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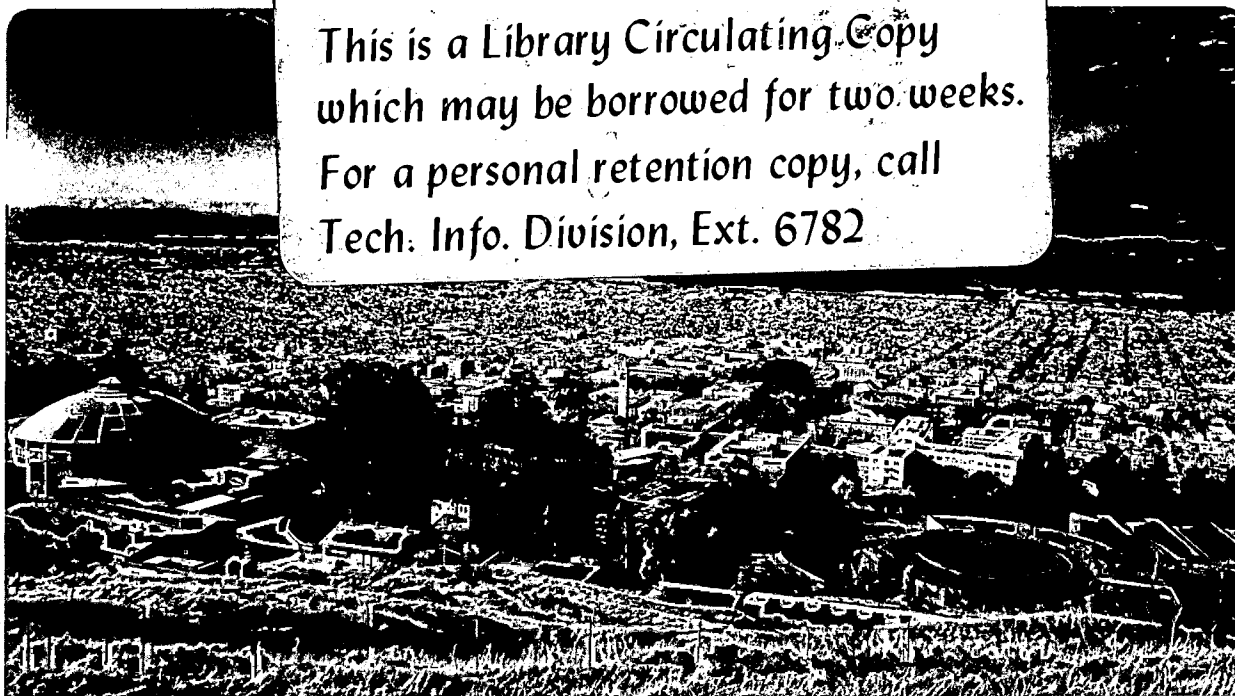
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MIGRATION OF BRINE INCLUSIONS IN SALT

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Abstract

Theories of the migration of brine inclusions in salt are interpreted as simple physical processes, and theories by Russian and American workers are shown to yield the same results. The migration theory is used to predict threshold temperature gradients below which migration of brine inclusions should not occur. The predicted threshold gradients are compared with the temperature gradients expected at the Waste Isolation Pilot Plant in New Mexico. The theory of a threshold gradient helps explain the existence of brine inclusions in natural salt deposits.

1. Introduction

Natural salt deposits, which are being considered as one of the geologic media for disposing of radioactive wastes, contain small inclusions of brine distributed throughout the salt. Temperature gradients, resulting from storing heat-generating wastes in the salt, can cause the inclusions to move through the salt, usually in the direction of higher temperatures. By this mechanism brine can accumulate within the cavity around the waste canister, where it may corrode the canister and contribute to the possible deterioration and dissolution of the waste material. Prediction of the rate and amount of brine-inclusion migration, and the interpretation of experimental data on such migration, are necessary for the evaluation of bedded or domed salt as possible media for waste repositories.

Here we review the theory of brine migration in salt and its application to a salt repository for radioactive wastes. We show that theories proposed independently by Russian and American workers yield the same results and can be interpreted in terms of simple physical processes. We then apply these theories to predict threshold temperature gradients below which migration of brine inclusions should not occur. These predicted threshold temperature gradients are compared with the

actual temperature gradients expected at the Waste Isolation Pilot Plant designed for the bedded-salt deposit near Carlsbad, New Mexico.

The theoretical threshold temperature gradients are compared with the geothermal gradient to explain the existence of brine inclusions in the crystals of these natural salt deposits.

