning transmission electron microscopy (STEM) mode. The TEM samples will be prepared by a solution-drop method deposition of a direct deposition of the dehydrated samples.
- 3. *X-ray diffraction (XRD).***
Powder diffraction analysis and in-situ characterization of structural changes occurring in secondary mineral phases associated with salt will be performed on a Bruker D8 diffractometer equipped with a humidity and temperature control cell that allows temperature control from ambient to up to 400 °C and RH of 10 to 90 % (Figure 6).
- 4. *Scanning electron microscope (SEM).***
SEM analyses will be performed using a FEI InspectF instrument available to us at the MST-6 facility at LANL.
- 5. *Thermogravimetric analyzer (TG-DSC).***
We will use a Simultaneous Thermogravimetry - Differential Scanning Calorimetry - STA (TG-DSC) available to the GGRL at Los Alamos national Laboratory. Data acquisition and interpretation will be coordinated with Dr. Hongwu Xu. The instrument allows the simultaneous application of Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) to a single sample and yields more information than separate application in two different instruments. The instrument allows the acquisition of TG and DSC signals under identical conditions (same atmosphere, flow rate, vapor pressure on the sample, heating rate, thermal contact to the sample crucible and sensor, radiation effect, etc.).
- 6. *High pressure, hydrothermal laboratory.***
The experiments will utilize LANL's unique high pressure, hydrothermal laboratory. Our experimental setup allows one to run reactions at high pressures of up to 200 bar and temperatures in excess of 300 °C.

The reaction cells that contain the experimental mixtures will be either gold (see Figure 5) or titanium bags and will be sealed within steel pressure vessels (Figure 8 right). The vessels will then be inserted in 400 °C/600 bar rocking autoclave.



Figure 8. Left: Rocking autoclave rack (400 °C/600 bar)
Right: AE (Bridgeman seal-type) pressure vessel, for 600 °C/1.5 kbar furnaces (vessel is ~24" tall).

Cold seal reaction vessels following the design of London will also be utilized. Cold Seal reaction vessels are depicted in (Figure 5, right). The vessels containing the reactive materials will be inserted into furnaces that can attain a maximum temperature of 800°C. A furnace designed by Mellon Co., similar to one depicted in Figure 9, is on order and will be used for heating the samples. This type of reaction vessel is extremely useful due to the smaller size and ability to track and contain samples. This allows for much more precise experimental material parameters.

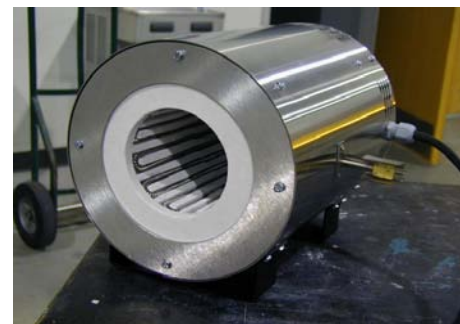


Figure 9. Furnace for Cold Seal reaction vessels. Note that inner mullite sleeve is not yet inserted in this photograph.

7.0 *Tri-axial high pressure system.*

A schematic representation of the high pressure system is shown in Figure 4. This apparatus, which has been used for multiple rock physics experiments was designed by the EES division at LANL and is unique in the following ways. The equipment is designed to hold a sample core with a diameter of 2.5 cm and up to 50 cm long. The salt core can be subjected to confining pressures of up to 10000 psi and temperatures of up to 300 °C. Thermocouples will be implanted at regular intervals (5 cm) to monitor for expected thermal gradients.

4.4 **Procedures development**

Performing work related to tasks 1 will require the development of work control documents (IWD's) to specifically address the hazards related to working with localized heat sources of up to 300 °C. Work related to tasks 3.3 will require modification of an

existing IWD for the tri axial high pressure system to address the hazards related to the introduction of a point heat source of up to 300 °C.

Work related to task 3 (3.2 and 3.4) will be performed under our existing IWD's "EES14-GGRL-Core Flood" and "EES14-GGRL-Hydrothermal"

5. Timetable of Proposed Work

FY 2013. (anticipated budget -\$330 K) In the first fiscal year of the project we will begin the experiments on Task 1.1. We anticipate being able to track brine movement in both single crystals of salt and adjoining salt crystals (boundary conditions at interfaces). In addition, we will perform initial studies on Tasks 3.1, 3.2 and 3.4 (clay dehydration and sulfate dehydration, respectively).

FY 2014. (Request for budget of \$1300K) In the next year we will focus on detailed characterization of the following Tasks : 1.2, 2.1, and 3.3. In addition we will finish Tasks 1.1, 3.2, and 3.4. Specifically, we will compare clay interaction with salt at elevated temperatures, make the transition from microscopic scale experiments to core size samples, and compare dehydration data to international published results. During this year we will submit for publication manuscripts on early results of brine migration at the microscopic scale and dehydration events. Our novel characterization methods will be transferred within LANL (and to Used Fuel Campaign) and used to assess two phase fluid flow in confined media. Additionally this research will be integrated with LANL SDI modeling efforts.

FY 2015. (Request for budget of \$1300K) In the next year we will focus on detailed characterization of the following Task :1.3. In addition we will finish Tasks 1.2, 3.1, and 3.3. Specifically, we will finish comparing clay interaction with salt at elevated temperatures, characterize the transition from microscopic scale experiments to core size samples, and compare all the brine migration data at multiple scales to international published results. During this year we will submit for publication manuscripts on all results of brine migration at the microscopic scale and dehydration events. Our novel characterization methods will be fully integrated with LANL SDI modeling efforts used to assess two phase fluid flow in confined media

FY 2016. (Request for budget of \$1400K) In this year we will investigate the mechanism(s) and rates of brine migration in salt core (dimensions) subjected to temperature gradient and axial pressure using a high pressure system. The rate of water release and the transformation of the water inclusions will be determined, analyzed and compared to existing literature data. Redistribution of water the salt core will be analyzed for the multiple scales (within a single crystal, at grain boundaries between crystals, and within the entire salt core). Results of these experiments will be analyzed to extract the mechanisms and parameters that affect brine migration.

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APPENDIX A

Review of Brines, Brine Chemistry, and Brine Migration in a Salt Repository for Spent Fuel or HLW

July 2, 2012

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1 BACKGROUND

This section briefly reviews the projects that investigated the disposal of spent fuel or high-level radioactive waste (HLW) in salt formations to provide the context for the studies of brines and brine migration described in subsequent sections.

The Federal Republic of Germany and the United States have investigated possible disposal of spent fuel or HLW in salt. Germany has investigated salt domes, the U.S. mainly bedded-salt formations. IN addition, the U.S. Department of Energy (DOE) opened the Waste Isolation Pilot Plant (WIPP) in March 1999 for disposal of defense-related transuranic (TRU) waste in a bedded-salt formation and has been emplacing TRU waste in the WIPP since then.

1.1 Recommendation of Salt for Disposal of Radioactive Wastes

The Earth Sciences Division of the National Research Council (NRC) organized a meeting of geologists and engineers in September 1955 to discuss possible deep geologic disposal of radioactive wastes (Boegly et al., 1966). Those present concluded that salt is the most promising geologic medium for the disposal of solid or liquid radioactive wastes. According to Boegly et al. (1966), the advantages of salt relative to other geologic media are:

1. Salt formations are widely distributed throughout the U.S. There exist formations in the U.S. that are located in areas with low seismicity (i.e., tectonically stable areas).
2. The thermal conductivity of salt is high relative to other rocks and would thus allow larger quantities of heat to be dissipated. Furthermore, the minerals in salt formations have high thermal stabilities.
3. Salt has a high compressive strength (similar to that of concrete) but, unlike most other rocks, it would flow plastically and remove the stress produced by mining and heating. Viscoplastic deformation of salt in response to the pressure imposed by overlying formations (creep) would close the boreholes and drifts used to dispose of radioactive waste and eventually encapsulate the waste. The rate of creep closure increases with pressure (depth) and the temperature of the waste.
4. Salt is essentially impermeable because of its plastic behavior under pressure. Therefore, any cracks that might develop would be self-healing.
5. The cost of mining salt is less than that of most other rocks.

As a result of this meeting and subsequent deliberations, the NRC recommended deep geologic disposal, especially in salt, for radioactive wastes in 1957 (NRC, 1957).

1.2 Disposal of Radioactive Wastes in Domal Salt Formations in Germany

In 1963, the Second German Atomic Program also recommended salt for disposal of radioactive wastes, including spent fuel and HLW. A report by the Federal Institute for Soil Research, now the Federal Institute for Geosciences and Natural Resources (the German Geologic Survey) agreed with these recommendations (DBE, 2011).

As a result, the German government purchased the abandoned Asse salt mine in 1964 for research and development (R&D) related to radioactive waste disposal. The Asse mine, located in the state of Lower Saxony in one of the more than 200 salt domes in northern Germany, had produced potash and rock salt from 1909 to 1964. Research and development began at Asse in 1965; disposal of low-level waste (LLW) began there in 1967; and disposal of intermediate-level waste (ILW) began in 1972. During the 1970s, a series of high-temperature in situ experiments were carried out to study the thermal and thermomechanical behavior of domal salt. In the 1980s, a new drift was excavated for brine-migration tests; data on room closure were collected during construction of this drift. The brine-migration tests simulated borehole disposal of HLW (DBE, 2011). In the 1990s, the Thermal Simulation of Drift Emplacement experiment simulated HLW disposal in drifts (Rothfuchs et al., 1988).

