

see minor comments/suggestions on text from
A.D. Kelmers and R E Meyer
06/06/85

DRAFT

SITE TECHNICAL POSITION
DOE HIGH-LEVEL WASTE REFERENCE REPOSITORY LOCATION
HANFORD SITE

Use Of Hydrazine To Experimentally Simulate
Expected Site Redox Conditions And Reactions

NRC/NMSS/WMGT/Geochemistry Section

INTRODUCTION

The DOE/Hanford Staff performs laboratory and field investigations to acquire data needed to address repository performance based on site geochemical conditions. The Nuclear Waste Policy Act (NWPA) and Nuclear Regulatory Commission (NRC) regulations (10CFR60) and agreements governing licensing of a geologic repository, provide for consultation between DOE and NRC staffs prior to formal licensing to assure that licensing information needs and requirements are identified at an early time. This determination depends, in part, on whether the geochemical data being collected is adequate to characterize repository performance.

Technical criteria of 10CFR60.113, includes a limit on the amount of radionuclides permitted to be released from the engineered barrier system and to the accessible environment. In order to demonstrate compliance with this limit, DOE/Hanford must identify the particular barriers that will be relied upon to retard radionuclide migration. Based on discussions presented by DOE in the Hanford Draft Site Characterization Report (DSCR), the Draft Environmental Assessment (DEA), and at site workshops, DOE/Hanford is taking

All sites
Must do this →

8507120023 850611
PDR WMRES EXIORNL
B-0287 PDR

DRAFT

DRAFT

the position that under the anticipated site Eh of -0.3 volts (or lower), the reference repository location has chemically reducing conditions that will maintain redox-sensitive radionuclides such as uranium, plut⁰onium, ~~and~~ neptunium, ^{and Technetium} in their least mobile state, thus contributing to the control of the release of radionuclides from the repository (DOE, 1982 and 1984). Therefore, site redox conditions have been identified in NRC issues 3.1, 3.2 and 3.3 as a significant site condition that DOE/Hanford needs to address in order to characterize the Hanford site (NRC, 1984). This site technical position presents the major concerns of the NRC staff regarding the adequacy of DOE experimental results that make use of hydrazine to simulate "expected" redox conditions and reactions.

BACKGROUND

DOE/Hanford anticipates that the redox condition in the undisturbed host rock and in the repository will reduce redox-sensitive radionuclides to their least mobile valence state. To support this expectation, a calculated or proposed groundwater Eh as low as -0.48 volts is frequently cited (Salter, 1981a). Assuming that these expected repository conditions will be chemically reducing, DOE/Hanford adds 0.05 to 0.1 M hydrazine (as hydrazine hydrate, $N_2H_4 \cdot H_2O$) to synthetic groundwater solutions used in experiments, in order to simulate the expected site redox conditions and reactions. The justification for the use of hydrazine has not been well developed in DOE/Hanford reports which describe its application to sorption tests (Barney 1982a, Barney 1982b, Salter 1981b, Salter 1981c, SCR 1982.) In order to confirm the validity of these experiments, DOE/Hanford is currently evaluating experimental results that use hydrazine to control radionuclide behavior (DOE, 1984).

Some of the advantages and disadvantages of using hydrazine are discussed in Barney 1983.

DRAFT

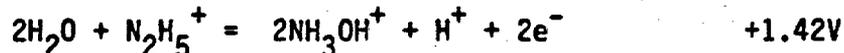
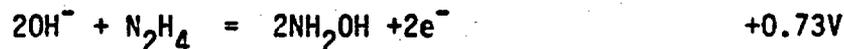
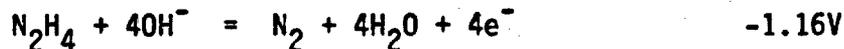
DRAFT

TECHNICAL POSITION

The effective solution redox conditions generated by hydrazine are strongly dependent upon the specific reduction reaction(s) involved. DOE/Hanford has not identified the reaction(s) occurring between hydrazine and any reducible radionuclide species in groundwater; thus, the effective Eh or redox conditions/reactions in these experiments must be considered to be unknown. Therefore, the NRC position is that the use of hydrazine to simulate Hanford site redox conditions and reactions will not provide defensible data that can be used to characterize expected radionuclide behavior.

DISCUSSION

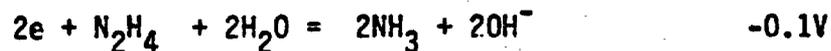
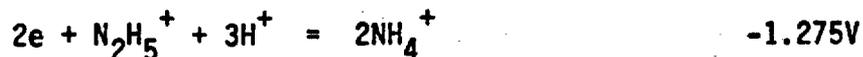
Four completely different reactions with widely varying standard potentials are commonly cited for hydrazine reduction reactions (Kirk-Othmer, 1980). These are:



Hydrazine can also act as an oxidant in the same Eh potential range. For example:

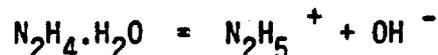
DRAFT

DRAFT



Thus, without knowledge of the specific reaction(s) occurring between hydrazine and the solute of interest, it is not possible to estimate what Eh value or redox condition is effective in experimental solutions.

Further, the dissociation of hydrazine hydrate is most likely the dominant influence on the experimental groundwater pH. For example, hydrazine in aqueous solution is present as the hydrate, which dissociates to generate hydroxide ions:



The dissociation constant is 1.7×10^{-6} (Audrieth, 1951). Since the hydrazine is added to DOE/Hanford experiments at 0.05 to 0.1 M concentration, while the carbonate/bicarbonate concentration in the synthetic groundwater used is only about 0.001 M, it is probable that all of the synthetic groundwater samples containing hydrazine are buffered by the hydrazine rather than by the synthetic groundwater carbonate/bicarbonate components or by the basalt rock phases. Also, according to Kelmers et al. (1984), the addition of hydrazine is observed to raise the groundwater pH by about one-half to one unit. Thus, the synthetic groundwater/hydrazine is no longer representative of in situ pH conditions.

