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**Brine Migration in Salt and Its
Implications in the Geologic
Disposal of Nuclear Waste**

G. H. Jenks
H. C. Claiborne

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CHEMICAL TECHNOLOGY DIVISION

NUCLEAR WASTE PROGRAMS

**Technical Topical Report on Brine Migration
(Activity No. AP 05 15 15; FTP/A No. ONW-2813)**

**BRINE MIGRATION IN SALT AND ITS IMPLICATIONS
IN THE GEOLOGIC DISPOSAL OF NUCLEAR WASTE**

G. H. Jenks and H. C. Claiborne

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**OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
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SYMBOLS AND ABBREVIATIONS

SF	spent fuel
CHLW	commercial high-level waste
CHLW	defense high-level waste
SENM	Southeast New Mexico
WIPP	Waste Isolation Pilot Plant
MTHM	metric tons of heavy metal
ONWI	Office of Nuclear Waste Isolation
m	meter
kg	kilogram
L	liter
y	year
mol	gram mole
<u>m</u>	molal
<u>M</u>	molar
k, kilo	prefix meaning 1000
m, milli	prefix meaning 0.001
μ , micro	prefix meaning 1 E-06
n, nano	prefix meaning 1 E-09
p, pico	prefix meaning 1 E-12
f, femto	prefix meaning 1 E-15

Lists of symbols used with particular topics are presented or referenced at appropriate locations in the text. See particularly Sects. 3.1.2, 3.1.3, and 3.1.4.

BRINE MIGRATION IN SALT AND ITS IMPLICATIONS IN THE
GEOLOGIC DISPOSAL OF NUCLEAR WASTE

G. H. Jenks and H. C. Claiborne

1. EXECUTIVE SUMMARY

1.1 Introduction

Bedded and domal salt deposits within the United States that are being considered for use in the disposal of spent light-water reactor (LWR) fuel and/or solidified high-level wastes contain a small volume fraction of brine inclusions, which are located within salt crystals and/or at crystal boundaries. These inclusions can migrate through the salt to the waste package when sufficiently large gradients (primarily temperature gradients) exist in the chemical potential of the salt around the inclusions. The fluids could also move hydraulically if sufficiently large microcracks are formed in the salt.

Information concerning the rates and total amounts of brine migrating to a waste package within a salt repository are needed in evaluating the suitability of a given disposal concept. Brine migration in salt has been studied extensively during the past 15 years, and the objective of the present report is to provide a comprehensive review and analysis of this available information for use in the preparation of a licensing topical report (LTR) on brine migration. The objectives of the licensing report are discussed elsewhere.

The topics covered in this report relate to three general areas: (1) the characteristics of salt formations and waste packages germane to considerations of rates, amounts, and effects of brine migration, (2) experimental and theoretical information on brine migrations, and (3) means of designing to minimize any adverse effects of brine migration. Flooding, brine pockets, or other factors will presumably be precluded by appropriate site selection and repository design.

1.2 Baseline Repository Characteristics

These are discussed in Sect. 7.2 (Table 11) for the three waste types considered in this report. The repository is mined by the room and pillar method, and the waste packages are placed in vertical holes drilled in the floor of each room.

The salt walls of the holes in which the commercial high-level waste (CHLW) is emplaced will reach maximum temperatures about 15 y after emplacement; these temperatures will be $\sim 210^{\circ}\text{C}$ for the 37 W/m^2 loading and $\sim 155^{\circ}\text{C}$ for the 25 W/m^2 loading, with maximum temperature gradients of $\sim 1.6^{\circ}\text{C/cm}$. The lower loading (and lower maximum temperature) will most likely be used. The maximum salt temperatures and temperature gradients for the other waste types will be less than those for the CHLW.

1.3 Rock Salt Characteristics Pertinent to Brine Migration in Salt Repositories

Most of the information on bedded salt summarized in this section pertains specifically to (1) the Salado salt in southeast New Mexico (SENM) at the depths where the Waste Isolation Pilot Plant (WIPP) would be located (one level at about 600 m and the other at 800 to 830 m below the surface), and (2) the Hutchinson salt member of the Wellington formation, where the Project Salt Vault Experiment was conducted (at the 1000-ft depth in the Carey Salt Company mine), at Lyons, Kansas.

Other bedded salt formations were not considered, either because of insufficient information on the composition, lithology, and texture of the formation, or because of incomplete information on the effects of the known impurities on brine migration, or both.

Most of the summarized information on domal salt pertains specifically to the Rayburn and Vacherie domes in Louisiana, although some pertinent information is also available from studies at other locations, including the mine at Avery Island, Louisiana and the dome at Grand Saline, Texas. In situ and other experiments were conducted with the Avery Island salt.

Sections 1.3.1-1.3.4 summarize the characteristics of the referenced salt formations that might affect the rates and total amounts of brine migrating to a waste package and/or the effects of the brine on the waste package.

1.3.1 Characteristics of salt crystals

Rock salt formations are composed of tightly bound aggregates of crystals of NaCl containing anhydrite impurity and small amounts of other impurity minerals and brines. The crystals are anhedral in shape, with characteristic dimensions in the range of 3 to 30 mm.

1.3.2 Characteristics of mineral impurities

Detailed examinations of core samples of Salado salt at depths of ~800 to 850 m indicated that halite and/or anhydrite are major constituents. The observed fractions of anhydrite ranged up to ~90 wt %. Other impurities include trace amounts of clay and one or more of the following: polyhalite, iron oxide, K-feldspar, talc, chlorite, carnallite, bloedite, and quartz. The anhydrite and the clays are usually located intercrystalline (to the halite) but disseminations of these impurities within halite crystals also occur.

Detailed examinations of a shallow core (3.2 m) from the floor of the Project Salt Vault experimental area in the Lyons, Kansas mine showed that the salt composition and structure were very similar to those for the Salado salt described above. The reported amounts of anhydrite in samples taken at depths of 0.6, 1.0, 1.5, 2.0, and 3.2 m below the floor were: 18, 8, 5, 47, and 32 wt %, respectively.

Chemical analysis indicates that the referenced domal salt consists primarily of halite with average anhydrite impurity of 1.6 wt % in Vacherie and of 2.3 wt % in Rayburn.

1.3.3 Characteristics of brine inclusions

Bedded salt. Brine inclusions occur within the single crystals of NaCl; these inclusions are generally cubical in shape and range in size from <1 μ m to a few millimeters on edge. Most of the brine volume is

contained within the larger inclusions (i.e., those greater than ~0.5 mm). Some brine also occurs on the boundaries between crystals.

Measurements of weight loss after heating to ~500°C showed that the total volatile content of samples of the referenced Salado salt was <0.5 wt %. Similar measurements with samples of the Lyons, Kansas, salt showed about 0.25 wt % volatiles. The total weight-fraction of H₂O in the undisturbed referenced salt (including that occurring as bound H₂O) may be somewhat less than the volatile fraction, but it could be greater since some inclusions could have been lost during the coring and sample preparation. It is also possible that drilling fluid was driven into the core during the drilling operation. Evidence has been reported that supports the possibilities for the occurrence of both gains and losses of fluids in core samples taken from ERDA Core No. 9 in the Salado in SENM. Hydrous minerals occur as impurities at certain levels in both salt formations, but these levels would be avoided in a high-level waste repository.

Domal salt. The available evidence showed the amount of H₂O in domal salt to be much less than that in bedded salt. There are very few brine inclusions within crystals, and the total amount of H₂O in core samples was <0.03 wt % in Rayburn and Vacherie. Larger amounts (<0.2 wt %) were reported for core samples from the experimental area in Avery Island.

1.3.4 Brine composition

Bedded salt. The best available information indicates that the encapsulated brine is rich in MgCl₂ (~2.4 m), saturated in CaSO₄ (~0.03 m), contains appreciable amounts of Br⁻ (~0.05 m) and some K⁺, and, of course, is saturated in NaCl (<2.0 m). There is apparently little or no Ca²⁺ that is not stoichiometrically balanced by SO₄²⁻. Any brine formed by the thermal decomposition of hydrous minerals within the rock would presumably be saturated in NaCl and CaSO₄. It might also contain appreciable concentrations of K⁺, Mg²⁺, and additional Ca²⁺, since thermal decomposition of hydrous minerals other than gypsum and clays would release these ions.

Domal salt. The encapsulated brine probably has low concentrations of solutes other than NaCl.

1.3.5 Permeability of rock salt

Studies of the permeability of bedded rock salt in the absence of a temperature gradient have been reported by several groups of investigators. There is agreement that undisturbed bedded salt at repository depths has a negligible permeability in the regions which are free of impurity stringers. Laboratory samples usually have sensible permeabilities that result from the presence of interconnected microcracks, which probably formed during the mining, drilling, and/or machining operations. There is strong evidence that the microcracks within a sample can be healed by application and maintenance of hydrostatic confining pressures comparable to those prevailing in the undisturbed formation.

1.4 Experimental and Theoretical Information on Migration of Fluids Within Walls of Waste Emplacement Holes

Migration of brine within the rock salt walls of a waste emplacement hole in the salt will depend upon the transport properties of the in situ aggregates, as well as upon the migration of inclusions within individual crystals.

Information concerning the brine and vapor transport properties of the rock salt walls of a waste emplacement hole is available from several reported experimental and theoretical studies. The general conclusions of these studies are given in Sections 1.4.1 and 1.4.2.

1.4.1 Possible mechanisms of brine migration

Brine inclusions within crystals. The most probable mechanism is thermal-gradient-induced migration in which salt dissolves at the hot interface and precipitates at the cooler interface, after diffusing through the inclusion. Completely filled brine inclusions within a single crystal of NaCl (or other alkali halide) migrate up a temperature gradient in the crystal by this mechanism.

Several different investigators have reported theoretical equations relating the velocity of migration of an inclusion to the temperatures and other physical and chemical characteristics of the brine-salt

system. The factors affecting the rate of migration of liquid-filled inclusions are well known and are identified in Eq. (1) (derived by Anthony and Cline) and elaborated upon in Sect. 3 and Appendices A, C, D, and E.

Included among the factors is an allowance K (or ΔC^*) for deviations from equilibrium between solid salt and solution at the interfaces. These deviations are caused by the undersaturation and supersaturation prevailing in the solutions at the dissolving and precipitating interfaces during migration of the inclusions. They act to reduce the rate of migration, V , below that which would prevail with no significant deviations from equilibrium at the interfaces, i.e., with K or $\Delta C^* = 0$ or negligible relative to effects of other factors which affect the migration rate in the given system.

The values of K and of ΔC^* have been related theoretically and/or experimentally to the migration rate, V , (which is proportional to the rates of dissolution and of precipitation at the interfaces) as shown in Eqs. (4) and (12) in the text:

$$K = \beta V + b, \quad (4)$$

$$\Delta C^* = VC_g/k + \Delta C^{\ddagger}, \quad (12)$$

where the quantities other than K , ΔC^* , and V are system constants at a given temperature. It was shown that these relationships are equivalent.

Both relationships indicate that the value of K (or ΔC^*) remains finite at $V = 0$. One implication of this is the indicated occurrence of a threshold value for the temperature gradient, VT_L , which can cause migration of an inclusion. The existence of such a threshold in alkali halides was shown by the experimental findings of Cline and Anthony for the migration of brine inclusions in KCl crystals at $\sim 40^\circ\text{C}$. The occurrence of a threshold gradient can also be inferred from considerations of the presence and distribution of brine inclusions in bedded salt.

Other workers have recently proposed a model for thermal-gradient induced migration of brine inclusions in alkali halides which has no threshold quantities for either temperature gradient or inclusion size [see Eq. (33)]. However, there is no evidence that this model applies to migration of inclusions in rock salt under the exposure conditions

which will prevail in a salt repository, and we believe that it does not apply.

$$\Delta C^* = v^{1/2} C_s^{1/2} C_l \left(\frac{1}{\sqrt{k_r}} + \frac{1}{\sqrt{k_d}} \right) \quad (33)$$

In general, the values for the system constants in Eqs. (4), (12), and (33), other than those for C_s and C_l , are not well established for NaCl, especially at the conditions which may prevail in rock salt and for inclusions in a repository. Accordingly, a semiempirical relationship between temperature gradient in the rock salt and V_{max} at a given temperature has been proposed and used in conducting estimates of brine migration in repositories. This relationship, referred to as the Jenks equation [Eq. (42) of the text] was based on correlations of experimental data and theories of brine migration in alkali halides. The use of this relationship is the equivalent of assuming that K or $\Delta C^* = 0$ in the system under consideration.

In addition to uncertainties regarding the value of K or ΔC^* in rock salt, there is also some uncertainty regarding the effective value for the coefficient of thermal diffusion (the Soret coefficient) of the solutes in the brine within an inclusion. Any practical effects of this uncertainty on the prediction of maximum migration rates is eliminated when the Jenks equation is used to calculate V_{max} .

Inclusions that contain a gas-vapor phase as well as a liquid phase might move down a temperature gradient in the salt, away from the heat source. A gas-vapor phase might result from the formation of radiolytic gas pressures high enough to force expansion of the salt walls of the inclusion. A gas-vapor phase could also result from escape of some of the liquid from an inclusion through microcracks into a region of lower pressure. Our analyses indicate that the amount of material transfer by down gradient movement of inclusions within crystals will have negligible consequences in a salt repository.

Brine inclusions intersecting crystal boundaries. Experimental information from the in situ Project Salt Vault experiment showed that most of the brine in bedded salt does not migrate from one crystal into

another but instead stops on the boundary between the crystals. Theoretical considerations indicate that large brine inclusions could move across crystal boundaries under a thermal gradient in the salt if they move within the crystals under the same gradient. The experimental observation that most inclusions are trapped on the boundaries might have resulted from the presence of impurities, such as clay and anhydrite, on the boundaries.

For domal salt there is no experimental information on the behavior of inclusions reaching crystal boundaries. However, this lack of information is probably unimportant since the amount of H_2O occurring as brine inclusions within crystals in the reference dome salt is insignificant.

Brine on crystal boundaries. Any significant movement of the liquid brine on crystal boundaries into an emplacement hole must take place through connected pores and/or microcracks. Such movement could result from gradients of pressure that could arise in the vapor pressure of H_2O , the radiolytic gas, and/or in the stress state of the salt. Other mechanisms for movement include transport in a thermal gradient analogous to that occurring for brine inclusions within crystals, and capillary action along previously unwetted surfaces. Water vapor, as opposed to liquid brine, could move under gradients of vapor pressure of H_2O and radiolytic gas from a receding liquid front within a microcrack or pore.

1.4.2 Permeability of salt around waste emplacement holes

Experimental results from Project Salt Vault and from more recent in situ and laboratory heater experiments indicate only slight permeability of the salt during the first 1 or 2 y after emplacement of the waste. No direct information is available on the subsequent permeability. Indirect information indicates that the permeability will be negligible if the emplacement is designed such that compressive forces are maintained on the rock salt and if radiation damage in the salt and the accumulation of brine on crystal boundaries in bedded salt have no significant adverse effects on the permeability. The latter reservation is particularly significant, since the collection of brine on boundaries

might lead to an increase in the number of connected pores in the salt, possibly extending to the distance beyond which the temperature gradients are no longer sufficient to cause migration of large inclusions to the surface of a crystal, i.e., to the distance beyond which the value of VI_2 is less than the threshold value. For domal salt, however, brine migration from crystals will probably not contribute significantly to the amount of brine on crystal boundaries. Upper-bound estimates for migration of H_2O that employ estimated values for the threshold temperature gradient are summarized in Sect. 1.5.

1.5 Estimated Rates of Migration of Water to a Waste Package in Salt

1.5.1 Bedded salt

The estimated H_2O migration rates during the first 1 to 2 y after emplacement of waste are approximately equal to those calculated by the MIGRAIN code (or by a similar method), assuming 0.5 vol % liquid H_2O (with liquid rates of migration given by the Jenks equation). This assumes that all of the liquid is located within crystals and that there are no effects of crystal boundaries on the thermal-gradient-induced migration. Rate values in bedded salt that are estimated in this way are: 250 mL/y and 80 mL/y for packages of CHLW and spent fuel (SF), respectively, and 10 mL/y for a package of defense high-level waste (DHLW).

This method for estimating rates of in-migration was based on observed agreement between experimental values and values calculated as described above. This agreement is probably fortuitous since it is likely that experimentally observed in-migration took place by movement of brine and/or vapor along crystal boundaries as well as by movement of brine inclusions through crystals. Also, the amounts of liquid H_2O may have differed from 0.5 vol %, and the rates of migration through crystals by all but the largest inclusions were very likely less than the rates shown by the Jenks equation. This method still seems an adequate means for estimating the amounts of brine in-migration during the first 1 to 2 y after emplacement of waste.

Longer-term rates and total amounts of in-migration will depend upon the permeability of the rock salt adjacent to the emplacement hole,

which, as summarized above, is uncertain. We have speculated that the average rates of in-migration will not significantly exceed the average rates during the initial 1- to 2-y periods. Assuming constant rates equal to the initial rates, the total amounts of in-migration during 100 y after emplacement in bedded salt are: 25 and 8 L for packages of CHLW and SF, respectively, and 1 L for a package of DHLW. If it is deemed necessary to establish the long-term brine migration characteristics more accurately for a repository, additional in situ experiments of many-year duration, with actual waste emplaced in the salt formation of interest, are required.

Estimates of the upper bounds for in-migration of H_2O to CHLW and SF waste packages in reference repositories from the surrounding salt were made employing the assumption that all of the brine reaching a crystal boundary will reach the emplacement hole at some unspecified later time, presumably by movement through connected pores and microcracks that may develop on the crystal boundary as a result of the collection of brine there. We have also assumed that a threshold temperature gradient exists (below which no migration of inclusions within crystals takes place), and that we can predict this temperature gradient using theoretical and experimental information discussed in this report.

The results indicate that, at the upper-bound, the volumes of salt which could contribute to in-migration of H_2O are about 24 m^3 and 6.0 m^3 for reference packages of CHLW and SF, respectively, in reference repositories with thermal loadings of 25 W/m^2 for each type of waste. These maxima occur at about 10 y and 25 y, respectively, after emplacement of the 10-y aged reference wastes. The estimates also show that reductions in the amount of radioactive waste (and the thermal power) charged to packages of CHLW cause marked reductions in the estimated volumes of salt which could contribute to brine in-migration.

1.5.2 Domal salt

The estimated rates of in-migration of H_2O during the first 1 to 2 y after emplacement of waste are approximately equal to those calculated

by the MIGRAIN code (or by a similar method), assuming 0.03 wt % (~0.065 vol %) liquid H_2O as brine, and rates of migration of brine as shown by the Jenks equation. This assumes that all of the brine is located within crystals and that there are no effects of crystal boundaries on the thermal gradient-induced migration. Rate values thus estimated for domal salt are 25 mL/y or less and are considered negligible.

As in the case of bedded salt considered previously, this method for estimating rates of in-migration was based on the results of comparisons and correlations between experimental values and those calculated by a method analogous to that employed with the MIGRAIN code. Again, the inferred agreement is probably fortuitous, since it is likely that experimentally observed in-migration took place by movement of brine and/or vapor along crystal boundaries as well as by movement of brine inclusions through crystals. Also, the amount of liquid H_2O probably differed from the assumed value, and the rates of migration were very likely less than the rates shown by the Jenks equation. Nevertheless, the above method comprises an adequate means for estimating the amounts of brine in-migration during the first 1 to 2 y after emplacement of waste.

The total amounts of in-migration during 100 y after emplacement of waste, estimated as described above for bedded salt, are 2.5 L for CHLW, and smaller volumes for the SF and DHLW. We believe that these are conservative estimated values for the reference domal salt.

1.6 Recommendations

1.6.1 Potential siting and design constraints

There is general agreement that contact between liquid H_2O (brine) and the metallic surfaces of the waste canister (or overpack if present) should be avoided for as long as possible after waste emplacement (conceivably several centuries) in order to avoid corrosive reactions at the metallic surfaces. Also, it can be argued that the amount of liquid brine within the emplacement hole at any time should be as low as possible in order to avoid conceivable adverse effects on the stability of the waste package and surroundings. Achievement of these general

criteria would be favored by the following site selection and/or design specifications.

1. Locate the emplacement holes within the rock salt formation where there is a minimum amount of brine which could conceivably migrate from the salt into the emplacement hole.
2. Employ designs and practices such that the walls of the emplacement hole are maintained under compressive stresses. In order to accomplish this, it may be necessary to employ canister dimensions and backfill materials which will minimize closure movement of the salt walls.
3. Avoid impurities in the rock salt that could yield water upon thermal or radiolytic decomposition and thus contribute to the amount of water which might migrate into the emplacement hole.
4. Design the emplacement so that the maximum temperature of the salt walls does not exceed about 250°C in order to avoid possible decrepitation of salt, with release of trapped water.
5. Design so that the maximum pressure of gas-vapors within the emplacement hole remains less than the compressive stresses on the salt walls to avoid forcing the expansion of microcracks within the salt.
6. Use a desiccant-barrier material as part of the backfill (between the metal enclosures and the salt walls) with the general objectives of sorbing water; shielding the metal from brine, gases, and vapors; and conceivably sorbing radioactive nuclides, if any should be released from the enclosures.

Strong desiccants such as CaO or MgO, or mixtures of these, in combination with sand or crushed salt might prove satisfactory as a backfill material to protect the metallic parts of the waste package from contact with corrosive liquids and vapors and also to minimize the amount of liquid brine within the emplacement hole. A mixture of CaO with sand or crushed salt filling the backfill space around the active length of a reference CHLW canister would react with more than 45 kg of water. Still more desiccant oxide could be contained within the larger backfill volumes around reference SF and DHLW canisters. Additional

experimental work, including in situ experiments, will be required to completely establish the characteristics of the oxide-sand or crushed salt backfill and to verify their suitability for the task.

1.6.2 Recommendations for additional experimental and analytical work

Additional in situ experiments of many-year duration, with actual waste emplaced in the salt formation of interest, are needed to establish the long-term, brine-migration characteristics for a repository in bedded salt. These experiments should be designed so that the exposure conditions closely reproduce those occurring in the repository with a given type of waste. The exposure parameters of interest include the following:

1. size and shape of waste package and of emplacement cavity in salt,
2. age of waste, thermal power, and radiation intensity,
3. states of stress in the salt adjacent to the emplacement cavity,
4. closure movements of the walls of the cavity,
5. composition and physical characteristics of backfill, and
6. amounts and distributions of pressure within the emplacement cavity and on the waste package.

Other recommendations relating to site selection and/or design of the repository were discussed in Sect. 1.6.1.

The experimental work should include several emplacements of individual waste packages, as in a reference repository. One or two waste packages should then be exhumed at intervals of 1 to 2 y, and the package and surroundings examined for evidence of the amounts and characteristics of brine migration and of the behavior within the emplacement cavity of brine, backfill, and metallic waste enclosures.

Similar in situ experiments are recommended for planned repositories in domal salt. The objectives in this case would be to establish the behavior within the emplacement cavity of brine, backfill, and metallic waste enclosures and to verify that the rates of in-migration of brine remain as low as expected with the given salt formation and repository design.

In situ experiments designed to provide information on aspects of brine in-migration and behavior within an emplacement cavity are underway in the domal salt mine at Avery Island, Louisiana; experiments are also planned for the dome salt mine at Asse, Germany, and in the potash-bearing bedded salt in the Carlsbad, New Mexico area. Laboratory experiments are also underway, or planned, which will provide information on certain aspects of brine migration in salt. The results of these in situ laboratory experiments will not, however, abate the need for the many-year in situ experiments described in the preceding paragraphs.

BRINE MIGRATION IN SALT AND ITS IMPLICATIONS
IN THE GEOLOGIC DISPOSAL OF NUCLEAR WASTE

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ABSTRACT

This report represents a comprehensive review and analysis of available information relating to brine migration in salt surrounding radioactive waste in a salt repository. The topics covered relate to (1) the characteristics of salt formations and waste packages pertinent to considerations of rates, amounts, and effects of brine migration, (2) experimental and theoretical information on brine migration, and (3) means of designing to minimize any adverse effects of brine migration. Flooding, brine pockets, and other topics were not considered, since these features will presumably be eliminated by appropriate site selection and repository design.

The fractional amount of water in the salt around a waste package varies with the salt deposit and with the purity of the salt. Fairly pure bedded salt, such as that at the WIPP site in New Mexico, probably contains less than 0.5 wt % water, and a large fraction of this occurs as brine inclusions within salt crystals. Domal salt, such as that in the Vacherie and Rayburn domes in Louisiana, probably contains <0.1 wt %, and the amount occurring as inclusions within crystals is much less.

Migration of brine within the rock salt walls of a waste emplacement hole in the salt will depend upon the brine-transport properties of the in situ aggregates as well as upon the migration of inclusions within individual crystals.

It is well established, both by experiment and by theory, that liquid-filled brine inclusions within salt crystals migrate up a temperature gradient in the salt, and the maximum migration rates that will occur within crystals in a repository can be estimated with reasonable confidence. A review and discussion of theory of the brine migration of all-liquid inclusions in salt crystals is included in the report, and it is demonstrated that the various theoretical equations that have been reported are either equivalent or in error.

However, experimental and theoretical data also indicate that most of the brine may not migrate from one crystal into another but instead may be trapped on the boundary between the crystals. Some of this trapping can be explained in terms of differences in energy between an inclusion on a crystal boundary and one within the adjacent crystal. Impurities on the boundary could also be a

contributing factor. In any case, it seems likely that extensive trapping on crystal boundaries will occur in the repository salt. Any significant movement of the brine on crystal boundaries into an emplacement hole will probably take place through connected pores and/or microcracks.

Experimental results from Project Salt Vault and from more recent in situ and laboratory heater experiments indicate that the permeability of the salt will be very small during the first 1 or 2 y after emplacement of the waste. No direct information is available on the permeability that will prevail subsequently. Indirect information indicates that the permeability will be negligible if the emplacement is designed such that compressive forces are maintained on the rock salt and if radiation damage in the salt and the accumulation of brine on crystal boundaries in bedded salt have no significant adverse effects on the permeability. We speculate that long-term migration rates will not exceed the average rates for the first few years after emplacement that are found by MIGRAIN calculations, and we present calculated values based on this speculation. Illustrative values are ~180 mL/y and ~60 mL/y of brine migration to each reference package of commercial high level waste (CHLW) and spent fuel (SF), respectively, emplaced in a bedded-salt repository. We believe that the rates and total amounts of in-migration estimated in this way are very conservative for domal salts, and are reasonably conservative for bedded salts.

Canister backfills that contain strong desiccants such as CaO or MgO might prove suitable for absorbing the H₂O migrating to a waste package at rates comparable to those mentioned above.

This report also includes estimates of the upper bounds for in-migration of H₂O to CHLW and SF waste packages in reference repositories from the surrounding salt.