2. Characteristics of Brine Inclusions in Salt

Fluid inclusions were trapped when the salt crystallized. The composition of an inclusion was initially that of the residual liquid when the salt crystals were formed. Subsequent recrystallization may have substantially altered the fluid composition. The inclusions may also contain gas and/or solid phases, and all three phases may be present in a single inclusion. The gas phase is predominantly water vapor, but it may also contain CO_2 , CH_4 , N_2 , and/or H_2S . Gas phases in fluid inclusions are more prevalent in domed salt, where the sedimentary halite has undergone plastic deformation at elevated temperatures and has subsequently cooled^{1,2}. Salt domes generally contain less water than bedded salt.

Bedded salt at Lyons, Kansas and at the Carlsbad site in New Mexico also contains some inclusions in which gas-vapor bubbles are found. In the Lyons salt the gas phase occurs in the larger inclusions, at depths of about 300 m. The gas phase was found to occupy a few percent of the inclusion volume and disappeared upon heating to 80° to 100°C ^{3,4}. Similar gas-phase bubbles were reported for samples of salt from the Carlsbad site in New Mexico, taken at depths of 550 to 850 m. These bubbles disappeared when heated to temperatures of 20° to 45°C ⁵.

Fluid inclusions in salt are composed of brines or bitterns containing calcium or magnesium and varying amounts of Na^+ , K^+ , Cl^- , SO_4^{2-} ,

and trace constituents. Samples of the brine inclusions in the bedded salt at Lyons, Kansas were found to contain about 2.1 molar MgCl_2 and 1.9 molar NaCl , with small amounts⁶ of Ca^{2+} , Br^- , SO_4^{2-} , and probably K^+ . Analyses from salt cores taken near the Carlsbad site, referred to as "Permian Salado Salt", show similar compositions.

The salt cores near the Carlsbad site are found to contain inclusions of two main types⁷:

- o Type A inclusions exist in primary or unrecrystallized salt. The inclusions are small, less than 5 μm , and occur in dense populations in sheets and zones.
- o Type B inclusions exist in the recrystallized salt, which comprises about 99% of the total salt. The inclusions are large, 100 μm to 2 mm, and randomly oriented. It is within these larger inclusions that a gas phase is found.

Fluid inclusions in salt deposits generate appreciable partial pressure of water vapor as the salt is heated. At a high-enough temperature the resulting internal stresses can cause fracture of the salt, i.e., "decrepitation". Decrementation will set an upper limit to the temperature at which a salt repository can be operated, but current repository designs are well below this limit. Decrementation and fissures opened in the solid by internal stress provide additional pathways for releasing brine from salt.

In laboratory experiments with Permian salt most of the inclusions of size 100 μm were released by decrementation in several days at 250°C. The very large inclusions, >1 mm, were released by decrementation at temperatures as low as 60°C⁷. These laboratory releases are probably

greater than would occur under the compressive conditions in a salt repository.

3. Mechanisms of Migration of Brine Inclusions in Salt

In a thermal gradient the all-liquid inclusions migrate up the gradient, towards the heat source, because the solubility of salt in the brine inclusion increases with temperature. The temperature at the inclusion surface nearer the heat source is greater than at the surface away from the heat source. Consequently, salt dissolves into the inclusion across the hot surface and crystallizes out at the cold surface. The net diffusion of salt from the hot face to the cold face of the inclusion causes the inclusion to move in the opposite direction, i.e., in the direction of higher temperature.

The gas-liquid inclusions can, under some conditions, migrate down the temperature gradient, away from the heat source. The brine near the hot surface of the inclusion exerts a higher partial pressure of water vapor than exists near the cold surface. There is then a net transfer of water vapor from the hot surface to the cold surface, accompanied by crystallization of salt from the evaporated liquid at the hot surface and dissolution of salt into the pure condensate near the cold surface. The net transport of salt from the cold surface to the hot surface of the inclusion, through the liquid within the inclusion, causes the inclusion to move in the direction of lower temperature. However, such two-phase inclusions do not necessarily move down the temperature gradient under all conditions, since the driving force from temperature-dependent solubility remains in the opposite direction. Migration down the gradient is more important at higher average temperatures, where the

partial pressure of water vapor above the brine becomes appreciable.

It is possible for an all-liquid inclusion to transform into a gas-liquid inclusion when the former reaches the surface of the cavity in which a waste canister is emplaced. When exposed to the lower pressure of the cavity, a portion of the brine can evaporate. If the evaporation is accompanied by a resealing of the inclusion, now containing trapped water vapor, it is possible that the inclusion can then migrate back down the temperature gradient.