In addition, hydrazine can react with the bicarbonate anion to form the carbamate anion (Staal 1951):



DRAFT

[DRAFT]

This reaction could deplete the bicarbonate concentration due to the large excess of hydrazine relative to bicarbonate in the synthetic groundwaters used in the experiments. This could also affect the ground/hydrazine solution pH, in addition to hydrazine hydrate dissociation. In any case, the solution would no longer be representative of in situ groundwater conditions. Also, the carbamate anion could form complexes with transition elements or actinides similar to the well-known amine complexes (NOTE: NEED REF.). Little information is available in the literature concerning hydrazine carbamate chemistry. *delete*

Hydrazine has been reported to interact with clay minerals in a number of ways. For example:

(1) hydrazine may be preferentially adsorbed onto surface exchange sites and therefore compete with anticipated ion exchange sorption processes (Hayes, 1982). This potential problem has been recognized by DOE/Hanford (Ames, 1982). In addition, irreversible chemisorption of hydrazine also has been reported (Hayes, 1982).

(2) Hydrazine apparently disrupts the silicate layering and leads to mineral disaggregation (Bleakley, 1968, and El-Messide, 1977). Further, the use of hydrazine hydrate solutions for chemical disaggregation of rock has been patented (Huff, 1971). (NOTE: THIS NEEDS TO BE EXPANDED)

Such reactions between hydrazine in the synthetic groundwaters and basalt and/or secondary minerals could lead to significant alteration of the solids in the reducing condition tests, as well as alter the apparent radionuclide sorption behavior through sorption competition. The possibility of significant chemical reactions between hydrazine and the basalt or secondary minerals that

[DRAFT]

would lead to alteration of the basalt phases and/or surfaces, raises significant concerns about the use of hydrazine.

The chemistry of the basalt/groundwater system seems to be primarily dominated by the rock components. Thus, reactions leading to radionuclide removal from solution by sorption or precipitation ^{may} ~~must~~ involve heterogeneous reactions between basalt solid phases and radionuclide species in solution. Some of these reactions are likely to be kinetically ~~slow~~ ^{slow}. The addition of hydrazine, or any exogenous reducing chemical, seems likely to result in ~~rapid~~ ^{rapid} homogeneous solution reactions ~~(NOTE: NEED REF.)~~. These reactions have not been shown to model heterogeneous, in situ radionuclide reactions, and it seems unlikely that such test systems could be shown to be accurate measure of the expected behavior of radionuclides. For example, the rate of reaction between hydrazine and technetium(VII) has only been studied at a pH of 11 and the reaction was reported to proceed more slowly or not at all at a higher or lower pH (Galateanu, 1977). The reaction products were not identified, but were assumed to be Tc(IV) compounds. To date, DOE/Hanford reports do not identify the products formed from the reaction of hydrazine with technetium (or any other radionuclide). Further, there is considerable uncertainty as to the reduced form of technetium produced by hydrazine. It has been reported that metallo-organic compounds containing a Tc-N bond are formed (the formal valence of the technetium was not established) (Baldas, 1982). The possible formation of at least transiently stable Tc(V) complexes cannot be ruled out (Davidson, 1982). Recent work has shown that a number of what were believed to be Tc(VI) organic compounds are actually Tc(III) compounds, and that Tc(III) is generally more stable in aqueous solutions than had been generally believed (Jones, 1982). Two different DOE/Hanford reports have suggested that the solid formed by the reaction of hydrazine with the pertechnetate anion are $TcO_2 \cdot 2H_2O$ (Barney, 1981) or $TcO_2 \cdot xH_2O$ (Barney, 1982b). According to Kelmers et al.

DRAFT

7

(1984), a black solid is formed, presumably a hydrated Tc(IV) oxide, when hydrazine is added to pertechnetate solutions. The technetium solution species in equilibrium with this solid are undefined.

Finally, hydrazine is a very aggressive chemical and reacts with plastics. According to Kelmers et al. (1984), the rapid reaction of hydrazine visibly attacks polycarbonate test tubes, either causing them to crack with resulting loss of solution or causing etching of the tube and a brown discoloration of the groundwater solution. Further, Kelmers et al. (1984), reported a slight reaction with polypropylene. To date, all of the radionuclide sorption work performed by DOE/Hanford under hydrazine-induced "reducing" conditions ~~have~~ ^{has} been conducted in polycarbonate tubes. While the details of the hydrazine-polycarbonate reaction are not known, it clearly represents a loss of hydrazine from solution. In addition, the formation of brown-colored groundwater solutions strongly suggests the presence of organic degradation products in the radionuclide sorption tests. This practical experimental problem would seem to render suspect all of the work for all radionuclides under hydrazine-induced reducing conditions. In fact, DOE suggests that results from these experiments are suspect (Barney (1982b)).

SUMMARY

In order to simulate expected redox conditions and reactions, DOE/Hanford has conducted much of their reported radionuclide sorption experimental work by adding 0.05 to 0.1 M hydrazine hydrate to the synthetic groundwater used in their experiments. They have identified these tests as "reducing condition" tests with basalt (Salter, 1981c), secondary minerals (Salter, 1981b), and interbed materials (Barney, 1982a and Barney, 1982b). As a result of laboratory work, the NRC has a number of fundamental concerns about the use of

DRAFT

hydrazine in experiments to poise the experimental system at some predetermined Eh or redox condition (Kelmers et al., 1984). These general major concerns are:

1. Hydrazine can exhibit four different reduction reactions and two oxidation reactions which have widely different standard potentials.
2. Hydrazine hydrate dissociates to release hydroxide ions.
3. Hydrazine can react with the bicarbonate anion to form the carbamate anion.
4. Hydrazine is reported to disrupt the mineral structure of clays, and disaggregate rock.
5. The chemistry of basalt rock/groundwater systems seems to be primarily dominated by the rock components. Thus, reactions leading to radionuclide removal from solution by sorption or precipitation must involve heterogeneous reactions between basalt solid surfaces and radionuclide species in solution. The addition of hydrazine, or any exogenous reducing chemical, seems likely to result in ~~rapid~~ homogeneous solution reactions involving radionuclides.
6. Hydrazine is a very aggressive chemical and reacts with plastics in the experimental apparatus.

Therefore, it is the position of the NRC that the use of hydrazine to simulate Hanford site redox conditions and reactions will not provide defensible data that can be used to characterize radionuclide behavior.