1. INTRODUCTION

Salt deposits within the United States that are being considered for use in the disposal of spent light-water reactor (LWR) fuel and/or solidified high-level wastes may contain a small volume fraction of brine inclusions within the salt crystals and/or at crystal boundaries. Sufficiently large gradients in the chemical potential of salt around the inclusions can cause their migration through the salt. The fluids

may also move hydraulically when and if sufficiently large microcracks are formed in the salt.

Information relative to the rates and total amounts of brine migrating to a waste package within a salt repository and also for effects of the brine on the package are needed in evaluating the suitability of a given disposal concept. These subjects have been studied and discussed extensively during the past 15 years. The objective of the present report is to provide a review and analysis of available information for use in the preparation of a licensing topical report (LTR) on brine migration. The objectives of a licensing report are discussed elsewhere.¹

Three general areas of information are considered in this report: (1) the characteristics of salt formations and waste packages that are germane to considerations of rates, amounts, and effects of brine migration; (2) experimental and theoretical information on brine migrations; and (3) means of designing to minimize any adverse effects of brine migrations. Only information relating to the brine located within the salt is reported, since factors such as flooding and brine pockets will presumably not be factors because of appropriate site selection and repository design.

This report also includes estimates of the upper bounds amounts for in-migration of H_2O to CHLW and SF waste packages in reference repositories from the surrounding salt. These estimates employed the assumption that all of the brine collecting on a crystal boundary will reach the emplacement hole at some unspecified later time, and that a predictable threshold temperature gradient exists. The results indicate that at the upper bound, the salt volumes which could contribute to in-migration of H_2O are $\sim 24 \text{ m}^3$ and 6.0 m^3 for reference packages of CHLW and SF, respectively, in reference repositories with thermal loadings of 25 W/m^2 for each type of waste. These maxima occur at about 10 y and 25 y, respectively, after emplacement of the 10-y aged reference wastes. The estimates also show that reductions in the amount of radioactive waste (and the thermal power) charged to packages of CHLW cause marked

reductions in the estimated volumes of salt which could contribute to in-migration of H_2O .

We believe that additional in situ experiments of many-year duration, with actual waste emplaced in the salt formation of interest, are needed if it is considered necessary to accurately establish the long-term, brine-migration characteristics for a salt repository. These experiments should be designed so that the exposure conditions closely reproduce those that will occur in the repository with a given type of waste.

2. Rock Salt Characteristics Affecting Brine Migration

The characteristics of salt deposits which might affect the rates and total amounts of brine migrating to a waste package and/or the effects of the brine on the package include the following:

1. number, size, shape, and locations of brine inclusions within the salt,
2. composition of brine within inclusions,
3. size, shape, and texture of salt crystals composing the salt deposit,
4. identities, amounts, and locations of hydrous and other mineral impurities, and
5. temperature, temperature gradients, stress, and radiation damage in the salt.

These characteristics for both bedded and domal salts are discussed in the following sections of this report.

2.1 Bedded Salt

Bedded salt deposits are sedimentary deposits composed of evaporites that accumulated on the sea floor through precipitation following water evaporation. The usual mineral associates of halite in these bedded deposits are other saline evaporites, dolomite, and shale, which may occur in layers of varying thickness as illustrated in Figs. 1 and 2. These figures show the identities, depths, and thicknesses of major mineral layers found in cores from the Cary salt mine at Lyons, Kansas², and from the proposed WIPP site in New Mexico³ (SENM area). The mineral impurities may also occur within and among the crystals that compose the deposits of halite. Brine inclusions occur within the halite crystals and on the crystal boundaries.^{4,5}

Waste repositories at the WIPP site (SENM) would be located within the Salado formation at depths of about 600 m and 790 to 820 m for the low- and high-level wastes, respectively.³ At Lyons, the Project Salt Vault experiment was conducted in the Hutchinson salt member at ~300 m depth.^{2,6}

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Fig. 1. Generalized stratigraphic column taken from AEC#1 (AEC#1: 15-cm core drilled at the northeast corner of the Cary Salt Company mine at Lyons, Kansas).

ORNL DWG 81-15418

Fig. 2. Stratigraphic column of the WIPP (SENM) site geologic formation.

2.1.1 Size and shape of salt crystals

Most of the information on this topic was reported for the Salado salt^{5,7,8} and for the Hutchinson salt in the Lyons, Kansas area,^{2,9,10} and it indicated that the salt crystals are mostly anhedral with characteristic dimensions in the range of ~0.3 to ~3.0 cm. Little information is available from other regions in the United States, but a cursory examination of bedded salt specimens from Detroit, Michigan,⁴ indicated that the crystal sizes and the aggregates of crystals are similar to those from the Lyons area and from the Salado in SENM.

2.1.2 Identities, amounts, and distribution of mineral impurities

Detailed examinations of core samples^{5,7,8,11} of Salado salt at depths of ~790 to 820 m (the probable horizons within which the high-level waste repository would be located) indicated that halite and/or anhydrite are major constituents. The observed fractions of anhydrite ranged up to ~90 wt %. Trace amounts of clay were also reported for some samples, as well as one or more of the following impurities: polyhalite, iron oxide, K-feldspar, talc, chlorite, canallite, bloelite, and quartz. The anhydrite and the clays are usually intercrystalline (to the halite) but disseminations of these impurities within halite crystals also occur.

Sampling of a shallow core (3.2 m) from the floor of the Project Salt Vault experimental area in the Lyons, Kansas, mine showed that the composition and structure were very similar to those for the Salado salt.^{2,9,10} The reported amounts of anhydrite in samples taken at depths of 0.6, 1.0, 1.5, 2.0, and 3.2 m below the floor were: 18, 8, 5, 47, and 32 wt % respectively.

2.1.3 Physical characteristics and distribution of brine inclusions within bedded salt

The following summary of results for Salado salt in samples from ERDA Core 9 is quoted from Ref. 12.

Fluid inclusions have been studied in core samples from nineteen horizons above and below the levels of the proposed

repository in Salado salt beds. The techniques used include mainly petrography, freezing stage, heating stage, crushing stage, and decrepitation tests. The purpose was to determine those inclusion parameters that might be pertinent to an understanding of the origin and geological history of these salt beds.

Four general types of inclusions were found in these samples: type A - extremely abundant but minute primary liquid inclusions ($<100\text{ }\mu\text{m}$), with or without a tiny vacuum bubble, outlining primary growth features; type B - much larger liquid inclusions trapped during several stages of recrystallization of the primary salt, some with a small vacuum bubble and/or unidentified daughter crystals; type C - scarce, large liquid inclusions with large and variable gas bubbles under pressure, and type D - empty (i.e., gas) inclusions, found principally along grain boundaries, that have leaked and hence have lost their liquid contents.

The total weight percent of liquids as fluid inclusions in these 19 samples, as measured, ranged from 0.1 to 1.7% mostly as type B inclusions; the amount of liquid in these same samples in situ was larger, since many of the largest inclusions, that are the major contributors to the total percentage, and the intergranular fluids, have been drained during the boring and sample preparation. The temperatures at which these inclusions were trapped were generally in the range of 25-45°C. The brines in them are never simple saturated NaCl-KCl solutions; freezing temperatures indicate that they must contain considerable amounts of other ions such as Mg and Ca.

The shape of both type A and B inclusions was nearly cubic.

Also quoted from Ref. 12 is the following summary of results from volatile-constituent analyses of samples of Salado salt from ERDA Core 9.*

Amounts and composition of volatile constituents in the evaporite minerals were determined by heating rock samples to 600°C, recording mass loss, and in some cases analyzing the effluent in a gas chromatograph/mass spectrometer. Except for samples rich in hydrous minerals (polyhalites, clay partings, potash zones), the vast majority of rock salt contains less than 0.5 weight percent total volatiles.

*500°C (rather than 600°C) was the maximum temperature given in the body of the report (Ref. 5, pp. 7-31 to 7-35) which contained the detailed experimental information.

The most abundant volatile constituent in that 0.5% or less is water. Next most abundant is nitrogen, followed by CO_2 . Traces of hydrocarbons and fluorides from drilling operations were detected as contaminants in the core.

Similar results were reported by others for AEC Cores 7 and 8 of the Salado salt.^{7,8,11}

Studies of Lyons salt from the Project Salt Vault experimental area (Rooms 1 and 4) indicated that the types of brine inclusions were similar to those reported for the Salado salt. The results from measurements of weight loss upon heating were also similar, averaging 0.25% loss in weight upon heating to 625°C.¹³

Roedder and Bassett¹⁴ have recently reported considerations of possible sources of error in analyses for a specific form of water in rock salt. They concluded that most determinations made in the past are seriously low. However, we see no reasons to question the statement of Powers et al.,¹² with respect to maximum values for the total amount of H_2O within samples of repository-level rock salt at the proposed WIPP site in SENM (see quotation above). Note that the quoted statement excludes samples rich in hydrous minerals (polyhalites, clay partings, potash zones) which could contribute significantly to the total amount of H_2O within a sample. Similarly, we see no reason to question the reported maximum values for the total amount of H_2O within salt in experimental Rooms 1 and 4 of the Project Salt Vault experiment in the Carey Mine at Lyons, Kansas.¹³ The analyses made as part of the Project Salt Vault experiment showed an average of ~0.25 wt % H_2O . Hydrous minerals occur as impurities at certain levels in both salt formations, but these levels would be avoided in a high-level waste repository.

Many of the larger brine inclusions in the Lyons salt exhibit a low-pressure gas vapor bubble when examined at temperatures near those prevailing in the salt formation (~25°C at a depth of ~300 m).¹⁵ These bubbles, which generally occupied several percent of the inclusion volume, disappeared in the temperature range of 80 to 100°C.¹⁵ The disappearance-temperatures of these relatively large bubbles are accounted for on the bases of the known dependence of salt solubility on temperature, the partial molal volume of the dissolved salt, and the

thermal expansion coefficients of the solution and solid. However, the presence of bubbles in unheated specimens at laboratory temperatures has not been fully explained. It seems unlikely that the low-pressure bubbles could exist under natural conditions because of the plastic creep of the salt at high overburden pressures (~7 MPa at Lyons) over very long time periods. The bubbles were probably formed during or after the salt was removed from the formation, possibly as a result of the loss of some liquid through microcracks in the surrounding crystal.⁴

Low pressure bubbles were also reported in samples of New Mexico salt obtained from ERDA Core 9 at depths of 550 to 850 m, but they disappeared when heated to temperatures between 20.4 and 45.5°C.⁵ The occurrence of these bubbles and their disappearance-temperatures can probably be explained by the maximum temperatures prevailing in the undisturbed geologic formation (30 to 35°C) at the depths from which the cores were taken and/or by other factors such as leakage through microcracks.

2.1.4 Composition of brine inclusions in bedded salt

The best available information indicates that the encapsulated brines in the experimental areas of Project Salt Vault and in the Salado salt at the depths where the high-level waste repository would be placed are rich in MgCl_2 (~2.4 m), saturated in CaSO_4 (~0.03 m), contain appreciable amounts of Br^- (~0.05 m) and some K^+ , and, of course, are saturated in NaCl (~2.0 m). There is apparently little or no Ca^{2+} that is not stoichiometrically balanced by SO_4^{2-} (Ref. 4).

Any brine which is formed by thermal decomposition of hydrous minerals within the rock would presumably be saturated in NaCl and CaSO_4 . A thermal decomposition of hydrous minerals other than gypsum and clays could release K^+ , Mg^{2+} , and additional Ca^{2+} ions.¹⁶

2.1.5 Depth and site effects

No significant effects on brine amounts and composition or on salt composition have been shown with changing depth within the relatively pure layers of halite studied as possible locations for waste repositories. Also, there were no appreciable differences between the salt in the relatively pure layers in the Salado in SENM and in the Hutchinson salt member of the Wellington formation in the Lyons, Kansas, area.

It is notable that the relatively pure salt in both the Salado and the Hutchinson formations contains appreciable amounts of anhydrite, as well as small amounts of clay. Most of these impurities are inter-crystalline and thus can be expected to influence movement of brine along crystal boundaries.

Insufficient information is available regarding conceivable repository sites in other bedded salt deposits for evaluation of their characteristics relative to those of the Salado and Hutchinson formations.

2.1.6 Age of brine inclusions

Roedder and Belkin¹⁷ concluded that the brine inclusions in crystals of Salado salt had not moved measurably since deposition approximately 200 million years ago.

Additional evidence for little or no movement of brine inclusions can be inferred from their fairly uniform distribution; either upward or downward movement would have caused accumulation at a parting of shale or other relatively insoluble material or, conceivably, on boundaries between crystals of salt. The crystals would then have been cleared of inclusions.

2.2 Domal Salt

Domal, or dome salt, refers to the flowage deposits which occur in the Gulf Coast district of the United States.¹⁸ It is generally believed that these originated in deposits of bedded salt and that the

flowage resulted from the static weight of sediment and elevated temperatures, combined with differences in the densities of the flowing salt and the contacting country rock.¹⁸⁻²¹ Depths of the Gulf Coast salt domes are believed to be ~10 km.¹⁸⁻²¹

Analyses indicate that naturally occurring domal salts contain less H₂O as inclusions than does bedded salt.^{22,23} They are apparently free of the significant amounts of clay and silt commonly found in bedded salt. The principal contaminant is anhydrite.

Recent studies²⁴ of cores from the Vacherie and Rayburn salt domes (interior Louisiana domes), have reported information on crystal sizes, shapes, and salt composition that is summarized in the following section.

2.2.1 Lithology and mineralogy of the Vacherie and Rayburn salt domes

The following summaries are quoted from the studies of J. D. Martinez et al., of Louisiana State University. (Ref. 24).

A salt core recovered from the upper 2500 feet of Vacherie salt dome was studied to determine its petrologic and geochemical properties.

- + The salt consists mostly of halite with anhydrite inclusions occupying 5 to 10 percent of the volume.
- + The anhydrite inclusions appear as laminated layers and chunks, and dismembered, broken and folded layers up to 10 cm thick.
- + Diffuse segregations and sparsely disseminated crystals of anhydrite are also common.
- + Some large halite crystals (up to 10 cm) are locally present, sometimes associated with laminated anhydrite.
- + No major zones of shear, no major fluid inclusions, and no sedimentary rocks other than salt and anhydrite were encountered.

A similar 2500-foot core from Rayburn's salt dome revealed some similarities as well as some significant differences when compared to the Vacherie core.

- + The anhydrite content of the core is probably less than 5% by volume.
- + Sand-size anhydrite crystals commonly outline halite grains as intergranular trails.
- + No major fluid inclusions were found; however, sparse, minute fluid inclusions (up to a few mm) are more common in the very coarse halite than elsewhere in this core or in the Vacherie core.

- + No zones of shear, and no sedimentary rocks other than salt and anhydrites were found.
- + The upper 1000 feet of the Rayburn's core consists of elongate halite grains (0.5 to 3 cm) with many near vertical diffuse anhydrite bands up to about 5 cm thick.
- + The lower 1500 feet of this core contain mosaic bands of equi-dimensional halite grains (1 to 3 cm) separated by broad bands of very coarse-grained crystals (up to 50 cm).
- + Diffuse, near-vertical anhydrite bands in the lower 1500 feet are broader, more widely spaced, and commonly border the coarse halite bands.

Chemical analyses of samples taken at intervals over the full lengths of the salt cores (~760 m) showed that the cored materials were essentially pure halite, with an average anhydrite impurity of 1.6% and 2.3% in Vacherie and Rayburn, respectively.²⁵ No statistically significant differences could be observed between the average compositions of the two northern Louisiana domes, or between those domes and two domes in southern Louisiana (not specifically identified). There were no appreciable effects of changing depth on the average compositions.

2.2.2 Fluid inclusions in the salt

The following is quoted from the abstract of a report by Edwin Roedder and H. E. Belkin²⁶ on this subject.

Core samples from the Rayburn and Vacherie salt domes in Louisiana were examined for fluid inclusions, in connection with the possible use of such domes for nuclear waste storage sites. Three types of fluid inclusions were found: brine, compressed gas, and oil (in decreasing volume percent abundance). The total amount of such fluids is small, certainly <0.1 vol % and probably in the range 0.01 to 0.001 vol %, but the inclusions are highly erratic in distribution. Unlike many bedded salt deposits, the brine inclusions in this salt contain fluids that are not far from simple NaCl-H₂O solutions, with very little of other ions.

Knauth and Kumar²³ have recently reported very sensitive measurements of the water content of salt from six Louisiana salt domes, including core samples from the Rayburn and Vacherie domes. The average water content in samples from each dome was about 0.004 wt %, while anomalous zones were found with eight times this average amount.

3. THEORETICAL ASPECTS OF LIQUID BRINE MIGRATION WITHIN CRYSTALS OF NaCl

This section reviews theory concerning the migration of all-liquid inclusions in salt crystals and demonstrates that the various theoretical equations that have been reported are either equivalent or in error. Information is presented on values of the exposure and system variables and their predicted effects on migration rates.

3.1 Brine Migration Induced by a Thermal Gradient

3.1.1 Introduction

Completely-filled brine inclusions within a single crystal of NaCl (or other alkali halide) migrate up a temperature gradient in the crystal by a mechanism in which NaCl dissolves at the warmer brine-solid interface and precipitates at the cooler interface, after diffusing through the inclusion. Several investigators have reported theoretical equations relating the velocity of migration of an inclusion to the temperatures and other physical and chemical characteristics of the brine-salt system. Anthony and Cline²⁷ were the first to publish an apparently correct derivation, followed by Geguzin,²⁸ who used an independent, but apparently adequate approach. Subsequent reports of others have reviewed and discussed the derivations of Anthony and Cline^{4,29} and of Geguzin³⁰⁻³² and have expanded the Geguzin derivation to include thermal diffusion processes within the body of the brine inclusion.³⁰⁻³² These studies have concluded that the Anthony and Cline and the modified-Geguzin equations are equivalent.³⁰⁻³²

Such theoretical equations are useful for the collation and interpretation of experimental data on brine migration and for the prediction of migration rates at conditions of interest in a salt repository, as shown in later sections of this report. These equations and their derivations, as well as useful alternate forms and relationships between the equations, are briefly discussed here.

Some incorrect theoretical equations for brine migration rates^{33,34} that were reported prior to the work of Anthony and Cline

are described in Appendices A and E, where it is also demonstrated that these equations are in agreement with Anthony and Cline when their errors are corrected.

3.1.2 Anthony and Cline²⁷ equation for brine migration velocity

The theoretical equation derived by Anthony and Cline is

$$V = \frac{DC_L}{C_S} \left[\left(\frac{1}{C_E} \frac{\partial C_E}{\partial T} - \sigma \right) \nabla T_L - \frac{K}{RTL} \right] \quad (1)$$

where

V = migration velocity, cm/s,

C_L = concentration of salt in brine droplet, mol/L,

C_E = equilibrium concentration of salt in brine, mol/L,

C_S = concentration of salt in solid salt, mol/L,

D = diffusivity of salt in brine, cm²/s,

R = gas constant, ergs mol⁻¹ °C⁻¹,

T = absolute temperature, K,

K = kinetic potential, $K_d + K_p$, ergs/mol,

K_d = change in chemical potential at the dissolving interface generated by irreversible processes associated with the transfer of salt between the solid and liquid phases, ergs/mol,

K_p = change in chemical potential at the solidifying interface generated by irreversible processes associated with the transfer of salt between the solid and liquid phases, ergs/mol,

L = dimension of droplet parallel to thermal gradient, cm,

∇T_L = temperature gradient in the brine droplet, °C/cm,

σ = Soret coefficient of salt in brine, °C⁻¹.*

Figure 3 illustrates some of the quantities included in Eq. (1) and/or used in the derivation of the equation.³⁵

*The Soret coefficient, σ , is conventionally negative when thermal diffusion causes transport of solute from the hot to the cold regions of a solution.

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Fig. 3. Chemical potential profiles across a brine droplet: $\Delta\mu_s$ represents the difference between the chemical potentials of the solid salt at the dissolving and solidifying interfaces, and $\Delta\mu_l$ represents the difference between the chemical potentials of the solutions at the interfaces.

The following Eqs. (2) and (3), together with chemical potential considerations (including an allowance, K , for deviation from equilibrium between solid and solution at the interfaces), were used by Anthony and Cline in deriving Eq. (1). (See Appendix D for a review of the derivation.)

$$V = -J/C_s \quad (2)$$

$$J = -DVC_l + D\sigma C_l VT_l \quad (3)$$

Equation (2), in which J is the flux of salt through the brine in a direction parallel to the temperature gradient, results from material balance considerations. Equation (3) states the relationship between the flux and the gradients of concentration, VC_l , and of temperature, VT_l ; $D\sigma$ is the thermal diffusion coefficient.

The values of K are representative of the undersaturation and supersaturation at the dissolving and precipitating interfaces, respectively, required in order for these processes to occur at rates sufficient to support the rate of migration of the droplet. Values of K as a function of brine droplet velocity in KCl at room temperature were reported by Cline and Anthony³⁶ for accelerational as well as thermal fields. The values of K and V were linearly related, at least up to 1 nm/s, according to the general equation

$$K = \beta V + b, \quad (4)$$

where β and b represent system constants at a given temperature.

3.1.3 Rearrangement of Anthony and Cline equation to include the empirical relationship between migration velocity and kinetic potential

Assuming that the relationship shown by Eq. (4) is generally valid, we can substitute from Eq. (4) into Eq. (1), and solve explicitly for V . Therefore,

$$V = \frac{C_l D}{C_s + (BC_l D/RTL)} \left[\left(\frac{1}{C_E} \frac{\partial C_E}{\partial T} - \sigma \right) VT_l - \frac{b}{RTL} \right] \quad (5)$$

3.1.4 Theoretical equations of Geguzin and later workers

Geguzin²⁸ and later workers³⁰⁻³² assumed a brine-migration model based on the concentration profiles illustrated in Fig. 4.* Their assumptions are expressed mathematically by Eqs. (6-8). This model and the resulting equations are analogous to those of Anthony and Cline because of the thermodynamic relationship between chemical potential and concentration (see Sect. 3.1.5 and Appendix D).

$$-J = k_d (\Delta C_d^* - \Delta C_d^\ddagger) \quad (6)$$

$$-J = k_p (\Delta C_p^* - \Delta C_p^\ddagger) \quad (7)$$

$$\Delta C_d^* + \Delta C_p^* + \Delta C_l = \Delta C_E = \frac{dC_E}{dT} LVT_l \quad (8)$$

where k_d and k_p are transfer coefficients at the surfaces and ΔC_d^* and ΔC_p^* (not shown in Fig. 4) are threshold values for the onset of dissolution and precipitation at the respective interfaces, i.e., $\Delta C^* > \Delta C^\ddagger$, or no transfer occurs. Noting that, for a linear concentration distribution, $\nabla C_l = \Delta C_l/L$ and solving Eqs. (2), (3), (6), (7), and (8) explicitly for V ,

$$V = \frac{C_l D}{C_s + (DC_s/kL)} \left[\left(\frac{1}{C_l} \frac{dC_E}{dT} - \sigma \right) VT_l - \frac{(\Delta C_d^\ddagger + \Delta C_p^\ddagger)}{LC_l} \right] \quad (9)$$

*Geguzin did not include a thermal diffusion parameter, but later workers included this.

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Fig. 4. Concentration profiles across a brine droplet.

where

$$1/k = 1/k_d + 1/k_p .$$

To demonstrate the equivalence of Eqs. (5) and (9), the relationship between ΔC^* and V must be developed by combining Eqs. (2) and (6):

$$\Delta C_d^* = VC_s/k_d + \Delta C_d^{\ddagger} . \quad (10)$$

An analogous relation obtains for the cold interface, which, when summed with Eq. (10) yields

$$(\Delta C_d^* + \Delta C_p^*) = VC_s \left(\frac{1}{k_d} + \frac{1}{k_p} \right) + (\Delta C_d^{\ddagger} + \Delta C_p^{\ddagger}) . \quad (11)$$

This reduces to

$$\Delta C^* = VC_s/k + \Delta C^{\ddagger} , \quad (12)$$

because of the definition of the parenthetical expressions. Both sides of Eq. (23) may be multiplied by RT/C_l to obtain

$$\frac{\Delta C^* RT}{C_l} = \left(\frac{C_s RT}{k C_l} \right) V + \left(\frac{\Delta C^{\ddagger} RT}{C_l} \right) . \quad (13)$$

Comparison of Eq. (13) with Eq. (4) reveals that they are of the same form and become identical if

$$K = \frac{\Delta C^* RT}{C_l} , \quad (14)$$

$$\beta = \frac{C_s RT}{k C_l} , \text{ and} \quad (15)$$

$$b = \frac{\Delta C^* RT}{C_l} . \quad (16)$$

In Sect. 3.1.5, the validity of Eq. (14) is demonstrated from thermodynamic considerations.

When the values of β and b are substituted into Eq. (5), it becomes identical to Eq. (9), except for C_E in the denominator of the first term. However, $C_E \equiv C_l$.

3.1.5 Thermodynamic relationship between kinetic potential and interface concentration

The validity of the relationship between kinetic potential and ΔC^* shown by Eq. (14) is demonstrated through use of the thermodynamic relationship between the chemical potential, μ , and the concentration

$$\mu = \mu^\circ + RT \ln fC , \quad (17)$$

where

μ = chemical potential of the dissolved salt,

μ° = standard chemical potential of the dissolved material in a standard reference state in which $fC = 1$,

fC = activity of the solute (i.e., the corrected concentration).

Differentiating Eq. (17) and expressing it in difference form,

$$\Delta\mu = RT\Delta C/C . \quad (18)$$

Using the nomenclature shown in Figs. 3 and 4, and assuming that

$K_d = \Delta\mu_d$, then

$$K_d = \Delta\mu_d = RT\Delta C^*_d / C_{Ed} . \quad (19)$$

Similarly, at the solidifying interface,

$$K_p = \Delta\mu_p = RT\Delta C^*_p / C_{Ep} . \quad (20)$$

Therefore

$$K = RT\Delta C^*/C_l \quad (21)$$

since $K = K_d + K_p$, and

$$\Delta C^*_d/C_{Ed} + \Delta C^*_p/C_{Ep} = \Delta C^*/C_l \quad (22)$$

It can be further noted that the relationship between K and V shown by Eq. (4) can now be translated to the following relationship between ΔC^* and V by combining Eqs. (4) and (21):

$$\Delta C^* = \frac{\beta C_l V}{RT} + \frac{b C_l}{RT} \quad (23)$$

Equation (23) is identical with the equation obtained by substituting from Eqs. (15) and (16) and in Eq. (12) of Sect. 3.1.4.