4. Theory of Migration of All-Liquid Inclusions

The mechanisms and associated parameters which control the rate of migration of brine inclusions have been analyzed by Anthony and Cline^{8,9,10,11,12,13}, Jenks³, Olander and Balooch¹⁴, and Geguzin and Dzyuba¹⁵. The two initial investigations and theoretical analyses, carried out separately by Anthony and Cline and by Geguzin and Dzyuba, can be shown to be essentially identical for all-liquid inclusions, and both investigations have obtained laboratory data to test these predictions. Experimental data were obtained for inclusions in KCl crystals with [100] orientation, rather than in the NaCl which would have been more appropriate to the halite deposits of bedded and domed salt. There are many instances in the literature wherein these data for KCl have been applied, without correction, to NaCl systems.

Here we derive the theory to predict the rate of migration of a liquid inclusion in a temperature gradient, using the terminology of Geguzin and Dzyuba, and we use this theory to interpret terms which appear in the derivation by Anthony and Cline. This theory is then used to predict and interpret threshold temperature gradients below which

brine inclusions should not migrate but should remain stationary within the salt crystals or at the grain boundaries.

Consider a brine inclusion with planar surfaces surrounded by solid salt, as shown in Figure 1. The temperature profile shown is that existing across the liquid inclusion, which is of thickness L in the direction of the temperature gradient. The concentration C_s of salt in the liquid near a given surface is expected to be near the saturation concentration determined by the temperature of that surface. Because the solubility of salt increases with temperature, the concentration C_{sh} near the hot surface is greater than the concentration C_{sc} at the cold surface. This concentration difference can cause salt to diffuse across the inclusion. A simple diffusional mechanism can result in a linear change in concentration of the dissolved salt across the inclusion. The concentration profile may appear as shown in Figure 1.

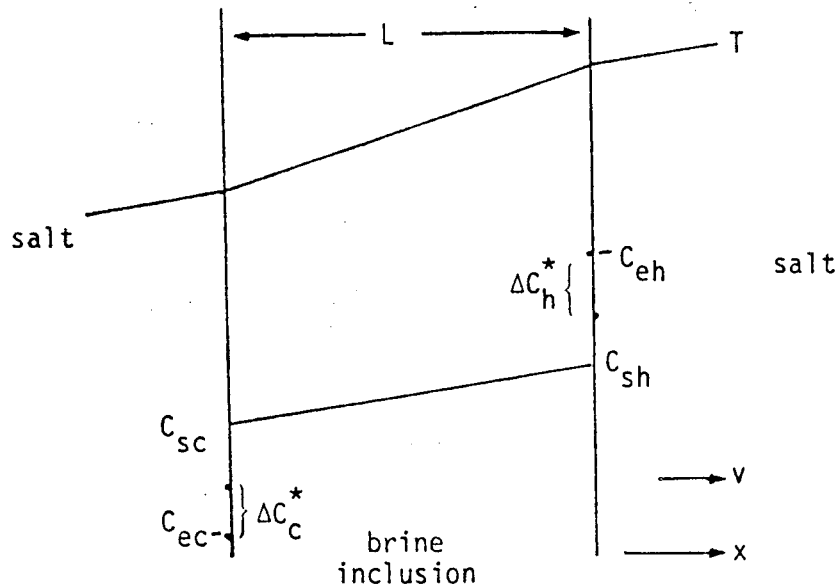


Figure 1. Concentration profiles

In order to nucleate crystallization at the cold surface, the concentration C_{sc} of dissolved salt at that surface must be greater than the saturation concentration C_{ec} , as shown in Figure 1. Similarly, to promote dissolution, the concentration C_{sh} of dissolved salt at the hot surface must be less than the saturation concentration C_{eh} .

Geguzin and Dzyuba propose that the actual driving force to nucleate crystals at a finite rate is less than $C_{eh} - C_{sh}$ by an amount ΔC_c^* , where ΔC_c^* is a critical concentration difference to nucleate a step on the crystalline surface. The mass rate dw/dt of crystallization of salt at the cold surface can be expressed in terms of a kinetic crystallization coefficient k_c :

$$\frac{dw}{dt} = k_c A (C_{sc} - C_{ec} - \Delta C_c^*) \quad (1)$$

where A is the interfacial area of the inclusion at the cold surface.