DRAFT

REFERENCES

Ames, L. L., P. F. Salter, J. E. McGanah, and B. A. Walker, Selenium Sorption on a Columbia River Basalt, PNL-SA-10750, Pacific Northwest Laboratory, Richland, Washington, 1982.

Audrieth, L. F., and B. A. Ogg, The Chemistry of Hydrazine, John Wiley and Sons, New York, 1951.

Baldas, J., J. Bonnyman, P. M. Pojer, and G. A. Williams, "The Influence of Reducing Agents on the Composition of Technetium-99 Complexes: Implications for ^{99m}Tc -Radiopharmaceutical Preparation," Eur. J. Nucl. Med. 187-189, 1982.

Barney, G. S., Radionuclide Reactions With Groundwater and Basalts from Columbia River Basalt Formations, RHO-SA-217, Rockwell Hanford Operations, Richland, Washington, 1981.

Barney, G. S., Radionuclide Sorption of Columbia River Basalt Interbed Materials, RHO-BW-SA-198P, Rockwell Hanford Operations, Richland, Washington, 1982.

Barney, G. S., Radionuclide Sorption on Basalt-Interbed Materials. Annual Report FY 1981, RHO-BW-ST-35P, Rockwell Hanford Operations, Richland, Washington, 1982.

Bleakely, W. B., "Research Shows How Chemical Action Enlarges Boreholes," Oil Gas J. 66, 91-93 (1968).

Barney, G. S., Radionuclide Sorption Kinetics and Column Sorption Studies with Columbia River Basalts, SD-BWI-TI-168, Rockwell Hanford Operations, Richland, Washington, 1983. DRAFT

DRAFT

10

Davison, A. and A G. Jones, "The Chemistry of Technetium(V)," Int. J. Radiat. Isot. 33, 875-881, 1982.

DOE, Site Characterization Report for The Basalt Waste Isolation Project, DOE/RL 83-3, 1982.

DOE, Draft Environmental Assessment, Reference Repository Location, Hanford Site, Washington, DOE/RW-0017, 1984.

EL-Messide, A., "Effects of Hydrazine Hydrate on Berea Sandstone," presented at the American Nuclear Society Topical Meeting on Energy and Mineral Recovery Research, Golden, CO, April 12, 1977.

Galateanu, I., C. Bratu, and A. Petride, "The Reduction of ^{99m}Tc -Pertechnetate by Hydrazine," Radiochem. Radional. Letts. 28, 95-104, 1977.

Hayes, M. H. B., P. J. Isaacson, K. Y. Chia, and A. M Lees, Interaction of Hydrazine and of Hydrazine Derivatives with Soil Constituents and with Soils. Annual Report December 1, 1980 - December 1, 1981, AD-A-113067/3, Birmingham University, United Kingdom, 1982.

Huff, R. V., and L. J. Heath, "Chemical Disaggregation of Rock," U.S. Patent 3,567, 427 (1968).

Jones, A. G., and A. Davison, "The Chemistry of Technetium I, II, III, and IV," Int. J. Radiat. Isot. 33, 867-874 (1982).

Kelmers, A.D., J.H. Kessler, W.D. Arnold, R.E. Meyer, N.H. Cutshall, G.K. Jacobs and S.Y. Lee, Progress in Evaluation of Radionuclide Geochemical

DRAFT

DRAFT

Information Developed by DOE High-Level Nuclear Waste Repository Site Projects: Report for October-December, 1983, NUREG/CR-3851, Vol. 1, 1984.

Kirk-Othmer, Kirk-Othmer Encyclopedia of Chemical Technology, Volume 12, p. 736, John Wiley and Sons, New York, 1980.

NRC, Draft Issue-Oriented Site Technical Position (ISTP) For Basalt Waste Isolations Project (BWIP), 1984.

Salter, P. F., and G. K. Jacobs, Evaluation of Radionuclide Transport: Effect of Radionuclide Sorption and Solubility, RHO-BW-SA-192A, Rockwell Hanford Operations, Richland, Washington, 1981.

Salter, P. F., L. L. Ames, and J. E. Mc Garrah, Sorption of Selected Radionuclides on Secondary Minerals Associated with the Columbia River Basalts, RHO-BWI-LD-43, Rockwell Hanford Operations, Richland, Washington, 1981.

Salter, P. F., and L. L. Ames, The Sorption Behavior of Selected Radionuclides on Columbia River Basalts, RHO-BWI-LD-48, Rockwell Hanford Operations, Richland Washington, 1981.

Staal, E. and C. Faurholt, "Carbamates. IV. The Carbamate of Hydrazine," Dansk. Tid. Farm. 25, 1-12 1951.

DRAFT

LR-287-5
06/11/85

LETTER REPORT

TITLE: Review of "Brine Migration in Salt," by W. Kelly
AUTHOR: G. K. Jacobs
PROJECT TITLE: Technical Assistance in Geochemistry
PROJECT MANAGER: Susan K. Whatley
ACTIVITY NUMBER: ORNL #41 37 54 92 4 (189 #B0287)/NRC #50 19 03 01

The subject document provides a concise and clearly written summary of work related to the migration of brine inclusions in salt. The organization of the document is good, and most important aspects of brine migration are covered to some extent (assuming that the section on Project Salt Vault will be completed). Although the document is in good shape, I do have a few suggestions for improvement (H. C. Claiborne kindly provided some helpful input that is included in my comments). My major concern is with the purpose of the report. Although the document provides an excellent summary of previous work, essentially no guidance is provided to the DOE projects currently involved in the investigation of salt as a host rock for a repository. Addition of a short section addressing remaining concerns and potential areas for future work would greatly increase the value of the document. Additional specific editorial and technical comments are marked within the text of the document.