The German government also began a survey in 1974 to determine a suitable location for an integrated nuclear waste management center. Preliminary site-characterization studies were started at three locations in Lower Saxony, but were terminated in 1976 after protests at all three sites and opposition from the government of Lower Saxony. The government of Lower Saxony appointed its own task force to select suitable locations for the integrated nuclear waste management center in 1976 and nominated the Gorleben salt dome as a possible repository for LLW, ILW, and HLW in 1977. Surface exploration (geologic mapping, geophysical surveys, hydrogeologic studies, etc.), started at Gorleben in 1979, and was essentially completed in 1985. The first shaft was excavated from 1986 to 1997, and a second shaft was excavated from 1989 through 1995. Excavation of drifts and development of underground infrastructure began in 1995 (Anonymous, 2005, DBE, 2011).

A coalition of the Social Democrats and the Alliance '90/The Greens took control of the Bundestag after winning the 1998 German federal election held that year. In 2000, this coalition government decided to: (1) phase out the use of nuclear power in Germany, (2) stop reprocessing spent fuel after June 30, 2005, (3) halt most work on the Gorleben site for a period of three to ten years, and (4) consider the disposal of heat-generating radioactive waste in argillaceous rock (shale) and crystalline rocks (granite or related igneous or metamorphic rocks), two rock types that have been studied extensively in other European countries (Anonymous, 2005). In Germany, all radioactive waste is classified as “waste with negligible heat generation,” (LLW and some ILW) or “heat-generating waste” (spent fuel, HLW, and some ILW) (Stenhouse et al., 2010).

Comparisons of the disposal of heat-generating radioactive waste in clay, granite, and salt resulted in renewed interest in salt; the moratorium on characterization of Gorleben ended in 2010. However, clay and granite are still under consideration in Germany (Stenhouse et al., 2010).

Furthermore, concerns about carbon-dioxide emissions and global warming led many to reconsider Germany's decision to phase-out nuclear power. However, reaction to the recent Fukushima Daiichi accident in Japan has reinvigorated public pressure to phase-out the use of nuclear power in Germany (DBE, 2011).

In addition to Asse and Gorleben, Germany has conducted studies at Morsleben, an abandoned salt mine in the East German state of Saxony-Anhalt, and Konrad a former iron mine in Lower Saxony. Both of these mines were used for disposal of LLW and/or ILW (Anonymous, 2005; DBE, 2011).

1.3 Disposal of Radioactive Wastes in Bedded Salt Formations in the U.S.A.

Meanwhile, back in the U.S.A., Oak Ridge National Laboratory (ORNL) carried out Project Salt Vault for the Atomic Energy Commission (AEC) from 1965 to 1967 to evaluate disposal of HLW in salt. ORNL conducted this project in a mine in a bedded salt formation near Lyons, Kansas. The results initially appeared to be favorable and did not identify any processes that ruled out bedded salt for disposal of HLW. Therefore, the AEC tentatively selected Lyons as a potential site for a repository in 1970 and the NAS tentatively endorsed this selection (NRC, 1970).

The Hutchinson Member of the Permian Wellington Formation (Fm.), which was tentatively selected to host the repository, is about 300 ft thick at the Lyons site and extends from a depth of 780 to 1080 ft subsurface. It consists of about 60% halite (NaCl) interbedded with shale and anhydrite (CaSO₄) (NRC, 1970).

The NRC (1970) recommended that the AEC carry out several studies to resolve “several site problems ... before radioactive materials are committed to the salt beds.” One of these issues was that:

Location of previous oil and gas wells and inspection of records, where available, should determine if these former wells have been adequately plugged to avoid an entrance of water to the salt.

Recommendation: A survey should be made of neighboring wells in order to avoid threats to the integrity of the proposed bedded salt disposal site.

The AEC completed a conceptual design for a repository for HLW and TRU waste in 1971. However, two serious problems with the Lyons site arose in 1971: (1) numerous exploratory boreholes for oil and gas discovered near the site had not been identified or recorded during site characterization; (2) solution mining about three miles from the proposed site often resulted in large, unexplained losses of water, which was considered to be an unfavorable characteristic. Consequently, the AEC abandoned the Lyons site in 1972 (Mora, 1999).

ORNL and the U.S. Geological Survey (USGS) restarted site-selection activities for the AEC in the Permian Basin in 1972. The AEC designated the Los Medaños (“The Dunes”) area as its “prime study area in 1973; this area included the current WIPP site. The U.S. Congress passed the Energy Reorganization Act in 1974. This legislation split the AEC into the Energy Research and Development Administration (ERDA) and the Nuclear Regulatory Commission in 1975. Also that year, the ERDA chose Sandia National Laboratories (SNL) as the scientific advisor for the new bedded-salt project. SNL and the USGS identified a “prime exploration zone” within the Los Medaños area in early 1976, and identified the current site within this zone by the end of 1976. The ERDA also designated the project as the WIPP Project in 1976. These site-selection activities all focused on the Salado Formation (Fm.), a thick, Permian bedded-salt formation, as the host formation for the WIPP.

Congress combined the ERDA and the Federal Energy Administration into the U.S DOE, America's 12th cabinet-level department, in 1977. During the mid-to-late 1970s, the ERDA and the DOE considered the possibility of using the WIPP for disposal of commercial spent fuel and HLW and/or defense HLW in addition to TRU waste. Some ERDA and DOE officials envisioned a two-level repository with TRU waste in the upper level of the repository and spent fuel and HLW 500 m below it. However, the WIPP Authorization Act, passed by Congress in 1979, restricted the WIPP to defense-related TRU waste.

Nevertheless, the DOE used an experimental area in the northern part of the WIPP underground workings to carry out studies relevant to the behavior of spent fuel or HLW in bedded salt during the 1980s and early 1990s (see Subsection 2.1.3 below). The DOE also funded laboratory studies of waste-package materials for spent fuel or HLW (Subsection 3.2.1). The objective of these studies was to provide information applicable to a potential salt repository for spent fuel or HLW at sites other than the WIPP site. Furthermore, the DOE's characterization and licensing of the WIPP for TRU waste provided invaluable information that can be applied to the disposal of spent fuel or HLW in salt, especially bedded salt. Therefore, results obtained from studies of the WIPP site are included in many of the following discussions.

The DOE developed the WIPP site as a repository for defense-related, TRU waste from 1981 through 1988. This included: (1) excavation of four shafts, access drifts, design-validation, and experimental rooms; (2) construction of surface waste-handling facilities and support buildings; (3) excavation of Panel 1, the first of the ten panels required for disposal of the WIPP contact-and remote-handled TRU waste inventory. Congress passed the WIPP Land Withdrawal Act (LWA) in 1992. The LWA transferred the WIPP site to the DOE and designated the U.S. Environmental Protection Agency as the main WIPP regulator. The DOE submitted its Compliance Certification Application (CCA) to the EPA in 1996 (U.S. DOE, 1996). The EPA reviewed the CCA and certified that the WIPP complied with its regulations for TRU waste in 1998 (U.S. EPA, 1998). The WIPP opened in 1999. Because the LWA also specifies that the DOE must submit a compliance recertification application to the EPA every five years after the 1999 opening of the WIPP, the DOE submitted these applications in 2004 and 2009 (U.S. DOE, 2004; 2009); and the EPA recertified the WIPP in 2006 and 2010 (U.S. EPA, 2006, 2010).

The DOE's Salt Repository Project (SRP) also investigated the possible disposal of (mainly) commercial spent fuel and defense HLW in bedded salt. The SRP was one of three major projects that partially characterized sites for possible use as repositories for spent fuel and HLW under the Nuclear Waste Policy Act (NWPA) of 1982 (U.S. DOE, 1986). The other two were the Basalt Waste Isolation Project (BWIP), which investigated basalts of the Columbia River Group near Hanford, Washington; and the Nevada Nuclear Waste Storage Investigations (NNWSI) Project, which later became the Yucca Mountain Project (YMP). Congress terminated the SRP (and the BWIP) when it amended the NWPA in 1987 to designate Yucca Mountain as the only potential site for spent fuel or HLW to be characterized, and renamed the NNWSI Project the YMP.

The SRP selected a site in Deaf Smith County, TX, as the site to be characterized for a possible salt repository for spent fuel and HLW. As in the case of the WIPP Project, the SRP selected the Salado Fm. as the host formation. At the Deaf Smith Co. site, the Salado is also a bedded-salt formation. However, the salt section, which also includes evaporite deposits above and below the Salado, is thinner at the Deaf Smith Co. site than at the WIPP site.

In addition to these three major site-characterization projects, the DOE also carried out preliminary site-screening activities that included other bedded-salt formations and salt domes along the Gulf Coast. These activities included an in situ brine-migration experiment in the preexisting Avery Island salt mine, Avery Island, LA (Krause, 1983). This test is described in Subsection 2.1.2 (see below).

2 OCCURRENCE OF BRINES AND POSSIBLE BRINE MIGRATION IN A SALT REPOSITORY

2.1 Introduction

Roedder (1984) stated that:

The fluids in salt consist of two very different types that might be termed “external” and “internal.” “External” fluids consist of incursions of outside waters, as have taken place in numerous salt mines in the past. An artificial cavity far below the water table is basically unstable; those in salt are especially subject to flooding as the flow of water through any leak dissolves salt and opens the passage to more flow. The recent flooding of the salt mine at Jefferson Island salt dome, Louisiana (Groat, 1981) apparently started from a drilling accident, but many other mines have filled, some catastrophically, generally after starting with natural leaks of unknown source. ...