Similarly, at the hot surface the driving force for dissolution at a finite rate is $C_{eh} - C_{sh} - \Delta C_h^*$, where ΔC_h^* is a critical concentration difference required for the surface distortion accompanying dissolution. At steady state the rate of dissolution at the hot surface is equal to the rate of crystallization and is expressed in terms of a kinetic dissolution coefficient k_h :

$$\frac{dw}{dt} = k_h A (C_{eh} - C_{sh} - \Delta C_h^*) \quad (2)$$

The effects of the two kinetic coefficients k_c and k_h can be incorporated into one overall kinetic coefficient k , defined by

$$\frac{dw}{dt} = kA (C_{eh} - C_{sh} + C_{sc} - C_{ec} - \Delta C^*) \quad (3)$$

where

$$\Delta C^* = \Delta C_c^* + \Delta C_h^* \quad (4)$$

By eliminating common terms from equations (1), (2), and (3) we obtain

$$\frac{1}{k} = \frac{1}{k_h} + \frac{1}{k_c} \quad (5)$$

At steady state the rate of dissolution is equal to the rate of diffusion within the bulk of the inclusion, given by:

$$\frac{dw}{dt} = A \left(D \frac{dC_\ell}{dx} - D \sigma C_\ell \frac{dT}{dx} \right) \quad (6)$$

The first group on the right-hand side represents Fick's-law diffusion in the liquid due to a concentration gradient, where D is the diffusion coefficient. The second group represents thermal diffusion, where σ is the Soret coefficient.

The concentration gradient dC_ℓ/dx can be approximated by

$$\frac{dC_\ell}{dx} = \frac{C_{sh} - C_{sc}}{L} \quad (7)$$

where L is the thickness of the inclusion in the direction of the temperature gradient.

The mass flux $\frac{dw}{A dt}$ causes the inclusion surface to move with a velocity v , given by

$$\frac{dw}{dt} = AvC_s \quad (8)$$

where C_s is the concentration, i.e., the density, of the soluble species in the solid salt.

Since the concentrations C_{eh} and C_{ec} are each determined by the surface

temperatures and solubilities of the salt, the overall concentration difference shown in Figure 1 is the product of the overall temperature difference $L\nabla T_\ell$ across the inclusion and the temperature dependence of solubility dC_e/dT , so that

$$C_{eh} - C_{ec} = L\nabla T_\ell \frac{dC_e}{dT} \quad (9)$$

Combining equations (3), (6), (7), (8), and (9), and multiplying and dividing by RT , we obtain the migration velocity of an inclusion within a salt crystal;

$$v = \frac{C_\ell}{C_s RT} \left(\frac{D}{1 + D/Lk} \right) \left[\left(\frac{dC_e}{C_\ell dT} - \sigma \right) \nabla T_\ell RT - \frac{\Delta C^* RT}{C_\ell L} \right] \quad (10)$$

where R is the gas constant. The temperature difference across the small inclusions is expected to be quite small, so the term $dC_e/C_\ell dT$ can be approximated by the log derivative of solubility.

When the temperature gradient is negative, the temperature decreases with increasing x , the concentration profile of Figure 1 is reversed, and the inclusion migrates to the left with a negative velocity. For the derivation based upon Figure 1 to apply to this case, the critical concentration differences shown in Figure 1 must become negative. To allow for this condition, Equation (10) must be rewritten as

$$v = \frac{C_\ell}{C_s RT} \left(\frac{D}{1 + \frac{D}{Lk}} \right) \left[\left(\frac{dC_e}{C_\ell dT} - \sigma \right) \nabla T_\ell RT \mp \frac{\Delta C^* RT}{C_\ell L} \right] \quad (11)$$

where the minus sign before $\Delta C^* RT/C_\ell L$ is used when v is positive and the plus sign is used when v is negative. What happens at the condition of zero migration velocity will be discussed later.

An alternate form of Equation (11), which facilitates comparison with the Anthony-Cline model, is:

$$v = \frac{C_l D}{C_s RT} \left[\left(\frac{dC_e}{C_l dT} - \sigma \right) \nabla T_l RT \bar{f} \left(\Delta C^* + \frac{C_s |v|}{k} \right) \frac{RT}{C_l L} \right] \quad (12)$$

where $|v|$ is the migration speed, i.e., the magnitude of the velocity. The \bar{f} is used as described after Equation (11).

Anthony and Cline present a similar equation for the migration velocity within the crystalline lattice.

$$v = \frac{C_l D}{C_s RT} \left[\left(\frac{dC_e}{C_l dT} - \sigma \right) \nabla T_l RT \bar{f} \frac{K}{L} \right] \quad (13)$$

The two equations are equivalent if

$$K = \left(\Delta C^* + \frac{C_s |v|}{k} \right) \frac{RT}{C_l} \quad (14)$$

K is referred to by Anthony and Cline as the "kinetic potential", a term which represents the frictional effects of interface kinetics. A clearer meaning, in terms of concentration differences for nucleation and dissolution, has been identified by the above derivation.