3.1.6 Derivation of the transport equation with thermal diffusion and applications

Each of the derivations of the migration-velocity equation cited above included the assumption either implicitly or explicitly, that the concentration profile remained linear when thermal and molecular diffusion is present. We have derived the transport equation that is applicable when both thermal and ordinary diffusion are occurring. We found that the concentration profile is not linear, although the equation for the velocity of migration is the same as that resulting from the linear assumption. We also showed that the average concentration is the theoretically correct one to use, within the assumptions made. This derivation is described and discussed in Appendix C.

The theoretical differences that are evident, in this derivation and others, between the thermodynamic approach of Anthony and Cline and the mass balance-kinetic approach, are of no practical significance

since

$$\left(\frac{\partial C_E}{\partial T}\right)_{P, C_X} = \frac{dC_E}{dT} ,$$

$$\frac{dC_L}{dL} \cong \frac{\Delta C_L}{L} \cong vC_L ,$$

and

$$C_{Lp} \cong C_{Ld} \cong C_L .$$

3.1.7 Theoretical equations assuming nonlinear interface kinetics

Olander et al.,³¹ generalized the Geguzin model by assuming that the salt flux at the solid-liquid interfaces can be expressed in the general functional forms:

$$-J = k_d f(\xi_d) \quad (24)$$

at the dissolving face, and

$$-J = k_p g(\xi_p) \quad (25)$$

at the cold or precipitating interface, where ξ_d and ξ_p are the fractional undersaturation and supersaturation at the dissolving and precipitating interfaces respectively. That is, using terminology described as part of the presentation of Fig. 4,

$$\xi_d = \Delta C_d^*/C_{Ed} \quad (26)$$

and

$$\xi_p = \Delta C_p^*/C_{Ep} . \quad (27)$$

When it is assumed that $f(\xi_d) = \xi_d$, and that $g(\xi_p) = \xi_p$, it can be shown using Eqs. (2), (3), and (8) (and previous approximations) and solving for V , that

$$V = \frac{C_l D}{C_s} \left[\left(\frac{1}{C_l} \frac{dC_E}{dT} - \sigma \right) VT_l - \frac{(\xi_d + \xi_p)}{L} \right] \quad (28)$$

Comparison shows that $\xi_d + \xi_p$ in Eq. (28) is the equivalent of K/RT in the Anthony and Cline relationship of Eq. (1).

The relationship between J and $(\xi_d + \xi_p)$ discussed up to this point in this section is linear; i.e., the interface kinetics are assumed to be linear. Olander et al.,³¹ suggested that the linear kinetics may not hold for small departures from equilibrium. Consequently, they have suggested using the power law

$$g(\xi_p) = \xi_p^r \quad (29)$$

This is frequently used to represent crystallization kinetics at the surface of crystals, with a theoretical basis in which r approaches 2 at low supersaturation. Olander and coworkers³¹ assumed the same form for the dissolution process (which is probably the rate controlling process), that is,

$$f(\xi_d) = \xi_d^r \quad (30)$$

Using Eqs. (29) and (30) with $r = 2$, Eq. (24) and Eq. (25) become

$$-J = k_d \xi_d^2, \quad (31)$$

$$-J = k_p \xi_p^2. \quad (32)$$

Another assumption, which is implicit in Eqs. (29) through (32), is that there is no threshold potential gradient (or concentration gradient) for initiation of inclusion migration. This is illustrated by

the following relationship found by combining Eqs. (26), (27), (31), (32), and (2) and solving for ΔC^* :

$$\Delta C^* = v^{1/2} C_s^{1/2} C_l \left(\frac{1}{\sqrt{k_p}} + \frac{1}{\sqrt{k_d}} \right). \quad (33)$$

Equation (33) has no V -independent term that is analogous to b in Eq. (4) or to ΔC^* in Eq. (12).

Using Eqs. (31) and (32) with Eqs. (2), (3), and (8) (and approximations) and solving for V , we obtain the result of Olander et al.³¹:

$$V = \frac{DC_l Z}{4LC_s} \left\{ \sqrt{1 + \frac{4LVT_l}{Z} \left(\frac{1}{C_l} \frac{dC_E}{dT} - \sigma \right) - 1} \right\}^2, \quad (34)$$

where the parameter characterizing the relative magnitudes of the resistances due to liquid diffusion and interfacial kinetics is

$$Z = \frac{DC_l}{L} \left(\frac{1}{\sqrt{k_p}} + \frac{1}{\sqrt{k_d}} \right)^2. \quad (35)$$

When values for k_p and k_d are large, liquid diffusion controls. For this condition, Eq. (33), as $Z \rightarrow 0$, simplifies to the Anthony and Cline result of Eq. (1) with $K = 0$, representing the maximum migration velocity. For small k values, surface kinetics controls and Eq. (23), as $Z \rightarrow \infty$, simplifies to

$$V = \frac{1}{C_s} \left(\frac{1}{\sqrt{k_p}} + \frac{1}{\sqrt{k_d}} \right)^{-2} \left(\frac{1}{C_l} \frac{dC_E}{dT} - \sigma \right)^2 (LVT_l)^2. \quad (36)$$

For isothermal conditions with control by surface kinetics Eq. (36) indicates that a plot of V vs $(LVT_l)^2$ would produce a straight

line on log-log paper. Olander et al.,³¹ found that their isothermal data ($T = 65^{\circ}\text{C}$, with axial load of 10 kg/cm^2) for brine inclusions in KCl crystals could be reasonably correlated by such a plot with a slope of 2.2. However, their examination of NaCl data was inconclusive; both the linear and nonlinear kinetics models seemed to give consistent results within the limits of experimental error.

The types of interface kinetics that will actually prevail in a salt repository are of practical interest, since the kinetic relationships might significantly affect inclusion migration rates at low values of L and/or VT_L (see Sects. 3.1.10 and 7.3).

3.1.8. Numerical values of the migration equation parameters

Information on migration equation parameters in the temperature range to 200°C is summarized in the following sections for NaCl-saturated solution containing no other solutes and also for NaCl-saturated 2.4 m MgCl_2 solution. The latter solution is considered to be representative of the probable compositions of brine inclusions occurring within bedded salt.⁴ Composition of the few brine inclusions which occur within crystals of domal salt may approximate that of pure NaCl brine.²⁶ Pure NaCl solutions were used in laboratory studies and in theoretical considerations reported by Olander and coworkers.³¹

Concentrations, C_L and C_E (molar units). The concentrations C_L and C_E are conceptually different. C_L is the actual brine concentration, while C_E is the equilibrium value for a solid in contact with solution. This difference is not significant; for practical purposes, $C_L = C_E$.

Values for C_E in brine containing 2.4 m MgCl_2 , in the temperature range 25 to 200°C , are presented in Ref. 4. More recent values are reported by Chou;³⁷ we will adopt Chou's values, and they are listed below for convenient reference. Values for C_E in brine containing only NaCl which were recently reported by Olander et al.,³⁸ are also listed in the tabulation.

Temperature (°C)	Concentration of NaCl (mol/L)	
	In 2.4 <u>m</u> MgCl ₂	Without MgCl ₂
25	1.93	5.40
50	2.06	5.45
100	2.36	5.60
150	2.73	5.80
200	3.15	6.09

It is notable that the values of C_E in 2.4 m MgCl₂ solutions are less than those in pure NaCl solutions by factors ranging from about 2.8 at 25°C to 1.9 at 200°C.

Fractional concentration change with temperature. This parameter is expressed as:

$$\frac{1}{C_E} \frac{dC_E}{dT} \text{ or } \frac{1}{C_L} \frac{dC_E}{dT} \quad (\text{molar units}) .$$

Values in the temperature range of 50 to 200°C are presented in Ref. 4 for NaCl-saturated, 2.4 m MgCl₂ solutions. Chou³⁷ has recently pointed out that these values are in error by amounts ranging from ~16 to 30%; he has presented more nearly correct values, which are listed in the following tabulation. Values for C_L and dC_E/dT for pure NaCl solutions can be obtained from the recent report by Olander et al.,³⁸ and the fractional quantities determined from these values are presented in the following tabulation. Note that values for $(1/C_L) (dC_E/dT)$ in the 2.4 m MgCl₂ solutions are greater than those in the pure NaCl solutions by factors ranging from ~2.5 to 5.5.

(°C) Temperature	$(1/C_E) \frac{dC_E}{dT} (°C^{-1})$ (molar units)	
	2.4 <u>m</u> MgCl ₂	Without MgCl ₂
50	2.65 E-03	3.87 E-04
100	2.83 E-03	6.07 E-04
150	2.91 E-03	8.53 E-04
200	2.91 E-03	10.95 E-04

Diffusion coefficient. Estimated values for the diffusion coefficient, D , (also called diffusivity) of NaCl in saturated NaCl solutions over a range of temperatures to 200°C are listed in Ref. 4 and in the recent report by Olander et al.³⁸ These recent values of Olander et al., tabulated below, are adopted in this report.

Temperature (°C)	D , for NaCl in NaCl-saturated solutions (10^{-5} cm ² /s)
50	2.7
100	5.8
150	10.9
200	18.7

We assume that the values for D of NaCl in the NaCl-saturated MgCl₂ solutions are approximately equal to those in the solutions without MgCl₂.

Inclusion length, L . The brine inclusions observed within bedded salt from SENM and from the Lyons, Kansas, area exhibit a wide range of sizes, starting at <1 μ m.^{17,39-41} However, it has been estimated that most of the included brine is present within inclusions with sizes ≥ 1 mm.^{4,39}

These larger inclusions are roughly cubic. They may tend to elongate in the direction of motion during migration in a moderate temperature gradient ($\nabla T_{\infty} \approx 1.5 \text{ }^{\circ}\text{C/cm}$)³⁵ typical of the maximum gradients prevailing in the salt in a waste repository.^{22,42} Experimental information on changes in shape under conditions that are not typical of those in a repository will be summarized in a later section.

The inclusion length, L , in the theoretical equations is always measured parallel to direction of the thermal gradient.

Ratio of thermal gradient in brine inclusion to that in salt, $\nabla T_i / \nabla T_{\infty}$. The value for this ratio is >1 and is dependent upon the aspect ratio of the inclusion, as well as upon the difference between the thermal conductivities of the solution and the solid salt. The value for the ratio is ~ 1.4 for cubical and spherical brine inclusions in NaCl.^{4,43} Values become smaller as the inclusions become elongated in the direction of the thermal gradient, and approach unity as the limit.⁴ There may also be some temperature gradient between the center and the sides of an inclusion, in the directions perpendicular to ∇T_{∞} , depending upon the size and shape of the inclusion.³² The value of 1.4 for cubical inclusions, mentioned above, was partially based on the assumption of uniform temperature in the directions perpendicular to ∇T_{∞} .

Soret coefficient, σ . The reported experimental values for the Soret coefficient in concentrated NaCl solutions at 30 to 50°C is $\sim -0.002 \text{ }^{\circ}\text{C}^{-1}$, as illustrated in Fig. 5 (Refs. 4, 44-46). Some reported values for σ at $\geq 1 \text{ M NaCl}$ do not agree with those plotted in this figure,⁴⁷ however, we believe that the plotted values are the most reliable and pertinent.

No experimental or reliable theoretical values⁴⁸⁻⁴⁹ are available for higher temperatures in NaCl solutions or for the MgCl_2 solutions that occur as brine inclusions in bedded salt. However, analyses and correlations of experimental and theoretical information (presented in

Fig. 5. Plot of literature data for Soret coefficient, $-\sigma$, in NaCl solutions at several concentrations and temperatures.

Sect. 4.1.1) indicated $-\sigma$ values for the natural inclusions in bedded salt vary from 0.004 and $0.005^{\circ}\text{C}^{-1}$ in the temperature range 50 to 200°C ; these are greater than the value for $-\sigma$ in saturated NaCl solutions at $\sim 50^{\circ}\text{C}$ by factors of 2 to 2.5.

Experimental values for the kinetic potential. Analyses and correlations of experimental and theoretical information bearing on the values of these quantities for natural brine inclusions in rock salt are presented in Sect. 3.1.10 of this report.

Cline and Anthony³⁶ studied these quantities for brine inclusions in crystals of KCl, at temperatures averaging $\sim 30^{\circ}\text{C}$, using both accelerational and thermal fields. For their reported results in accelerational fields (V ranged up to 0.5 cm/s) the linear relationship between V and K shown by Eq. (4) prevailed, and calculations show that $\beta = 1.85 \text{ E}+14 \text{ erg-s mol}^{-1} \text{ cm}^{-1}$ and $b = 2.0 \text{ E}+06 \text{ ergs/mol}$. Approximately the same values were found for their thermal field results at V up to $\sim 1 \text{ nm/s}$; the linear relationship between V and K prevailed, and the values of β and b were $4.4 \text{ E}+13$ and $3.0 \text{ E}+06$, respectively. Above $\sim 1 \text{ nm/s}$ in the thermal fields, the values of K leveled off with further increases in V , and K appeared to be nearing a constant value of $\sim 1.2 \text{ E}+07 \text{ ergs/mol}$ at $V \geq 5 \text{ nm/s}$.

3.1.9 Predicted maximum rates of migration, V_{max} , of brine inclusions in single crystals of NaCl

Predicted values of V_{max} are obtained from Eq. (1), (5), or (9) when the value of the kinetic potential, K (or the equivalent of K), is negligible with respect to its effect on V . In order to illustrate values that are predicted from the theoretical equations, Table 1 lists calculated values of V_{max}/VT_L for NaCl-saturated brine inclusions containing 2.4 $\underline{\text{m}}$ and 0.0 $\underline{\text{m}}$ MgCl_2 migrating within single crystals of NaCl at 150°C .

It can be noted that the ratio of the values for V_{max}/VT_L in the pure NaCl brine to those in MgCl_2 -rich brine range from ~ 1.0 , when $\sigma = 0$, to higher values when $-\sigma > 0$.

Table 1. Calculated values for $V_{\max}/VT_l$ for brine inclusions in salt crystals at 150°C

Soret coefficient, σ (°C ⁻¹)	$V_{\max}/VT_l$ (nm/s)/(°C/cm) ⁻¹	
	NaCl-saturated 2.4 M MgCl ₂ ^a	Pure, saturated NaCl ^b
0.0	0.24	0.15
-2 E-03	0.40	0.49
-5 E-03	0.65	1.01
-10 E-03	1.05	1.88

^a $C_l/C = 0.0749$; $(1/C_l)(dC_l/dT) = 2.91 \text{ E-03}$; $D = 10.9 \text{ E-05}$.
Values from^s Sect. 3.1.8.

^b $C_l/C = 0.159$; $(1/C_l)(dC_l/dT) = 8.53 \text{ E-04}$; $D = 10.9 \text{ E-05}$.
Values from^s Sect. 3.1.8.

3.1.10 Ratio ($V/V_{\max}$) of calculated migration velocity to maximum migration velocity: effects of kinetic potential

For purposes of illustration, Eqs. (4) and (5) will be used, and pre-bracket and bracket terms in Eq. (5) will be considered separately. Values for RT and for other quantities which may enter the considerations will be assumed to be at 150°C .

Considering first the pre-bracket term in Eq. (5), let A = this term, and let $A_{\max}$ = the same term when the value of β is negligible. Then,

$$A/A_{\max} = \frac{1}{1 + \frac{DC_l \beta}{C_s LRT}} \quad (37)$$

Introducing the 150°C values for RT , D , and C_l/C_s for natural brine inclusions in bedded salt, then

$$A/A_{\max} = \frac{1}{1 + \frac{2.3 \beta E-16}{L}} \quad (38)$$

and further assuming that $\beta = 1.7 \text{ E}+14 \text{ erg s/mol cm}$ (see Sect. 4.1.2 and Table 4),

$$A/A_{\max} = \frac{1}{1 + \frac{0.039}{L}} \quad (39)$$

Setting $L = 0.01$, 0.1 , and 1.0 cm in Eq. (39) yields values for $A/A_{\max} = 0.20$, 0.72 , and 0.96 , respectively.

The values for $A/A_{\max}$ are seen to vary directly with the values of L and inversely with the values for β in this equation.

Now considering the bracket term in Eq. (5), let B represent this term and let $B_{\max}$ = the same term when the value of b is negligible. The ratio $B/B_{\max}$ can then be written as

$$B/B_{\max} = 1 - \frac{b}{RTLVT_L \left(\frac{1}{C_L} \frac{\partial C_F}{\partial T} - \sigma \right)} \quad (40)$$

Equation (40) shows that the value of $B/B_{\max}$ depends upon the combined value of several factors. Table 2 lists calculated values for $B/B_{\max}$ for the NaCl-saturated 2.4 M $MgCl_2$ brine and for the pure NaCl brine migrating in NaCl crystals at 150°C, for several values of σ and VT_L .

The effects of different values for various parameters can now be readily estimated using Eq. (40) and the values of $B/B_{\max}$ listed in Table 2. As the value of VT_L increases, the value of $B/B_{\max}$ increases and is near unity when $VT_L = 5^\circ\text{C}/\text{cm}$ for all of the assumed values of σ . As the value of L becomes smaller, the value of $B/B_{\max}$ also becomes smaller, and in fact, may remain zero for certain combinations of values of the other parameters including low values for σ .

The combined effects of $B/B_{\max}$ and $A/A_{\max}$ are found using Eq. (41) below:

$$V/V_{\max} = (A/A_{\max}) (B/B_{\max}) \quad (41)$$

This equation shows that when $B/B_{\max} = 0$, $V = 0$ also.

It should be noted that the above discussion and conclusions regarding $A/A_{\max}$ and $B/B_{\max}$ may be invalid if the interface kinetics are such that there is no threshold value for VT_L (see Sect. 3.1.7). For example, if the relationship between J and $\xi_d^2 + \xi_o^2$ are as shown by Eqs. (31) and (32) in Sect. 3.1.7, the value of V might remain >0 even at very low values of VT_L and/or L .

3.1.11 Effects of kinetic potential

Cline and Anthony have discussed theoretical explanations for the importance of a kinetic potential for brine migration in salt.^{27,35,36,50} They point out, as did previous investigators, that a moving solid-liquid interface is not in true equilibrium because of the irreversible

Table 2. Calculated $B/B_{\max}$ values for brine inclusions in salt crystals at 150°C

Soret coefficient (°C ⁻¹)	$B/B_{\max}$ ^a					
	NaCl-saturated 2.4 M MgCl ₂			Pure, saturated NaCl		
	5b	1b	0.1b	5b	1b	0.1b
0	0.96	0.82	0	0.88	0.40	0
-2 E-03	0.98	0.90	0	0.96	0.82	0
-5 E-03	0.99	0.94	0.35	0.98	0.91	0.12
-10 E-03	0.99	0.96	0.60	0.99	0.95	0.53

^aAssumed values for parameters:

$$L = 0.1 \text{ cm}$$

$b = 1.8 \text{ E}+06 \text{ erg/mol}$ (see Section 4.1.2 and Table 5 of this report.) $(1/C_L)(dC_E/dT) = 2.91 \text{ E}-03$.

^bAssumed value for ∇T_p , °C/cm.

nature of the processes of detachment and attachment of ions at the moving interfaces. The detachments at a dissolving interface are believed to occur at ledges in the solid surface, and the number of ledges present at any time may be limited by the time required to nucleate a ledge and/or by the number of dislocations in the solid that can promote the nucleation. Ledges may also be required at the precipitating interface in order for crystal growth to occur; however, it is likely that the number of ledges on this interface will be formed, or preserved, during crystal growth.

Olander and coworkers³¹ also studied and discussed the nature of the chemical potential. Their conclusions are in accord with those of Cline and Anthony summarized in the preceding paragraph.

3.2 Effects of Stress and of Gamma Irradiation on Kinetic Potential

The rock salt adjacent to a waste package in a repository will be subjected to several forces in addition to elevated temperatures and temperature gradients. The forces that have been recognized and discussed with respect to possible effects on brine migration of all-liquid inclusions are: stress and stress gradients, gamma irradiation, and accumulated radiation damage in the salt.

A possible effect of either stress or radiation damage in the crystal, or of both, would be a reduction in the value of the kinetic potential, K , as a result of the formation of dislocations within the salt crystal and/or of crystal damage at the salt-brine interfaces.⁴ The maximum expected effect on inclusion migration would be the elimination of any retarding effect of K on V , which would cause the value of $V/V_{\max}$ to approach unity at the given set of exposure conditions.⁴

Pressurizing (stressing) of the brine-crystal system would increase the solubility, but only by a small amount. This increase in solubility is expected to be nearly uniform over all interfaces within an inclusion,* so the maximum effect would be an equally small fractional increase in the thermal-gradient-induced migration rate of the inclusion.⁴

*Generally, liquid-filled brine inclusions in salt at elevated temperatures will pressurize the adjacent salt because of the greater thermal expansion of the brine.^{51,52}

In the event that a stress gradient prevails between the solid salt at the dissolving and precipitating interfaces in the same direction as the temperature gradient, Olander^{53,54} pointed out that another term, $(V_s)(\Delta E_{el}/2RT)$, would be added to those within brackets in Eq. (5) or (9) where:

V_s = molar volume of solid salt;

E_{el} = elastic strain-energy density of the solid at an interface.

Olander also suggested^{51,52} that the effect of this added term on the migration rate of an inclusion is probably very small.

Another conceivable effect of stress gradients on brine-inclusion movement may be called a "toothpaste tube effect" in which unequal squeezing forces cause an extrusive-type movement of the brine. The possibilities have not been fully evaluated that such an effect would occur in a salt repository.

Experimental information concerning the effects of radiation and stress on migration of brine inclusions will be reviewed in Sect. 4.4.

4. MIGRATION RATE DATA FOR LIQUID BRINE INCLUSIONS IN SINGLE CRYSTALS OF NaCl

In this section, the brine migration experimental data and their correlations are discussed for single crystals of NaCl from both bedded and domal salt and for synthetic NaCl crystals with pure NaCl brine inclusions. Summaries are also given of information and conclusions regarding maximum rates of brine inclusion migration in salt crystals around waste packages in repositories.

4.1 Natural Crystals of Bedded Salt with Natural Brine Inclusions

Experimental data were obtained with salt crystals from mines at Hutchinson, Kansas, and from cores near the WIPP site in SENM.

4.1.1 Data for bedded salt in the Cary mine, Hutchinson, Kansas

Bradshaw and Sanchez^{55,56} measured the rates of migration of large brine inclusions within natural single crystals obtained from the Carey mine at Hutchinson, Kansas, at temperatures ranging to ~250°C. Results of their rate measurements are reproduced in Fig. 6 and in Table 3. The data scattered appreciably, and the curve shown in Fig. 6 was assumed by Jenks⁴ to represent the maximum rates indicated by the data. The relationship between V and VT_{∞} along this curve is shown by Eq. (42) given below:⁴

$$\log V_{\max} / VT_{\infty} = 0.00656 T - 0.6036 , \quad (42)$$

where T is the temperature of the salt (°C) and V/VT_{∞} has the units ($\text{cm}^2 \text{ y}^{-1} \text{ } ^\circ\text{C}^{-1}$).

Other relevant data that were reported by Bradshaw and Sanchez or that can be inferred from their reports^{55,56} are summarized below:

1. Each single crystal sample was of the same size, ~25 mm on an edge.
2. The brine cavities ranged from 2 to 10 mm on an edge.

Fig. 6. Experimental data for rates of migration of brine inclusions in Kansas salt. (Source: Refs. 55 and 56 of this report.)

Table 3. Brine migration data for Cary salt^a

Crystal No.	Temperature (°C)	Gradient (°C/cm)	Migration (mm)	Time (h)	Rate (nm/s)
1	75	5	3.0	240.0	3.5
2	185	34	1.0	26.5	10.5
5	200	20	0.8	68.0	3.3
6	190	17	2.0	23.0	24.2
6	188	12	0.8	19.5	11.4
6	210	23	3.7	43.5	23.6
6	200	15	8.0	67.0	33.2
7 ^b	193	12	4.5	19.2	65.1
8	200	18	6.8	67.0	28.2
11	85	13	3.6	358.0	2.8
16	208	7	3.4	44.7	21.1
16	210	10	1.3	30.0	12.0
16	190	9	2.2	63.3	9.7
16	237	7	1.1	24.0	12.7
16	240	9	1.8	24.0	20.8
16	237	9	1.5	24.7	16.9
17	163	9	1.0	44.3	6.3
17	163	15	1.5	63.3	6.6
17	160	11	1.2	42.0	7.9
17	140	13	0.8	44.5	5.0
17	130	11	1.1	65.0	4.7
1	232	8	2.5	59.0	11.8
1	244	8	2.1	24.2	24.1
1	128	4	0.9	45.0	5.6
11	85	13	3.6	358.0	2.8
11	82	10	2.1	312.0	1.9
18	120	7	1.0	44.8	6.2
(Cavity A)					
18	120	7	1.0	44.8	6.2
(Cavity B)					
18	117	8	2.5	92.3	7.5
(Cavity A ^c)					
18	117	8	1.2	92.3	3.6
(Cavity B)					

^aSource of data: Refs. 55 and 56 of this report.

^bCavity in crystal 7 behaved differently than other cavities.

^cCavity A (the larger one) migrated toward an existing hole in crystal 18.

3. Heating was from the bottom.
4. The initially cubical shape of inclusions became oval during migration. No breakup was reported.

Jenks⁴ made comparisons between the experimental values for $V_{\max}/VT_{\infty}$ shown by Eq. (42) for the temperature range 50 to 200°C, and the theoretical values found using Eq. (1), with $K = 0$. He observed that the experimental and theoretical values were in near agreement for both sets of data when the assumed values for $-\sigma$ were in the range 0.003 to 0.004°C⁻¹ and the assumed values for the other quantities in Eq. (1) were near those described in Sect. 3.1.8.

Table 4 shows a similar comparison made using the revised values for C_l/C_s , $(1/C_l)(\partial C_l/\partial T)$ and D in Sect. 3.1.8. Near agreement between experimental and theoretical values is indicated when the values for $-\sigma$ are in the range 0.004 to 0.005°C⁻¹.

4.1.2 Data for bedded salt in SENM (ERDA Core 9)

Roedder and Belkin³⁹ reported studies of the rate of migration of small, liquid brine inclusions within natural single crystals obtained from the bedded salt in SENM (ERDA Core 9).

Pertinent experimental conditions are summarized below.

1. The single crystals of salt were taken from Core 9 at depths near 628 and 798 m.
 2. The temperature gradient, VT_{∞} , was 1.5°C/cm and was applied in a horizontal direction.
 3. The brine inclusions were initially cubical, with the initial sizes ranging downward from ~1.0 mm on edge.
 4. Inclusions with initial dimensions >0.1 mm on edge changed shape during migration, generally becoming elongated in the direction of motion.
 5. The exposure temperatures were 108, 160, 201, and 260°C.
- Experimental results were reported graphically.

