TITLE: TEST PLAN TO DEVELOP HYDROLOGIC LABORATORY METHODS: EXPERIMENTS OF BRINE MIGRATION IN SALT DUE TO THERMAL GRADIENT AND /OR DEHYDRATION OF SECONDARY MINERAL PHASES

Fuel Cycle Research & Development

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ACRONYMS

DTA:	differential thermal analysis				
ERDA-6:	(U.S.) Energy Research and Development Administration (WIPP well) 6 a synthetic brine representative of fluids in Castile brine reservoirs				
FFT	Fast Fourier transformed				
GWB:	Generic Weep Brine, a synthetic brine representative of intergranular Salado brines				
IR: Inf	rared spectroscopy				
RAMAN:	RAMAN spectroscopy				
SAED	selected area electron diffraction				
TEM	Transmission electron Microscopy				
TGA:	and thermal gravimetric analysis				
TG-DSC	Thermogravimetric analyzer				
WIPP:	Waste Isolation Pilot Plant				
XRD:	X-ray diffraction				

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TEST PLAN TO DEVELOP HYDROLOGIC LABORATORY METHODS: EXPERIMENTS OF BRINE MIGRATION IN SALT DUE TO THERMAL GRADIENT AND /OR DEHYDRATION OF SECONDARY MINERAL PHASES

1. 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?

2. Background and Significance

2.1 Water content of rock salt

2.1.1 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).

2.1.2 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).

2.1.3 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). Intracrystalline brine is not readily released



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

from salt even when heated to temperatures above 250 °C (Shefelbine, 1982). Brine contained in intracrystalline inclusions 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.

2.1.4 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 ($KMgCl_3 \cdot 6(H_2O)$), bischofite ($MgCl_2 \cdot 6H_2O$), kieserite

 $(MgSO_4 \cdot H_2O)$, gypsum (CaSO₄ · 2H₂O), polyhalite (K₂Ca₂Mg(SO₄)₄ · 2H₂O) 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 $^{\circ}$ C and 340 – 360 $^{\circ}$ 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 sitespecific minerals.

2.1.5 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.

Constituent	Duval mine	Brine	WIPP	WIPP	GWB	ERDA-6
		inclusions	Brine A	Brine B		
Na^+	49	33	42	115	81	112
\mathbf{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
\mathbf{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	-	-

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).

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 Ca^{2+} , Mg^{2+} and SO_4^{2-} 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).

2.2 Brine migration in salt.

2.2.1 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 of brine. The research proposed here will specifically focus on addressing knowledge gaps related to the effect of minor mineral phases under repository conditions applicable for the disposal of heat-producing radioactive nuclear waste.

2.2.2 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 (Shefelbine, 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.

2.2.3 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 $^{\circ}$ 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 $^{\circ}$ 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 $^{\circ}$ 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 60 Co (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.

2.3 Dehydration of secondary minerals associated with salt.

2.3.1 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 though 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.

2.3.2 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, manganesite, 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



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

motions typically

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-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).

2.3.3 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 (CaSO₄· 2H₂O) 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 (KMgCl₃· 6(H₂O)), bischofite (MgCl₂· 6H₂O), kieserite(MgSO₄· H₂O), and polyhalite (K₂Ca₂Mg(SO₄)₄· 2H₂O).Calcium sulfates are classified in three different mineral forms based on their degree of hydration. The phase changes of the calcium sulfates are: gypsum((CaSO₄· 2H₂O), hemihydrate (CaSO₄· 0.5H₂O), and anhydrite (CaSO₄). 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 (CaSO₄ $2H_2O$) also converts to anhydrite (CaSO₄) 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: MgCl₂·*n*H₂O (n = 1, 2, 4 and 6), MgOHCl·*n*H₂O ($0 \le n \le 1.0$), MgCl₂ and MgO (Sugimoto, 2007). Polyhalite minerals, which possibly formed as a result of the reaction of brine with gypsum or anhydrate, are described as a tipple salt and are represented by the formula (K₂ SO₄· MgSO₄· 2Ca SO₄· 2H₂O). It is the most wide spread sulfate mineral in evaporatic 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.

3. Task Implementation

3.1 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 <u>salt crystals and crystal aggregates</u> (e.g., behavior of water at grain boundaries, effect minor mineral phases on brine migration); 2) Brine transport within <u>salt core</u> (e.g., brine behavior under isotemperature 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 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 *isotemperature* 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 <u>radial and axial stress and</u> <u>temperature gradient created by a point heat source</u>
 - 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 <u>temperature and pressure loads</u>

- 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

3.2 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 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 indepth 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



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).

sealed using a heat resistant epoxy resin with thermal conductivity properties similar to that of salt (i.e. 7 $Wm^{-1}K^{-1}$) 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 indepth 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 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 microcopy 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 isotemperature 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 isotemperature conditions and how brine migration is affected by minor mineral phases under isotemperature 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 ^oC). 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 though 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 Discovesry 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 sate 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 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 clavs 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



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 %.

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⁺, Mg²⁺, Ca²⁺), 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



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

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 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 (< 30min), 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.

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



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

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 Simultaneus 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 similtanious 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).



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

The vessels will then be inserted in 400 °C/600 bar rocking autoclave.

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.

3.4 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"

4. 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 3.2 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, 3.1, 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.

5. Literature Cited

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