The “internal” fluids are those that are essentially inherent to the salt, although they may have originally come from external sources. They include the various types of fluid inclusions, and since radioactive waste will cause heating and decomposition of at least some hydrous minerals, they also include water in hydrous minerals in the beds.

Clearly, the possibility that fluids from external sources might enter a repository must be evaluated as part of the safety case for disposal of spent fuel or HLW in salt. However, these fluids will not be considered further in this report; instead, the reader is referred to sources such as Groat (1981), Kumar and Martinez (1981), Knauth et al. (1980), Knauth and Kumar (1983), and Kumar (1983).

The water (brine) content of domal salt is on the order of thousandths, hundredths, or tenths of a wt. %; that of bedded salt is on the order of tenths to a few wt % (Roedder and Belkin, 1979; Jockwer, 1981; Knauth and Kumar, 1981; Roedder and Bassett, 1981; Rothfuchs, 1986; De Las Cuevas and Pueyo, 1995). These brines are present within individual salt crystals (i.e., intragranular brine or fluid inclusions), along the boundaries between salt crystals (intergranular brine), and as structural water in hydrous minerals such as clay minerals and the evaporite minerals gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and polyhalite ($\text{K}_2\text{MgCa}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$).

The ionic strength of these brines is high relative to the fluids in most other geologic media, although brines can occur in nonevaporitic rocks such as granites.

Redox conditions in salt are usually poorly poised (i.e., neither oxidizing nor reducing agents are present in sufficient quantities to affect the oxidation states of elements that can speciate in more than one oxidation state). Because of this feature and the very low permeability of salt, the processes that occur in a salt repository for radioactive waste will determine the Eh or f_{O_2} . These include, but are not necessarily limited to reduction of

the water in brine by steels or other Fe-base materials in waste packages (see below), microbial consumption of organic constituents of ILW or TRU waste, and radiolysis.

2.2 Compositions of Some Representative Brines

The Germans typically use three standard brines for their laboratory and modeling studies: Brine 1, also referred to as “Q brine,” with 26.8 wt % MgCl₂; Brine 2, with 33.03 wt % MgCl₂; and Brine 3, which is essentially an NaCl-saturated brine with much lower concentrations of MgSO₄, K₂SO₄, and CaSO₄ (Kursten et al., 2004). Table 1 provides the chemical compositions of these brines.

Table 1. Chemical Compositions of Standard Brines Used for German Studies of Waste-Package Materials for Spent Fuel or HLW in a Salt Repository (Kursten et al., 2004, Table 4-3).

Dissolved Concentration (wt %) or Property	Brine 1 (Q Brine)	Brine 2	Brine 3
NaCl	1.4	0.31	25.9
MgCl ₂	26.8	33.03	-
MgSO ₄	1.4	-	0.16
K ₂ SO ₄	-	-	0.23
KCl	4.7	0.11	-
CaSO ₄	-	0.005	0.21
CaCl ₂	-	2.25	-
H ₂ O	65.7	64.3	73.5
Dissolved O ₂ (mg/L)	0.8-2.8	0.6-1.5	1.2-4.9
pH (scale unspecified)	4.3-4.6	4.1	6.5-6.9

The compositions of these brines are representative of those expected in the Gorleben salt dome (Kurstien et al., 2004). None of the publications or reports on the German waste-package work obtained to date explains why the standard brines 1, 2, and 3 were chosen. However, the choice of these brines appears to be analogous the SRP's choice of its intrusion brine PBB1 and its inclusion brine PBB3 (see below).

The WIPP Project initially used Brine A, an Na-Mg-K-Cl brine; and Brine B, an Na-Cl brine, as standard brines. Molecke (1976) and Dosch (1976) established these brines for use in WIPP-related laboratory studies, especially studies of the Ti-base alloy American Society for Testing and Materials (ASTM) Grade-12 Ti (usually referred to as TiCode-12) for possible use as a corrosion-resistant waste-package material in a salt repository for commercial spent fuel and HLW, and defense HLW. Because the 1979 WIPP Authorization Act restricted the WIPP to defense-related TRU waste (see Subsection 1.3 above), the objective of these studies was to provide information applicable to disposal of spent fuel or HLW in salt at possible sites other than the WIPP site.

Molecke (1983) described Brine A as:

[A] high Na-Mg-K chloride brine representative of brines that have interacted with potassium and magnesium minerals and could potentially intrude into a waste facility in bedded salt (e.g., a brine which might intrude into the WIPP waste horizon by percolation through an overlaying zone containing potash).

Molecke (1983) described Brine B as:

[A] near-saturated, predominantly NaCl brine representative of brines potentially intruding into either a domed salt repository or into relatively pure bedded halite.

Neither Brine A nor Brine B was necessarily representative of fluid inclusions in the Salado Fm. Molecke did not include brines typical of these fluid inclusions in studies of TiCode-12 as a possible waste-package material in a salt repository for thermally hot waste.

Stein (1985a, 1985b) studied the mineralogy of and fluid inclusions in the Salado Fm., respectively, and Stein and Krumhansl (1986, 1988) carried out additional studies of Salado fluid inclusions. They reported that there exist two populations of intragranular brines, based on differences in their major-element compositions. They concluded that: (1) both groups of fluid inclusions are compositionally and genetically distinct from brine weeps (intergranular brines that seep into the drifts immediately after excavation and evaporate, thereby depositing salts on the backs, floors, and ribs of the drifts); (2) these compositions could not be explained by a simple model of evaporation of Permian seawater; and (3) they resulted instead from the alteration of anhydrite or gypsum to polyhalite, and of various polymorphs of calcium carbonate (CaCO_3) to magnesite (MgCO_3).

Brush (1990) replaced Brine B with ERDA-6, and Snider (2003) replaced Brine A with GWB for the laboratory and modeling studies of near-field chemistry used in the long-term WIPP performance assessment (PA). GWB is a synthetic brine representative of intergranular

brines from the Salado Fm. at or near the stratigraphic horizon of the repository (Krumhansl et al., 1991; Snider, 2003). GWB does not simulate a specific, in situ, intergranular brine; rather, it is the average composition of numerous analyses of these grain-boundary fluids and, as such, it simulates the composition of brines that would accumulate in the repository after it is sealed, the panel closures are emplaced, and evaporation by the mine ventilation system ceases. ERDA-6 is typical of fluids in brine reservoirs in the underlying Castile Fm. (Popielak et al., 1983); this brine could enter the repository in the event that exploratory drilling for oil and gas, potash, or other resources inadvertently penetrates both the repository and a brine reservoir. Brines typical of fluid inclusions in the Salado were not included in these near-field chemical studies because intergranular (but not intragranular) brines, could enter the repository after it is filled and sealed. This is due to the fact that the contact- and remote-handled TRU waste being emplaced in the WIPP will not increase the temperature significantly above its in situ value of 28 °C at a subsurface depth of 655 m. Table 2 (see next page) provides the chemical compositions of Brine A, Brine B, GWB, and ERDA-6.

The U.S. DOE's WIPP management and operating contractor (M&O) also carried out the Brine Sampling and Evaluation Program (BSEP) to characterize the compositions and rates of accumulation of intergranular brines in the underground workings (Deal and Case, 1987; Deal et al., 1987; Deal, 1988; Deal and Roggenthen, 1989; 1991; Deal et al., 1989; 1991a; 1991b; 1993). Brush (1990) used the results of these studies to develop SB-3, another synthetic brine representative of intergranular Salado brines at or near the repository horizon.

It is worth noting that (1) the compositions of GWB and SB-3 are essentially identical, despite the fact that they were established independently from separate sets of samples analyzed by different laboratories; and (2) geochemical modeling has shown that these brines are at or close to equilibrium with the Salado minerals, which comprise ~93 % halite and 1-2 % each anhydrite, gypsum, polyhalite, magnesite, and clays (Stein, 1985a; Brush, 1990).

It is also worth noting that the compositional heterogeneity of the intergranular brines on the scale of a few centimeters implies that there is no interconnected porosity in the undisturbed, nearly pure halitic units of the Salado. However, dilation of the disturbed rock zone around newly excavated drifts does result in fracturing, and there are even some fractures in the relatively brittle anhydritic marker beds prior to excavation.

Table 2. Compositions of Brine A, Brine B, GWB, and ERDA-6 (M) and Other Parameters (units as noted).

Element or Property	Brine A ^A	Brine B ^A	GWB ^B	ERDA-6 ^C
B	0.020	0.020	0.158	0.063
Na	1.83	5.00	3.53	4.87
Mg	1.44	< 0.005	1.02	0.019
K	0.770	< 5	0.467	0.097

Ca	0.020	0.020	0.014	0.012
S	0.040	0.040	0.177	0.170
Cl	5.35	4.93	5.86	4.8
Br	0.010	0.010	0.0266	0.011
TIC	0.010	0.010	-	0.016
pH (Pitzer ^D)	6.5	-	-	6.17
SG	1.2	1.2	1.2	1.216

- A. Molecke (1983)
 B. Krumhansl et al. (1991) and Snider (2003b)
 C. Popielak et al. (1983)
 D. The “Pitzer scale” is an unofficial pH scale consistent with pH values calculated using single-ion activity coefficients based on the Pitzer activity-coefficient model for brines and evaporite minerals of Harvie et al. (1984), extended to include Nd(III), Am(III), and Cm(III); Th(IV); and Np(V). The term “Pitzer scale” was proposed unofficially by T. J. Wolery of Lawrence Livermore National Laboratory (LLNL) in Livermore, CA.