All values reported by Roedder and Belkin³⁹ for V were less than those predicted for $V_{\max}$ using the relationship of Eq. (42). Values for β and b [in Eq. (5)] that would account for the lower values for certain

Table 4. Calculated and experimental values for maximum rates of thermal gradient-induced brine migration, V/VT_m , at 50 to 200°C^a

Temperature (°C)	C_L/C_S	Concentration change with temperature, ^b $\frac{1}{C_L} \frac{\partial C_E}{\partial T}$ (°C ⁻¹)	Diffusion coefficient, D^c (cm ² /s)	Values of V/VT_m (nm/s)/(°C/cm)					Experimentale
				Soret coefficient, σ (°C ⁻¹) ^d					
				0	-0.002	-0.003	-0.004	-0.005	
50	0.0557	2.65×10^{-3}	2.7×10^{-5}	.057	.100	.122	.143	.164	.168
100	0.0642	2.83×10^{-3}	5.8×10^{-5}	.148	.252	.304	.356	.408	.356
150	0.0749	2.91×10^{-3}	10.9×10^{-5}	.332	.561	.676	.790	.904	.762
200	0.0872	2.91×10^{-3}	18.7×10^{-5}	.664	1.12	1.35	1.58	1.81	1.62

^aCalculated values obtained using Eq. (1) with $K = 0$, $VT_L = 1.4 VT_m$, and listed values for other parameters.

^bSource of data in this column is Ref. 37 of this report. See also Sect. 3.1.9.

^cSource of data in this column is Ref. 38 of this report. See also Sect. 3.1.8.

^dValues for Soret coefficient are assumed for comparison of calculated and experimental values for V .

^eCalculated using Eq. (42) of this report.

of the smaller brine inclusions (which did not change shape) are listed in Table 5; the smoothed data for inclusion sizes of 0.046 and 0.1 mm on edge (reported by Roedder and Belkin in Fig. 2 of Ref. 39) were employed in the calculations leading to these values. The calculational procedure, using Eq. (5), was to assume $\sigma = -0.004^\circ\text{C}^{-1}$, as stated in Table 5, and also to assume values for other quantities as described in Sec. 3.1.8 of this report. The values for β and b were then calculated using the two simultaneous equations with the smoothed experimental values for V and L .

The values calculated for V when $L > 0.1$ mm, using the data for σ , β , and b shown in Table 5, are somewhat greater than the smoothed experimental values. The changes in shape of the inclusion during migration possibly accounted for some of these differences.

The experimental values for the largest inclusions (and highest migration velocities) studied by Roedder and Belkin³⁹ are plotted in Fig. 7. These experimental values are substantially less than the maximum values predicted by the Jenks equation.⁴

4.1.3 Data for bedded salt in the Carey mine at Lyons, Kansas

Shor and Baes⁵⁷ have reported experimental observations of naturally occurring brine inclusions within a single crystal of salt from the Carey mine at Lyons, Kansas. One inclusion measured 150×100 μm ; the other measured 65×65 μm . With a temperature of 100°C in the salt around the inclusions and with $\nabla T_\infty = 35^\circ\text{C}/\text{cm}$, these inclusions migrated at rates (V) of 3.5 mm/s and 2.0 mm/s, respectively. These experimental values are also plotted in Fig. 7.

Values for β and b were calculated for this study using the data from the two different-sized samples and following the calculational procedure described in Sect. 4.1.2. The calculated values are included in Table 5. The value for β is in good agreement with, but the value for b is 4 times greater than, the values for the Roedder and Belkin data³⁹ at 100°C .

Table 5. Calculated values^a for β and b

Experimenter ^b (Ref. No.)	Temperature (°C)	β (erg s/mol cm)	b (erg/mol)
Shor and Baes (Ref. 57)	100	2.5 E+14	7.4 E+06
Roedder and Belkin (Ref. 39)	160	1.7 E+14	1.8 E+06
Roedder and Belkin (Ref. 39)	201	2.8 E+14	1.5 E+06
Krause and Carter (Ref. 58)	212	4.6 E+14	3.0 E+06

^a $\sigma = -0.004^\circ\text{C}^{-1}$ was assumed in these calculations.

^bCalculated values used experimental data reported by these experimenters in the references listed for this report.

4.1.4 Data for bedded salt in SENM (near Salt Block II site)

Krause and Carter⁵⁸ conducted studies of brine migration in crystals of salt within aggregates obtained from SENM at the site from which the Salt Block II material was obtained. Information for some of their inclusions is plotted in Fig. 7.

Values for β and b at 212°C were calculated using the data from the two different-sized samples tested. The calculational procedure was that described in Sect. 4.1.2, and the calculated values, shown in Table 5, are slightly greater than those found from the Roedder and Belkin data at 201°C.

4.1.5 Effects of stored radiation energy on brine migration

Although no direct information was available at the time, Jenks⁴ previously stated that the presence of stored radiation energy within a salt crystal could affect the rate of brine migration within the crystal if the stored energy caused an increase in the solubility of the salt.

Qualitative experimental evidence⁵⁹ now available indicates that stored radiation energy (~10 W/g) did not affect the general solubility significantly during a 21-month period of immersion of the irradiated sample in saturated brine (contacting solid NaCl) at room temperature. Some brine did migrate into the irradiated sample (initially cubic, 13 mm on edge) during immersion, as shown by the presence of some white salt in place of the original, coal-black, irradiated salt.

However, no penetration of brine into irradiated crystals was observed in the Project Salt Vault experiment,⁴⁰ so it is likely that the penetration observed in the laboratory sample took place through microcracks formed during the handling and fabrication of the irradiated specimen.

4.1.6 Evidence that the kinetic potential has a finite value at zero migration rate

Pigford⁶⁰ has recently pointed out that the evidence that brine inclusions within crystals of bedded salt have remained essentially sta-

Fig. 7. Experimental data for rates of migration of brine inclusions in crystals of bedded salt. (Sources of data are shown in figure legend.)

tionary since they were formed (see Sect. 2.16) can in turn be regarded as evidence for the occurrence of a finite value for the kinetic potential K , even at $V = 0$, as implied by Eq. (5).

Thus, it can be shown that a migration distance of ~ 60 m over a period of 200 million years is predicted using Eq. (42) ($K = 0$) with an average salt temperature of 28°C and a geothermal gradient of $7.9^\circ\text{C}/\text{km}$, and also assuming no grain boundary effects on the migration. If inclusions had migrated this large distance, both deficient regions and regions enriched in brine would be expected, respectively, below and above impervious partings (e.g., shale partings) in the rock salt deposit. If the migrating inclusions were trapped at grain boundaries, the crystals would be free of inclusions. No such indications of brine migration during geologic times have been reported.

Gravitational forces (buoyant forces) as well as thermal forces acted on the brine inclusions throughout their stay in the salt (Appendix B). It can be estimated that these buoyant forces were roughly equivalent (but opposite in direction) to the thermal forces at the temperature and temperature gradients mentioned (Appendix B), yet it is very unlikely that the forces could have been near enough to equivalency to cancel movement of a brine inclusion that would have occurred in the absence of either one of these forces. Accordingly, the Pigford observation regarding evidence for a finite value of K , at $V = 0$, is considered valid.

4.2 Natural Crystals of Dome Salt with Natural Brine Inclusions

Roedder and Belkin²⁶ studied the thermal migration at 157°C of several small, liquid brine inclusions (with sizes of $2.0 \text{ E}+04$ and $2.6 \text{ E}+06 \text{ } \mu\text{m}^3$) in crystals of NaCl from Rayburn and/or Vacherie domes. The equipment and procedures were the same as those used with the samples of bedded salt described above (see Sect. 4.1.2). The rates of migration were said to be in the same range as those obtained for equivalent-sized inclusions in the bedded salt.

4.3 Synthetic NaCl with Inclusions of Pure NaCl Brine

Olander and co-workers^{31,32} studied the thermal migration of small brine inclusions in synthetic NaCl crystals with experimental conditions

that included large temperature gradients. The inclusions were initially cubical in shape, but they flattened markedly in the direction of motion during thermal migration. The observed rates of migration generally were substantially below the maximum rates predicted by the relationship shown in Eq. (42). However, we were unable to make direct comparisons between their results and the results of investigations with natural brine inclusions in natural salt crystals.

4.4 Summary of Information on Maximum Rates of Migration of Brine Inclusions in Bedded Salt

The review and analysis of information conducted for this study confirm that the highest rate of migration for all-liquid brine inclusions within crystals of salt adjacent to a waste package in a bedded salt repository is represented by Eq. (42):

$$\log V/VT_{\infty} = 0.00656T - 0.6036 ,$$

where V = migration velocity, cm/y; VT_{∞} = temperature gradient in salt, °C/cm; and T = salt temperature, °C.

This relationship includes several assumptions and/or implications that are discussed in the following sections.

4.4.1 Kinetic potential effects

Comparisons of experimental and theoretical information on rates of brine inclusion migration in crystals of bedded salt (Sect. 4.1.1) indicate that Eq. (42) is applicable for systems in which the value of the kinetic potential, K , is negligible, i.e., systems in which the dissolution and precipitation processes at the salt-solution interfaces do not limit the rate of inclusion migration. The result of laboratory experiments with single crystals of salt as well as the presence of fairly uniformly distributed brine inclusions in bedded salt suggest that the kinetic potential, K , may not be negligible in a repository (see Sect. 4.1). However, the salt adjacent to (within ~20 cm) a waste package in a repository will be exposed to gamma radiations and

will accumulate radiation damage. It is conceivable that this damage may promote equilibrium conditions at the solution-salt interfaces (i.e., reduce the value of K from that which would occur in the absence of radiation damage). Thermal stresses in the salt might produce effects similar to those of radiation damage. The assumption that $K = 0$ covers these possibilities as well as being on the conservative side.

4.4.2 Shape of brine inclusions

The value of $V T_i / V T_\infty \approx 1.4$ for brine inclusions which are cubical or spherical in shape. This value changes if the shape of an inclusion changes during migration; it decreases and approaches unity if the inclusion elongates, but increases if the inclusion flattens, in the direction of motion. Experimental results for natural inclusions in natural crystals of bedded salt, using values of $V T_\infty$ comparable to those expected in a waste repository, showed that most changes in shape are elongations in the direction of motion.

4.4.3 Other effects of gamma radiation

The available experimental evidence indicates that radiation damage within crystals of NaCl has no significant effects on the solubility of the NaCl or on penetration of a crystal by the contacting brine. This indicates that radiation has no significant effects on the migration of brine inclusions within single crystals of NaCl, other than the possible reduction of the value of K already discussed.

Information relating to the effects of radiation on migration of brine through aggregates of salt crystals is discussed in Sect. 6.

4.5 Summary of Information on Maximum Rates of Migration of Brine Inclusions in Domal Salt

The available evidence indicates fewer brine inclusions within crystals and/or on crystal boundaries in the reference domal salt than in bedded salt. It can be reasonably assumed that the maximum rates of migration are approximately the same as those for inclusions in bedded salt, as given by Eq. (42).

5. MIGRATION OF GAS-LIQUID INCLUSIONS IN NaCl

Brine inclusions containing a gas-vapor bubble may respond differently to a temperature gradient than all-liquid inclusions. Experimental observations with essentially pure NaCl or KCl brine inclusions in crystals of the respective salt showed that some or all of the inclusions containing a gas-vapor bubble could move down a temperature gradient within the crystals, away from the heat source.

Qualitative and quantitative explanations for some of the observed phenomena have been presented by several investigators. Brief summaries are presented in this section of reported experimental and theoretical information on migration of gas-liquid inclusions and of possible effects in a waste repository in rock salt.

5.1 Experimental Information on Migration of Gas-Liquid Inclusions

5.1.1 Synthetic NaCl crystals

Wilcox⁶¹ investigated movement of inclusions through synthetic NaCl crystals; the inclusions were 0.75-mm-diameter cylinders, and each contained NaCl brine and an air-vapor bubble.

Temperature gradients were in the range of 60 to 100°C/cm, with average temperatures ranging up to 100°C. In all cases, regardless of the orientation of the inclusion with respect to the temperature gradient, the bulk of the solution migrated toward the heat source, while the air bubble and some of the solution traveled in the opposite direction. When the inclusion was vertically oriented and heated from the top, the air bubble moved to the bottom of the inclusion and then into the solid salt. Rates of migration of the air bubbles were appreciably greater than those of the liquid; perhaps by a factor of 10.

Bubbles were introduced into all-liquid inclusions, when the inclusions reached a surface, by leakage of liquid followed by gas and/or vapor replacement.

5.1.2 Synthetic KCl crystals

Brine (KCl) inclusions in synthetic KCl crystals were investigated by Anthony and Cline.⁶² A gas-vapor phase was introduced into all-liquid inclusions when they migrated through a thermal gradient to a crystal surface. The two-phase inclusions then moved back into the salt. The all-liquid inclusions were in the size range 2-150 μm . Migration behavior of the two-phase inclusions was studied using a thermal gradient of $3^\circ\text{C}/\text{cm}$ at 40°C during a period of 6 h. In all cases, the air-vapor bubble moved to the cooler side of the inclusion.

Several of the larger inclusions eventually divided to form an all-liquid inclusion and an inclusion in which gas-vapor was predominant. Migration rates for the two-phase inclusions exceeded those expected for all-liquid inclusions by appreciable factors.

5.1.3 Synthetic NaCl crystals with NaCl brine

Olander et al.³² studied NaCl brine inclusions in synthetic NaCl crystals. Down-gradient migration rates, V/VT_∞ , for gas-liquid inclusions at 50, 100, and 150°C were reported to average about 6, 20, and 35 (nm/s)/($^\circ\text{C}/\text{cm}$) at the respective temperatures, $\pm 50\%$ around the average at each temperature. Other experimental conditions included temperature gradients of 5 and $10^\circ\text{C}/\text{cm}$ and gas fractions of 0.1 and 0.2.

The migration rates per unit of temperature gradient at 50°C were within the range of values reported by Anthony and Cline for inclusions in KCl with comparable fractions of gas (Sect. 5.1.2).

5.1.4 Natural NaCl crystals

Roedder and Belkin³⁹ measured the down-gradient migration rates of two-phase inclusions found in crystals of bedded salt from SENM, ERDA Core 9, at a depth of 628 m. Figure 8 and Table 6, adapted from their report, summarize the experimental conditions and results. These experimental values for migration rates are generally in agreement with those reported by Olander et al., for synthetic crystals³² (Sect. 5.1.3).

Roedder and Belkin noted that the down-gradient rates were 1.25 to 10 times greater than the up-gradient rates observed for liquid-filled inclusions of the same size. However, as shown in Fig. 8, the down-

Fig. 8. Experimental data for down-gradient migration of two-phase inclusions in bedded salt crystals. (Source of data: Roedder and Belkin, Ref. 39 of this report; also Table 6 of this report.)

Table 6. Down-gradient migration of two-phase inclusions
in salt crystals from SENM

Temp. (°C)	VT_{∞} (°C/cm)	Time (h)	Initial size (μm) ^a	Vol. of gas (%)	V/VT_{∞} (nm/s)/(°C/cm)
108	1.5	252	21	28	0.089
108	1.5	252	21	28	0.095
108	1.5	252	158	14	0.353
160	1.5	183	117	28	0.145
160	1.5	183	177	25	0.655

^aThese values were calculated from the reported volumes,
assuming cubical shapes.

gradient rates were still less than the up-gradient rates predicted by the Jenks equation, Eq. (42).

5.1.5 Effects of stress on two-phase inclusions in salt

Powers et al.⁶³ reported an experiment in which a uniaxial stress imposed on a two-phase inclusion in natural rock salt caused rapid dissolution of portions of the salt walls and shrinkage of the gas-vapor space to zero in a short period of time.

A possible explanation for this behavior is mentioned in Sect. 5.2.

5.2 Theoretical Information

In this section, the theoretical models developed to describe the migration rates of two-phase inclusions are discussed, and comparisons with experimental results are made. Possible effects of stress are also considered.

5.2.1 Qualitative models for migration of two-phase inclusions in salt

The model which was assumed by Olander et al.^{31,64} as a basis for qualitative and quantitative descriptions of migration of two-phase inclusions in salt is reproduced in Fig. 9. The following description is quoted from Ref. 31.

Water vapor evaporates from the hot side of the gas bubble in the brine and is transported to the cold side, where it condenses. The condensed water is recycled to the hot side by backflow of the brine, which provides the mechanism for moving salt from the cold face of the inclusion to the hot face. The inclusion thus moves in the opposite direction from the salt flow.

A similar model was assumed by Anthony and Cline.⁶² These models made no provisions for division of an inclusion into an all-liquid inclusion and an inclusion in which gas-vapor was predominant.

Wilcox⁶¹ ascribed the down-gradient migration of an inclusion to the effects of surface tension gradients accompanying gradients in salt concentration within the inclusion.

One of the significant inferences which can be drawn from the qualitative models is that the down-gradient migration might depend upon the

Fig. 9. Schematic of the migration mechanism for gas-liquid inclusions in a temperature gradient. (Source of model: Olander et al., Refs. 31 and 64 of this report.)

composition of the liquid within the inclusions. For example, the water vapor pressure over a brine containing a high concentration of MgCl_2 will be significantly less than that over a pure NaCl brine at the same temperature. Also, the transfer of water by the backflow of brine might be reduced by the presence of MgCl_2 . Accordingly, it has been suggested that two-phase inclusions with MgCl_2 -rich brines may not migrate down-gradient in the low temperature gradients that will prevail in a repository.²² The experimental information reported by Roedder and Belkin (Sect. 5.1.4) does not support this suggestion. However, they do not completely discount the idea because neither the brine nor the gas compositions were determined in these experiments for gas-liquid inclusions.

5.2.2 Comparisons of theoretical and experimental rates

Glander et al.^{31,64} derived and reported theoretical relationships for velocity of migration of two-phase inclusions in the presence of a thermal gradient in the salt. Their most recent studies indicated⁶⁵ that the predicted results for NaCl were in reasonable agreement with the experimental results. Results for KCl were apparently in poorer agreement.

A less sophisticated, but basically similar, theoretical relationship was previously derived by Anthony and Cline.⁶²

5.2.3 Possible effects of stress on two-phase inclusions in salt

Theoretical considerations indicate that the solubility of NaCl can be substantially increased by application of pressure to the crystalline salt while leaving the contacting solution unpressurized.⁴ This system can be visualized as producing a solution adjacent to the stressed surface which is supersaturated in NaCl with respect to equilibrium solubility at the lower pressure prevailing over the solution. The supersaturated solution near the surface would lose salt by diffusion into the body of the solution as well as by precipitation on the nearest unstressed surface. These surfaces could be crystallites of NaCl formed and suspended within the solution.

Such effects might occur when brine inclusions within salt crystals contain low-pressure, gas-vapor bubbles, and these effects could influence migration of the inclusions when there are stress gradients in the salt surrounding the inclusions. This could account for the results of uniaxial stress experiments reported by Powers et al.⁶³ (Sect. 5.1.5.)

5.3 Conclusions Regarding Possible Effects of Two-Phase Inclusions in a Salt Repository

As discussed in Ref. 4, it is unlikely that low-pressure, gas-vapor bubbles will occur naturally within brine inclusions in the solid salt around waste packages in a repository. They might occur salt located at the edge of an emplacement cavity, should a portion of the liquid escape into the cavity through temporary fractures or small blowouts formed when inclusions approach the surface of the cavity.* High-pressure gas-vapor bubbles might be formed within brine inclusions that contain Br^- (likely in bedded salt) because the Br^- inhibits the recombination of H_2 and O_2 formed by the radiolysis of H_2O .^{4,22}

Two-phase inclusions could also be formed within crushed salt backfill around a waste package under circumstances causing formation of closed cavities containing brine during the consolidation of the backfill. Gas bubbles could be trapped along with the brine, or they could be generated within a cavity by radiolytic and/or corrosion processes.^{4,22}

Insufficient information prohibits confident predictions regarding the fates of two-phase inclusions occurring within the salt around a waste package in a repository. Some general comments and/or conclusions are listed below.

- 1 It is possible that no down-gradient migration will occur in bedded salt, where the brines are likely to be rich in MgCl_2 .

*Such fractures could also develop in crystals within the body of the salt if there is a lower-pressure, gas-vapor space into which the brine inclusion liquid could escape; however, this is considered unlikely.

2. If radioactive nuclides are present in the open spaces surrounding a waste package, they could enter two-phase inclusions during the brief period of formation near the surface of salt surrounding the package (or during formation within the crushed salt backfill around a waste package).¹⁶ These nuclides could then be carried into the salt through a down-gradient migration of the inclusion.^{25,51,53} The maximum migration distance within a repository can be estimated from the available experimental and theoretical information. It appears very unlikely that the migration distances would be great enough to compromise satisfactory containment of the wastes within the repository.
3. The formation of high-pressure, two-phase inclusions within the body of the salt might decrease the rate of up-gradient migration of the inclusions.
4. The formation or occurrence of two-phase inclusions in a salt repository will probably not adversely affect either the amount of brine reaching a waste package or the satisfactory containment of radioactive nuclides within the repository.

6. EXPERIMENTAL AND THEORETICAL INFORMATION ON MIGRATION OF FLUIDS WITHIN ROCK SALT WALLS OF WASTE EMPLACEMENT HOLE

Rock salt is composed of aggregates of single NaCl crystals along with impurity minerals, dirt, and brine — the latter occurring as inclusions within the crystals and on the crystal boundaries (see Sect. 2). Migration of brine within the walls of a waste emplacement hole in the salt will depend on the brine-transport properties of the in situ aggregates, as well as the migration of inclusions within individual crystals.

Several experimental and theoretical studies have reported information on the brine and vapor transport properties of the rock salt walls of a waste emplacement hole. The general conclusions of these studies are the following:

1. Very few inclusions undergo thermal-gradient-induced migration from one crystal into an adjacent one; they are usually stopped on boundaries between crystals.
2. Brine on salt boundaries can move along microcracks or connected pores to the spaces around a waste package. Microcracks could occur along crystal boundaries and/or through crystals.
3. Liquid brine migration through microcracks and connected pores could result from pressure gradients on the liquid caused by gradients in the vapor pressure of H_2O , radiolytic gas, and/or the stress state of the salt. Brine might also move by a thermal gradient mechanism analogous to that within salt crystals or by capillary action along previously unwetted surfaces. Water vapor, as opposed to liquid brine, could move under gradients of vapor pressure of water and radiolytic gas from a receding liquid front within a microcrack or pore.
4. The effective permeability of the rock salt walls around a waste package in bedded or domal salt of repository quality, and free of impurity stringers, will be very low: $<5 \text{ fcm}^2$.

5. The available results of MIGRAIN-type calculations of rates of in-migration of H_2O in the Salt Block II experiment and in an in situ experiment in salt similar to that in Salt Block II were in near agreement with the experimental values. We believe that this agreement is fortuitous since it is likely that in-migration took place by movement of brine and/or vapor along crystal boundaries as well as by migration through crystals. However, the near agreement does suggest that the MIGRAIN-type calculations constitute a means for making rough estimates of the rates of in-migration to a waste package during the first 1.5 to 2 y after emplacement in a repository. (The experimental data on in-migration do not extend beyond ~1.6 y.)
6. Calculations of the type outlined above for in situ experiments in the Avery Island domal salt gave calculated values that were appreciably higher than the experimental results.

The experimental and theoretical studies leading to these conclusions are reviewed in the following sections.

6.1 Rock Salt Permeability in the Absence of a Temperature Gradient

Studies of the permeability of bedded rock salt without a temperature gradient have been reported by several groups of investigators. There is general agreement that undisturbed bedded salt which is located at repository depths has a very low permeability, probably $<5 \text{ fcm}^2$ in the regions free of impurity stringers. Laboratory samples usually have sensible permeabilities resulting from the presence of interconnected microcracks. It is believed that the microcracks formed within the rock salt are disturbed by mining, drilling, and/or machining. There is strong evidence that microcracks within a sample can be healed by application and maintenance of hydrostatic confining pressures comparable to those prevailing in the undisturbed formation.

The fewer laboratory studies on samples of domal salt indicated permeabilities much greater than those for bedded salt, with the other permeability characteristics being very similar. In situ measurement of

the nitrogen permeability in the Avery Island domal salt around a 38-mm-diameter borehole showed an average value of 3 fcm^2 . These laboratory studies are summarized in following sections.

6.1.1 Studies by Gloyna and Reynolds

Gloyna and Reynolds^{66,67} were the first to report careful studies of the permeability of rock salt. Their tests were conducted at room temperature. Other pertinent information on their test materials, procedure, and results are summarized below.

Source of sample material:

Bedded salt from the Carey Salt Company mine at Hutchinson, Kansas;

Dome salt from the Morton Salt Company mine at Grand Saline, Texas.

Finished sample size:

$32 \times 32 \times 43 \text{ mm}$.

Permeating fluids:

The liquids tested with most of the brine samples were either saturated NaCl brine or kerosene. Supersaturated NaCl brine and helium gas were also tested.

Confining pressure:

3.4 to 21 MPa. This pressure was applied to the top surface of the confined specimen.

Average fluid pressure:

0.07 to 3.4 MPa. The fluid pressure was always $< 1/3$ of the confining pressure. The fluid pressure was applied at a vertical surface and fluid was withdrawn from the opposite vertical surface.

Test Procedures:

The confining pressure was applied, and the creep (vertical movement) of the specimen was followed until further movement became negligible, usually 7 to 14 d. The test-permeation liquid was maintain at a pressure of 1.0 to 1.4 MPa, with no flow during this time (no liquid was applied when helium was tested).

The permeation-flow of the test fluid was measured on each of the next several days. A measurement at a given confining pressure was made by opening the exit line from the specimen and collecting the exiting fluid during a period of 1 h.

Results:

Permeability measurements for samples of bedded salt are summarized in Table 7. Some of the measurements with samples of dome salt are summarized in Table 8. Studies of the "nonreactive liquid" permeability,* K_L , of samples of the domal salt with helium gas and certain liquids were also reported. Illustrative values for K_L for the domal salt obtained using helium were 2.3 and 72 pcm^2 at mean stresses of 10 and 3.4 MPa, respectively.

Additionally it was found that a single crystal of NaCl (Harshaw Co.) exhibited zero permeability.

Limits of detection were not discussed; they were apparently $<5 \text{ fcm}^2$.

Tables 7 and 8 show that the liquid permeabilities decreased with exposure time whenever the initial (maximum) permeability was >0 . The experimenters had some evidence that these reductions resulted from clogging of the pores (rather than from pore-closure under the confining stresses), and they assumed that clogging may have caused some or all of the reductions in all studies of liquid permeation.

Gloyne and Reynolds noted that the permeability of the bedded salt specimens were mostly below the limits of detection, and the permeabilities of the domal salt specimens were generally much greater than

*Nonreactive liquid permeability, K_L , indicates that the permeating liquid does not react chemically with the solid. K_L is related to the gas permeability, K_G , by the equation

$$K_L = K_G / (1 + C/\bar{P}) ,$$

where $\bar{P}$ is the mean gas pressure and C is a system constant called the Klinkenberg constant.