Enclosure 6. Draft Topical Report

BRINE MIGRATION IN SALT

TOPICAL REPORT

MARCH 28, 1985

by

Walton Kelly

~~8505069429~~

TABLE OF CONTENTS

INTRODUCTION.....1

FLUIDS IN SALT

 Types of Fluids.....2

 Composition of Included Water.....3

THEORY OF BRINE MIGRATION.....5

EXPERIMENTAL ~~EFFORTS~~ ^{DATA} ~~TECHNIQUES~~.....7

 Laboratory Studies.....7

 In Situ Studies.....12

MODELING ~~EFFORTS~~ ^{of BRINE MIGRATION}.....14

→ ~~UNCERTAINTIES IN PREDICTION~~ ^{subheading}.....18

SUMMARY AND CONCLUSIONS.....22

I suggest expanding somewhat and make more general - then introduce salt - why it's good - & problem of brine migration

I. INTRODUCTION

In order to dispose of high-level ^{radioactive} waste (HLW), the Department of Energy (DOE) is mandated to build a deep geologic repository. One of the proposed rock types in which this repository may be built is (bedded or domal) salt. A favorable aspect of salt is that it has ^(is the most important) very low permeability, thus inhibiting the flow of groundwater. Groundwater ^{is considered to potentially be the main} agent for corrosion of the waste package, solubilization of ^{radionuclides from} the waste form, and transport of the ^{radionuclides} waste to the accessible environment. However, salt deposits ^{do contain a certain amount of water that was either, deposited with the salt or} ^{trapped during deposition of} ^{into the salt} ^{placed during some secondary process.} This water may be present in intercrystalline inclusions (e.g., brine pockets), intracrystalline inclusions, and hydrated or hydrous minerals. The significance of brine inclusions in salt is that, under a temperature and/or pressure gradient, they have been shown to migrate. The water can move either up or down a gradient, depending upon the nature of the inclusion. Therefore, despite the basic impermeability of salt, ^{will not "compromise" if taken into account} water may still reach the waste package and compromise its performance under ^{in repository - the design} repository-induced conditions. ^{Information on the nature of} Inclusions in the salt ^{can be useful in developing an} ~~will also aid in the~~ understanding of the depositional and diagenetic history of the salt. It is therefore important to understand the nature of these inclusions and their ^{potential impact on the performance of a HLW repository,} ~~significance in affecting a repository's ability to isolate HLW.~~ This report attempts to summarize ^s the work that has been completed to date on inclusions in salt and brine migration and to discuss ^{es} uncertainties in predicting the effects of brine migration on repository performance.

awkward

II. FLUIDS IN SALT

Types of Fluids

As stated above, fluids in salt deposits are basically found in three settings: (1) intercrystalline inclusions; (2) intracrystalline inclusions; and (3) hydrated or hydrous minerals. Intercrystalline inclusions contain water found between the mineral crystals and in any fractures. These inclusions can contain large amounts of brine (i.e., brine pockets) and can be under high pressure. ^{WIPP Reference?} All salt crystals contain some amount of water within the crystal structure, i.e., intracrystalline inclusions. These inclusions are commonly ^{most?} between 2 and 250 ^{micrometers} ^{in diameter?} microns, although inclusions of several millimeters have been found (Isherwood, 1979). Inclusion sizes and shapes can vary greatly within a single crystal, although the smaller the inclusion, the more cubic its shape tends to be. The amount of ^{syndepositional} fluids present in ^{salt} inclusions depends on the crystallization history of the salt. The higher the growth rate of salt crystals precipitating out of solution, the greater the amount of fluid trapped in inclusions (see Roedder, 1984, for a more complete discussion).

Most salt, however, undergoes ^{some sort of} recrystallization during its diagenetic history. This recrystallization process may be isochemical but also may involve the loss and/or gain of fluids (Roedder, 1984). An example of such an effect is the diapirism of salt beds (i.e., the formation of salt domes). Salt domes generally contain less included water than bedded salts, often more than an order of magnitude less. This is postulated to be ~~due to~~ ^{a result of} the squeezing

out of fluids, apparently along grain boundaries, as the salt is forced toward the surface (Baes and others, 1983).

Certain minerals commonly associated with salt deposits can contain significant amounts of water. The common minerals that make up the vast majority of salt deposits, halite and anhydrite (and sylvite), contain no water in their crystal structures. Minerals such as carnallite, kieserite, gypsum, and polyhalite, however, do contain bound water and are commonly found in salt deposits. In addition, sedimentary units such as shales which contain clay minerals are always associated to some extent with salt deposits. Under repository-induced temperatures, these minerals may ^{become} ~~tend to be~~ unstable and undergo dehydration reactions. The more "pure" the salt is, the less likely it is to contain significant amounts of water in hydrous and hydrated minerals.

Composition of Included Water

The total water in salt deposits may range from ~~as little as~~ approximately 30 ppm in some dome salts (Knauth and Kumar, 1981) to ~~up to~~ several weight percent total in some bedded salts (Roedder and Belkin, 1979a). ^{Because of} ~~Due to~~ the small size of inclusions, ^{Found in most salt deposits,} ~~very~~ little quantitative work has been done studying the composition of fluid inclusions. Most of the work has been done on the rare, large inclusions (cm-sized); the smaller inclusions (mm-sized) have been studied particular in the USSR (see Petrichenko, 1973). The data suggest that

specific to salt?

Found in most salt deposits,

the fluids are Ca-Mg brines with varying amounts of Na^+ , K^+ , Cl^- , $\text{SO}_4^{=}$, and other trace constituents (Isherwood, 1979). The ^{total dissolved solids} (TDS) values range from 32 to 36 weight percent, depending on the Ca:Mg ratios (Clyne and Potter, 1977). Very little is known about the identity and concentration of the trace constituents. Solid phases are found in some inclusions, including halite, sylvite, anhydrite, carnallite, epsomite, bischofite, and possibly cryptomelane (Isherwood, 1979; Roedder, 1984). A number of gas phases in fluid inclusions have been identified, including CO_2 , CO , H_2 , N_2 , CH_4 , C_2H_6 , H_2S , O_2 , Ar , Xe , Ne , and He (Roedder, 1972). Oil globules have also been observed (Roedder and Belkin, 1979b). Inclusions formed ^{during} at different periods of crystal growth and ^{because of} due to post-depositional processes can have very dissimilar chemical compositions. Inclusions in the same deposit or even adjacent to one another can differ significantly. } Combine sentences?