The U.S. DOE’s SRP specified various standard brines and solids for use in their laboratory studies: For example, Westerman et al. (1984) used Permian Basin Brines No. 1 and 2 (PBB1 and PBB2); Westerman et al. (1986) used PBB1, PBB2, and PBB3; and reagent-grade NaCl; Westerman et al. (1988) used the same three brines, but used PBB1 solids (the solids dissolved in PBB1) and a standard salt referred to as “surrogate salt.” It should also be noted that the reported compositions of these “standard” brines changed with time, especially that of PBB3 (compare Westerman et al., 1986, Table 2; and Westerman et al., 1988, Table 4.3) Table 3 (see next page) provides the chemical compositions of these brines and solids from Westerman et al. (1988, Table 4.3).

Table 3. Chemical Compositions of Standard Brines and Solids Used by PNNL for the SRP’s WPP (Westerman et al., 1988, Table 4.3)

Total Dissolved Elemental Concentrations	PBB1 Brine (mg/L)	PBB2 Brine (mg/L)	PBB3 Brine (mg/L)	Surrogate Salt (ppm)
Na	123,000	123,000	23,000	377,000
Mg	134	122	60,000	258
K	39	39	11,000	78
Ca	1,560	1,110	18,700	11,200
Sr	35	35	NA	78
HCO ₃	30	23	NA	246
SO ₄	3,200	1,910	250	26,900
Cl	191,000	191,000	240,000	583,000
Br	32	24	3,400	NA

The SRP established these standard brines based on its conclusion that there were two scenarios under which brines could form, migrate, and contact the waste packages in a bedded-salt repository for spent fuel or HLW (Westerman et al., 1988):

1. In the dissolution-brine scenario, low-ionic-strength groundwater was assumed to enter the repository horizon from some external source and dissolve rock salt, thereby attaining a composition a saturation similar to the overall composition of the formation (i.e., essentially an NaCl-saturated brine). This brine, referred to as “PBB1,” was established by dissolving samples of rock salt obtained from a subsurface depth of 743.77 to 785.01 m in the G. Friemel Hole No. 1; a depth corresponding to the halite horizon the San Andres Cycle 4 at the SRP’s study site in Deaf Smith County (Westerman et al., 1988).

PBB2, obtained by maintaining PBB1 in a pressurized autoclave at 150 °C for several days and then analyzing the supernatant solution, represents the composition of PBB1 after approaching or contacting the waste packages, heating, and precipitation of solids with retrograde solubilities (solubilities inversely proportional to temperature). Westerman et al. (1988, p. 4.7) concluded that these solids comprised mostly carbonates, but comparison of the compositions of PBB1 and PBB2 in Table 7 shows that anhydrite and/or gypsum also precipitated. Use of PBB2 also solved the problem of precipitation of these solids from PBB1 in the inlet lines of the flow-through autoclaves used for many of PNNL’s experiments.

2. In the inclusion-brine scenario, which the SRP considered more likely than the dissolution-brine scenario, fluid inclusions in the formation were assumed to migrate up the thermal gradient or down the pressure gradient towards the waste packages. The SRP expected that these inclusion brines would have higher $MgCl_2$ and $CaCl_2$ concentrations than the dissolution brines, based on analyses of fluid inclusions from the halite horizon in the San Andres Cycle 4 at the site (Westerman et al., 1988). (This report did not provide the actual results of these analyses, but did give the composition of PBB3 derived from them.)

2.3 Laboratory and Modeling Studies of Brine Migration

Numerous investigators carried out laboratory and/or modeling studies of the possible migration of fluid inclusions in thermal gradients imposed on NaCl, other alkali halides, or other soluble solids (e.g., Whitman, 1926; Young et al, 1959; Hoekstra et al., 1965; Bradshaw and Sanchez, 1969; Wilcox, 1969; Anthony and Cline, 1971; 1972; 1973; Cline and Anthony, 1972; 1977; Hohlfelder and Hadley, 1979; Lambert, 1979; Roedder and Belkin, 1980; Hadley, 1981; Hadley and Faris, 1981; Jenks and Claiborne, 1981; Jockwer, 1981; Olander, 1982; Olander et al., 1982; Pigford, 1982; Carter and Hansen, 1983; Yagnik, 1983; Olander, 1984; Müller, 1985; Schlich and Jockwer, 1985; Yih, 1986; Hwang et al., 1990). Nevertheless, this process remains controversial. Some investigators who have worked on disposal of spent fuel or HLW in salt, but not necessarily on brine migration, have concluded that this is a “showstopper”; others have concluded that is an “urban legend.” (No references have been identified yet for either one of these strong but often-stated opinions.)

Some conclusions that might be relevant to the behavior of waste-package materials, and their potential effect on repository conditions, are:

1. All-liquid (brine-filled) fluid inclusions may move up the thermal gradient toward the heat source. Clearly, this process would bring intragranular and (perhaps) intergranular brine (see below) into contact with the waste packages if it were to occur in a repository for spent fuel or HLW. However, this remains controversial because, while some investigators concluded that fluid inclusions cannot cross grain boundaries, others reported that they did cross grain boundaries, or at least moved along these boundaries with a component of motion in the direction of the heat source.

2. Gas-liquid fluid inclusions may move down the thermal gradient if the gas bubble in the inclusion is large enough. Based on all of the references identified to date, Wilcox (1969), paraphrasing the discussion of Young et al. (1959), offered the best explanation for this phenomenon:

The experimental evidence shows that gravity is not required for the solution to return from the cool to the hot side of the bubble. It is proposed that surface tension supplies the driving force for this circulation. Due to the evaporation-condensation process, the salt concentration is higher on the hot side of the bubble. Since surface tension increases with salt concentration, a surface tension gradient is produced. The gradient in surface tension then causes circulation from the low- to the high-surface tension region and also causes a net force on the bubble directed toward the low-surface tension region [Young et al., 1959]. Thus, for example, heating the crystal from above causes the bubble to move down the inclusion and produces dissolution at the bottom.

The above mechanism must also be responsible for bubbles moving away from the heat source in liquid inclusions of natural crystals.

Movement of gas-liquid fluid inclusions down the thermal gradient has been identified as a process that could transport radioelements away from breached waste packages, albeit for short distances. However, this process could just as likely be beneficial for the performance of a salt repository for spent fuel or HLW, inasmuch as it could also transport brine away from the waste packages before it could corrode waste-package materials.

3. Brine migration up (or down) a thermal gradient is more likely to be significant in a bedded-salt repository than in a domal-salt repository, because the brine content of the former typically exceeds that of the latter by a factor of 50 to 100 (see above).

2.4 Field Studies of Brine Migration

There have been at least four in situ studies of brine migration in response to thermal gradients in bedded or domal salt formations. These included: (1) the cavity-migration test included in Project Salt Vault (Bradshaw and McClain, 1971), (2) the Avery Island, LA, brine-

migration test (Krause, 1983); (3) the WIPP brine-migration study (Nowak, 1986; Nowak and McTigue, 1987), and (4) the German-American brine-migration test in the Asse salt mine in Lower Saxony, Germany (Rothfuchs et al., 1988).

2.4.1 Project Salt Vault Cavity-Migration Test

ORNL carried out Project Salt Vault in a mine near Lyons, KS, from 1965 to 1967 for the AEC. ORNL conducted several in situ tests with electrical heaters and spent-fuel assemblies to simulate the response of a bedded-salt repository to spent fuel or HLW (Bradshaw and McClain, 1971). In one of these tests, ORNL quantified the amount of brine that migrated into three boreholes, each with a 1.5 kW heater, in separate rooms (designated rooms 1, 4, and 5) in new workings excavated for the project. Each of these boreholes contained an “off-gas condensate collection system” to quantify the amount of brine collected during the ~12-to-19-month tests. ORNL turned on the electrical heaters in rooms 1 and 4 on November 15, 1965; and began the test in room 5 on June 6, 1966. ORNL intended to maintain a maximum temperature of 200 °C in the salt adjacent to the midplanes of the boreholes. However, various problems resulted in variable maxima of 150–200 °C in rooms 1 and 4, and a maximum of 142 °C in room 5, despite increases to the power applied to the heaters (eventually up to 2.1 kW) and modifications to prevent loss of heat from the salt through the floors of the rooms. ORNL turned off all three heaters on June 5, 1967 (Bradshaw and McClain, 1971).

The total amounts of water collected (and the rates at which they were collected) during the heater tests were ~1.7 L (0.43 mL/day) in room 1; 0.8 L (0.22 mL/day) in room 4; and 3.1 L (10–93 mL/day) in room 5 (Bradshaw and McClain, 1971, described the uncertainties responsible for the range of rates reported for room 5).