Anthony and Cline have observed that K depends linearly upon the migration speed $|v|$ according to:

$$K = \alpha + \beta |v| \quad (15)$$

From the above analysis we can now identify:

$$\alpha = \Delta C^* RT / C_l \quad (16)$$

and

$$\beta = C_s RT / k C_l \quad (17)$$

The equation for the migration velocity can be interpreted^{8,9,10} as the force F on the inclusion multiplied by the inclusion mobility M , or

$$v = MF \quad (18)$$

where

$$M = \frac{C_l D \bar{V}_s}{C_s RT V_l} \quad (19)$$

\bar{V}_s is the molar volume of the solid salt, and V_l is the inclusion volume.

For thermally induced migration within a crystal

$$F = F_t + F_f \quad (20)$$

where F_t is the thermal force:

$$F_t = \left(\frac{dC_e}{C_l dT} - \sigma \right) \frac{V_l}{\bar{V}_s} \nabla T_l RT \quad (21)$$

and F_f is the frictional force due to interface kinetics, i.e., due to the finite concentration differences at the inclusion surfaces for nucleation and dissolution:

$$F_t = \mp \left(\Delta C^* + \frac{C_s |v|}{k} \right) \frac{RT}{C_l L} \quad (22)$$

Migration Across Grain Boundaries

A brine inclusion which has reached a grain boundary is in a position of minimum energy, since the surface area of the grain boundary must be increased if the inclusion is moved from the boundary into an adjacent crystal. Thus, an inclusion migrating through a crystalline solid may either penetrate or be stopped by the grain boundary, depending on whether or not the force on the inclusion is sufficient to move the inclusion out of the energy well associated with a grain boundary¹².

If we imagine an inclusion in the form of a platelet of square cross section, of length X on a side in a plane perpendicular to the direction of migration, the retarding force $-F_{gb}$ due to surface tension at the grain boundary is

$$- F_{gb} = 4 \gamma X \quad (23)$$

where γ is the surface tension of the grain boundary, and $4X$ is the perimeter of the inclusion.

Migration of Inclusions Through Polycrystalline Salt

To predict the overall migration of an inclusion through a polycrystalline solid, the net force F on the inclusion is given by extending Equation (20):

$$F = F_t + F_f + F_{gb} \quad (24)$$

Combining Equations (18), (19), (21), (23), and (24), we obtain the working equation for predicting the velocity at which a brine inclusion migrates in a thermal gradient in polycrystalline salt:

$$v = \frac{C_\ell D}{C_s RT} \left[\left(\frac{dC_e}{C_\ell dT} - \sigma \right) \nabla T_\ell RT \mp \left(\frac{\Delta C^* RT}{C_\ell L} + \frac{C_s |v| RT}{k C_\ell L} + \frac{4\gamma \bar{V}_s}{XL} \right) \right] \quad (25)$$

Because the nucleation-dissolution and grain-boundary terms in the second parentheses on the right hand side retard the migration of an inclusion, the minus sign is used when the velocity is positive and the positive sign when the velocity is negative.

The validity of this theory when applied to experimental data on brine inclusions has been demonstrated by Anthony and Cline^{8,9,10,12}, by Geguzin and Dzyuba¹⁵ for KCl, and by Jenks³ for NaCl.

Effect of Pressure On Migration

The effect of pressure on brine migration has been analyzed by Jenks³, who shows that corrections to the above theory due to the lithostatic pressure in a geologic repository are relatively small.

Obtaining ∇T_ℓ From the Temperature Gradient in the Salt

To apply Equation (25), the temperature gradient within the brine inclusion must be known. Because the thermal conductivity of the brine is less than that of the surrounding salt, the presence of the inclusion perturbs the temperature distribution within the salt immediately surrounding the brine inclusion and results in a gradient across the inclusion greater than the unperturbed gradient in the salt. It is generally assumed that the migration velocity is determined by the maximum temperature gradient, which exists at the center of the inclusion. This value of ∇T_ℓ can be obtained from the unperturbed gradient ∇T_s in the salt by

$$\nabla T_\ell = \xi \nabla T_s \quad (26)$$

where ξ is a correction factor determined from a multidimensional analysis of heat conduction in the vicinity of the inclusion⁸.

For a cubic inclusion

$$\xi = \frac{3}{2 + \frac{k_\ell}{k_s}} \quad (27)$$

where k_ℓ and k_s are the thermal conductivities of liquid and solid, respectively.

For a platelet inclusion of large aspect ratio,

$$\xi = \frac{k_s}{k_\ell} \quad (28)$$

4. Threshold Temperature Gradients for No Migration of Brine Inclusions

Equation (25) applies for both positive and negative temperature gradients and for both positive and negative velocities. It has been assumed that the critical concentration difference ΔC^* is constant and

independent of the migration velocity. The migration velocity as a function of temperature gradient would appear as in Figure 2.