Very little ^{information available concerning} is known about the redox and pH conditions of the inclusion fluids. inclusion fluids. Quantitative data are limited to a few Russian studies. The pH is generally acidic (between 3 and 6.5) while redox conditions (Eh was measured) varies considerably (Isherwood, 1979). Petrichenko (1973) observed that ^{fluids from inclusions in} salt domes ^(value-?) fluid inclusions tended to be reducing while those in bedded salt tended to be more oxidizing ^(value-?). "more oxidizing than reducing" ^{can't still be reducing - need give idea of values.}

~~A few isotopic studies (i.e., hydrogen and oxygen) have been performed on~~

~~inclusion fluids (Beeunas and Knauth, 1983; see Roedder, 1984). The results of~~
~~these studies generally show that the fluids are not essentially seawater~~

Information from hydrogen & oxygen isotope studies

~~residues, but rather mixtures of seawater and local meteoric waters from a~~
variety of possible sources^{(B+K, 1983, R (1985), rather than seawater residues only.} Studies by Knauth and others (1980) and Knauth and Kumar (1983) show that some water from brine leaks in Weeks Island, Jefferson Island, and Avery Island salt mines in Louisiana is meteoric in origin.

III. THEORY OF BRINE MIGRATION

^{migration}
The behavior of intracrystalline inclusions under a temperature gradient has been extensively studied (e.g., Anthony and Cline, 1971; Cline and Anthony, 1972; Geguzin and others, 1975; Olander and Machiels, 1979; Olander, Machiels, and Yagnik, 1980; Jenks and Claiborne, 1981; Pigford, 1981; Biggers and Dayton, 1982; Yagnik, 1983; Olander, 1984). The nature of the movement is dependent upon whether the inclusion is all liquid or contains a gas phase.

When a temperature gradient is applied to an all-liquid inclusion, migration is driven by solubility differences; i.e., since the solubility of salt increases with temperature, salt will dissolve at the interface closest to the heat source (the "hot" face), molecularly and thermally diffuse through the brine, and precipitate at the interface furthest from the heat source (the "cold" face). This^{process?} is brought about because the thermal conductivity of the salt is higher than that of the brine, which produces a higher temperature gradient within the liquid than the applied gradient to the solid (Yagnik, 1983). Thus, the inclusions will migrate toward the heat source. The processes which that

brine migration will occur whether thermal and is the same or not - the difference in and simply speeds the process up.
through the dissolution - precipitation process

control migration velocity are the diffusional transport within the inclusion and the kinetics of interfacial mass transfer (i.e., the dissolution and precipitation within the inclusion) (Yagnik, 1983).

The presence of a gas phase within the inclusion will profoundly affect brine migration. The increase in vapor pressure of water over brine with temperature controls inclusion behavior. Water will evaporate at the hot side of the gas bubble and be transported to the cold side, and condense, ^{and dissolve salt until saturation is reached} (Anthony and Cline, 1972). The condensed water in turn backflows to the hot side, carrying dissolved salt from the cold face of the inclusion to the hot face. This backflow effect overwhelms any solubility-driven salt flux if the gas volume fraction is ≥ 0.1 . Thus, the gas-liquid inclusion will migrate away from the heat source.

The behavior of intercrystalline inclusions under a temperature gradient is unknown. It has been postulated, ^(Reference?) however, that their migration is driven by pressure gradients; i.e., intercrystalline inclusions will migrate down a pressure gradient. This phenomenon is observed in salt mines where water in the salt under lithostatic pressure leaks into the mine, which is under atmospheric pressure. It is also unknown how water released ⁹ from hydrated and hydrous minerals will migrate. The dehydration effect may be most pronounced in salt-poor zones, e.g., clay interbeds. Released water may undergo significant migration in these clastic zones in a manner not predicted by brine migration theory.

IV. EXPERIMENTAL ^{DATA} EFFORTS

Laboratory Studies

As stated above, almost all of the experimental studies on brine migration to date have been concerned with intracrystalline migration. Some of the pioneering laboratory work was done by T.R. Anthony and H.E. Cline (1971, 1972, 1974; Cline and Anthony, 1971). They studied thermal migration of both liquid droplets and biphasic vapor-liquid droplets in solids and through grain boundaries. They used high-purity KCl crystals and produced their own brine inclusions by drilling holes into the crystals, filling them with deionized water, and sealing them with wax to prevent evaporation. A temperature gradient was then applied and inclusion behavior observed. Initially, the large inclusions tended to break up into many smaller inclusions under the temperature gradient. As the inclusions began to migrate under the temperature gradient, Anthony and Cline (1971) observed that the inclusions changed shape, becoming more disk-like. Larger inclusions traveled faster than smaller ones and were observed to collide and coalesce with smaller ones as they migrated. The investigators noted that migration was heterogeneous and should be treated as such. They suggested that interfacial kinetics control inclusion migration occurrence and velocity and that there will be no migration below a certain critical inclusion size (Anthony and Cline, 1971).

In other studies, Anthony and Cline observed migration behavior at grain boundaries (Cline and Anthony, 1971) and biphasic vapor-liquid inclusion migration (Anthony and Cline, 1972). The investigators observed that the surface tension of a grain boundary tended to pull droplets that had passed through a boundary back towards the boundary plane under a temperature gradient. This effect was negated if the temperature gradient was increased. Anthony and Cline found that a vapor phase in an inclusion would cause it to move down a temperature gradient (see Section III) and that the nature of the vapor phase affects the velocity. If the gas phase is only water vapor, viscous gas flow controls transport of water through the vapor phase. If a significant "foreign" gas is present, diffusion controls the transport of water vapor through the gas phase and thus the migration velocity is significantly less.

substantial?

There is a significant body of work by Soviet investigators on brine migration (Geguzin and Dzyuba, 1973b, 1973c, 1974; Geguzin and others, 1975; Sedletskii and others, 1973). Isherwood (1979) presents an annotated bibliography on these works.

Thermal experiments were conducted at Sandia National Laboratories on large salt blocks as a prelude for subsequent in situ experiments at the Waste Isolation Pilot Plant (WIPP). In the Salt Block I tests, a cylinder of salt one meter high was heated and various tests were performed (Duffey, 1979).

Some water loss data were collected and are reported but not interpreted. The

diameter ?