ORNL conducted pretest modeling and laboratory studies to predict the amount of brine migration that would occur during the in situ tests (Bradshaw and McClain, 1971). Bradshaw and McClain (1971) used: (1) the equations for theoretical predictions of the temperature-dependent solubility and diffusion of H₂O from the high- to low-temperature ends of fluid inclusions in ice (Hoekstra et al., 1965), corrected for the different densities of and thermal gradients in seawater inclusions and the surrounding ice (Seidensticker, 1966); (2) the assumption that the salt in the Lyons mine contains 0.5 vol % brine; and (3) confirmatory laboratory experiments with fluid inclusions in single crystals of halite. They concluded that

“[O]ne might expect a total inflow per waste [package] disposal hole of perhaps 2 to 10 liters, taking place over a period of 20 to 30 years after burial. The peak inflow rate would occur at around one year after burial and be somewhere in the range of 200 ml to 1 liter per year per hole. This corresponds to about ½ to 3 ml per day per hole, a range similar to that estimated in the demonstration waste container holes. This water inflow rate would be expected to taper off and approach zero after 20 to 30 years. Other considerations indicate that such volumes and inflow rates will be tolerable in a waste disposal facility.

Therefore, the predicted and observed values were in good agreement.

2.4.2 Avery Island Brine-Migration Test

RE/SPEC Inc. carried out brine-migration tests in domal salt in the Avery Island salt mine, near New Iberia, LA, from 1979 to 1981 as part of the DOE's National Waste Terminal Storage Program (NWTS). RESPEC used three boreholes, spaced 15 m apart in the same room, to quantify: (1) migration of the naturally occurring brine in the salt under ambient (unheated) conditions (Site AB), (2) migration of naturally occurring brine under heated conditions (Site NB), and (3) migration of naturally occurring and synthetic, isotopically (D_2O -)labeled brine under heated conditions (Site SB) (Krause, 1983). Each of the three central boreholes at Sites AB, NB, and SB each contained a water-collection system; the central boreholes at Sites NB and SB also contained ~ 1.0 kW electrical heaters. RESPEC turned on these heaters on October 4, 1979. According to Krause (1983, p. 2) the heater at NB operated at or near its nominal power for ~ 350 days, after which the power was reduced by ~ 30 watts per day for 30 days; the heater at Site 3B operated at nominal power for ~ 325 days, after which it was reduced by 20% per day for 5 days. Krause (1983, Table 3), however, stated that both heaters operated for 315 days. After steady-state conditions had been attained, the maximum temperature in the salt adjacent to the midplanes of the boreholes was 51 °C. Krause (1983) did not explain why the maximum temperature was so low during these tests. (Most in situ, laboratory, and modeling studies carried out under the NWTS around this time assumed a maximum near-field temperature of 200 °C or higher.)

Krause (1983) reported that the masses of water collected from the heated salt at Sites NB and SB and the steady-state rates at which it was collected were approximately twice those observed under ambient conditions (Site AB). He subtracted the mass of water collected at Site AB and the steady-state rate at which it was collected from the measured masses and rates at Sites NB and SB. The total masses collected at Sites NB and SB that were attributed to heating were 8.27 and 5.10 g, respectively; the steady-state rates attributed to heating were 0.0175 and 0.0107 g/day. Note that the duration of water collection, 205 days at Site NB and 235 days at Site SB, was less in both cases than the duration of heating (see above).

Krause (1983) used the model of Antony and Cline (1971) to predict the masses of brine to be collected at Site NB and SB. This model included: (1) the equations for the temperature-dependent solubility and diffusion (both Fickian and Soret) of KCl from the high- to low-temperature ends of fluid inclusions in single crystals of sylvite (KCl) (Antony and Cline, 1971), and (2) temperature-dependent material properties for saturated NaCl solutions and halite from various sources. For example, Martinez et al. (1980) reported that the brine content of the brine content of intact Avery Island salt varies from 0.02-0.10 wt %; but Krause (1983) concluded that the brine content of the salt adjacent to the heated boreholes contained 0.054 wt %. Krause (1983) computed that the maximum thermal gradient in the salt was 1.44 °C/cm, and the maximum depth in the salt from which brine was removed during the heater tests was about 5 mm. Most important, Krause (1983) calculated that, for a period equivalent to that of the operation of the heaters at Sites NB and SB, the total brine migration would be 5.44 g with a steady state rate of 0.0173 g/day. Therefore, the predicted and observed values agreed well. Krause (1983) did not predict the total amount of brine that would migrate during the thermal period expected for spent fuel or HLW in domal salt.

2.4.3 WIPP Brine-Migration Study

SNL performed brine-migration tests in the northern (experimental) part of the WIPP underground workings in the mid-to-late 1980s (Nowak, 1986; Nowak and McTigue, 1987). SNL used four boreholes in two rooms (boreholes A1041 and A1042 in room A1; and boreholes B041 and B042 in room B). Boreholes A1041 and A1042 each contained a 470 W electrical heater to simulate a defense HLW (DHLW) canister. Boreholes B041 and B042 contained 1.5 kW electrical heaters to establish near-field overtest conditions. All four boreholes contained water-collection systems. During the 7.1 days prior to heating in room A1, SNL collected a total of 230 g of water from borehole A1041 (32 g/day) and 90 g from borehole A1042 (13 g/day). In the 4.2 days prior to heating in room B, SNL collected a total of 22.4 g of water from borehole B041 (5.33 g/day) and 19.3 g of water from borehole B042 (4.60 g/day).

SNL turned on the heaters in room B on April 23, 1985, and in room A1 on October 2, 1985 (Nowak, 1986). The maximum temperatures in the salt adjacent to the midplanes of the boreholes increased exponentially throughout the 441- and 600-day periods described by Nowak and McTigue (1987), eventually rising to 55 °C in boreholes A1041 and A1042 at 441 days, and to 120 °C in borehole B041 and 130 °C in borehole B042 by 600 days. After the heaters were turned on, the water-collection rates rose to a peak, decreased, and then remained nearly constant for 441 days (boreholes A1041 and A1042) or 600 days (boreholes B041 and B042). The total masses of water collected in the boreholes in room A1 were both 4.3 kg at 441 days. Neglecting a couple of outliers, the collection rates in these boreholes peaked at about 17 g/day in borehole A1041 and 14-15 g/day in borehole A1042 then decreased to about 8 g/day in both boreholes by 441 days. The total masses collected in room B and were 36 and 38 kg in boreholes B014 and B042, respectively, at 600 days. The maximum rates could not be determined in these boreholes because they exceeded 30 g/day, the most that could be measured by these systems. The rates decreased to about 20 and 50 g/day at 600 days.

Nowak and McTigue (1987) used a Darcy flow model to predict the brine-migration rate prior to heating. Their model used one-dimensional radial flow to a circular tunnel caused by the pore-pressure gradient established by mining the rooms used for their study. Their results were relatively insensitive to whether the upper end of the pore-pressure gradient was hydrostatic or lithostatic, and obtained water mass-flow rates of 10 g/day with permeabilities in the range of 10^{-20} to 10^{-18} m² (10^{-8} to 10^{-6} darcy), which they considered to be representative of the permeabilities measured in the Salado by that time. However, their attempt to predict the effect of heating on the brine-migration rate by incorporation of temperature-dependent viscosity was unsuccessful; they predicted increases that were significantly less than those observed. Nowak and McTigue (1987) did not attempt to include brine migration in response to the thermal gradients caused by heating in their model and concluded that vapor-phase migration of water was insignificant in their experiments.

2.4.4 Asse Brine-Migration Test

The German-American brine-migration test was carried out in the Ass salt mine in Lower Saxony, Germany, during the early-to-mid 1980s. The Institut für Tieflagerung (IfT), or Institute for Underground Disposal, in Braunschweig, Lower Saxony; part of the Gesellschaft für Strahlen- und Umweltforschung mbh München (GSF), or Corporation for Radiation and Environmental Research, participated on behalf of Germany. The Office of Nuclear Waste Isolation (ONWI), in Columbus, OH, managed by the Battelle Memorial Institute for the DOE's Civilian Radioactive Waste management Program, participated on behalf of the U.S. Westinghouse – Advanced Energy Systems (WAESD), a subcontractor to ONWI, designed the test facility and fabricated most of the test equipment and instrumentation, except for the radiation source handling system, which was designed and fabricated by GANUL mbh under a subcontract with the GSF-IfT. Rothfuchs et al. (1988) provided the final report for this test.

The Asse brine-migration test was conducted in a test room mined from December 1981 through March 1982 at the 800 m level of the mine. The boreholes for the test, including the pretest core samples, were drilled from June through December 1982. The test equipment and instrumentation were installed from March through May 1983. The test comprised four test sites spaced 15 m apart. Each test site contained a central borehole for an electrical heater and, in the case of test sites 3 and 4, two 9430 Ci ^{60}Co sources ($t_{1/2} = 5.3$ years) with an initial power of 145 W. In addition to the central heater and (at test sites 3 and 4) the ^{60}Co sources, there were eight “guard heaters” (peripheral heaters) in an octagonal array of boreholes 1.5 m from the centerline of the central borehole.

All four test sites were deployed in the Main Halite, which contains more water than most of the other units in the Asse (see below). Test sites 2 and 4 collected water continuously from their central boreholes, at tests sites 1 and 3, the pressure was allowed to build-up and the water content was determined at the end of the test.