Table 7. Permeabilities of Hutchinson bedded salt^a

Permeation fluid	Mean stress (MPa)	Maximum permeability (fcm ²)	Minimum permeability (fcm ²)	Test period (d)	Days of flow	Days without flow
Kerosene	16	230	5.0	23	23	0
NaCl brine	6.8	0	0	7	0	7
NaCl brine	6.8	72	0	9	3	6
NaCl brine	14	15	0	11	6	5
Helium	10	0	0	2	0	2
Helium	3.4	0	0	2	0	2
Kerosene	3.4	0	0	2	0	2

^aAdapted from a table by Gloyne and Reynolds in Ref. 66.

Table 8. Permeabilities of Grand Saline domal salt^a

Permeation fluid	Mean stress (MPa)	Initial permeability (pcm ²)	Minimum permeability (pcm ²)	Duration to minimum (d)
NaCl brine	6.8	4.5	1.4	3
NaCl brine	21	0.60	0.0020	36
kerosene	16	5.0	0.0050	22
NaCl brine	6.8	1.0	0.25	4
Kerosene	3.4	10	1.7	9
Kerosene	3.4	42	32	3
Kerosene	10	2.1	0.54	10
Supersaturated NaCl brine	10	0.50	0	9
Kerosene	3.4	62	17	6
NaCl brine	3.4	40	1.1	4

^a Adapted from a table by Gloyne and Reynolds in Ref. 66.

those of the bedded salt. They pointed out that, since the single crystals of NaCl were impermeable, the permeating flows occurred through cracks or fractures in the crystal aggregates. Such fractures may have been caused by the relaxation of stress occurring when underground samples are removed from a compressed formation.

6.1.2 Studies by Sutherland and Cave

Sutherland and Cave⁶⁸ studied the permeability of core samples of bedded salt from ERDA Core No. 9 in SENM at depths of ~640 m and ~790 m, using argon as the permeation fluid. The samples were cylindrical, 76 mm in diameter, and 102 mm long. Permeability was measured along the length of the sample, which corresponded to the vertical direction of the core; the salt samples were under uniform hydraulic pressure in a rig described by Wawersik and Hannum.⁶⁹ The minimum permeability that could be measured was 0.5 fcm^2 , with estimated experimental error of $\pm 4\%$ or $\pm 0.3 \text{ fcm}^2$ (whichever was greater).

These studies showed that relatively high initial permeabilities prevailed; these decreased during pressurization, and the rate of decrease increased with increasing hydraulic pressure. One sample from a depth of 796 m (No. 9-2613) was pressurized at a constant level of 14 MPa for 336 h. Argon pressures used in these permeability measurements were 8.5 to 10.2 MPa. The measured permeability, K_L , decreased from an initial value of 45 fcm^2 to 2.0 fcm^2 after 336 h. The minimum value of K_L measured for this and for other samples at higher hydraulic pressures was $<0.5 \text{ fcm}^2$.

These experimenters concluded that the in situ permeability of the undisturbed salt formation was $<0.5 \text{ fcm}^2$. They suggested that the microcracks formed as a result of mining and working the rock salt formation will heal when (and if) the formation is returned to its pre-mining pressure state.

6.1.3 Other laboratory investigations of bedded salt permeability

Other laboratory investigations of the permeability of bedded salt from SENM were reported by Cooley et al.⁷⁰ and by others cited in

Ref. 68. The results and conclusions from these studies were similar to those reported by Sutherland and Cave.⁶⁸

6.1.4 In situ permeability of Avery Island domal salt

Workers at RE/SPEC, Inc. conducted in situ measurement of the N_2 permeability of the salt around a 38-mm borehole in the Avery Island domal salt^{71,72} and reported an average value of 3 fcm².

6.1.5 Other laboratory investigations of domal salt permeability

C. S. Lai⁷³ conducted permeability investigations of a "Louisiana dome salt" using kerosene.

6.2 Studies Relating to Thermal-Gradient-Induced Transfer of Brine Across Crystal Boundaries

Theoretical and experimental information shows that brine inclusions undergoing thermal-gradient-induced migration within crystalline NaCl (and other alkali halides) may either be stopped on a tight crystal boundary or migrate into the adjacent crystal, depending upon several factors: (1) the size and shape of the inclusion, (2) the presence of impurity solids on the boundary, and (3) the temperature gradient in the salt. If the boundary is not tight, the arriving brine inclusion will merge with the boundary region. Laboratory and in situ experiments (Project Salt Vault) indicate that very few inclusions in bedded salt continue their migration from one crystal into another, because of this trapping and/or spreading.

Spreading implies the presence of a microcrack at the boundary. The spreading and trapping behavior around a waste package will depend upon the stress on the surrounding rock salt. We note here that the results of the Project Salt Vault in situ experiment indicated that brine was generally immobilized on crystal boundaries and was released only when tension stresses developed as the salt cooled.

These considerations apply to brine occurring naturally on a crystal boundary as well as brine originating within a salt crystal.

The available theoretical and experimental information on this subject is summarized in more detail in the following subsection.

6.2.1 Theoretical aspects of brine migration across crystal boundaries

Cline and Anthony⁷⁴ point out that brine droplets on crystal boundaries in KCl and other alkali halides are in positions of minimum energy; therefore, the thermal-gradient force required to propel a droplet across a boundary can exceed that required for motion through the body of a crystal. Their theoretical expression for the retarding effects of the grain boundary tension force is given by the final term in Eq. (43), for droplets in which the leading edge has a square shape.

$$V = \frac{C_l D}{C_s + (\beta C_l D / RTL)} \left[\left(\frac{1}{C_E} \frac{\partial C_E}{\partial T} - \sigma \right) VT_l - \frac{b}{RTL} - \frac{4Y\bar{V}_s}{RTXL} \right] \quad (43)$$

where

γ = grain boundary tension, ergs/cm²;

X = dimension of droplet perpendicular to thermal gradient, cm;

$\bar{V}_s$ = molar volume of solid salt, cm³/mol; (other symbols have been previously defined in Sect. 3.1.2).

Pigford³⁰ has recently reviewed the derivation of Eq. (43) in his discussion on transport through grain boundaries.

In order to compare the theoretical minimum value for the temperature gradient, $(\nabla T_\infty)_{b,min}$, required to propel a droplet across a crystal boundary, with the temperature gradient, $(\nabla T_\infty)_{c,min}$, required to induce movement of the same droplet within the body of a crystal, we can use the relationship shown:

$$\frac{(\nabla T_\infty)_{b,min}}{(\nabla T_\infty)_{c,min}} = 1 + \frac{4Y\bar{V}_s}{Xb} \quad (44)$$

This was derived by setting the bracket functions in Eqs. (5) and (43) equal to zero, solving for ∇T_l in each case, dividing one ratio by the

other, and simplifying. It was assumed that the value of L , [as well as values of the other parameters within brackets in Eq. (5)], does not change significantly when the droplet (inclusion) migrating within the body of the crystal reaches the boundary.

Values for the quantities on the right side of Eq. (44) are known or can be estimated. For illustrative purposes, Table 9 gives calculated values for Eq. (44), using several assumed values for X , two values for γ , and the values for $\bar{V}_g$ and b which apply to NaCl at 150°C. The higher value for γ (150 ergs/cm²) corresponds to the maximum of the range of values for NaCl which were estimated by Jenks;⁴ the minimum value was 50 ergs/cm². Pigford³⁰ recently reviewed possible values for γ in NaCl and estimated 45 ergs/cm² as the minimum.

The calculated values listed in Table 9 indicate that brine inclusions for which $X \gtrsim 0.1$ cm will move across a crystal boundary if they move within the crystal, under the given thermal gradient. Inclusions with smaller values for X might be trapped on a boundary even though they move within the crystal, depending upon several factors including the actual value for γ for NaCl and the prevailing value for ∇T_∞ .

Values for $(\nabla T_\infty)_{c,\min}$ can be estimated by setting $B/B_{\max} = 0$ in Eq. (40) and solving for $(\nabla T_\ell)_{c,\min}$. As an example of values estimated in this way, the relationship shown by Eq. (30) for cubical and spherical inclusions migrating in bedded salt at 150°C may be expressed as

$$(\nabla T_\infty)_{c,\min} \cong \frac{5.3 \text{ E-03}}{L} \text{ } ^\circ\text{C/cm} \quad , \quad (45)$$

where assumed values are: $b = 1.8 \text{ E+06 ergs/mol}$, $[(1/C_\ell)(dC_\ell/dT) - \sigma] = 0.0069 \text{ } ^\circ\text{C}^{-1}$, and $\nabla T_\ell/\nabla T_\infty = 1.4$.

6.2.2 Experimental studies of brine migration in bedded salt

Shor and Baes^{57,75}. These researchers investigated some characteristics of brine migration in two small samples of bedded salt from the Lyons, Kansas, mine. Figure 10, reproduced from Ref. 57, illustrates their

Table 9. Calculated Values for $\frac{(VT_{\infty})_{b,min}}{(VT_{\infty})_{c,min}}$
for NaCl at 150°C^a

x^b (cm)	$(VT_{\infty})_{b,min}/(VT_{\infty})_{c,min}$	
	$\gamma = 45 \text{ ergs/cm}^2$	$\gamma = 150 \text{ ergs/cm}^2$
0.001	3.8	10.3
0.01	1.3	2.0
0.05	1.06	1.2
0.1	1.03	1.1
0.2	1.01	1.03

^a $\bar{V}_S = 27.5 \text{ cm}^3/\text{mol}$ (Ref. 4).

^b $b = 1.8 \text{ E+06 erg/mol}$ (Section 5).

^b x = dimension of droplet perpendicular to thermal gradient.

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Fig. 10. Microscope stage designed for observation of brine inclusion migration under thermal gradients and mechanical stress.

observation cell. The sample dimensions were $0.65 \times 1.3 \times 2.5$ cm. The brine inclusion sizes were in the range 100×100 μm . Temperature gradients were ~ 35 $^{\circ}\text{C}/\text{cm}$, and the high temperature end was held at 100 – 110°C . The plunger pressures used were 0.52 MPa and 2.2 MPa for the first and second samples, respectively. Walls of the sample holder parallel to the plunger and motion were rigid; however, the experimenters found no significant compression of the specimens during testing.

In the first sample, where two inclusions reached a crystal boundary, one merged completely and the other partially with the boundary; the latter inclusion developed a gas-vapor space during migration, after which it ceased to move.

Information concerning the second specimen is quoted from Ref. 75 as follows:

A second halite specimen from the same core section was mounted on the microscope stage assembly and subjected to a lengthwise temperature gradient of $\sim 35^{\circ}\text{C}/\text{cm}$ and a mechanical pressure of ~ 300 psig. One rectangular inclusion (132 $\mu\text{m} \times 117$ μm) after elongation slightly in the direction of motion and moving at an average rate of about 90 μm per day appeared to pass into a concentration of much smaller inclusions and to break up. Another reached what appeared to be a grain boundary and merged with it. Small inclusions adjacent to grain boundaries developed gas bubbles similar to those observed in a prior experiment at 60 psig. Finally, another rectangular inclusion (145 $\mu\text{m} \times 130$ μm), half of whose area was opaque and the other half containing a bubble, showed very little movement. Similar to previous observations, no significant compression of the salt specimen occurred at the increased pressure of 300 psig during the 90 -hour heating period.

Roedder and Belkin.⁷⁶ These investigators continued the experimental work reviewed in Sect. 4.1.2, studying the behavior of inclusions reaching crystal boundaries. The boundaries were curved and were marked by gas and/or liquid inclusions and dark particles. The inclusions had volumes equal to those of cubes with edge dimensions of 0.1 to 0.45 mm. There was no pressurization of the specimens.

They reported that the inclusions lost 50 to 90% of the liquid on intersecting a boundary. Each inclusion then resealed and the gas-vapor-liquid inclusion moved back from the boundary.

This boundary behavior is typical of that expected at an unconfined surface and the subsequent down-gradient movement is as expected for inclusions in which the brine solute is primarily NaCl.

Lambert.⁷² The Salt Block II experiment utilized a block of rock salt containing about 88% NaCl, 8% polyhalite, and 4% sylvite. The block was machined into a right-circular cylinder 1-m diameter and 1 m high. This block was fitted with an axial heater, thermocouples, and an off-gas collection system. The block was heated for about 100 d. The maximum temperature and temperature gradients were $\sim 200^{\circ}\text{C}$ and $12^{\circ}\text{C}/\text{cm}$.^{77,78} The average gradient was $\sim 3^{\circ}\text{C}/\text{cm}$. No external stresses were applied to the block.

Lambert⁷⁷ examined the block after heating and reported on the mineralogical aspect of fluid migration. He found that fluid inclusions within 15 cm of the heater hole had migrated, but rarely across grain boundaries. Intergranular liquid had been mobilized within this region. He also reported that fluid inclusions had not been mobilized at distance greater than ~ 15 cm from the heater hole. Koedder and Belkin⁷⁶ have questioned the validity of the latter statement, implying that the temperature and temperature gradients in Salt Block II were such that significant migration of inclusions within crystals would have taken place beyond 15 cm.

Project Salt Vault.^{4,79} Project Salt Vault was conducted in the Carey Mine at Lyons, Kansas. The experiment included two different arrays of seven heated canisters. Each canister in one array contained a radiation source consisting of spent fuel elements from the Engineering Test Reactor (ETR); these fuel elements supplied radioactive decay heat, which was supplemented by the electrical heat. The other array served as an unirradiated control, and electrical heat was supplied to each canister to match the total in the irradiated canisters.

The experimental design, results, and analyses have been reported in detail.^{4,79} The result to be pointed out here is that a large amount of brine in-flow to the emplacement holes occurred when the salt walls were allowed to cool after heating. The explanation offered for the marked release of brine during cooling of the salt⁷⁹ was that the tangential stresses created by thermal expansion of the salt during heating were released during cooling, allowing the trapped water in the salt to break free and enter the air space. A further explanation⁴ might be that the brine was trapped on grain boundaries during heating and that release of tangential stresses allowed the grain boundaries to open sufficiently for the brine to escape to the air gap space. In support of these ideas, it should be noted that the thermal contraction of the salt at the surface of a cylindrical hole comparable in size to those in Project Salt Vault produces a decrease in area of $\sim 1.5 \text{ cm}^2/^{\circ}\text{C}$. (The dimensions of the holes in Project Salt Vault are given in Table 10.)

Holdaway.^{10,80} Petrofabric examinations of salt samples from a region adjacent to irradiated Array Hole 2 in Project Salt Vault were conducted by Holdaway. This region was located in an outward direction from the periphery of the array of waste canisters. Evidence for brine migration within crystals was observed, but only a few trails crossed crystal boundaries. There was some evidence that droplets spread on grain boundaries. These observations appear to support the postulation that brine was trapped on grain boundaries during the heating phases of the Project Salt Vault experiment.

6.3 Summary and Correlation of Brine In-Migration Measurements

The conditions and results for these experiments are summarized in Table 10. Values for rates of in migration were calculated by assuming that all in-migration resulted from thermal gradient-induced movement of brine inclusions through crystals, with no crystal boundary effects, and also assuming that the migration obeyed Eq. (42). Notable features of the in-migration experiments are discussed below, and other pertinent experimental information is given in footnotes to Table 10.

Table 10. Rates of in-migration of H₂O

Experimental parameters	Project Salt Vault ^a	Sandia Salt Block II experiment, ^b	Sandia in situ in SENM ^{b,c}	Sandia in situ, Avery Island ^b	ONWI in situ, Avery Island ^d
Salt type	bedded	bedded	bedded	dome	dome
weight fraction of H ₂ O	~0.0025 ^d	0.0025	0.0025	0.002	0.002
Dimensions of heated hole					
diameter, m	0.30	0.13	0.13	0.13	0.076
length, m	1.85	0.61	1.0	1.0	4.25
surface area, m ²	1.75	0.24	0.41	0.41	1.02
Max. temp. of salt walls, °C	150 200	200	200	200	55
Max. temp. gradient, °C/cm	0.7 2	12	7	7	1
Length of test, d	1 580	140	113	138	350
Total H ₂ O collected, g	<1 <1400 ^e	110	190	12	20
Steady-state rate of collection of H ₂ O, g/d	<1	<2.4 ^e	0.5	0.02 (0.01) ^g	0.04 (0.015) ^f
g/d m ²	<0.4	<1.4 ^e	2.0	0.05 (0.025) ^g	0.04 (0.015) ^f
Calculated steady-state H ₂ O collection rate (assuming only thermal gradient diffusion through crystals), g/d		0.39 ^h	0.37 ⁱ		0.10 ^j

^aData in center column were common to both experiments. Data in the left column represent results of a 1-d test, and data in the right column are for the entire experimental period of 580 d.

^bInformation not otherwise referenced or discussed was obtained from Ref. 81.

^cThis experiment was conducted in the mine area from which the Salt Block II material was taken (See Ref. 82).

^dSee Sect. 2.1.3.

^eSee Ref. 4.

^fAfter subtracting 0.026 g/d measured for the unheated control emplacement hole (Ref. 83).

^gAfter correcting for the background inflow/unit area found in the ONWI in situ experiment (see preceding note).

^hMIGRAIN calculation assuming 0.25 wt % H₂O in the salt. Also assuming use of the Jenke equation (see Sect. 7).

ⁱFound by analogy with MIGRAIN calculation for Salt Block II: $(0.39)(7/12)(1/0.61) = 0.37$.

^jThe value calculated by Krause (Ref. 84) for 0.03 wt % H₂O was 0.015 g/d. This table value, 0.10 g/d, was obtained by multiplying 0.015 by the ratio: $0.2/0.03$.

6.3.1 Project Salt Vault measurements

Two sets of data for Project Salt Vault are included in Table 10; one set for the entire experimental period of 580 d, and one set showing results of a 1-d test aimed at accurately establishing the rate of in-migration in the irradiated array during periods of continuous heating. (At the time of the test, the array had operated for 70 d with no collection of H_2O and, presumably, no heater failure.) To accomplish the test, the central experimental hole of the irradiated array was flushed with dry N_2 and sealed for a period of 1 d. The moisture collected in the hole was then swept into a cold trap using dry N_2 . This experiment was not completely successful, and only the upper limit for the amount of H_2O entering the hole during the 24-h period was established.⁸⁵

The steady-state rate of collection of H_2O per unit area in the 1-d experiment was lower (and possibly much lower) than that in the in situ experiment in the Sandia potash salt. The lower temperatures, temperature gradients, and possibly smaller amount of brine, in the salt for Project Salt Vault probably accounted for the lower in-migration rates.

6.3.2 In situ measurements at Sandia and Avery Island

The in situ experiments in the Avery Island mine were located in a section of the floor that appeared dry and had not been covered with crushed salt.⁸⁶ The surfaces in some other sections of the experimental area were covered with ~1 m of crushed salt at some unspecified time before the heater test work began. This crushed salt was damp, possibly as a result of water leaking from a nearby shaft to the surface. The damp, crushed salt was scraped from the floor of the experimental area during preparation of the site. The fraction of H_2O in the salt immediately adjacent to the in situ experiments has not been fully established. Recent measurements were done at ORNL of the volatile content of samples from the core-barrels which were formed during core drilling (dry) of the experimental heater sites SB, NB, and AB. The samples were from depths of ~320 mm below the floor. Measurements were made by heating crushed samples to 650°C for 1 h, with observed losses of ~0.2 % for each of the core-samples. The amount of H_2O found in samples from other locations in the Avery mine have been in the range of 0.004 wt % to 0.17 wt %.^{23,87} For reference

purposes, we arbitrarily assume a value of 0.20 wt % for the salt in the immediate neighborhood of the in situ experiments.

The exposure conditions for the Sandia in situ experiments in the potash mine salt and in the Avery Island salt were comparable in all respects except for the properties of the rock salt being tested. The rate of in-migration of H_2O in the Avery Island experiment was much lower than that in the Sandia potash salt; this cannot be explained in terms of smaller amounts of H_2O in the Avery Island salt and remains unexplained.

6.3.3 Salt Block II measurements

The block used for Salt Block II was machined from bedded salt removed from the Mississippi Chemical Company's potash mine in SENM.⁷⁸ The area from which the block was taken contains appreciable amounts of polyhalite ($K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$) ranging to >10 wt %. The volatile content, measured by loss of weight upon heating to 424°C, ranged to 1.2 wt %, with an average of 0.5 wt %. Measurements of weight loss vs temperature indicated that weight losses >0.25 wt % resulted from decomposition and loss of H_2O from polyhalite.⁸⁸

The steady-state rate of collection of H_2O per unit area in the Salt Block II experiment was nearly twice that in the Sandia in situ experiment in SENM, although the salt used in fabricating Salt Block II came from the same mine area. It is likely that the lower in situ rate resulted from the higher compressive stresses during heating of the salt.

6.3.4 Calculated brine in-migration rates

MIGRAIN-type calculations of in-migration rates for the bedded salt experiments, using Eq. (42) and probable values for fractions of liquid H_2O in the salt (line 2 of Table 10), were in near agreement with the experimental values. This agreement is probably fortuitous, since it is likely that in-migration took place by movement of brine and/or vapor along crystal boundaries as well as by brine inclusion migration through crystals. Also, only the largest inclusions would migrate through crystals at the rates given by Eq. (42). However, the near agreement between calculated and experimental values suggests that the MIGRAIN-type calculations constitute a means for making rough estimates of the rates of

in-migration to a waste package in a bedded salt repository during the first 1.5 to 2 y after emplacement.

MIGRAIN-type calculations for the Avery Island domal salt experiments gave values appreciably higher than the experimental results. While the differences between experimental results for the bedded and domal salt experiments have not been explained, it is reasonable to assume that the MIGRAIN-type calculations constitute a means for making conservative estimates of the in-migration rates of H_2O to a waste package in a domal salt repository during the first 1.5 to 2 y after emplacement.

The in-migration rates for Salt Block II have been modeled by Hadley⁸⁹ assuming vapor transport from a receding liquid front within the microcracks and an effective permeability of 0.4 fcm^2 with a porosity of 0.25%.

Salt Block II in-migration was also modeled by Bloom and Hulbert⁹⁰ by assuming two simultaneous transport mechanisms: thermal gradient diffusion (dissolution at the hot side and precipitation at the cold side of the inclusion) and vapor transport through microcracks from a receding liquid front. Their fit to the experimental data yielded values of 0.5% for the porosity of the salt and 0.06 fcm^2 for the permeability.

These models and the results of fitting to experimental data are summarized in Sect. 6.6.

6.4 Other Laboratory Experiments with Rock Salt

6.4.1 Lyons bedded salt

Shor and Baes⁵⁷ conducted brine migration experiments with a section of core from the Carey Mine at Lyons, Kansas. The core-section was 150 mm in diameter and 70 mm long. The upper and lower faces were held at 190 and 105°C, respectively, during 17 d of the 22-d experiment. Dry air, from which moisture was extracted downstream, was passed over both the hot and cold faces. The results showed totals of 235 and 175 mg H_2O from the hot and cold faces, respectively.

These data were modeled by Bloom and Hulbert⁹⁰ by the methods discussed in Sect. 6.6; they obtained values of 0.09% and 0.03% for the

porosity of the cooler and hotter sides, respectively, and 0.2 fcm^2 for the effective permeabilities of these sides.

6.4.2 Salt Block I

The Salt Block I experiment, using 1 kg of salt from SENM, was described and the H_2O -collection data modeled, by Hohlfelder and Hadley.⁹¹ The model assumed vapor transport from a receding front, as mentioned in Sect. 6.3. The assumed values for the effective permeability (0.4 fcm^2) and porosity (0.25%) gave a satisfactory fit to the data. This model is summarized in Sect. 6.6.

6.5 Synthetic Aggregates with Synthetic Inclusions

Biggers and Dayton⁹² conducted brine migration experiments with synthetic aggregates of very small crystals. No load was applied to the aggregates during the migration experiments. They found that very rapid migration along grain boundaries took place when a thermal gradient was applied and brine supplied to the hot side. This suggests that capillary action pulled the brine along the previously unwetted surfaces of the grain boundaries.

6.6 Vapor Transport Models

Investigations of brine migration in blocks of halite at Sandia Laboratories have led to a proposed model of vapor transport along grain boundaries or cracks, with no consideration given to migration of the intra-crystalline inclusions. The observed behavior of increased flow after the heat source was turned off is accounted for by including stress relaxation effects in the model. The first model was developed on the assumption of Darcy flow of vapor through a porous medium; this was applied to the Salt Block I⁹¹ and later to the Salt Block II⁸⁹ experiments at Sandia Laboratories. A second model, which apparently produced a better correlation of the experimental data, assumed that the vapor flow was entirely in the Knudsen regime (the mean-free path of the vapor molecules is on the order of pore diameter or equivalent spacing). This second model was applied to Salt Block I but not yet to the Salt Block II experiment.

6.6.1 Darcy vapor flow models

The Darcy vapor flow models that were applied to both Sandia experiments were conceptually similar, except that Salt Block I was considered as a sphere and Salt Block II as a cylinder. In addition, stress relaxation by creep was approximated for Salt Block II so that thermal stresses were effectively eliminated from the calculations until a change in power occurred.

Salt Block I. The experiment used a 1-kg halite cylinder, 5 cm high and 10.8 cm in diameter, with electrical heat around the circumference. Water vapor removal was from the top of the block. In this model, the following assumptions were made.

1. The cylindrical salt block was modeled in one dimension by a sphere with volume equal to that of the cylinder.
2. Water motion within the salt was by Darcy flow of vapor from a receding evaporation front.
3. The permeability of the salt was constant except where radial cracks were predicted, in which case it was increased by a factor of 40. The uncracked permeability (0.4 fm^2) and the factor of 40 were determined on the basis of the best fit to the data.
4. The porosity was estimated to be 0.25%, based on weight loss measurements.
5. Steady-state was assumed for vapor motion but not for the temperature distribution.
6. The pressure causing flow was the equilibrium vapor pressure for pure water at the interface temperature.

The following five equations (and the elastic stress-strain equations) were solved simultaneously to calculate the vapor flow from the sample. The equations were:

the steady-state continuity equation:

$$\frac{\partial}{\partial r} (r^2 \rho_v V) = 0 , \quad (46)$$

the ideal gas equation:

$$P = R \rho_v T , \quad (47)$$

Darcy's Law:

$$V = \frac{\kappa}{\mu} \left(\frac{\partial P}{\partial r} \right), \quad (48)$$

the evaporation front velocity equation:

$$\mu = \frac{\rho_v V}{\rho_w \phi}, \quad (49)$$

and the time-dependent heat conduction equation for a sphere:

$$\frac{\alpha}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) = \frac{\partial T}{\partial t}, \quad (50)$$

where

- P = pressure, dynes/cm²,
- r = radial dimension, cm,
- V = Darcy velocity of water vapor, cm/s,
- ρ_v = water vapor density, g/cm³,
- R = gas constant,
- T = absolute temperature, K,
- κ = effective permeability, cm²,
- μ = viscosity,
- ρ_w = brine density, g/cm³,
- ϕ = porosity, dimensionless.