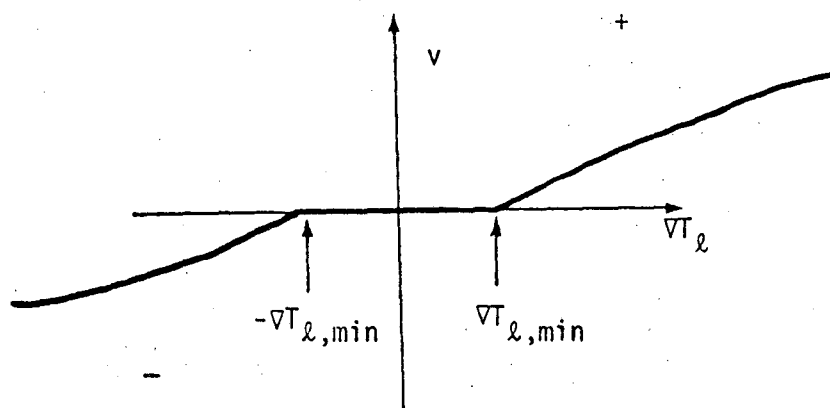


Figure 2. Migration velocity as a function of temperature gradient, as predicted from Equation (25).

Figure 2 illustrates that when the magnitude of the temperature gradient is reduced below some limiting value, the inclusion remains stationary. The inclusion is then either immobile within the crystal and does not reach grain boundaries, or it is trapped at the grain boundary. Each of these processes is considered in the following sections.

4.1 Threshold Temperature Gradient for No Migration Within Crystals

Equation (12) applies to the motion of an inclusion within a crystal and away from a grain boundary. It predicts behavior illustrated in Figure 2, which shows that at some limiting temperature gradient the inclusion becomes immobile. At this limiting condition the temperature difference from the hot to the cold surfaces of the inclusion is just sufficient for the brine concentration adjacent to the cold surface to exceed the saturation concentration by an amount equal to the threshold

concentration difference required to nucleate a crystal surface. Similarly, there exists at this limiting condition a threshold difference between the saturation concentration and actual concentration at the hot surface, below which the local crystal disorder accompanying dissolution cannot occur. At any smaller absolute value of the temperature gradient the velocity remains zero, the inclusion is immobile, and Equation (12) is not valid.

The threshold temperature gradient below which the inclusions are not predicted to migrate within a crystal can be obtained from Equation (12) by setting v equal to zero. There results:

$$\nabla T_{l,\min} = \frac{\Delta C^*}{LC_l} \left(\frac{1}{\frac{1}{C_l} \frac{dC_e}{dT} - \sigma} \right) \quad (29)$$

To obtain the minimum temperature gradient $\nabla T_{s,\min}$ in the salt, we must apply the correction from Equation (21). Stationary inclusions in solid NaCl are cubic, so Equations (26), (27), and (29) are combined to yield:

$$\nabla T_{s,\min} = \frac{2\Delta C^*}{3LC_l} \left(1 + \frac{k_l}{k_s} \right) \frac{1}{\frac{1}{C_l} \frac{dC_e}{dT} - \sigma} \quad (30)$$

For the Soret coefficient we adopt the value from Jenks³:

$$\sigma = -0.002/^\circ\text{C} \quad (31)$$

From Olander's¹⁴ data on NaCl at room temperature;

$$\frac{\Delta C^*}{C_l} = 2 \times 10^{-5} \quad (32)$$

For the inclusion composition we adopt a representative bittern of 2.35 M MgCl₂ saturated with NaCl. For small inclusions the concentration changes are small enough that $C_l \approx C_e$. For the temperature

dependence of solubility of NaCl in 2.35 M MgCl_2 we adopt the data of Jenks³, shown in Table 1.

Table 1. Solubility of NaCl in 2.35 M MgCl_2 (J1)

$T, ^\circ\text{C}$	$\frac{1}{C_e} \frac{dC_e}{dT}, ^\circ\text{C}/\text{cm}$
25	1.67×10^{-3}
50	2.17×10^{-3}
100	3.54×10^{-3}

Using the data for 25 $^\circ\text{C}$ in Equation (30), with $k_s/k_l = 7$, we calculate the threshold temperature gradients in Table 2.

Table 2. Threshold temperature gradients for no migration within a crystal at 25 $^\circ\text{C}$.

<u>Inclusion size, cm</u>	<u>$\nabla T_{s,\text{min}}, ^\circ\text{C}/\text{cm}$</u>
5×10^{-4}	8.1
1×10^{-2}	0.39
2×10^{-1}	0.019

The larger inclusions have the greatest temperature difference from the hot face to the cold face and therefore migrate most easily.