Power was applied to the heaters at tests sites 1 and 2 on May 25, 1983. To obtain a maximum temperature of ~ 210 °C in the salt adjacent to the midplanes of the central boreholes the power on the central heater was set to 2530 W and the total power on the guard heaters was set to 7220 W. However, this power was inadequate to establish a maximum temperature of 210 C, so the power on the central heater was increased to 3000 W on September 12, 1983. The ^{60}Co sources were installed at test sites 3 and 4 on December 13 and 14, 1983, and the power was turned on at these test sites on December 15 (central heater power = 2710 W; guard heater power = 7220 W). The guard heater power at test site 4 was increased to 7600 W on March 14, 1984; the central heater power at that site was increased to 2810 W on June 5, 1984, and to 2850 W on June 12 of that year. These adjustments maintained the maximum temperatures in the salt close to 210 °C. On October 4, 1985, power reductions began on the central and guard heaters at all four test sites after 863 days of heating at test sites 1 and 2 and 659 days of heating (and 660 and 661 days of irradiation, respectively) at test sites 3 and 4.

The power on all the heaters was turned off completely on October 28.

Rothfuchs et al. (1988) reported that the total volumes of brine that flowed into the central boreholes were 125, 125, 100, and 137 mL at test sites 1, 2, 3, and 4, respectively.

The average collection rates, obtained by dividing these volumes by 863 or 659 days of heating, were 0.145, 0.145, 0.152, and 0.208 mL/day.

Pretest modeling of the Asse brine-migration test was conducted using: (1) a model that assumed that transport would occur by migration of fluid inclusions up the thermal gradient, and (2) a vapor-phase transport model. The brine content of the salt was assumed to be 0.05 wt % for both of these models. The fluid-inclusion model predicted that about 400 mL of brine would flow into the central borehole after about 2 years; the vapor-phase transport model predicted about 2 L (assuming a permeability of $0.1 \mu\text{darcy}$) and 4 or 5 L ($1 \mu\text{darcy}$). Rothfuchs et al. (1988) concluded that despite the fact that the brine volume predicted by the fluid-inclusion model was “in the same range as the measured values” (100–137 mL), “this agreement is of no significance” because the quantity of fluid inclusions assumed to be present for this calculation (0.05 wt %) was much higher than that present in the Main Halite at test sites 1, 2, 3, and 4 (see below). They also concluded that, although the shape of the water volume versus time curve predicted using the vapor-phase transport model was similar to the measured curves, the predicted volumes were much higher than the measured values.

The average, pretest, total water content of the Main Halite at test sites 1, 2, 3, and 4 was 0.213 wt % (Rothfuchs et al, 1988, Table 7-1). However, most of this water was present as structurally bound water in the mineral polyhalite ($\text{K}_2\text{MgCa}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$), which varied from 1.88 to 6.68 wt % of the samples of the Main Halite obtained for pretest analysis. (The other minerals present at significant concentrations were halite, which varied from 92.00 to 96.58 wt %; and anhydrite, which varied from 0.47 to 5.48 wt %.) Rothfuchs et al. (1988) subtracted the water content of the polyhalite from the total water content and reported the difference as “adsorbed water.” The average, pretest adsorbed water content of the Main Halite was 0.030 wt %. However, they did not specify how much, if any, of the adsorbed water was present as fluid inclusions, intergranular brine, or in other forms. The average, posttest, total water content of the Main Halite at test sites 1, 2, 3, and 4 was 0.123 wt % and the average, posttest, adsorbed water content was 0.023 wt % (Rothfuchs et al., 1988, Table 7-2). The difference between the average, pretest and the average, posttest, total water contents ($0.213 \text{ wt } \% - 0.123 \text{ wt } \% = 0.090 \text{ wt } \%$) probably does not represent the amount of brine that migrated to the central boreholes during the test, because most of the total water content of the Main Halite is contained in polyhalite, which does not start to dehydrate until the temperature exceeds $235 \text{ }^\circ\text{C}$. Instead, the difference in the average, pretest and the average, posttest, total water contents — and the average, pretest and the average, posttest, adsorbed water contents — probably represents the small-scale, heterogeneous distribution of polyhalite and adsorbed water in the Main Halite at test sites 1, 2, 3, and 4 (Rothfuchs et al., 1988).

2.4.5 Comparison of Results and Conclusions

Table 4 (see next page) compares the experimental parameters and results of the four in situ studies of brine migration described above. The amounts of brine collected under heated conditions and the rates at which brine was collected in these studies decreased in the order WIPP > Project Salt Vault > Asse > Avery Island. This is consistent with the observation that bedded salt contains significantly more brine than domal salt, because both

the volumes collected and the rates at which they were collected were higher in the WIPP and Project Salt Vault than in the Asse and Avery Island. In the case of the domal salts, it is also consistent with the maximum temperatures attained in these tests, because the volumes and rates in the Asse were higher than those at Avery Island. The only inconsistency is that more brine was collected in the WIPP than in Project Salt Vault, despite the fact that the maximum temperatures in Project Salt Vault were higher than those in the WIPP. It is unclear why so much more brine was collected in the WIPP than in Project Salt Vault.

The uncertainties described in this brief summary of the brine-migration literature clearly identify this process as one that would require additional investigation, if a salt site were considered for disposal of spent fuel or HLW. This is especially true for bedded salt, which contains more brine than domal salt (see above).

Table 4. Comparisons of Four In Situ Studies of Brine Migration.

Characteristic or Parameter	Project Salt Vault ^A	Avery Island ^B	WIPP ^C	Asse ^D
Type of salt	Bedded	Domal	Bedded	Domal
Brine content	0.5 vol %	0.054 wt %	0.1-1 or 2 wt %	0.02-0.03 wt % ^E
Duration of test	~12–19 months	325 & 350 days	441 & 600 days	659 & 863 days
Heater power	1.5-2.1 kW	1.0 kW	470 W & 1.5 kW	9.75-10.74 kW
Maximum temperature	150–200 & 142 °C	51 °C	55, 120, & 130 °C ^J	~210 °C
Brine collected, prior to heating or unheated	NA	NA	230, 90, 22.4, & 19.3 g	NA
Average rate, prior to heating or unheated	NA	NA	32, 13, 5.33, & 4.60 g/day	NA
Brine collected, heated	1.7, 0.8, & 3.1 L	8.27 & 5.10 g	4.3, 4.3, 36, & 38 kg	100, 137, 125, & 125 mL
Avg. or steady-state rate, heated	0.43, 0.22, & 10-93 mL/day	0.0175 & 0.0107 g/day	8, 8, 20, & 50 g/day	0.152, 0.208, 0.145, & 0.145 mL/day

A. Bradshaw and McClain (1971)

B. Krause (1983)

C. Nowak (1986), Nowak and McTigue (1987)

D. Rothfuchs et al. (1988)

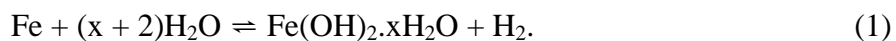
3 SOME CHEMICAL EFFECTS ASSOCIATED WITH BRINE MIGRATION IN A SALT REPOSITORY FOR SPENT FUEL OR HLW

3.1 Possible Effects of Brine-Steel Interactions on Chemical Conditions

Perhaps the most important consequence of possible brine migration towards the waste packages in a salt repository for spent fuel or HLW is that water could react with steel, other Fe-base materials, or other metallic components of the waste packages and produce hydrogen (H₂) gas via anoxic corrosion. Anoxic corrosion is the corrosion of steel, other Fe-base materials, or other metals such as Al and Al-base alloys by the oxygen in H₂O instead of by the free molecular O₂ dissolved in the aqueous or gaseous phase (Westerman et al., 1986; Haberman and Frydrych, 1988; Westerman et al., 1988; Simpson and Schenk, 1989; Brush, 1990; Grauer et al., 1991; Telander and Westerman, 1993; 1997; Smart et al., 2002a; 2002b; Roselle, 2009; 2010; 2011a; 2011b).

Telander and Westerman (1993; 1997) carried out a laboratory study of anoxic corrosion as part of a series of studies of gas generation by TRU waste in the WIPP (Brush, 1990; Brush et al., 1990; 1991a; 1991b; Davies et al., 1991; Mendenhall et al., 1991; Webb, 1991; Brush et al., 1993; Brush et al., 1994; Brush, 1995; Freeze et al., 1995a, 1995b; Wall and Enos, 2006; Roselle, 2009; 2010; 2011a; 2011b). Although conducted for the WIPP, these studies of anoxic corrosion and the hydrologic and mechanical responses of bedded salt to gas generation have provided insights applicable to a salt repository for spent fuel or HLW.

Telander and Westerman (1993, 1997) concluded that, absent microbial production of CO₂ and H₂S — which might occur in the WIPP (Francis and Gillow, 1994; Francis et al., 1997; Gillow and Francis, 2003) but would not be expected in a repository for spent fuel or HLW, anoxic corrosion occurs in WIPP brines at 30 °C via the reaction:



In this reaction, Fe represents metallic iron in the mild-steel waste containers being employed in the WIPP and the Fe-base materials in TRU waste; H₂O is the water in WIPP brines; Fe(OH)₂·xH₂O is a solid, Fe(II)-bearing, corrosion product similar in composition to the mineral amakinite, but with a distinct and unidentified X-ray diffraction (XRD) pattern; and H₂ is the gaseous corrosion product released by the reduction of the water in brines.