The experimentally measured temperatures and the heat flux on the periphery were used as the boundary conditions.

Tests were made on 3 different blocks. The results were not reproducible in detail, but the general features of a peaked profile after each heater power increase and the sudden water flow after heater turn-off were consistent with the calculations. The increased flows (as in Project Salt Vault) apparently resulted from stress relaxation. The maximum tensile stress predicted by the calculation during heatup remained

below the measured tensile strength. However, the cooldown tensile stresses were in excess of the strength, which implied cracking of the salt. It was recognized that a more elaborate model was needed, although the results seemed to demonstrate the overall feasibility of the model.

Salt Block II. The Darcy flow model discussed in the previous section was improved and applied to the Salt Block II experiment.

This experiment was performed on a block of SENM rock salt machined into a right circular cylinder, ~1 m in height. A central hole contained the heater, and water was collected from the hole by a flow of dry nitrogen gas. The block was completely enclosed in a jacket equipped with cooling coils around the periphery for heat removal. The heater power was increased in discrete steps to a maximum of 1.5 kW.

The model used to analyze this experiment was essentially the same as described in the previous section, with the following exceptions:

1. The salt block was modeled as a one-dimensional cylinder.
2. The same permeability and porosity was assumed but a crack enhancement factor of 50 was used.
3. The vapor pressure at the evaporation front was calculated using a mixture formula and components specific to WIPP brine.
4. An allowance for creep was made by an approximate method that involved resetting the reference temperature profile after one week at a given power level, so that the thermal stresses were effectively eliminated from the calculations until a change in power occurred.
5. The stress-strain behavior of salt in one region depends upon fractures in adjacent region since the latter can no longer support its share of the stress. Consequently, the stress normal to a fracture plane was decreased by 0.01 when fracturing occurred. The justification for this higher than the normal 10^{-4} to 10^{-6} decrease is based on the belief that microfractures occurred rather than a total failure of the salt. Consequently, it was to be expected that some stress normal to the fracture plane could be supported.

The experiment and this improved Darcy flow model showed reasonably good agreement. Each increase or decrease in power was followed by an immediate increase in the experimental water loss rate, followed by a gradual decline, which was modeled well by the Darcy flow model. Hadley⁸⁹ therefore concluded that the model is viable and is worthy of further investigation.

6.6.2 Knudsen diffusion model

Hadley and Paris⁹³ have developed a refinement of the vapor flow model that assumes Knudsen diffusion and binary gaseous diffusion to be the important transport mechanisms. Also, the total porosity is considered as two contributions: a small connected porosity that reflects the flow "channel" dimensions limiting the vapor flow rate, and a larger "inclusion" porosity that reflects the total water content influencing the rate of recession of the evaporation front. Since this model was applied to the Salt Block I experiment, a spherical configuration was assumed.

The technique of vapor flow calculation was similar to that described in the previous sections, except that it was assumed that Darcy flow was small compared to Knudsen diffusion flow, and Eq. (48) was replaced by equations describing Knudsen flow with concomitant water vapor-air diffusion.

Stresses and strains due to thermal expansion of the salt were calculated in the same manner as before. It was felt that residual strains might cause a considerable change in channel properties; consequently, the connected pore radii were considered to vary as a linear function of the residual strain in the tangential direction. The initial values for the equivalent pore radius and the connected porosity were treated as fitting constants that gave the best fit to the experimental data. In this analysis, the fitting constants were multiplied by a factor of 7 whenever the tensile strength of the salt was exceeded. This is in contrast to the Darcy flow model, where the permeability was the modified transport property.

Generally better experimental agreement was obtained with this model. However, none of the vapor flow models gave good agreement near the peak of the second increase of power to 116W. The authors suggested

that this indicates some undiscovered mechanisms. They speculated that absorption effects in the small pores may require activation energy to free the water molecules and that the mechanical effects were not treated accurately enough. They also pointed out that three sets of data were taken in the experiments and only one was used in the comparison. The other runs showed considerable variation in water loss, so that close agreement with experiments could not be expected.

6.6.3 Combined diffusion and Darcy vapor flow models

Alcom and Hulbert⁹⁰ developed a preliminary model that combined the temperature-dependent, dissolution-deposition, diffusion model with the Darcy vapor flow model proposed by Sandia Laboratories.⁹¹ This was applied to the ORNL (Sect. 6.4.1) and the Salt Block II experiments.

The main assumptions used for the combined model were that the two mechanisms act independently (the two flows are additive) and that a distinct and moving vapor-liquid interface exists within a uniformly porous medium. The basic equation expresses a mass balance between the vapor loss from the vapor-liquid interface and the brine loss that produces the motion of the interface.

The results of the analysis were three equations, giving the flow rate as a function of time from the hot and cold faces of the ORNL experiment and into the centrally heated hole of the Salt Block II experiment at Sandia Laboratories. Properties of the salt and brine and the vapor-liquid interface positions were lumped together into convenient groups, which were treated as arbitrary fitting constants in correlating the theoretical equations and experimental data. The theoretical equation for the cold face of the ORNL experiments contained three fitting constants and the hot face and the Salt Block II experiments, four fitting constants. A good fit was obtained, particularly for the Sandia data. However, this does not necessarily validate the model, since one would expect a good fit using four arbitrary constants. We obtained a fit to the Sandia data that was as good, or slightly better, by using a two-constant equation of the form

$$t = a + bw^2, \quad (51)$$

where

a and b = fit constants,

t = time,

w = flow rate .

Using the fitted constants and making estimates for the individual parameters that were contained in the fit constants, Bloom and Hulbert calculated a porosity of 0.09% and permeability of 0.2 fcm^2 for the cooler side and 0.03% and 0.06 fcm^2 for the hotter side in the ORNL experiments. The corresponding values for the Sandia experiment were 0.5% and 0.06 fcm^2 . The ratio of diffusion to Darcy flow was 0.65 for both sets of the ORNL data and 0.84 for the Sandia data.

It must be pointed out that the density of pure water was used in the basic mass balance equation, rather than the correct partial water density of the brine. This does not change the values of the fit constants but does affect the derived values of porosity and permeability.

6.7 Comparison of Vapor Transport and Inclusion Migration Models

Neither the vapor transport nor the inclusion migration model completely represents the phenomenon of brine transport up the thermal gradient. The former assumes transport only along cracks or openings in the grain boundaries, and the latter assumes only intracrystalline transport. Obviously, both of these transport phenomena, and probably others, could exist simultaneously with one or the other dominant, depending on conditions.

The a priori application of either model is not possible, since some of the basic parameters are unknowable without resorting to empiricism that produces some of the parameters on a best-fit basis. The various predictions with the inclusion migration model use the Jenks equation, which is empirical, and apparently conservative, for the temperature gradients expected in a salt repository. Other empirical equations relating the migration velocity to the temperature and temperature gradient could be used in a computer code such as MIGRAIN.

The preceding exhaustive discussions of theoretical and experimental information on inclusion migration in salt crystals showed that the various treatments of theory can be made consistent and demonstrated the

compatibility of the Jenks equation with such theory. Obviously, theory alone cannot predict brine movement along the grain boundaries, but it can act as a basis for postulating possible brine behavior.

The vapor transport model has conceptual difficulties with the receding liquid-vapor interface and with the assumption of exclusively vapor transport. Probably the interface is not sharply defined but extends over a region, and two-phase transport likely occurs.

The improved vapor transport model with Knudsen flow agreed with the Salt Block I experiment better than the original model, which is not surprising since two additional fit parameters were used in correlation of the experimental data. The inclusion migration model using the Jenks equation also gave a very good fit to the heating phase of the Salt Block II experiment when the thermal conductivity of salt was treated as a fit parameter.

A considerable effort has been made to include the stress relations in developing the vapor transport model in order to predict the sudden flow increase occurring when the heat source is turned off. This can help substantiate the postulate that stress relaxation causes this flow phenomenon, although this information is purely academic since nuclear heat cannot be turned off abruptly.

On the basis of the available information, it appears that any model can be used, provided that it is based on, or normalized to, empirical data. If it is deemed necessary to have accurate values for brine migration in a repository, only in situ testing at the disposal horizon can produce values with relatively small uncertainties.

7. BRINE FLOW ESTIMATES IN REFERENCE SALT REPOSITORIES

Estimates of brine inflow for many-year periods of time after waste emplacement have assumed thermal-gradient-induced migration of brine inclusions, as in single crystals, at the maximum rates shown by Eq. (42) (or shown by a similar relationship between rate of brine inclusion migration, temperature gradient, and temperature). It has also been assumed that crystal boundaries do not affect brine migration from one crystal into another through aggregates of crystals.

Early estimates of the brine inflow for specific repository configurations were made by Bradshaw and coworkers^{55,81} and by Jenks.^{22,94} Later, a more sophisticated method based on the time-dependent continuity equation was incorporated into a computer code called MIGRAIN.^{42,95} This code and its applications to reference repositories are discussed in Sects. 7.1 and 7.2.

As discussed, it is unlikely that the assumptions regarding continuous brine migration from one crystal into another will be valid for an actual repository in salt. It is much more likely that the brine inclusions will be stopped on crystal boundaries and that any significant movement of this brine into an emplacement hole would take place through connected pores and/or microcracks.

Information on brine migration obtained from in situ heat and radiation experiments in rock salt was summarized and discussed in Sect. 6.3. The Salt Block II laboratory experiment, which studied brine migration through a large block of rock salt, was included in that presentation. For the experiments in bedded salt, the results of MIGRAIN-type calculations using the Jenks equation, along with probable values for fractional amounts of liquid H₂O in the salt, were in near agreement with the experimental values for rates of in-migration. For the reasons indicated previously, this agreement is probably fortuitous. However, the near agreement between calculated and experimental values suggests that the MIGRAIN-type calculations constitute a means for making rough estimates of the rates of in-migration to a waste package in a bedded salt repository.

during the first 1.5 to 2 y after emplacement. Results of MIGRAIN-type calculations for the Avery Island domal salt experiments showed calculated values appreciably higher than the experimental results. While the differences between experimental results in bedded and domal salt have not been explained, it seems reasonable to assume that MIGRAIN-type calculations constitute a means for making conservative estimates of the rates of in-migration of H_2O to a waste package in a domal salt repository during the first 1.5 to 2 y after emplacement. Section 7.2 presents MIGRAIN calculations that are our best estimates of the rates of brine in-migration during the first few years in repositories located in rock salt conforming to the site selection and/or design specifications listed in Sect. 3. The amount of liquid H_2O in bedded salt is assumed to be ~0.5 vol % for these particular estimates. Larger or smaller amounts of H_2O would result in proportionately larger or smaller calculated inflow rates.*

No direct information is available on the permeability that will prevail after the first 1 or 2 y following waste emplacement. Indirect information reviewed and discussed in Sect. 6 indicates that the permeability will be negligible if the emplacement is designed to maintain compressive forces on the rock salt⁹⁶ and if radiation damage in the salt and the accumulation of brine on crystal boundaries (in bedded salt) have no significant adverse effects on the permeability. In the absence of direct experimental information for given emplacement designs, we have assumed that the long-term migration rates will not exceed the average rates found by MIGRAIN calculations for the first few years after emplacement, and we present calculated values in Sect. 7.2 that are based on this assumption. The rates and total amounts of H_2O in-migration estimated in this way are probably conservative for bedded salt where brine inclusions occur within the salt crystals and very conservative for domal salt where few inclusions occur within crystals.

Estimates of the upper-bounds for in-migration of H_2O to CHLW and SF waste packages in reference repositories from the surrounding salt have

*As discussed in Sect. 2.1.3, the amount of H_2O in the WIPP bedded salt is probably ~1 vol %.

employed the assumption that all of the brine reaching a crystal boundary will reach the emplacement hole at some unspecified later time, presumably by movement through connected pores and microcracks that may develop on the crystal boundary as a result of the collection of brine there. We have also assumed that a threshold temperature gradient exists (below which no migration of inclusions within crystals takes place), and that we can predict this temperature gradient using theoretical and experimental information discussed in earlier sections of this report.

The results indicate that, at the upper-bound, the volumes of salt which could contribute to in-migration of H_2O are about 24 m^3 and 6.0 m^3 for reference packages of CHLW and SF, respectively, in reference repositories with thermal loadings of 25 W/m^2 for each type of waste. These maxima occur at about 10 y and 25 y, respectively, after emplacement of the 10-y aged reference wastes. The estimates also show that reductions in the amount of radioactive waste (and the thermal power) charged to packages of CHLW cause marked reductions in the estimated volumes of salt which could contribute to brine in-migration.

7.1 The MIGRAIN Computer Code

7.1.1 Theory and description

Brine inclusions in the model are considered in terms of a density of particles that obey the time-dependent continuity equation, namely,

$$\frac{\partial \rho}{\partial t} + \nabla(v\rho) = 0 \quad , \quad (52)$$

where

ρ = inclusion density, vol %;

t = time;

v = velocity of migration;

∇ = gradient operator.

A computer code (MIGRAIN) was developed for Cartesian coordinates (1-, 2-, and 3-dimensional) and for 2-dimensional cylindrical coordinates

(R-Z with azimuthal angle symmetry). The required input of temperatures and temperature gradients as a function of time and space is supplied by separate heat-transfer calculations. This code greatly facilitates brine migration calculations and properly accounts for brine volume densities along flow paths.

Any equation representing the velocity of brine migration as a function of temperature and temperature gradient can be used in the MIGRAIN code, although Eq. (42) was used for these subsequent applications.

The current version of the code is written for an IBM-360 computer but could be converted to other systems. The MIGRAIN code is presently designed to interface with the HEATING5 heat conduction code,⁹⁷ but the modification to accept temperature files generated by other codes is straightforward.

7.1.2 Validation of the MIGRAIN code

The accuracy of the MIGRAIN code in solving the time-dependent continuity equation has been independently verified.⁹⁸ Other efforts to validate the MIGRAIN code, by Claiborne et al.,⁴² compared calculated and experimental results for inflow of H₂O in Salt Block II (see Sect. 6). The temperature field was computed using the heat conduction code, HEATING5. Since thermal properties of the salt sample were not known, the temperature-dependent conductivity of Birch and Clark⁹⁹ was used.

The brine migration into the heater hole was computed for the model, and results are given in Fig. 11. The calculated values for net collection of water into the heater hole are shown as the lowest curve in Fig. 11 and are based on an initial 0.5 vol % of brine in the salt. Experimental data are also shown. For comparison, the results with a constant heat source of 1.5 kW are also shown, and the shape of the curve is different. This figure suggests that the model predicts the shape of the curve reasonably well, although the calculated results are lower than the experimental data by ~30%.

Aside from the probability that other phenomena existed (such as flow along cracks or opened grain boundaries), Claiborne et al.⁴² also

Fig. 11. Comparison of calculated brine inflow with experimental results for the Salt Block II experiment.

concluded that a possible explanation for the high brine inflow is that the actual temperature distribution may have been different than that computed. The thermal conductivity used in the calculation was for pure salt, but since the salt block was taken from a salt bed, the actual conductivity may have been lower. This would give a steeper temperature gradient and higher migration rates. If a constant thermal conductivity of 3 W/m K is used (which is lower than the values used), calculated results (bottom curve of Fig. 11) agree quite well with the experimental ones. Assuming a higher brine content would also produce good agreement (not shown in Fig. 11). The calculational model cannot be used to explain the brine spike that occurred after the heater was turned off.

7.2 Applications of MIGRAIN to Reference Repositories

7.2.1 General applications

Claiborne et al.,⁴² and Rickertsen et al.,¹⁰⁰ applied the MIGRAIN code to calculate brine inflows for commercial high-level waste (CHLW), spent fuel (SF), and for Savannah River defense high-level waste (DHLW). The pertinent characteristics of these repositories are shown in Table 11. It was assumed in all cases that the brine inclusions were 0.5 vol % of the halite, and calculations did not distinguish between domal and bedded salt. Since the calculated inflows are directly proportional to the volume percentage of brine, a smaller inflow would be expected from domal salt.

The calculated values⁴² for the brine flow into the emplacement hole for the baseline repository in bedded salt are shown in Fig. 12. For the 37 W/m^2 (150 kW/acre) CHLW case, the total flow is $<10 \text{ L}$ in the first 100 y (0.1 L/y) and $\sim 12 \text{ L}$ after 1500 y (note the logarithmic scale over time). Essentially all of this water would come from the salt within 60 cm of the emplacement hole. The total flow for the 14.8 W/m^2 (60 kW/acre) SF case in 1500 y is $\sim 6 \text{ L}$. The dependence on areal loading causes a roughly proportional decrease in flow.

The results¹⁰⁰ for the DHLW, shown in Fig. 13, indicate that less than 0.5 L of brine is calculated to flow into the emplacement hole during 1000 y after emplacement.

Table 11. Baseline repository characteristics

Characteristics	CHLW ^a	SP ^b	DHLW ^c
Repository depth below surface, m	600	600	600
Age at emplacement, y	10	10	15
Thermal loading (at emplacement), W/m ²	24.7	14.8	11.6
Local areal thermal loading W/m ²	37	9.9	11.6
Canister thermal power, kW	2.16	0.55	0.31
Room description			
Room length, m	very long	165	165
Room width, m	5.5	5.5	5.5
Room height, m	5.5	7.6	5.5
Adjacent pillar thickness, m	18.3	18.3	18
Canister emplacement holes			
Rows per room	1	1	2
Row separation, m			2.28
Hole pitch (along row), m	3.66 and 2.45	1.50 and 2.34	2.28
Emplacement hole depth, m	5.50	7.60	5.50
Emplacement hole diameter, m	0.51	0.51	0.76
Canisters per hole	1	1	1
Waste description			
Active length, m	2.4	3.7	2.28
Mass loading, MTHM ^d equivalent	2.1	0.46	

^aCHLW = commercial high-level waste.

^bSP = spent fuel.

^cDHLW = defense high-level waste.

^dMTHM = metric tons of heavy metal.

Fig. 12. Brine migration histories for a baseline repository.

ORNL-DWG 80-1800

Fig. 13. Brine inflow to defense high-level waste (DHLW) emplacement hole.

7.2.2 MIGRAIN-calculated rates of brine in-migration

Short-term rates of brine in-migration to reference waste packages in salt repositories have been calculated with the MIGRAIN code; these calculated and extrapolated values for salt with 0.5 vol % H₂O are listed in Table 12.

As stated previously, we have estimated long-term migration rates by assuming that they will not exceed average rates for the first few years after emplacement. Values in Table 12, which are found by MIGRAIN calculations, are based on this assumption. We believe that the rates and total amounts of in-migration estimated in this way are very conservative for domal salts and are reasonably conservative for bedded salts.

7.3 Upper-Bound Estimates of H₂O In-Migration

This section presents a more detailed discussion of the model and assumptions used for estimating upper bounds for brine in-migration. A description of the calculations and results are also presented here.

7.3.1 Description and discussion of brine in-migration model

Threshold temperature gradient. The existence of a threshold temperature gradient for the thermal-induced migration of brine inclusions within salt crystals was indicated by the theoretical equations of Anthony and Cline [Eqs. (1), (4), (5)] for the rate of migration of brine inclusions within alkali halides and by the experimental findings of Anthony and Cline³⁶ for migration of brine inclusions in KCl crystals at ~40°C. The occurrence of a threshold gradient can also be inferred from considerations of the presence and distribution of brine inclusions within bedded salt (see Sect. 4.1.6 and Appendix B).*

*Olander and coworkers have recently proposed a model for thermal-gradient-induced migration of brine inclusions in alkali halides, which has no threshold quantity for either temperature gradient or inclusion size (see Sect. 3.1.7). However, there is no evidence that this model applies to migration of inclusions in rock salt under the exposure conditions prevailing in a salt repository, and we assume that this model does not apply to rock salt in a repository.

Table 12. MIGRAIN-calculated rates of brine in-migration^a

Waste type and thermal loading at emplacement	Calculated initial rates for 0.5 vol % H ₂ O in salt		Total volume of H ₂ O after 100 y assuming continuation of initial rate
	(mL/m ² ·d) ^b	(mL/y)	(L)
CHLW			
37 W/m ²	0.18 ^c	250 ^c	25.0
25 W/m ²	0.13 ^c	180 ^c	18.0
CF			
15 W/m ²	0.038 ^d	82 ^d	8.2
10 W/m ²	0.028 ^d	60 ^d	6.0
DHLW			
12 W/m ²	0.005 ^e	10 ^e	1.0

^aSee Table 11 for repository characteristics. The MIGRAIN calculations included all of the salt surrounding the waste package emplaced in the reference repositories.

^bThis refers to the surface area of salt walls of the emplacement hole over a length equal to the active length of the waste.

^cAverage rate between 1 and 2 y after emplacement (read from graph in Fig. 12).

^dAverage rate between 5 and 10 y after emplacement (read from graph in Fig. 12).

^eAverage rate between 0 and 15 y after emplacement (read from graph in Fig. 11).

The value for the threshold gradient, $VT_{\infty\min}$, is related to other system parameters as shown by Eq. (53),

$$LVT_{\infty\min} = b \left[1.4RT \left(\frac{1}{C_L} \frac{\partial C_E}{\partial T} - \sigma \right) \right]^{-1}. \quad (53)$$

Eq. (53) was derived from Eq. (5) by setting the bracket term in Eq. (5) equal to zero and solving for $LVT_{\infty\min}$ or by substituting 1.4 for the ratio, VT_L/VT_{∞} . The quantities represented by the symbols have been described and discussed in Sects. 3 and 4 of this report. The pertinent values for these quantities that are employed in the upper-bounds estimates are discussed and/or referenced as follows:

1. The assumed maximum size, L , of brine inclusions in a salt crystal within the given salt formation is 2 mm on edge, and it is assumed that essentially all of the brine within the crystals is contained within these maximum-size inclusions. No inclusions larger than ~2 mm on edge (if cubic) have been reported for representative crystals from the rock salt within a salt formation.
2. The salt temperatures of interest in our upper-bounds estimates were in the range 65 to 145°C.
3. Available information on the values of b (erg/mol) for inclusions in crystals of bedded salt was discussed in Sect. 4. The pertinent experimental information consisted of values for migration rates for two inclusions of different sizes at a given temperature and temperature gradient. Values of b which were deduced from the experimental information are listed in Table 5. Table 5 also indicates that the lowest temperature for which values of b could be deduced from experimental information was ~100°C and the next lowest temperature was 160°C. Values of b at temperatures between 100 and 160°C that were used in our upper-bounds estimates were found by linear interpolation between the values at 100 and 160°C, viz.,

$$b = 1.67 \text{ E}+07 - 9.3 \text{ E}+04 \text{ t, } 160^\circ\text{C} > \text{t} > 100^\circ\text{C} . \quad (54)$$

Values of $VT_{\min}$ at temperatures $<100^\circ\text{C}$ were assumed to remain constant and equal to the value at 100°C (12.5 K/m).

Values for the term $[(1/C_g)(\partial C_g/\partial T) - \sigma]$ were obtained from those listed in Table 4 with $\sigma = -0.004, ^\circ\text{C}^{-1}$.

Collection of brine on crystal boundaries. It is assumed that the migrating brine that is trapped on crystal boundaries will move into the emplacement hole at some later time, via connected pores or microcracks which are assumed to form along crystal boundaries as a result of the collection of brine there.

As discussed previously, indirect information indicates that the long-term permeability will be negligible if the emplacement is designed to maintain compressive forces on the rock salt (with the highest forces immediately adjacent to the hole) and if radiation damage in the salt and the accumulation of brine on crystal boundaries have no significant adverse effects on the permeability. In making these upper-bound estimates, we have assumed that the accumulation of brine on boundaries does significantly increase the permeability of the salt.

7.3.2 Estimation of the salt volume contributing to brine in-migration

The procedure followed in estimating the volume of rock salt around a waste package emplacement that could contribute to in-migration of H_2O to the emplacement hole is indicated by the information given in Tables 13-15. The total area was found for the virtual shell surfaces (surrounding a waste package in the salt) that were required for uniform and instantaneous passage of the heat from the package at the assumed value for $VT_{\min}$ in the salt located at the shell surfaces. The volume of salt bounded by the virtual shell surfaces was then evaluated.

Table 13. Parameters used in estimations of upper bounds for in-migration of water to reference CHLW packages in salt^c

Time after emplacement	Temperature, T, and thermal conductivity, k, of salt in horizontal midplane at 1.4 m from canister center ^{b,c}		Thermal power of canister relative to that at emplacement	Assumed value for threshold temperature gradient at assumed temperature, ^d $\nabla T_{\infty \min}$	Area of shells in salt around waste package required to pass heat from canister at the assumed value ^e for $\nabla T_{\infty \min}$	Radius, r, of cylinder corresponding to the area of shells, and the volume of salt within shells ^f	
	Temperature (°C)	Conductivity (W/m K)				Radius (m)	Volume (m ³)
(y)			(P/P10)	(K/m)	(m ²)		
1	80	4.45	0.95	12.5	36.9	1.40	20
3	96	4.19	0.87	12.5	35.8	1.37	19
5	105	4.08	0.81	11.6	37.0	1.40	20
10	118	3.93	0.69	9.3	40.5	1.50	24
20	127	3.81	0.53	7.5	40.1	1.48	23
30	127	3.81	0.40	7.5	30.2	1.22	15
50	120	3.88	0.23	8.8	14.6	0.7	3.2

^a10-y aged waste at emplacement; 2.16 kW thermal power, 2.4-m active length of canister; 0.51-m diameter hole in salt; 3.68 m between canister centers within row of canisters.

^bIn a direction normal to the plane through the axes of the row of canisters in the room. Temperature values were obtained from those supplied by L. D. Rickertsen in Ref. 102 of this report. These temperatures were used in estimating the temperature gradients values in Column 5.

^cBirch and Clark values for thermal conductivity of salt (see Ref. 42 of this report). These values were used in the evaluations of A, in footnote e below.

^dSee discussion in Sect. 7.3.2 of text.

^eUsing the relationship, thermal power/unit area = $\frac{P}{A} = k \nabla T_{\infty \min}$.

^fUsing relationships, $A = 2\pi r h + 4\pi(0.8r)^2$ and $V = \pi r^2 h + 4/3\pi(0.8r)^3 - \pi/4(.51)^2 h$.