A representative heat-generating canister of defense waste for the proposed WIPP site generates 600 W of thermal energy. At an areal loading of 7.3 W per square meter of repository, the maximum temperature gradient is estimated by Hunter¹⁶ to be 0.2 $^\circ\text{C}/\text{cm}$. Based upon the threshold gradients estimated above, it is the more populated smaller inclusions (less than about 10^{-2} cm) which are predicted not to migrate. The larger inclusions (>2mm) are predicted to migrate through the crystal at a finite but slow rate until they arrive at the grain boundary. Even inclusions of this size may terminate their migration if, in the process of migration,

they fission into smaller inclusions. Fissioning of inclusions in the process of migration has been observed in the laboratory by Muchowski and Olander¹⁷ and in the Salt Block II experiment by Lambert¹⁸.

A typical canister of commercial high-level waste could generate as much as 3.5 kW of heat at the time of emplacement. At the relatively high areal loading of 37 W/m² the maximum temperature gradient in the salt is 1 °C/cm, at a maximum salt temperature of 176°C¹⁹. Again, the expected temperature gradients lie within the range of the threshold gradients appearing in Table 2, so only the smaller inclusions will migrate.

The existence of a finite concentration difference ΔC^* for a finite inclusion at rest within a temperature gradient has been observed experimentally²⁰. ΔC^* can be interpreted as a measure of the free energy that must be supplied to distort the inclusion surface so that dissolution and crystallization can occur.

4.2 Threshold Temperature Gradient For No Migration Across Grain Boundaries

Here we examine the conditions for no migration across the grain boundaries. Treating the grain boundary as a surface between adjacent crystals, all the terms in Equation (25) apply to the motion of an inclusion across the surface. To obtain the threshold temperature gradient for no migration across the grain boundary, we set v equal to zero in Equation (25) and solve. There results:

$$\nabla T_{l,\min} = \frac{\frac{\Delta C^*}{C_l} + \frac{4\gamma\bar{V}_s}{XRT}}{L \left(\frac{dC_e}{C_l dT} - \sigma \right)} \quad (33)$$

Not knowing the shape of an inclusion at the grain boundary, a cubic inclusion will be assumed, so that:

$$X = L \quad (34)$$

From Equations (27), (33), and (34) there results:

$$\nabla T_{s,\min} = \frac{2 \left(\frac{\Delta C^*}{C_l} + \frac{4\gamma \bar{V}_s}{LRT} \right)}{3L \left(\frac{dC_e}{C_l dT} - \sigma \right)} \quad (35)$$

To illustrate, we adopt from Jenks³:

$$\bar{V}_s = 27.0 \text{ cm}^3/\text{mole for solid NaCl}$$

$$\sigma = -0.002/^\circ\text{C}$$

$$\frac{dC_e}{C_l dT} = 2.17 \times 10^{-3}/^\circ\text{C}$$

The theoretical surface energy of NaCl is a minimum of 150 erg/cm² on the [100] surfaces and is a maximum of 400 erg/cm² on the [110] surfaces³. Use of the lower value for γ would be more conservative, in that it would predict a lower surface tension and a lower threshold gradient. However, an even lower possible value can be estimated from the data of Cline and Anthony¹², who studied the trapping of inclusions at a grain boundary in KCl, with the boundary formed by a 15° tilt between [100] planes of adjacent crystals. They estimated a surface tension of about 32 erg/cm², about one third the free-surface energy of the [100] planes of KCl. This seems to correlate findings obtained with metal systems. Therefore, for a 15° tilt boundary in NaCl we might expect a grain-boundary tension of 150/3 or 45 erg/cm². This more conservative estimate of γ will be adopted for the present estimates.

Using the above data, together with the data on ΔC^* estimated in Section 4.1, we use Equation (35) to predict threshold temperature gradients as a function of inclusion size, as listed in Table 3.

Table 3. Threshold temperature gradients for no migration across grain boundaries at 25°C, with finite ΔC^*

<u>Inclusion size, cm</u>	<u>$\nabla T_{s,min}, ^\circ\text{C/cm}$</u>
5×10^{-4}	142
1×10^{-2}	0.72
2×10^{-1}	0.020

Assuming the gradients of 0.2 to 1 C/cm for the WIPP wastes quoted earlier, the very large inclusions are predicted to migrate across the grain boundaries. However, inclusions slightly smaller than 2×10^{-1} cm may migrate through the lattice but will be stopped at the grain boundaries.

On the basis of these predictions, only the very large inclusions (> 0.01 cm) are predicted to migrate in NaCl in the presence of the heat generating WIPP wastes. These large inclusions represent only a very small fraction of the inclusions observed in the WIPP halite. However, most of the liquid in WIPP halite is contained in the few relatively large inclusions, with diameters of about 0.1 cm and greater²¹.