Westerman et al. (1986, 1988) observed anoxic corrosion similar reactions in three synthetic Permian Basin brines at 90, 150, and 250 °C in a laboratory studies carried out for the SRP (see Subsection 3.2.2 below). The corrosion product in their experiments depended on the Mg concentration of these brines. Anoxic corrosion of mild steel representative of the candidate waste package material for a commercial salt repository for spent fuel or HLW produced magnetite (Fe₃O₄) or magnesioferrite (MgFe₂O₄) in the two brines with low Mg concentrations (134 and 122 mg/L, respectively). The simplified, Mg-free reaction is:



In reaction 2, Fe_3O_4 is a solid, Fe(II,III)-bearing corrosion product in which one third of the Fe is present as Fe(II)O and the other two thirds are present as Fe(III) $_2\text{O}_3$. (In magnesioferrite, the Mg is present as Mg(II)O and the Fe occurs as Fe(III) $_2\text{O}_3$.) However, anoxic corrosion produced Mg-bearing amakinite ((Fe,Mg)(OH) $_2 \cdot x\text{H}_2\text{O}$) in a high-Mg brine (60,000 mg/L).

Simpson and Schenk (1989) calculated that the equilibrium H_2 fugacities (similar to the partial pressure) for reactions 1 and 2 are approximately 100 and 500 atm, respectively. In other words, reactions 1 and 2 will proceed, as long as both reactants (metallic Fe and H_2O) are present, until the fugacity of H_2 reaches ~ 100 or ~ 500 atm. At these fugacities, metallic Fe and H_2O are in equilibrium with Fe(OH) $_2 \cdot x\text{H}_2\text{O}$ or Fe_3O_4 and H_2 , and these reactions stop. Brush (1990) calculated that the equilibrium values of f_{H_2} for these reactions are ~ 60 and ~ 400 atm. Wall and Enos (2006), however, used recently obtained thermodynamic data from Chivot (2004) and obtained values of ~ 600 and ~ 500 atm.

The calculations by Wall and Enos (2006) imply that both of these reactions would produce H_2 partial pressures well in excess of lithostatic pressure prior to reaching equilibrium in repositories at depths of several hundred meters. (Lithostatic pressure at 655 m, the depth of the WIPP repository horizon, is about 150 atm.) Therefore, fracturing of the host geologic formation at pressures at or near lithostatic pressure would probably prevent the build-up of H_2 partial pressures to values high enough to stop reactions 1 and 2.

However, Telander and Westerman (1993, 1997) found this reaction is self-limiting: it proceeds if brine is present but stops once all of the brine has been consumed, because the relative humidity of water vapor in the WIPP (~ 73 -75%) is too low for anoxic corrosion to occur, at least at 30 °C.

The WIPP PA code Brine and Gas Flow (BRAGFLO) (U.S. DOE, 2009, Appendix PA-2009) predicts that, for various combinations of the parameters sampled by PA, the quantities of brine that will enter the repository after it is filled and the panel closures are emplaced are only sufficient to react with about 40 to 50% of the steel waste containers and Fe-base materials in the waste. Therefore, anoxic corrosion in the WIPP will probably be brine-limited. Furthermore, most of the PA personnel familiar with these calculations think that the quantities of brine predicted to enter the repository are probably highly conservative (i.e., greatly overestimated), mainly because of the highly conservative assumptions and parameter values that were “grandfathered” into the PA baseline when the EPA certified the WIPP in 1998.

WIPP PA also predicts (U.S. DOE, 2009, Appendix PA-2009) that: (1) the gas generated by TRU waste could increase the pressure to lithostatic pressure (~ 150 atm at 655 m) under some combinations of the parameters sampled for PA calculations; (2) any additional gas generation and pressure increases will enlarge preexisting fractures in the anhydritic (CaSO_4 -rich) marker beds in the Salado Fm., or initiate new fractures in these units; (3) storage of gas in these fractures will preclude pressures in excess of lithostatic in the repository; (4) gas will migrate upward and outward into fractures above the waste and brine will migrate downward and outward into fractures below the waste, thereby preventing additional anoxic corrosion and H_2 production even before all of the brine in the near field has been consumed;

(5) fracturing is limited in extent relative to the regulatory boundaries of the WIPP site and hence will not deleteriously affect the performance of the WIPP. The fifth conclusion is especially significant, given that the quantities of brine predicted to enter the repository by WIPP PA are probably highly conservative.

On the other hand, anoxic corrosion of the steel waste containers and Fe-base materials in the waste will create strongly reducing conditions in the WIPP, or in a salt repository for spent fuel or HLW. These conditions will be so strongly reducing that they would plot below the lower stability limit of water on an Eh-pH diagram. This is because the lower stability limit of water on such a diagram is typically calculated for a total pressure of 1 atm but, according to Wall and Enos (2006), the equilibrium H_2 partial pressure at equilibrium between metallic Fe and its corrosion products is ~500 to ~600 atm, well below the stability field of water. Consequently, the conditions created by anoxic corrosion would reductively immobilize radioelements such as Se, Tc, U, Np, Pu, and Am, if the waste packages were breached and they were released to the near field. Laboratory and field studies too numerous to cite here have shown that metallic Fe, and Fe(II)- and Fe(II,III)-bearing corrosion products such as amakinite and magnetite effectively reduce Se, Tc, U, Np, Pu, and Am from their higher to their lower oxidation states. In the case of the WIPP, the beneficial effects on the long-term performance of the repository of the lower solubilities and higher K_{ds} of U(IV), Np(IV), and especially Pu(III,IV), predicted for these strongly reducing conditions far outweigh any concerns about highly localized fracturing from pressurization caused by H_2 production. Furthermore, it is possible that the same beneficial effects on performance could be demonstrated for a salt repository for spent fuel or HLW in thick, corrosion-allowance, Fe-base waste packages. Moreover, both German and American investigators have identified excellent candidate materials for corrosion-allowance waste packages (see Subsection 3.2 below).

3.2 Effects of Brine Chemistry on Corrosion of Fe-Base Materials

The German government and the European Commission funded laboratory and in situ studies of waste-package materials for spent fuel or HLW in salt at the Forschungszentrum Karlsruhe (FZK), or Research Center Karlsruhe; the Gesellschaft zur Förderung der Naturwissenschaftlich-technischen Forschung, or Corporation for the Promotion of Scientific Research, in Berlin-Adlershof e.V./Institut für Umwelttechnologien GmbH (GNF/IUT), or Institute for Environmental Technology; and the Empresa Nacional de Residuos Radioactivos (ENRESA), the Spanish national radioactive waste management company.

The Germans have carried out extensive studies of several corrosion-allowance and corrosion-resistant alloys during the 1980s, 1990s, and 2000s. Kursten et al. (2004) reviewed these results and other results from the German program, and the results of other European countries' studies of waste-package materials for spent fuel or HLW in other geologic media.

Based on this work, the Germans have identified carbon steels, especially the mild steel TStE 355, as “the most promising materials” for corrosion-allowance waste packages; and the Ni-base alloy Hastelloy C-4 and the Ti-base alloy Ti 99.8-Pd as the most promising for corrosion-resistant waste packages (Kursten et al., 2004). Table 5 provides the chemical compositions of these materials.

Table 5. Chemical Compositions (wt %) of TStE 355, Hastelloy C-4, and Ti 99.8-Pd “the Most Promising Materials” for Waste-Packages for Spent Fuel or HLW in a German Salt Repository (Kursten et al., 2004, Table 4.1).

Element	TStE 355	Hastelloy C-4	Ti 99.8-Pd
H ₂			0.001
C	0.17	0.006	0.01
O ₂			0.04
Si	0.44	0.05	-
Ti		0.33	Balance
Cr		15.4-16.8	
Mn	1.49	0.09	
Fe	Balance	0.05	0.05
Ni		Balance	
Mo		15.2-15.9	
Pd		-	0.18

Subsequently, however, Hastelloy C-4, exhibited crevice corrosion in high-Mg brine at 90, 170, and 200 °C in 3-year experiments, and pitting in this brine at 200 °C in a 3-year test (Kursten et al., 2004).

Both the brine composition and the temperature affected the corrosion rate of TStE 355. According to Kursten et al. (2004, Table 4-5), the rates measured after immersion in Brine 1 at

90, 170, and 200 °C for 4 years were 69.7 ± 1.8 , 199.4 ± 15.0 , and 462.8 ± 33.6 $\mu\text{m}/\text{year}$, respectively. The corresponding rates for Brine 2 were 37.6 ± 15.0 , 307.9 ± 45.3 , and 651.2 ± 155.2 $\mu\text{m}/\text{year}$. Those for Brine 3 were 5.1 ± 2.2 , 46.0 ± 7.3 , and 18.3 ± 3.6 $\mu\text{m}/\text{year}$ (Table 1 in Subsection 2.2 above provides the compositions of these brines.). These reviewers concluded that the uniform corrosion rate increased with temperature in all three brines because TStE 355 corroded by “a thermally activated process” and because the pH of all three brines decreased as the temperature increased. They concluded that the higher corrosion rates in Brines 1 and 2, especially at higher temperatures, were caused by the higher Mg concentrations of these brines, which affected the identity of the corrosion products (see below), and the higher Cl concentrations of these brines.

The U.S. DOE funded laboratory and in situ studies of waste-package materials for spent fuel or HLW at SNL as part of its research and development activities for the WIPP (see Subsection 1.3 above). SNL focused on the Ti-base alloy ASTM Grade-12 Ti, usually referred to as TiCode-12, for possible use as a corrosion-resistant waste-package material in a salt repository for commercial or defense HLW. Braithwaite and Molecke (1980), Molecke et al. (1981; 1982; 1983), Molecke and Van Den Avyle (1988), Tyler et al. (1988), and Molecke et al. (1993) reviewed these studies. Because the 1979 WIPP Authorization Act restricted the WIPP to defense-related TRU waste (see Subsection 1.3 above), the objective of this work was to provide information applicable to disposal of spent fuel or HLW in salt at potential sites other than the WIPP site. Table 6 (see next page) provides the composition of TiCode-12 specified by the ASTM.