(size? cylinder)

Salt Block II tests were specifically set up to observe brine migration in a salt block (Hohlfelder, 1979). The salt block used contained total volatiles (mainly water) of between 0.1 and 0.5 weight percent. The salt itself was 88% halite, 8% polyhalite, and 4% sylvite (Lambert, 1979). A maximum temperature and temperature gradient of 200°C and 12°C/cm, respectively, were induced. The experiment ran for approximately 140 days. Only 111.4 grams of water were released (compared to between 2.2 to 9.0 kg of water present initially), and 43% of that was released during the three-week-long period after the heater was turned off. In general, the greatest water release ^S rates were observed following decreases in heater power. The investigators suggest that "the thermochemical response of the salt, including the stress state and time-dependent stress relaxation, is an essential ingredient in predicting the measured water release rates" (Hohlfelder, 1979). The investigators suggest that when the heater power was decreased, the salt failed in tension and thus increased in permeability, resulting in an increase in water release. Similar results were found in additional tests at Sandia (Hohlfelder and Hadley, 1979).

Additional results from the Salt Block tests show that encrustations on the interior of the axial heater hole consisting of sodium, potassium, and magnesium chloride minerals (e.g., carnallite, bischofite, recrystallized polyhalite) not usually found in the host salt rock were formed (Lambert, 1979). Investigators also observed that, in general, only the larger inclusions crossed grain boundaries during thermal migration. However, the larger inclusions were also observed to stop at least 7 cm from the heater

hole; smaller inclusions were predominant closer in, with a vapor phase commonly present in the inclusions within 4 cm of the heater hole (Lambert, 1979). This may be due to a breakup of the larger inclusions and boiling of the fluids close to the heater.

Roedder and Belkin (1979, 1980) also performed laboratory studies on WIPP salt. The investigators found that the fluids in many large inclusions ($>100 \mu\text{m}$) were released by decrepitation at 250°C in several days (Roedder and Belkin, 1979). This decrepitation caused some fracturing and crumbling in the 100 gram pieces of core used. At grain boundaries, larger inclusions were found to cross the boundaries while smaller ones would not (if the boundary was tight). In a subsequent experiment, approximately one centimeter cubed blocks of salt cut from portions of single crystals were heated and intracrystalline inclusion behavior observed (Roedder and Belkin, 1980). Only relatively small inclusions ($<10^9 \mu\text{m}^3$) were present. Of greatest significance in this study was the discovery that migration rates could differ by a factor of three for different samples from the same core or even from different parts of the same piece of core. The investigators believe that the amount of included water in salt deposits is not trivial.

a factor of 3
would seem
to be quite
good for
tests such as
this

This statement
not relevant
to remainder
of paragraph

Investigators at the University of California-Berkeley have ^{performed} done considerable experimental work on brine migration (Olander and others, 1980; 1982; Yagnik, 1983; Olander, 1984). The investigators used a microscope with a hot stage and observed all-liquid and gas-liquid inclusions in both NaCl and KCl (Olander and

others, 1980). Two of their observations were that very large inclusions tended to break up into smaller ones under a temperature gradient and that migration velocities ^{were} affected by the number of dislocations present in the salt crystal (Olander and others, 1980; Yagnik, 1983). Additional studies showed that interfacial kinetics were rate-controlling for inclusion migration velocity except for large inclusions, for which diffusion is rate-controlling due to intersection by enough dislocations so that the kinetic resistance to dissolution is negligible (Olander and others, 1982; Yagnik, 1983). The effect of stress was also observed. Migration velocities rose abruptly under an increased axial loading and increased with time. The velocities did not return to initial values after removal of the load, indicating an inelastic property. A change in brine composition (i.e., $MgCl_2$ and $SrCl_2$ solutions) did not affect migration velocity (Yagnik, 1983). Gas-liquid inclusions were observed to behave similarly to all-liquid inclusions except for the direction of migration. Investigators also observed inclusion behavior at grain boundaries. Inclusions migrated up or down the temperature gradient (depending upon the inclusion make-up), but in an indirect, two-dimensional manner (Yagnik, 1983). This was interpreted to be due to the distortion in the solid lattice at the grain boundary and the fact that a grain boundary is an area of minimum energy which would promote inclusion migration along the grain boundary.

Biggers and Dayton (1982) performed brine migration experiments on polycrystalline salt samples that were hot-pressed to control the microstructures. Salt samples were put in contact with a brine source and a

temperature gradient was induced. Migration velocities were estimated by the timed appearance of brine at the hot face or by determining the penetration distance by migration artifacts in the microstructure. Visual observation was precluded due to the nature of the experimental apparatus. A significant result of the study is that migration velocities in dense polycrystalline salt may be at least an order of magnitude greater than velocities observed in single crystal experiments. The investigators found that brine prefers to migrate along paths of high crystalline activity (i.e., grain and subgrain boundaries and crystal defects) and may be enhanced along these paths.

Except for the Biggers and Dayton (1982) study, none of the laboratory studies discussed above was concerned with intercrystalline migration, and the Biggers and Dayton study was basically qualitative. Another uncertainty with the studies is the spatial effects. The majority of these studies dealt with small salt samples, usually single crystals. These effects are better understood in the in situ studies discussed below.

In Situ Studies

There have been a limited number of brine migration tests which have been in situ, i.e., performed in salt mines. ..(Salt Vault).....

implies that a discussion of Salt Vault will be included?

?

A five-year field testing program which included brine migration tests was performed in the Avery Island, Louisiana, salt mine (Krause, 1983a; 1983b). Three experimental configurations were set up: (1) natural brine movement with no heating; (2) natural brine movement under elevated temperature conditions; and (3) synthetic brine movement under elevated temperature conditions. For a complete description of the experimental set-up, see Krause (1983b). Tests were run for ^{approximately} about one year. The measured borehole wall temperature was ^{approx.} about 51°C at heater mid-height and the calculated temperature gradient was approximately 1.2°C/cm in the immediate vicinity of the borehole wall. The effective moisture content of the salt was determined to be about 0.054 weight-percent. The salt contains about 10% anhydrite. Approximately 23 grams of moisture were collected in the natural brine under elevated temperature experiment and approximately 18 grams in the synthetic brine experiment (collection rates ranged from 0.026 to 0.044 grams/day) (Krause, 1983b). During the cooling-down period of the synthetic brine test, the ^{rate of} moisture collection increased significantly. Subtracting the brine collected in the unheated test gives a net accumulation of approximately 10 grams of moisture collected in the natural brine test and 5 grams in the synthetic brine test (before cooling).

The investigators found that the region of significant brine migration in these tests was very small, i.e., about 5 mm from the heater surface after one year.