Table 14. Parameters used in estimations of upper bounds for in-migration of water to CHLW packages with lower thermal loadings^a

Time after emplacement	Distance	Temperature, T, and thermal conductivity, k, of salt in horizontal midplane at indicated distance from canister center ^{b,c}		Thermal power, P, of canister rela- tive to that at emplacement of reference 2.16 kW canister	Assumed value for threshold temperature gradient at assumed temperature, d $\nabla T_{\infty \min}$	Area, A, of shells in salt around waste package required to pass heat from canister at the assumed value for $\nabla T_{\infty \min}$	Radius, r, of cylinder corresponding to the area of shells, and the volume, V, of salt within shells	
		Temperature	Conductivity	(P/P10)	(K/m)	(m ²)	Radius	Volume
(y)	(m)	(°C)	(W/m K)				(m)	(m ³)
1	0.8	64	4.72	0.95/2	12.5	17.6	0.82	5.7
3	0.8	71	4.60	0.87/2	12.5	17.1	0.80	5.4
5	0.8	75	4.53	0.81/2	12.5	16.2	0.76	4.9
10	0.7	82	4.42	0.69/2	12.5	14.0	0.68	3.8
20	0.4	91	4.28	0.53/2	12.5	10.4	0.54	2.0
30	0.4	88	4.32	0.40/2	12.5	7.4	0.40	0.9
1	1.2	71	4.60	0.95*3/4	12.5	27.3	1.13	12.2
3	1.1	85	4.37	0.87*3/4	12.5	27.0	1.12	12.0
5	1.1	96	4.20	0.81*3/4	12.5	26.2	1.10	11.4
10	1.1	101	4.14	0.69*3/4	12.5	22.6	0.98	8.8
20	1.0	108	4.04	0.53*3/4	11.5	18.6	0.85	6.3
30	0.6	112	3.98	0.40*3/4	10.4	14.8	0.71	4.1

^aThese packages and the emplacements are the same as those of reference CHLW packages and emplacements except that the thermal loadings are lower (0.5 to 0.75 of the reference thermal power).

^bIn a direction normal to the plane through the axes of the row of canisters in the room. These temperatures were estimated by assuming that they equaled 0.5 or 0.75, respectively, of those for the reference (2.16 kW) canister (see Table 13).

^cBirch and Clark values for thermal conductivity of salt (see Ref. 42 of this report). These values were used in the evaluations of A in footnote e below.

^dSee discussion in Sect. 7.3.2 of text.

^eUsing the relationship, thermal power/unit area = $\frac{P}{A} = k \nabla T_{\infty \min}$.

^fUsing the relationships, $A = 2\pi r h + 4\pi(0.8 r)^2$ and $V = \pi r^2 h + 4/3\pi(0.8 r)^3 - \pi/4(0.51)^2 h$.

Table 15. Identities and values for quantities used in estimations of upper bound amounts on in-migration of water to reference SF packages in salt^a

Time after emplacement	Distance	Temperature, T, and thermal conductivity, k, of salt in horizontal midplane at indicated distance from canister center ^{b,c}		Thermal power, P, of canister relative to that at emplacement	Assumed value for threshold temperature gradient at assumed temperature, ^d $\frac{P}{VT_{min}}$	Area, A, of half-shells in salt around waste package required to pass heat from canister at the assumed value for threshold temperature	Radius, r, of half-cylinder corresponding to the area of half-shells, and the volume, V, of salt within half-shells ^e	
		Temperature, T (°C)	Conductivity, k (W/m K)				Radius (m)	Volume (m ³)
(y)	(m)			(P/P10)	(K/m)	(m ²)		
1	0.8	75	4.53	0.96	12.5	9.4	0.66	2.4
3	0.6	95	4.22	0.89	12.5	9.4	0.66	2.4
5	0.6	105	4.08	0.84	11.6	9.8	0.68	2.7
10	0.6	119	3.90	0.75	9.2	11.7	0.79	3.8
25	0.95	137	3.68	0.57	5.8	14.7	0.96	5.9
50	0.8	144	3.61	0.40	4.9	12.5	0.83	4.7

^a0.554 kW/canister at emplacement of 10-y aged waste; 2 rows of canisters within room; canister pitch = 1.87 m; row separation = 1.77 m; 3.7-m active length of canister; 0.51-m diameter hole in salt.

^bIn a direction normal to and away from the plane through the axes of the row of canisters in the room. Temperature values were obtained from those supplied by L. D. Flickertsen in Ref. 102 of this report.

^cBirch and Clark values for thermal conductivity of salt (See Ref. 42 of this report). These values were used in the evaluations of A, see note e below.

^dSee discussion in Sect. 7.3.2 of text.

^eUsing the relationship, thermal power/unit area = $\frac{P}{A} = kVT_{min}$.

^fUsing the relationships, $2A = 2\pi rh + 4\pi(0.8r)^2$ and $2V = \pi r^2 h + 4/3\pi(0.8r)^3 = \pi/4(.51)^2 h$.

Three shells were assumed for each package. One was a cylinder surrounding the package with a height equal to the active length of the package. The other surfaces were hemispheres at the top and bottom of the active portion of the package. The ratio of the radii of these hemispheres to that of the cylinder was determined to be about 0.8 in our evaluations of calculations of salt temperatures around CHLW packages reported by G. H. Llewelyn.^{22,101} The temperatures of the horizontal midplanes at the approximate radii of the shells were used in obtaining values for the threshold temperature gradient, VT_{min} , and thermal conductivity, k . These midplane temperatures were determined from the results of temperature calculations supplied by L. D. Rickertsen.¹⁰²

The areas of the virtual shells for the SF were determined by analogous procedures with the exception that heat from a waste package was assumed to flow only outward from the row of packages; none was assumed to flow toward the adjacent row of packages within the room. Therefore, the surfaces considered were equal in area to 1/2 of the cylindrical shells plus 1/2 of the hemispherical shells at the top and bottom of the waste packages.

7.3.3 Results and comments

The results of salt volume estimates are listed in Tables 13-15 and plotted in Fig. 14. They indicate that the upper-bound volumes of salt which could contribute to in-migration of H_2O are about 24 m^3 and 6.0 m^3 for reference packages of CHLW and SF, respectively, in reference repositories with thermal loadings of 25 W/m^2 for each type of waste. These maxima occur at about 10 y and 25 y, respectively, after emplacement of the 10-y aged reference wastes. The estimates also showed that reductions in the amount of radioactive waste (and the thermal power) charged to packages of CHLW caused marked reductions in the estimated volumes of salt contributing to in-migration of H_2O .

The volumes of H_2O contained in the 24 m^3 and 6.0 m^3 of salt mentioned in the preceding paragraph are, respectively, 240 L and 60 L at

Fig. 14. Estimated volume vs time after emplacement for upper-bound volumes of salt in which the temperature gradient is greater than or equal to the threshold temperature gradient for brine migration.

the estimated maximum of ~1 vol % H_2O in bedded salt. The value of 240 L for CHLW is 26 times greater than the volume calculated by MIGRAIN for 0.5 vol % H_2O in the salt and a period of ~1500 years after emplacement (see Fig. 12). The volume difference would be reduced to a factor of ~13 if 1 vol % H_2O was assumed in the MIGRAIN calculations.

Similarly, the difference between the results of these upper-bound estimates for SF and the results of MIGRAIN calculations for a period of 1500 y after emplacement would be a factor of ~8 if the MIGRAIN calculations assumed 1 vol % H_2O in the salt.¹⁰³

8. POTENTIAL SITING AND DESIGN CONSTRAINTS

There is general agreement that contact between liquid water and the metallic surfaces of the waste canister, or overpack if present, should be avoided for as long as possible after waste emplacement (conceivably many centuries) in order to avoid corrosive reactions. Also, the amount of liquid brine within the emplacement hole at any time should be as low as possible in order to avoid conceivable adverse effects on the stability of the waste package and surroundings.^{22,104} Achievement of these general criteria would be favored by the following site selection and/or design specifications.

1. Locate the emplacement holes within the available rock salt formation where there is a minimum amount of brine.
2. Employ emplacement designs and practices that maintain compressive stresses on the walls of the emplacement hole. In order to accomplish this, it may be necessary to employ canister dimensions and backfill materials which will minimize closure movement of the salt walls.
3. Avoid impurities in the rock salt which could yield H_2O upon thermal or radiolytic decomposition and thus contribute to the amount of H_2O available for migration.
4. Design emplacements so that maximum temperatures of salt walls do not exceed $\sim 250^\circ C$, in order to avoid decrepitation of salt and the release of trapped H_2O .
5. Design so that maximum gas-vapor pressure within the emplacement hole remains below compressive stresses on salt walls, in order to avoid forcing expansion of microcracks within the salt.
6. Use a desiccant barrier material as part of the backfill (between the metal enclosures and the salt walls) with the general objectives of sorbing H_2O ; shielding the metal from brine, gases, and vapors; and, conceivably, sorbing radioactive nuclides if any are released from the enclosures. (Information on two types of such materials is summarized in Sects. 8.1 and 8.2)

8.1 Backfills Containing CaO and/or MgO as Desiccants

Both CaO and MgO are strong desiccants; either one, or mixtures of both, in combination with other materials such as sand or crushed salt, might comprise a satisfactory desiccant-backfill material.^{22,105-107} Since swelling occurs upon hydration of either of the oxides, the desiccant-backfill would tend to become impervious upon sorption of H₂O.²² Relevant physical and chemical properties of CaO, Ca(OH)₂, MgO, and Mg(OH)₂ are listed in Table 16. Amounts of either oxide which might be used in backfills in combination with sand or crushed salt in reference repositories, and the amounts of H₂O which would be removed by complete hydration of the oxide, are shown in Table 17.

These amounts of sorbed H₂O, ranging from 43 kg for CaO in the backfill around the reference CHLW to 151 kg for MgO in the backfill around the DHLW package, exceed the conservatively estimated amounts (Table 12) of in-migration during 100 y after emplacement of the waste in bedded salt and greatly exceed the estimated in-migration in domal salt. The desiccant-backfill which would be placed above and below the waste package would also present additional H₂O-sorbing capacity.

The vapor pressure of H₂O over Ca(OH)₂ is extremely low (350 Pa at 301°C); that over Mg(OH)₂ is somewhat higher, but still low (84 kPa at 171°C). In practice, hydroxy chlorides rather than hydroxides might be formed when a brine solution comes into contact with CaO or MgO.¹⁰⁷ Formation of these compounds would neither decrease the H₂O-sorbing capacity of the oxide nor increase the vapor pressure of H₂O over the hydrated material as long as some oxide was present to react with liquid or vapor. However, the amount of swelling when these compounds are formed might differ from that which would occur with hydroxides.

The considerations in Ref. 22 and the information in Table 17 indicate the feasibility of adjusting the relative amounts of sand and oxide to favor the formation of imperviousness yet avoid the formation of excessive pressures on the salt walls.

It seems likely that desiccant backfills using CaO and/or MgO would prove satisfactory for sorbing in-migrating H₂O and shielding the metal from brine, gases, and vapors. However, chemical properties and phase behavior are uncertain for the systems resulting from contact of brine

Table 16. Chemical and physical properties of oxides and hydroxides of Ca and Mg relevant to backfills for reference repositories

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

^aHandbook values.

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

Table 17. Backfill desiccant-oxide capacities in reference salt repositories

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

^aFor reference repositories; the height of annular space is assumed to equal the active length of the waste canister (see Table 11). Spaces above and below waste are not included here.

^bAssuming packing to 60% of theoretical density.

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

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

solutions with hydrated oxide on the edges of the backfill or on the surface of cracks within the backfill. These properties must be established before a final recommendation can be made to use an oxide-sand or an oxide-salt mixture as backfill for the waste package. Also, experimental tests on radiation effects and corrosion of metallic packages in this backfill material are required for final verification of the suitability of the material. Other factors that should be investigated experimentally include: (1) identities, physical properties, and phase behavior of the products formed by reactions between the oxides and the MgCl_2 -rich brines; (2) the fractional amounts of oxides actually available for reaction with brine over 100–200 y periods of time; and (3) investigations to determine whether paths develop in the backfill through which brine could migrate to the canister without contacting the oxide.

8.2 Backfill Containing Clay and Other Getter Materials

Sandia Laboratories has conducted a backfill-getter development program since 1977.¹⁰⁸ They are attempting to incorporate the following chemical and physical functions:

1. to act as a barrier to hydrologic intrusion,
2. to act as an actinide and fission product radionuclide sorptive barrier or getter,
3. to chemically modify any intruding groundwater/brine, e.g., for pH, Eh, or ionic composition,
4. to buffer mechanical stresses and deformation in the waste package, and
5. to serve as a thermal transport medium.¹⁰⁸

Sandia investigators report that bentonite was selected as a major backfill component because of "its favorable properties in contact with salt and brine solution; good sorptive capacity for the actinides and rare earths; sorptive properties retained in mixtures with other components; brine pH buffered in a near-neutral range; low liquid permeability; favorable swelling properties in brine; adequate thermal conductivity and high-temperature performance; mechanical buffer properties; and reasonable cost for bulk materials."¹⁰⁸ Other materials having desirable sorption properties would be mixed with the bentonite in the backfill.

Results of the Sandia study to date are illustrated in Table 18, which gives compositions and other attributes of backfill-getter materials suggested for use with packages of HLW in salt.¹⁰⁹ The performance of these proposed backfill materials remains to be demonstrated with further considerations of temperature, pressure, and radiation which might be encountered in a repository, and with in situ tests in salt with actual or simulated wastes. The feasibility and necessity of employing such complicated backfill materials in large-diameter emplacement holes also remains to be demonstrated.

Table 18. Properties of backfill-getter materials suggested by Sandia workers for HLW packages in sa^{1-a}

Composition of mixture (wt %)	Retention time for radionuclides ^b	
	Nuclide	Time (ky)
Mixture 1		
30% bentonite, 70% charcoal	Pu	50
	Am	20
	TcO ₄ ⁻	4
	I ⁻	1
Mixture 2		
30% bentonite, 20% charcoal, 40% mordenite, 10% sodium titanite	Pu	50
	Am	20
	TcO ₄ ⁻	4
	I ⁻	0.4
	Cs ⁺	0.6
	Sr ²⁺	0.7

^aBackfill parameters used: thickness = 1 m; density = 2 g/mL; porosity = 10%.

^bRetardation of ion movement is by linear sorption, tested in WIPP brine A. Retention time is the time to breakthrough, which is assumed to be when the exiting concentration is 1% of the entering concentration. Migration is by molecular diffusion.

9. SUMMARY AND CONCLUSIONS REGARDING BRINE MIGRATION TO PACKAGES OF HLW AND SF IN SALT REPOSITORIES

This section summarizes our conclusions regarding factors important to consideration of brine migration to packages of HLW or SF in salt repositories, or to control of the possible brine migration effects on the waste packages and repositories. We assume that the general characteristics referred to as "reference repositories" and "reference wastes" will prevail and that the suggested site selection and/or design specifications discussed in Sect. 8 are adopted.

9.1 Bedded Salt

9.1.1 Initial amount of H₂O

The probable maximum amount of liquid H₂O initially present is <0.5 wt%.

9.1.2 Location of liquid brine

Liquid brine is present as inclusions within salt crystals and is also located on boundaries between the crystals. The fraction of the brine at each location is unknown.

9.1.3 Probable mechanisms of brine migration

Brine inclusions within crystals. The most probable mechanism is thermal-gradient-induced migration in which salt dissolves at the hot interface and precipitates at the cold interface. The qualitative aspects of this mechanism are well understood, and the quantitative aspects are understood to the extent necessary to enable close estimates of the maximum rates of migration of a brine inclusion of given dimensions and geometry under any of the conditions of temperature and temperature gradient found in the reference repositories. The maximum migration rate at a given temperature and temperature gradient is closely approximated by the Jenks equation for liquid-filled inclusions with shapes which are cubical, spherical, or elongated in the direction of the thermal gradient.

Most of the brine does not migrate from one crystal into another but instead is stopped on the boundary between the crystals.

It is likely that threshold values exist for the temperature gradients which can cause migration of a liquid inclusion within a given salt formation. These threshold values can be predicted and used in the estimation of upper bounds for the amount of H_2O that could migrate to a waste package from the surrounding salt.

Inclusions containing a gas-vapor phase in addition to a liquid phase might move down a temperature gradient in the salt, away from the heat source.

A gas-vapor phase might result from the formation of radiolytic gas pressures that are high enough to force expansion of the salt walls of the inclusion or from escape of liquid from an inclusion through microcracks into a region of lower pressure. Our analyses indicate that the amount of material transfer by down-gradient movement of inclusions within crystals will have negligible consequences in a salt repository.

Brine on crystal boundaries. Any significant movement of the brine from crystal boundaries into an emplacement hole must take place through connected pores and/or microcracks. Such brine movements could result from gradients of pressure on the liquid which, in turn, could arise from gradients in the vapor pressure of H_2O , radiolytic gas and/or stress state of the salt. Brine might also move by a thermal-gradient mechanism analogous to that which occurs within crystals. Also, capillary action could cause brine to move rapidly along previously unwetted surfaces formed by fresh fractures, old fractures, or loose crystal boundaries not previously contacted by brine or water. Water vapor, as opposed to liquid brine, could move under gradients of H_2O vapor pressure and radiolytic gas from a receding liquid front within a microcrack or pore.

9.1.4 Permeability of salt around a waste emplacement hole

No direct information is available on the permeability which will prevail following the first 1 or 2 y after emplacement of the waste. Indirect information indicates negligible permeability if the emplacement is designed so that compressive forces are maintained on the rock salt and if radiation damage in the salt and the accumulation of brine

on crystal boundaries have no significant adverse effects on the permeability. The latter reservation regarding brine on crystal boundaries is particularly significant, since the collection of brine on boundaries might lead to an increase in the number of connected pores in the salt — possibly extending to the distance beyond which the temperature gradients are no longer sufficient to cause migration of large brine inclusions to the crystal surface.

9.1.5 Estimated short-term rates of in-migration of H₂O

During the first 1 to 2 y after emplacement of waste, the estimated rates are approximately equal to those calculated by the MIGRAIN code (or by a similar method), assuming 0.5 vol % liquid H₂O, with rates of liquid migration given by the Jenks equation. This assumes that all brine is located within crystals and that there are no effects of crystal boundaries on the thermal-gradient-induced migration. Rates estimated in this way are: 250 mL/y and 80 mL/y for packages of CHLW and SF, respectively, and 10 mL/y for a package of DHLW.

9.1.6 Estimated longer-term brine in-migration rates

The long-term rates and total amounts of in-migration will depend upon the permeability of the rock salt adjacent to the emplacement hole, and this permeability is uncertain. Assuming constant rates of in-migration equal to the average rates during the initial 1 to 2 y period, the total amounts of in-migration during 100 y after emplacement are: 25 and 8 L for packages of CHLW and SF, respectively, and 1 L for a package of DHLW. Additional in situ experiments of many-year duration, with actual waste emplaced in the salt formation of interest, are required to establish the long-term brine migration characteristics more accurately for a repository, if these are deemed necessary.

Estimates were made of the upper-bound amounts of in-migration of H₂O to CHLW and SF waste packages in reference repositories from the salt surrounding the packages, employing the following assumptions:

1. that the upper bound is that for which all of the brine that reaches a crystal boundary will reach the emplacement hole at

some unspecified later time, presumably by movement through connected pores and microcracks that are assumed to develop on the crystal boundaries as a result of the brine collection,

2. that a threshold temperature gradient exists below which no migration of inclusions within crystals takes place, and
3. that we could predict this temperature gradient using theoretical and experimental information discussed in this report.

The results indicate that at the upper-bound, the volumes of salt which could contribute to in-migration of H_2O are about $24 m^3$ and $6.0 m^3$ for reference packages of CHLW and SF, respectively, in reference repositories with thermal loadings of $25 W/m^2$ for each type of waste. These maxima occur at about 10 y and 25 y, respectively, after emplacement of the 10-y aged reference wastes. The estimates also showed that reductions in the amount of radioactive waste (and the thermal power) charged to packages of CHLW caused marked reductions in the estimated volumes of salt which could contribute to in-migration of H_2O .

9.1.7 Desiccant-barrier materials around a waste package within an emplacement hole

If the metallic canister (or overpack) should remain intact for as long as possible after waste emplacement, it would be desirable to avoid contact between liquid water and the metallic surface as long as possible in order to avoid corrosive reactions.

Both CaO and MgO are strong desiccants, and either one of these or mixtures of the two, in combination with other materials such as sand or crushed salt, might prove satisfactory as a backfill material to protect the waste package from contact with corrosive liquids and vapors and could also minimize the amount of liquid brine within the emplacement hole. More than 45 kg of H_2O would react with the CaO in a mixture with sand or crushed salt in the backfill space around the active length of a reference CHLW canister. Even more desiccant oxide could be contained within the larger backfill volumes around reference SF and DHLW canisters. Additional experimental work, including in situ experiments, are required to completely establish the characteristics of the oxide-sand or oxide-crushed-salt backfills and to verify their suitability.

9.2 Domal Salt

9.2.1 Initial amounts of H₂O

The maximum amounts of liquid H₂O initially present in domal salts are probably <0.2 wt %.

9.2.2 Liquid brine location and migration

Some of the brine may be located on crystal boundaries. Very small amounts occur as inclusions within crystals. The probable mechanism for brine migration in domal salt is the same as that discussed for bedded salt (Sect. 9.1.3).

9.2.3 Permeability of salt around a waste emplacement hole

Permeability considerations for domal salt are the same as those discussed for bedded salt (Sect. 9.1.4) with the important exception that brine migration from crystals will probably not contribute significantly to the amount of brine on crystal boundaries. Accordingly, the salt permeability will probably not increase significantly over long time periods after emplacement of waste.

9.2.4 Estimated short-term rates of in-migration of H₂O

During the first 1 to 2 y after emplacement of waste, the estimated rates are approximately equal to those calculated by the MIGRAIN code (or by a similar method), assuming 0.03 wt % liquid H₂O, and rates of brine migration given by the Menks equation. This assumes that all brine is located within crystals and that there are no effects of crystal boundaries on the thermal-gradient-induced migration. Rates estimated for domal salt are 25 mL/y or less and are considered negligible.

This method, which we believe is an adequate means for estimating rates of in-migration, was based on the results of comparisons and correlations between experimental values and those calculated by a

method analogous to that employed with the MIGRAIN code. The inferred agreement is probably fortuitous, for reasons already discussed.

9.2.5 Estimated longer-term brine in-migration rates

The total amounts of in-migration during 100 y after emplacement of waste, estimated as described in Sect. 9.1.6, are 2.5 L for CHLW and smaller volumes for the SF and DHLW. We believe that these are conservative estimates for the domal salt.

9.2.6 Desiccant-barrier materials around waste packages within an emplacement hole

The discussion of these materials in Sect. 9.1.7 applies to domal salt as well. However, much smaller amounts of desiccants would be needed to sorb the smaller amounts of H_2O expected in domal salts.

The discussion of estimates of upper-bounds amounts of salt which could contribute to the in-migration of H_2O in bedded salt (Sect. 9.1.6) also applies to domal salt. The amount of H_2O within crystals is much less for domal salt, however, and the possibility that brine migrating to and collecting on crystal boundaries would increase the permeability of the rock salt is much lower.

10. RECOMMENDATIONS FOR ADDITIONAL EXPERIMENTAL AND ANALYTICAL WORK

As stated in Sect. 9, we believe that additional in situ experiments of many-year duration, with actual waste emplaced in the salt formation of interest, are needed to accurately establish the long-term brine-migration characteristics for a repository in bedded salt. These experiments should be designed so that the exposure conditions closely simulate actual repository conditions with a given type of waste. The exposure parameters of interest include the following:

1. Size and shape of the waste package and of the emplacement cavity in salt.
2. Age of the waste, thermal power, and radiation intensity.
3. States of stress in the salt adjacent to the emplacement cavity.
4. Closure movements of the cavity walls.
5. Composition and physical characteristics of backfill.
6. Amounts and distribution of pressure within the emplacement cavity and on the waste package.

Other recommendations relating to site selection and/or design of the repository are discussed in Sect. 8.

The experiments should include several emplacements of individual waste packages as in a reference repository. One or two waste packages should then be exhumed and examined at intervals of 1 to 2 y for evidence of the amounts and characteristics of brine migration, and of the behavior within the emplacement cavity of brine, backfill, and metallic waste enclosures.

Similar in situ experiments are recommended for planned repositories in domal salt. The objectives of the experiments in this case would be to establish the behavior within the emplacement cavity of brine, backfill, and metallic waste enclosures, and to verify that the rates of brine in-migration remain as low as expected with the given salt formation and repository design.

In situ experiments aimed at providing information on certain aspects of brine in-migration and brine behavior within an emplacement cavity are underway in the domal salt mine at Avery Island, Louisiana,^{89,110-112} and

are planned for the domal salt mine at Asse, Germany,⁹⁸ and in the potash-bearing bedded salt in the Carlsbad, New Mexico area.¹¹³ Laboratory experiments are also underway or planned to provide information on certain aspects of brine migration in salt.^{114,115} Results of these in situ and laboratory experiments probably will not abate the need for many-year in situ experiments necessary to establish long-term brine migration rates more accurately.

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Appendix A

Review of the Wilcox Derivation and Comparison With Others

Wilcox¹ derived the following time-dependent, one-dimensional differential equation for the concentration of an impurity in a multipliers zone melting process for the liquid zone moving at a uniform rate:

$$D \frac{\partial^2 w}{\partial z^2} + V \frac{\rho_s}{\rho_l} \frac{\partial w}{\partial z} = \frac{\partial w}{\partial t}, \quad (\text{A.1})$$

where w = weight fraction of the impurity at z , and the other symbols have been previously defined.

This equation is analogous to the equation describing the diffusion or dispersion of a nuclide in a flowing aquifer, but the convection term has opposite sign because both the diffusion and mass flow in an aquifer are in the same direction whereas for brine migration these flows are opposed to one another. In addition, $\rho_s/\rho_l = 1$ in the latter case. Wilcox² later applied the equation to the motion of liquid inclusions in pure crystals that are subjected to a temperature gradient under steady-state conditions.

We will first review the Wilcox work and compare his results with those obtained by the others and then show that the model described by Eq. (A.1) is not in agreement with other derivations because of the convective term in Eq. (A.1).

The solution to Eq. (A.1) with $(\partial w/\partial t) = 0$ is

$$w = C_1 + C_2 \exp[-(V\rho_s/D\rho_l)z] \quad (\text{A.2})$$

The arbitrary constants were evaluated by letting $w = w_{lp}$ at $z = 0$ (crystallizing end) and $w = w_{ld}$ at $z = L$ (length of solution zone).

To eliminate w_{ld} , Wilcox made the assumption that

$$w_{ld} = w_{lp} + \frac{L \Delta T_l}{m}, \quad (\text{A.3})$$

where m is the slope of the liquidus on the crystal-solvent phase diagram. This assumption is only rigorous for a linear liquidus, but the error is of no significance for the small temperature difference across a migrating inclusion. Note that it is not necessary to make this equilibrium assumption at this point and eliminate w_{ld} .