The DOE also funded similar studies at Pacific Northwest National Laboratory (PNNL) as part of the SRP (Subsection 1.3). PNNL studied the cast mild steel alloy ASTM A216, Grade WCA, for use as in corrosion-allowance waste packages for spent fuel or HLW as part of the SRP’s Waste Package Program (WPP) (Westerman, 1980; Westerman et al., 1982; 1984; 1986; 1988). Table 7 (see next page) provides the chemical compositions of the two lots of A216 used for the PNNL studies (Westerman et al., 1988). PNNL also studied TiCode-12 as an alternative, corrosion-resistant material (Westerman et al., 1988).

Table 6. Chemical Composition of TiCode-12
(Molecke et al., 1983, Table 1).

Element	Concentration (wt %)
H (max.)	0.015
C (max.)	0.08
N (max.)	0.03
O (max.)	0.25
Fe (max.)	0.30
Ni (range)	0.6–0.9
Mo (range)	0.2–0.4
Other (total)	0.30
Ti	Balance

Table 7. Chemical Composition of Two Lots of ASTM A216, Grade WCA
(Westerman et al., 1988, Table 4.1)

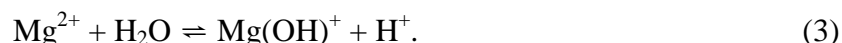
Element	Lot 1 (wt %)	Lot 2 (wt %)
C	0.23	0.16
Si	0.45	0.58
P	0.018	0.014
S	0.018	0.014
Cr	0.41	0.13
Mn	0.71	0.60
Ni	0.23	0.08
Cu	0.14	0.08
Fe	Balance	Balance

Based on this American work, A216 mild steel appears to be an excellent candidate material for corrosion-allowance waste packages (Westerman et al., 1984; 1986; 1988). However, TiCode-12 is susceptible to crevice corrosion, at least under some of the conditions expected in a salt repository for spent fuel or HLW (Ahn and Soo, 1982a; 1982b; 1982c; Westerman et al., 1988).

High temperatures and Mg concentrations increased the corrosion rates of the Fe-base materials considered by Braithwaite and Molecke (1980) on their initial screening study, and of A216 mild steel (Westerman et al., 1988). Clearly, the dissolved Mg concentration

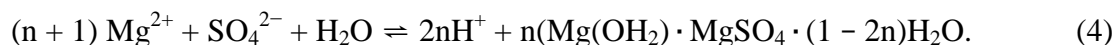
has a significant effect on the corrosion of A216 and TStE 355 mild steels and other Fe-base materials, especially at high temperatures. There are at least two reasons for this behavior:

1. The pH of high-Mg brines decrease significantly as the temperature increases and acidification increases the corrosion rates of mild steels such as A216 and TStE 355. This phenomenon has been studied extensively, both in terms of the reactions that cause acidification and the implications of this process for disposal of spent fuel and HLW (Baes and Mesmer, 1976; Bischoff and Seyfried, 1978; Janecky and Seyfried, 1983; Molecke et al., 1983; Thornton and Seyfried, 1985; Krumhansl, 1989). One of the reactions that causes acidification of both Mg-rich brines and seawater is hydrolysis of Mg^{2+} (Baes and Mesmer, 1976; Westerman et al. 1988):



This reaction produces more acid as the temperature increases because the stability constant for the complex species $Mg(OH)^+$ increases with temperature.

Another reaction that causes acidification of seawater and could cause acidification of Mg-rich brines is the formation of magnesium hydroxide sulfate hydrate (MHSH), which precipitates as the temperature increases (Bischoff and Seyfried, 1978; Janecky and Seyfried, 1983; Thornton and Seyfried, 1985; Krumhansl, 1989). According to Krumhansl (1989), this reaction can be written as:



Based on his review of the literature, Krumhansl (1989) concluded that precipitation of MHSH becomes important in seawater at ≥ 250 °C. Therefore, this reaction would probably not be important in salt repositories for spent fuel and HLW unless it occurs at lower temperatures in Mg-rich brines than in seawater.

Yet another reaction that results in acidification of seawater and could acidify Mg-rich brines is the formation of Mg-rich smectites in clay minerals. Molecke et al., (1983), Thornton and Seyfried (1985) and Krumhansl (1989) wrote this reaction as:



Molecke et al. (1983) hypothesized that reaction 5 could proceed with $SiO_2(aq)$ from the dissolution of clay minerals or quartz (SiO_2) that could be present as accessory minerals in evaporite formations, or from the dissolution of a borosilicate glass waste form. Thornton and Seyfried (1985) concluded that, although a reaction similar to reaction 4 (see above) was the most important cause of acidification during the first few hours of their experiments on the interactions of seawater and deep-sea sediments at 200 and 300 C and 500 bars, reaction 5 rapidly superseded reaction 4 as the more important cause. They reported that dissolution of amorphous silica and quartz (both SiO_2) were the source of the $SiO_2(aq)$ in their experiments, and that talc ($Mg_3Si_4O_{10}(OH)_2$) formed either as a distinct smectite phase with most of

its octahedral sites occupied by Mg, or as talc-like layers in existing clay minerals. Krumhansl (1989) reported, based on posttest analysis of the run products from his hydrothermal experiments with analytical transmission electron microscopy, that $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ was present as smectite.

The other major reason that the dissolved Mg concentration of brines has a significant effect on the corrosion of A216 mild steel and other Fe-base materials is that Mg either promotes the formation of an Mg-rich form of amakinite or prevents the formation of magnetite (Westerman et al., 1988; Kursten et al., 2004). Westerman et al. (1988) and Telander and Westerman (1993, 1997) typically reported that amakinite was nonadherent in their experiments and thus provided no protection for the corroding A216 surfaces. The only exception to this behavior occurred in some of the longer-term (12-month), excess-salt tests with PBB3 (see below), in which the salt in the welded cans held the amakinite in place next to the corroding surfaces. This caused the corrosion rate of the A216 specimens to decrease with time, but not enough to approach the significantly lower rates observed in the excess-salt tests with PBB1 and PBB2. On the other hand, the magnetite that formed in tests with PBB1 and PBB2 developed an “onion-skin” structure that provided some protection from corrosion by these brines, even though the outer layers tended to slough off after the formation of a rind that was a few layers thick (Westerman et al., 1988).

4 CONCLUSIONS

The issue of possible brine migration in a salt repository would require additional investigation, if salt were considered for disposal of spent fuel or HLW. This is especially true for corrosion-allowance waste packages in bedded salt. This is because the corrosion-allowance concept requires reliable predictions of how much brine will migrate up the thermal gradient and contact the waste packages during the thermal period, and because bedded salt contains more brine than domal salt. The four in situ studies of brine migration reviewed in Subsection 2.4 and summarized in Table 4 (see above) showed that the amounts of brine collected under heated conditions and the rates at which brine was collected were greater during the tests in bedded salt than in domal salt, consistent with the observation that bedded salt contains more brine than domal salt.

Both the corrosion-allowance and the corrosion-resistant concepts also require reliable predictions of the composition(s) of the brine(s) that will contact the waste packages. This is because the Mg concentration of brines affects the corrosion rates of the mild steels identified as candidate waste-package materials, especially at high temperatures (see Subsection 3.2). The Mg concentration could also affect the behavior the corrosion-resistant alloys identified as promising. None of the publications or reports on the laboratory or in situ brine-migration studies obtained to date has determined the compositions of these brines.

Brine migration up the thermal gradient will probably be less of an issue for both corrosion-allowance and corrosion-resistant waste packages in domal salt. Intrusion of brine could be a more important issue than brine migration up the thermal gradient in domal salt.

Anoxic corrosion of steel waste containers could create strongly reducing conditions in a salt repository for spent fuel or HLW. These conditions would reductively immobilize radioelements such as Se, Tc, U, Np, Pu, and Am, if the waste packages were breached and they were released to the near field. Numerous laboratory and field studies have shown that metallic Fe, and Fe(II)- and Fe(II,III)-bearing corrosion products effectively reduce Se, Tc, U, Np, Pu, and Am from their higher to their lower oxidation states. The beneficial effects on the long-term performance of a salt repository of the lower solubilities and higher K_{ds} of these radioelements observed under these strongly reducing conditions far outweigh any concerns about localized fracturing from pressurization caused by H_2 production. Furthermore, both German and American investigators have identified excellent candidate materials for corrosion-allowance waste packages (Subsection 3.2).

Although brine migration up the thermal gradient could be an important process for both corrosion-allowance and corrosion-resistant waste packages in bedded salt, intrusion of brine(s) could also be important. The quantities and compositions of such brine(s) will also have to be included in the design of both corrosion-allowance and corrosion-resistant waste packages if bedded salt were considered for disposal of spent fuel or HLW.

Additional site-specific studies of brine migration will probably be required, because the brine content of both bedded and domal salt formations can vary significantly. Furthermore,

it might be necessary to carry out full-scale, in situ tests that include the effects of high-temperature creep closure on the mechanical properties of grain boundaries to determine the extent to which both intragranular and intergranular brines migrate along and across these boundaries towards the heat source. It is also important that the brines be collected and analyzed from the vicinity of the heaters.

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