Distance? { Tracers (deuterium water and magnesium) were observed to increase ^{? in concentration?} toward the heat source, although there had not been sufficient time for them to reach the

heater borehole. The synthetic brine was not observed to migrate into salt crystals (nor was any salt dissolution observed), leading the investigators to conclude that the brine moved along microcracks or grain boundaries.

Brine migration tests are also being conducted in the Asse salt mine in West Germany (Westinghouse, 1983). The investigators plan to run tests for longer durations (up to two years) and higher temperatures (over 200°C) than were conducted at Avery Island. The investigators are also interested in testing the effects of radiation, stress, gas pressure, and petrology and mineralogy on brine migration. The tests are designed to model salt types in both the United States and West Germany. To date, no data have been published from the Asse Mine tests.

Asse salts are NOT a good analog for US salts under consideration → water content is too high; too much carnallite - sentence should be reworded

V. MODELING EFFORTS ~~6~~ BRINE MIGRATION

The first investigators to formulate a relatively complete mathematical model for predicting theoretical brine migration were Anthony and Cline (1971, 1972, 1974; Cline and Anthony, 1971). Their equation for all-liquid intracrystalline inclusion migration is:

$$v = D \frac{C_1}{C_s} \left[\left(\frac{1}{C_1} \cdot \frac{C_1}{T} + \sigma \right) \frac{G_1}{RT} - \frac{1}{RT} \left(\frac{K}{L} + \frac{4\gamma V_s}{XL} \right) \right] \quad (1)$$

where, v = droplet velocity
 D = diffusion coefficient
 C_1 = concentration of salt in brine droplet
 C_s = concentration of salt in solid
 σ = Soret coefficient
 G_1 = temperature gradient in brine droplet
 R = gas constant
 T = absolute temperature, °K
 K = kinetics potential at interface
 L = dimension of droplet parallel to temperature gradient
 X = dimension of droplet perpendicular to temperature gradient
 γ = grain boundary tension
 \bar{V}_s = partial molar volume of solid

The equation can be simplified conceptually as:

$$v = v_T + v_G - v_K - v_\gamma \quad (1a)$$

where, v_T = velocity due to ordinary diffusion
 v_G = " " " thermal diffusion
 v_K = " " " kinetics at interface
 v_γ = " " " surface tension at grain boundaries

Cheung and others (1979) evaluated the Anthony and Cline model and compared it with several earlier, more simplistic models. They found that the first two terms (i.e., v_T and v_K) in equation (1a) dominated the calculated velocity. The final two terms, v_K and v_Y , had relatively little effect on the calculated velocity. Furthermore, although the equation is the most complete available, it requires data for the final two terms that is presently ~~very~~ difficult or impossible to measure. Roedder and Chou (1982) found some errors in the work of Cheung and others (1979). These include the improper use of models and inaccurate estimation of diffusion coefficients.

which models

do these errors impact conclusions of Cheung + others?

The most advanced theoretical modeling of intracrystalline brine migration has been done by researchers at the University of California-Berkeley (Olander and Machiels, 1979; Olander and others, 1980; Pigford, 1981; Olander and others, 1982; Yagnik, 1983; Olander, 1984). Their work has basically expanded on that the work of Anthony and Cline, ~~involving investigation of~~ ^{by including} the variables for kinetics and surface tension effects on migration velocities. For a complete discussion of their work, see Yagnik (1983) and Olander (1984). There have been some disagreements with the Berkeley work (see Roedder and Chou, 1982; Chou, 1983). These disagreements are mainly centered around the magnitude of interfacial kinetics and surface tension effects and on the existence of a threshold temperature gradient (see section VI).

summarize next effect of disagreements in brine mig. non-cons?

Some empirical models have also been developed and, due to the lack of data for the theoretical models, are enjoying widespread use. Jenks developed the

"Most" of the data do fall below the curve -
 If a curve with "all" data below it was chosen - the model would be totally irrelevant for the data -
 I think Jenks made a reasonable compromise between conservatism + realism.

so-called Jenks equation, an empirical equation based on the work of Bradshaw and Sanchez (1968) on the Salt Vault Project (Jenks, 1972; 1979; Jenks and Claiborne, 1981). The ^{curve-fit} equation is based on migration rate versus temperature data:

$$\log V/G_s = 0.00656 T - 0.6036 \quad (2)$$

where, V = migration velocity (cm/yr)
 G_s = temperature gradient (°C/cm)
 T = temperature (°C)

~~It is a curve fit equation that is asserted to be conservative, although all the data do not fall below the curve.~~ Jenks and Claiborne (1981) compared rates calculated by the Jenks equation with experimental data and concluded that the equation gives conservative values. The equation is incorporated into a computer program, MIGRAIN, which was validated with data from the Salt Block II experiments (Hohlfelder, 1980). McCauley and Raines (1984) developed a modification of the MIGRAIN code, called BRINEMIG, which was also validated with Salt Block II data. BRINEMIG also uses the Jenks equation to model brine migration. Roedder and Chou (1982), however, disagree with the assertion by Jenks and Claiborne (1981) that the equation is conservative. Some of their concerns include: ⁽¹⁾ that the assumptions ^{relevant to the quantities in the salt} of fluid amounts and the Soret coefficient used are not conservative, ⁽²⁾ that the ^{assumption} existence of a threshold gradient for brine migration was not proven, ⁽³⁾ that assuming that salt formations

need to explain (in 1-2 sentences) why each of these results in non-conservative predictions of brine migration & approx by how much.

are homogeneous or that brine migration can be modeled as if in single crystals is incorrect, and that intercrystalline water was ignored in the analyses.

UNCERTAINTIES (subheading of modeling)
~~VI. UNCERTAINTIES IN PREDICTION~~

There a number of uncertainties involved in the prediction of brine migration in a potential HLW repository in salt. Perhaps the most significant uncertainty involves intracrystalline versus intercrystalline inclusion behavior. Intracrystalline migration of brine inclusions is a fairly well understood process, but intercrystalline migration is not. Roedder (1984) suggests that intercrystalline fluids could make up to 50% of the total water present in a salt deposit. Modeling of brine migration has generally considered only intracrystalline inclusions (see Jenks and Claiborne, 1981; McCauley and Raines, 1984), assuming that intercrystalline migration rates will not exceed intracrystalline migration rates. This assumption, however, is questionable. Intercrystalline migration may be driven by pressure gradients instead of temperature gradients, thus undermining the basis for the above assumption. It is clear that the process of intercrystalline fluid migration needs to be studied more thoroughly before the assumption that intercrystalline migration is not greater than intracrystalline migration can be fully evaluated.

the assumption of intra. only in homo. media could be conservative - I agree, though, that more information is needed.

can not arbitrarily conclude this →
low temp. gradients +
grain boundary conditions —
may prohibit migration into another crystal.