When the boundary conditions and Eq. (A.3) are applied to Eq. (A.1), the complete solution obtained by Wilcox becomes

$$w = w_{lp} + \frac{L \nabla T_l}{m} \left[\frac{1 - \exp(-zV\rho_s/D\rho_l)}{1 - \exp(-LV\rho_s/D\rho_l)} \right]. \quad (\text{A.4})$$

If the equilibrium assumption is not made, the result is

$$w = w_{lp} + \frac{(w_{ld} - w_{lp})}{L} \left[\frac{1 - \exp(-zV\rho_s/D\rho_l)}{1 - \exp(-LV\rho_s/D\rho_l)} \right]. \quad (\text{A.5})$$

Wilcox pointed out that, both theoretically and experimentally,

$$LV\rho_s/D\rho_l \gg 1. \quad (\text{A.6})$$

Since $\exp(x) \approx 1 - x$ for small x , Eq. (A.4) reduces to

$$w_{ld} = w_{lp} + \nabla T_l z/m, \quad (\text{A.7})$$

or, without the linear equilibrium assumption,

$$w_{ld} = w_{lp} + \frac{w_{ld} - w_{lp}}{L}, \quad (\text{A.8})$$

which is the linear concentration profile that was used in the other derivations either explicitly or implicitly.

Assuming a fixed boundary with flow into and out of the crystal-liquid interfaces, Wilcox used the following equations for the salt fluxes at the interfaces (which are correct when a net liquid flow into and out of the inclusion exists): At the crystallizing surface ($z = 0$),

$$-D(dw/dz) = V(\rho_s/\rho_l)(w_{lp} - 1), \quad (\text{A.9})$$

and at the dissolving surface ($z = L$),

$$-D(dw/dz) = V(\rho_s/\rho_l)(w_{ld} - 1). \quad (\text{A.10})$$

Combining Eq. (A.9) and Eq. (A.4) and noting that $w_{ld} \approx w_l$.

$$V = -(D\rho_l/L\rho_s)\ln\left[1 - \frac{LDVT_l}{m(1-w_l)}\right] \quad (\text{A.11})$$

Applying Eq. (A.6) to Eq. (A.11), the final result for the rate of movement of an inclusion is

$$V = \frac{DVT_l\rho_l}{m(1-w_{lp})\rho_s}, \quad (\text{A.12})$$

since Eq. (A.6) implies that the second term of the logarithmic argument is small and, consequently, $\ln(1 - x) \approx -x$.

Converting to concentration units, Eq. (A.12) becomes

$$V = \frac{V T_L D (\partial C_E / \partial T)}{(C_s - C_l)}, \quad (A.13)$$

since $w \propto C$ and $m = (\partial T / \partial w)$.

This differs from the other derived results for the case of no thermal diffusion and equilibrium at the interfaces in that C_l appears as a term in the denominator. Equality with the other derivations can only result for the special case of $C_l = 0$. Using Eq. (A.13) leads to rates of movement ~40% higher at 200°C, with smaller deviations at lower temperatures.

The following discussion shows that the model represented by Eq. (A.1), the boundary conditions represented by Eqs. (A.9) and (A.10), and the resulting Eq. (A.12) (which was derived for multipass zone melting purification), are in disagreement with the other results because of the convective term in Eq. (A.1).

The Lagrangian viewpoint seems applicable for brine migration problems, i.e., the observer moves with the solid-liquid interface and there is no net liquid flow to and out of the inclusion. For this condition, the convective term in Eq. (A.1) is zero and the salt flux at both ends is

$$D\rho_l \frac{dw}{dz} = V\rho_s. \quad (A.14)$$

The solution to Eq. (A.1) then becomes

$$w = C_1 + C_2 z. \quad (A.15)$$

Applying the conditions that $w = w_{lp}$ at $z = 0$, and $w = w_{ld}$ at $z = L$ in evaluating the arbitrary constants, the complete solution becomes

$$w = w_{lp} + \left(\frac{w_{ld} - w_{lp}}{L} \right) z . \quad (\text{A.16})$$

Differentiating Eq. (A.16) and substituting into Eq. (A.14),

$$v = \frac{D\rho_l}{\rho_s} \frac{(w_{ld} - w_{lp})}{L} = \frac{D\rho_l}{\rho_s} \nabla w_l ; \quad (\text{A.17})$$

or in concentration units,

$$v = \frac{D}{C_s} \nabla C_l . \quad (\text{A.18})$$

If the quite reasonable assumption used by Wilcox, that all concentrations are equilibrium values and the slope of the liquidus on the phase diagram is linear, is applied, then

$$\nabla C_l = \frac{\nabla T_l}{L} \frac{\Delta C_E}{\nabla T_l} \cong \nabla T_l \left(\frac{\partial C_E}{\partial T} \right) , \quad (\text{A.19})$$

and Eq. (A.18) becomes

$$v = \frac{D\nabla T_l}{C_s} \left(\frac{\partial C_E}{\partial T} \right) . \quad (\text{A.20})$$

This is the same as Eq. (A.13) except for the C_l term, and it is in agreement with other derivations when the Soret effect is neglected and the linear equilibrium assumption is made.

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Appendix B

Relative Effects of Geothermal and Gravitational Forces on
Brine Migration Over Geologic Times

The migration of a brine inclusion through a crystal of NaCl (or other alkali halide) occurs by dissolution at the forward, higher-potential-energy face and deposition at the rear, lower potential energy face of the inclusion. The driving forces which can cause inclusion-migration include thermal gradients and accelerational fields. Thermal-gradient-induced migration is discussed in detail in the text.

Migration in accelerational fields was discussed by Anthony and Cline,¹ Wilcox and Shlichta,² Cline and Anthony,³ and Wilcox.⁴

It was pointed out in the text (Sect. 4.1.6) that gravitational as well as thermal forces would have been acting on brine inclusions in bedded salt throughout their stay in the salt. Also, it was stated that the buoyant gravitational forces were roughly equal to the downward thermal gradient forces, assuming that frictional forces caused by interface processes were negligible. The bases for the latter statements are given in this appendix.

According to Cline and Anthony,³ the total driving force, F , on a brine inclusion in an alkali halide crystal is equal to the rate of change of the free energy of the system with respect to a virtual displacement of the inclusion, minus any frictional force, F_K , associated with the transfer of ions across the solid-liquid interfaces.

F_K is related to the kinetic potential, K , and to other characteristics of the solid-inclusion system as shown by

$$F_K = K V_s / L V_D \quad (B.1)$$

where

V_s = molar volume of solid salt,

$V_D = X^2 L$ = volume of inclusion,

L = dimension of inclusion parallel to the gradient of force.

Continuing to follow Cline and Anthony, the net force caused by a thermal gradient across an inclusion is

$$F = F_T - F_K, \quad (B.2)$$

while the net force caused by an accelerational field is

$$F = F_g - F_K, \quad (B.3)$$

where

$$F_T = \frac{V_D}{V_S} RT \left[\frac{1}{C_L} \frac{dC_E}{dT} - \sigma \right] VT_L, \quad (B.4)$$

and

$$F_g = V_D g(\rho_s - \rho_l). \quad (B.5)$$

Most of the symbols in Eqs. (B.2) to (B.5) have the meanings stated and discussed following Eq. (1) in the text and/or as stated above following Eq. (B.1). The symbols not previously identified are:

g = acceleration,

$\rho_s + \rho_l$ = densities of solid salt and of included liquid, respectively.

To compare the relative values of F_T and F_g for brine inclusions in bedded salt, divide Eq. (B.4) by Eq. (B.5) to obtain

$$\frac{F_T}{F_g} = \frac{(RT/V_S)[(1/C_L)(dC_E/dT) - \sigma] VT_L}{g(\rho_s - \rho_l)}. \quad (B.6)$$

Values for the several quantities in Eq. (B.6) which possibly prevailed in Permian bedded salt deposits are listed below.

$$T = 300K,$$

$$RT = 2.5 \text{ E}+10 \text{ ergs/mol},$$

$$g = 980.7 \text{ cm/s}^2 = 980.7 \text{ ergs/cm s},$$

$$V_S = 27 \text{ cm}^3/\text{mol},$$

$$\rho_s - \rho_l = 0.94 \text{ g/cm}^3,$$

$$(1/C_L)(dC_E/dT) - \sigma = 7.5 \text{ E}-03 \text{ } ^\circ\text{C}^{-1}.$$

The values for T and VT_L over a geologic time period of ~200 million years were discussed by Pigford and are summarized in Sect. 4.16 of this

report. The probable value for $[(1/C_p)(dC_g/dT) - \sigma]$ at 300K in bedded salt is discussed in the text. Values for the other quantities are readily available.

Introducing these values into Eq. (B.6) and carrying out the arithmetic, we have

$$F_T/F_g = 0.83 . \quad (B.7)$$

This result supports the idea that the gravitational and thermal forces may have been approximately balanced in the bedded salt over geologic times. However, the result does not discount the idea that the net difference between F_T and F_g was probably significantly greater than zero and that migration of inclusions was prevented by interface effects. That is, the value of the kinetic potential, K , was probably greater than zero and sufficient to account for the absence of inclusion migration. Using Eq. (25) of the text, it can be shown that $b = 2 \text{ E}+04 \text{ erg/mol}$ would account for zero migration of cubical inclusions $\leq 10 \text{ mm}$ on edge. This value for b is ~ 100 times smaller than any of the values deduced from experimental data for KCl or NaCl.

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Appendix C

Derivation of the Transport Equation with Thermal Diffusion
(Soret Effect) and Application

Previous derivations for the velocity of migration of a brine inclusion have usually either explicitly or implicitly assumed that the concentration profile was linear with thermal diffusion present (Soret Effect). Here we show that the profile is really not linear, but the equation for the velocity of migration is the same as the one resulting from a linear assumption.

Consider an increment of solution of thickness Δx , with the salt transporting in and out. This is described by

$$\text{salt flux in at } x - \text{salt flux out at } x + \Delta x = \text{salt stored} . \quad (\text{C.1})$$

The flux at any point x is given by

$$J = -D \nabla C_x + D \sigma C_x \nabla T_x \quad (\text{C.2})$$

Applying Eq. (C.2) to Eq. (C.1), we have

$$-\left[\left(\frac{\partial C}{\partial x} \right)_x - \sigma C_x \left(\frac{\partial T}{\partial x} \right)_x \right] + \left[\left(\frac{\partial C}{\partial x} \right)_{x+\Delta x} - \sigma C_{x+\Delta x} \left(\frac{\partial T}{\partial x} \right)_{x+\Delta x} \right] = \frac{\partial C}{\partial t} \left(\frac{\Delta x}{D} \right) \quad (\text{C.3})$$

Dividing through by Δx and setting $(\partial C / \partial t) = 0$ for steady state, Eq.

(C.3) becomes

$$\frac{\left[\left(\frac{\partial C}{\partial x} \right)_{x+\Delta x} - \left(\frac{\partial C}{\partial x} \right)_x \right]}{\Delta x} - \frac{\sigma \left[C_{x+\Delta x} \left(\frac{\partial T}{\partial x} \right)_{x+\Delta x} - C_x \left(\frac{\partial T}{\partial x} \right)_x \right]}{\Delta x} = 0 \quad (\text{C.4})$$

From the definition of partial derivatives as $\Delta x \rightarrow 0$, the differential equation becomes

$$\frac{\partial^2 C}{\partial x^2} - \sigma \frac{\partial}{\partial x} \left(C \frac{\partial T}{\partial x} \right) = 0 . \quad (C.5)$$

The form of the solution to Eq. (C.5) now depends on the assumptions regarding the relationship between C and T . We assume that $C = f(T)$ and $T = g(x)$. It then follows from a theorem for partial differentiation that

$$\frac{\partial C}{\partial x} = \left(\frac{\partial C}{\partial T} \right) \left(\frac{\partial T}{\partial x} \right) \quad (C.6)$$

Combining Eq. (C.5) and (C.6), we have

$$\frac{\partial^2 C}{\partial x^2} + C \left(\frac{\partial C}{\partial T} \right) \left(\frac{\partial T}{\partial x} \right)^2 - \sigma C \frac{\partial^2 T}{\partial x^2} = 0 . \quad (C.7)$$

Assuming that the temperature gradient is linear across the inclusion, and $\partial C / \partial T$ is a constant, $\partial^2 T / \partial x^2 = 0$ and Eq. (C.7) reduces to

$$\frac{d^2 C}{dx^2} + K = 0 , \quad (C.8)$$

where

$$K = \sigma \left(\frac{\partial C}{\partial T} \right) \left(\nabla T_l \right)^2 . \quad (C.9)$$

The solution to Eq. (C.8) is

$$C + A + Bx + \frac{Kx^2}{2}. \quad (C.10)$$

At $x = 0$, $A = C_{lp}$, and at the hot or dissolving end at $x = L$,

$$C_{ld} = C_{lp} + BL + \frac{KL^2}{2} \quad (C.11)$$

and

$$B = \frac{C_{ld} - C_{lp}}{L} - \frac{KL}{2}. \quad (C.12)$$

At both the hot and cold ends, the salt flux is $C_s V$. Therefore at $x = 0$,

$$-D \left(\frac{dC}{dx} \right)_l + D\sigma C_{lp} \left(\frac{dT}{dx} \right)_l = C_s V. \quad (C.13)$$

From Eq. (C.10),

$$\frac{dC}{dx} = B + Kx \quad (C.14)$$

Combining Eqs. (C.9), (C.12), (C.13), and (C.14) for $x = 0$ and solving for V , we get

$$V = \frac{D}{C_{sL}} \left[\frac{(C_{ld} - C_{lp})}{L} - \sigma \Delta T_l \left[\frac{L}{2} \left(\frac{\partial C}{\partial T} \right) \left(\frac{dT}{dx} \right) + C_{lp} \right] \right]. \quad (C.15)$$

Since $dT/dx \cong \Delta T/L$ and $\partial C/\partial T \cong (C_{ld} - C_{lp})/\Delta T$, Eq. (C.15) simplifies to

$$v = \frac{D}{C_s} \left[\frac{C_{ld} - C_{lp}}{L} - \sigma \nabla T_l \left(\frac{C_{ld} + C_{lp}}{2} \right) \right] \quad (C.16)$$

Since $(C_{ld} - C_{lp})/L$ is the average concentration gradient, and $(C_{ld} + C_{lp})/2$ is the average concentration, Eq. (C.16) can be written

$$v = \frac{DC_l}{C_s} \left[\frac{\nabla C_l}{C_l} - \sigma \nabla T_l \right], \quad (C.17)$$

which is identical to the equation obtained by simply considering the salt flux at a crystal surface and using average values for the gradient and the concentration.

Multiply the first term in Eq. (C.17) by $\Delta T/\Delta T$ and rearrange differentials to obtain

$$v = \frac{DC_l}{C_s} \left[\frac{1}{C_l} \frac{\partial C_l}{\partial T} - \sigma \right] \nabla T_l. \quad (C.18)$$

The $(\partial C_l/\partial T)$ function can now be converted to $(\partial C_E/\partial T)$ plus the chemical potential term for the irreversible effects as shown in Sect.

3.1.5. The final result is

$$v = \frac{DC_l}{C_s} \left[\left(\frac{1}{C_l} \frac{\partial C_E}{\partial T} - \sigma \right) \nabla T_l - \frac{K_p + K_D}{RTL} \right]. \quad (C.19)$$

Appendix D

Review of the Anthony and Cline Derivation
and Comparison with Others

In this appendix, the Anthony and Cline¹ derivation of the rate of brine migration is critically reviewed and compared with the others. The derivation uses a thermodynamic approach, as opposed to the more straightforward mass balance considerations of most of the others.

Here we neglect the surface tension terms since they cancel out in the Anthony and Cline derivation because of the necessary assumption of geometric similarity between the opposing faces.

The chemical potential of the salt in the liquid at the i th face is

$$\mu_l(i) = \mu_{ol}(i) + \bar{V}_l P_l + RT_i \ln f N_i, \quad (D.1)$$

where $\mu_{ol}(i)$ is a standard state that depends only on the temperature, N is the mole fraction of salt, and the other symbols are as previously defined.

For pure salt, the chemical potential of salt in the solid is

$$\mu(i) = \mu_{os}(i) + \bar{V}_s P_s(i) \quad (D.2)$$

At the solid-liquid interface, some irreversible processes occur that create a difference in the chemical potential between the solid and the dissolved salt. This difference is expressed by

$$\mu_l(i) = \mu_s(i) - K(i) \quad (D.3)$$

where $K(i)$ is the change in chemical potential at the solid-liquid interface generated by the irreversible processes associated with transfer of salt between the phases.

Combining Eqs. (D.1), (D.2), and (D.3), we get the concentration function

$$\ln f_i N_i = \frac{\mu_{os}(i) - \mu_{ol}(i)}{RT_i} - \frac{K(i)}{RT_i} + \frac{(V_s - \bar{V}_l)P_l}{RT_i}. \quad (D.4)$$

The analogous equation for the j th face, which is assumed opposite and parallel to the i th face, is

$$\ln f_j N_j = \frac{\mu_{os}(j) - \mu_{ol}(j)}{RT_j} - \frac{K(j)}{RT_j} + \frac{(V_s - \bar{V}_l)P_l}{RT_j}. \quad (D.5)$$

Assuming that $f_i = f_j$ and $T_i = T_j$ in the last two terms, subtracting Eq. (D.5) from Eq. (D.4) gives

$$\ln \frac{N_i}{N_j} = \frac{\mu_{os}(i) - \mu_{ol}(i)}{RT_i} - \frac{\mu_{os}(j) - \mu_{ol}(j)}{RT_j} - \frac{K(j) - K(i)}{RT}. \quad (D.6)$$

The differences in concentration at the two faces will be very small; therefore,

$$\ln \frac{N_i}{N_j} \approx \frac{N_i - N_j}{N_j} = \frac{C_i - C_j}{C_j} \quad (D.7)$$

since $\ln x \approx (x-1)$ when $x \rightarrow 1$.

Setting $C_i - C_j = C_{ld} - C_{lp}$, $K(i) = K_d$ and $K(j) = -K_p$, assuming that C_j is the average concentration C_l , and using Eq. (D.7), Eq. (D.6) becomes

$$\frac{C_{ld} - C_{lp}}{C_l} = \left[\frac{\mu_{os}(i) - \mu_{ol}(i)}{RT_i} - \frac{\mu_{os}(j) - \mu_{ol}(j)}{RT_j} \right] - \frac{K_d + K_p}{RT} \quad (D.8)$$

Anthony and Cline apparently replaced the chemical potential terms with $(\partial \ln C_E / \partial T)(T_i - T_j)$, based on the use of the relationship

$$\frac{\partial \ln C_E}{\partial T} = \frac{\partial}{\partial T} \left(\frac{\mu_{os} - \mu_{ol}}{RT} \right) \quad (D.9)$$

They stated that second-order terms were neglected, but no details were given.

We demonstrate below the correctness of the substitution but show that there are no second-order terms involved.

If the chemical potential terms of Eq. (D.7) are multiplied and divided by ΔT and expressed as a difference function, we get

$$\Delta T \left[\frac{\Delta \left(\frac{\mu_{os} - \mu_{ol}}{RT} \right)}{\Delta T} \right] \quad (D.10)$$

On applying the definition of a derivative as $\Delta T \rightarrow 0$, this becomes

$$\Delta T \frac{\partial}{\partial T} \left(\frac{\mu_{os} - \mu_{ol}}{RT} \right) \quad (D.11)$$

By rearranging and differentiating the thermodynamic relationship

$$\mu = \mu_o + RT \ln fN, \quad (D.12)$$

we get

$$\frac{\partial}{\partial T} \left(\frac{\mu - \mu_0}{RT} \right) = \frac{\partial}{\partial T} (\ln fN) . \quad (D.13)$$

On substituting Eq. (D.13) into the function (D.11), the chemical potential terms become

$$\Delta T \frac{\partial (\ln fN)}{\partial T} . \quad (D.14)$$

On substituting the function (D.14) into Eq. (D.8),

$$\frac{C_{ld} - C_{lp}}{C_l} = \Delta T \frac{\partial}{\partial T} (\ln fN) - \frac{K_d + K_p}{RT} . \quad (D.15)$$

Since

$$\frac{\partial}{\partial T} (\ln fN) \cong \frac{1}{N} \frac{\partial N}{\partial T} = \frac{1}{C_E} \left(\frac{\partial C_E}{\partial T} \right) , \quad (D.16)$$

Eq. (D.15) can be expressed as

$$\frac{C_{ld} - C_{lp}}{C_l} = \frac{\Delta T}{C_E} \left(\frac{\partial C_E}{\partial T} \right) - \frac{K_d + K_p}{RT} . \quad (D.17)$$

At an interface, the salt flux is

$$VC_s = D \left(\frac{\partial C_l}{\partial x} \right)_i - \sigma C_l \left(\frac{\partial T}{\partial x} \right)_i . \quad (D.18)$$

Anthony and Cline tacitly assumed that the concentration profile and temperature gradient were linear and that at either boundary the concen-

tration could be represented by the average concentration C_l . With these assumptions, Eq. (D.18) simplifies to

$$VC_s = D \left[\left(\frac{C_{ld} - C_{lp}}{L} \right) - \sigma C_l \nabla T_l \right]. \quad (D.19)$$

In combining Eqs. (D.17) and (D.19), the final result is

$$V = \frac{DC_l}{C_s} \left[\left(\frac{1}{C_E} \frac{\partial C_E}{\partial T} - \sigma \right) \nabla T_l - \frac{K_d + K_p}{RTL} \right]. \quad (D.20)$$

In place of the $(C_l/C_E)(\partial C_E/\partial T)$ term in the above equation, the straightforward mass balance derivation over the liquid regime results in $\partial C_l/\partial T$. The latter expression can be converted to the former by consideration of an under- or supersaturation ΔC^* at the interface, which will also lead to producing the last term of Eq. (D.20) (see Sect. 3.1).

This leaves only the difference exemplified by C_E and C_l that appear in the denominator of the terms in question. Obviously this is of no significance, since $C_E \cong C_l$.

Because of various approximations made in deriving the concentration difference by the chemical potential route and in the application of the boundary condition (all of which are quite justifiable), there appears to be no simple way of resolving this insignificant difference. The straightforward mass balance approach that considers on the liquid domain (as exemplified in Appendixes A and C) and then folds in the irreversible effects as shown in Sect. 3.1.5, also seems correct within the assumptions made and possesses the advantage that boundary conditions can be applied exactly.

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Appendix E

Discussion of the Brine Migration Equation
Derived by Hoekstra et al.

Hoekstra et al.¹ examined the migration of brine packets of KCl and NaCl under the influence of a temperature gradient in single ice crystals. They derived the migration equation (neglecting the Soret coefficient) based on the migration rate of the solute. The current of solute was

$$J = C_l v, \quad (E.1)$$

where C_l is the brine concentration, and v is the velocity of the liquid zone. The solute current is also

$$J = -D \frac{dC_l}{dx}. \quad (E.2)$$

On equating Eqs. (E.1) and (E.2), and making the usual assumptions that average values may be used and that $dC/dx = (\partial C_E / \partial T) \nabla T_l$, Hoekstra et al. obtained

$$v = - \frac{D}{C_l} \left(\frac{\partial C_E}{\partial T} \right) \nabla T_l. \quad (E.3)$$

The form of Eq. (E.3) is in agreement with other derivations, but it is conceptually incorrect and not in usable form, since $v \neq V$ (velocity of the interface). In this case, the water, not the salt, behaves as the solute; i.e., ice dissolves (melts) and precipitates (freezes). Consequently, the material balance should be based on the water. In

addition, the proper flux to use in Eq. (E.1) is $C_s V$ where C_s is the concentration of the diffusing component in the solid, since the velocity of migration is limited by the interface motion.

Seidensticker² recognized that density corrections were required to correct the velocity when viewed from the solid rather than the liquid. He also pointed out that a temperature gradient correction was required if the gradient in the solid was used, but that is not pertinent to this review and is discussed elsewhere.

Seidensticker corrected Eq. (E.3) to

$$v = - \frac{D}{C_l} \left(\frac{\rho_l}{\rho_s} \right) \left(\frac{\partial C_E}{\partial T} \right) \nabla T_l, \quad (E.4)$$

where ρ_l/ρ_s was defined as the ratio of the molecular volume of the solid to that of the liquid (he undoubtedly meant the ratio of the liquid to the solid). He did not mention the conceptual error that water, rather than salt, is the diffusing component in the model. However, it was tacitly recognized, since he used $(\rho_l/\rho_s) = 1.08$, which is the ratio of the molar densities (or mass densities) of water and ice. Actually this ratio should be somewhat smaller because of the salt content of the inclusion, since ρ_l is the molar or mass density of the solute alone (water in this case).

The minus signs in Eqs. (E.3) and (E.4) are unnecessary and can be dropped by making ∇T_l positive, which is common practice.

Equation (E.4) is of course applicable to brine migration in salt because the derivation is independent of which component is diffusing. Unfortunately, the use of the standard symbol, ρ , for total mass density

to represent the component molar or mass density and calling the component density simply "density," has contributed to a misconception leading to erroneous use of Eq. (E.4).

Bradshaw and Sanchez³ and others erroneously used the total mass density for ρ_l , instead of the salt component mass density. Therefore, all values calculated with Eq. (E.4) by these authors should be multiplied by the weight fraction (f) of the salt in the brine inclusion. Remembering that $C_s = \rho_s$, this is derived in the following manner:

$$\text{Correct value} = f\rho_l/\rho_s ;$$

$$\text{Incorrect value} = \rho_l/\rho_s ;$$

$$\text{Correction ratio} = \frac{\rho_l f}{\rho_s} \frac{\rho_s}{\rho_l} = f .$$

The weight fraction, f, varies from about 0.27 to 0.32 between 50 and 100°C, which means that the published theoretical curve of Bradshaw and Sanchez is about a factor of 3 high and should cause the theoretical curve to be significantly below the experimental results. However, the inclusion of a thermal diffusion term would raise the theoretical curve nearer the experimental points since Jenks has shown that thermal diffusion and molecular diffusion are comparable in magnitude.

Actually using Eq. (E.4) is unnecessary, and misconceptions can be eliminated by deriving Eq. (E.3) correctly in the first place. Using $J = \int_g V$ leads directly to the correct equation; namely,

$$V = \frac{D}{C_s} \frac{\partial C_E}{\partial T} \nabla T_l . \quad (E.5)$$

Eqs. (E.5) and (E.4) are actually identical since $\rho_s = C_s$ and, when ρ_l is defined properly, $\rho_l = C_l$.

References for Appendix E

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