Salt Vault
S.B. I/II

A related concern is the uncertainties regarding inclusion behavior at grain boundaries. When an intracrystalline inclusion reaches the grain boundary, various investigators observed that it either ceased migrating, crossed into the adjacent crystal, or began migrating along crystal boundaries. Its behavior depends on a number of parameters, including inclusion size (small inclusions were trapped), the nature of the boundary (i.e., how tight it is), and the magnitude of the temperature gradient. Since most of the fluids present in salt crystals are in the large inclusions, it can be concluded that the majority of the fluids will not stop migrating at crystal boundaries under a temperature gradient. It is apparent that long term, in situ experiments need to be run in order to determine the behavior of fluids at grain boundaries.

△ define; because Avery IS. could be considered long term

how much is sign.?

Many salt deposits contain significant amounts of hydrated or hydrous minerals. Repository-induced conditions may cause these minerals to dehydrate, thus producing fluids available for migration. However, it is unclear how these fluids will migrate, especially in clastic interbeds within the salt. Including dehydration fluids in intracrystalline migration models may be incorrect.

probably "up" as a result of density gradients thus - impact will depend on stratigraphy to some extent.

The existence of a threshold temperature gradient below which inclusion migration will not occur is a source of debate among investigators. Some investigators (see, e.g., Cline and Anthony, 1972; Jenks and Claiborne, 1981; Pigford, 1982; Yagnik, 1983; Olander, 1984) believe that a threshold gradient

does exist in salt. Jenks and Claiborne (1981) calculated a series of values for the threshold gradient, while McCauley and Raines (1984) used a threshold gradient of $0.125^{\circ}\text{C}/\text{cm}$ in their model, BRINEMIG. Other investigators, however, dispute the concept of a threshold gradient (see, e.g., Roedder and Chou, 1982; Chou, 1983). The disagreement centers around the magnitude of interfacial kinetics and grain boundary surface tension effects (Chou, 1983). Roedder and Chou (1982) also suggest that experimental data used to support the concept of a threshold gradient may not be applicable, while other data suggest that no threshold gradient exists. A scoping study by St. John and others (1982) suggests that a ^{mainly significant?} significant temperature gradient will exist in a salt repository ^{in salt} for over 10,000 years, although a more recent study suggests that temperature gradients will be insignificant well before that (McCauley and Raines, 1984). The use of a threshold gradient by McCauley and Raines (1984) does not decrease the predicted amount of brine accumulation at the waste package to a great extent. ^(how much - 90?) Because there is uncertainty about the existence of a threshold gradient, conservative predictions should presently not incorporate it. Additional experimental data modeling repository conditions should be collected to examine the threshold gradient concept.

The construction of a HLW repository and emplacement of waste may change the geochemical environment significantly enough to affect predicted brine migration rates and accumulated brine at the waste package. The actual construction may cause a number of changes, including fracturing of the salt, formation of brine inclusions, and the introduction of atmospheric oxygen.

by democracy
everyone should
must be
Right!?

(Reference)

and that

(Reference)

Fracturing will form pathways for fluid migration near the waste package; the extent of this problem will depend on the mining method used. Inclusions formed in the salt will probably be liquid-vapor inclusions. These inclusions would migrate down a temperature gradient, and their effect on the migration of all-liquid inclusions up the gradient is uncertain. Atmospheric pressures in the mined cavities will create a pressure gradient with respect to the salt rock that is under lithostatic pressure and possibly induce migration of intercrystalline fluids.

The irradiation of the rock salt by HLW may significantly influence the chemical environment. Radiation effects include the formation of colloidal sodium, dramatic changes in the pH, and gas formation (predominantly H₂; also CO₂, water vapor, and possibly O₂) (Panno and Soo, 1984). The nature and magnitude of these effects depends on the moisture present near the waste package during irradiation, impurities in the salt, and the rate and duration of the irradiation. Based on Salt Vault data, Jenks (1979) suggested that irradiation will not affect brine migration, but more recent studies may contradict this. Even if migration rates are not affected, the changes in redox and pH conditions and brine composition will certainly affect brine corrosion of the waste containers. Backfill and packing materials that are used will also affect the fluid composition and redox and pH conditions.

need to elaborate + defend assertion

NOT relevant to brine mig. TOP Rept

Some investigators observed the decrepitation of fluid inclusions in salt at high temperatures in a short period of time (e.g., see Roedder and Belkin,

1979). This breaking up of inclusions was not always observed in brine migration experiments. The effect of decrepitation on brine migration is uncertain.

VII. SUMMARY AND CONCLUSIONS

The migration of brine inclusions in a salt deposit under a temperature and/or pressure gradient may compromise the ability of a repository to isolate HLW from the accessible environment. Investigators have observed and modeled intracrystalline fluid behavior under a temperature gradient in a number of laboratory and some in situ experiments. This process is fairly well understood for both all-liquid and liquid-vapor inclusions. Intercrystalline fluid behavior, on the other hand, is poorly understood. The amount of fluids present in intercrystalline inclusions, however, can be significant. Their behavior under temperature and pressure gradients merits further study. Models predicting migration rates and amounts of fluid expected to reach the waste package in a HLW repository have incorporated only intracrystalline fluid behavior.

Additional uncertainties in predicting fluid behavior in a HLW repository in salt include behavior at grain boundaries, the migration behavior of fluids released by mineral dehydration, the possible existence of a threshold gradient, construction effects, radiation effects, and the effects of redox

*see comment on
p. 1 concerning
"compromise"*

conditions, and the occurrence of decrepitation. All of these uncertainties need to be better defined in order to accurately model brine migration in a HLW repository in salt.

of fluid inclusions -
but do they need to be better defined for conservative modeling?

References?