Large inclusions may still terminate their migration at the grain boundary or within the crystalline lattice if they fission into smaller inclusions, similar to the phenomenon observed by Muchowski and Olander¹⁷.

We can also use Equation (33) to estimate the temperature gradient which would trap inclusions at grain boundaries in the absence of resistance to dissolution and nucleation at the crystalline surfaces adjacent to the grain boundaries, i.e., with $\Delta C^* = 0$. Setting $\Delta C^* = 0$

and solving Equation (33) with the remaining parameters derived above, we obtain the threshold temperature gradients in Table 4.

Table 4. Threshold temperature gradients for no migration across grain boundaries, with $\Delta C^* = 0$

<u>Inclusion size, cm</u>	<u>$\nabla T_{s,min}, ^\circ\text{C/cm}$</u>
5×10^{-4}	134
1×10^{-2}	0.33
2×10^{-1}	8.4×10^{-4}

Comparing these estimates for grain boundaries with the threshold gradients in Table 2 for the crystalline lattice, we see that the grain boundary is the principal retarding force for small inclusions, less than about 10^{-2} cm. The crystalline lattice is the principal retarding force for larger inclusions.

5. Migration in the Geothermal Gradient

Brine inclusions in natural salt, such as in the halite at the Carlsbad site, seem to be distributed uniformly throughout a given layer of salt. During the 200-million-year age of these deposits there has existed a geothermal gradient which could have caused a net downward migration of inclusions. However, since the inclusions are distributed uniformly throughout a given halite layer, it is reasonable to assume that there has been no net migration on a macro scale during the geological age of the halite. It is also noted that many inclusions remain within the lattice of individual crystals, and we will assume that these inclusions were originally formed in the crystals wherein they now reside.

From the theory summarized in Section 4, and using the data developed by Jenks³, we can estimate the average velocity of an inclusion under the influence of the geothermal gradient. Assuming that this gradient has remained constant since the salt deposit was formed, we can test the validity of these theories in the region of low temperature gradient by estimating the distance over which inclusions should have migrated during this interval of geological time.

Measurements in the Carlsbad salt indicate a linear increase of temperature with depth. The temperature increases from 24.2 °C at 320 m to 32.0 °C at 1310 m, corresponding to a geothermal gradient of 7.85×10^{-5} °C/cm and an average temperature of 28 °C²².

Assuming no threshold resistance within a halite crystal and no surface-tension resistance at grain boundaries, i.e., with $\Delta C^* = \gamma = 0$, and using the data of Jenks, the theory would predict a migration distance of roughly 100 m over the geologic time of 2×10^8 yr, independent of inclusion size. Therefore, if ΔC^* and γ were zero, all inclusions would have migrated away from the top of the halite layer. This has not been observed.

In fact, in the Delaware basin, where the WIPP site is located, there are no beds of halite as thick as 100 m. The halite layers are separated by intervening beds of less soluble material such as anhydrite, clay, silt, or polyhalite. Consequently, even lesser rates of migration would have removed all brine inclusions from the halite and would have resulted in accumulations of brine at the interfaces of these intervening layers. No such accumulation has been observed.

If there were no dissolution-nucleation threshold within the crystalline lattice, i.e., $\Delta C^* = 0$, all inclusions would have migrated from the lattice of each halite crystal. With finite surface tension at the grain boundary, essentially all of these inclusions would have been trapped at the grain boundary, and there they would reside. However, this is not consistent with the observations of inclusions that do exist within natural salt crystals, so ΔC^* must be finite.

From Equation (30) we calculate that for the finite value of ΔC^* given by Equation (32) all inclusions smaller than about 5 cm will remain stationary within the crystalline lattice under the influence of the geothermal gradient. All of the inclusions in halite are much smaller than 5 cm. Therefore, the presence of brine inclusions in the crystals of natural halite, which has been under the influence of the geothermal gradient for the geologic time since its formation, is further confirmation of the existence of ΔC^* and of the theory of threshold temperature gradients below which inclusion migration does not occur.

6. Conclusion

The Anthony-Cline equation for brine-inclusion migration has been reasonably validated³ by its application to experimental data^{23,24,25} in natural single crystals from Kansas salt and to the data from Project Salt Vault²⁴. In predicting migration under the design conditions of geologic repositories, the migration resistances arising from the existence of ΔC^* (i.e., $K = 0$) and from grain-boundary surface tension are usually ignored²¹. This will overestimate the amount of brine that can migrate into the cavity around a waste canister.

The theory developed herein shows that for some repository conditions the expected temperature gradients are in the neighborhood of the threshold gradients below which no migration of inclusions will occur. This

suggest that the migration resistances in the crystal lattice and at grain boundaries should be taken into account in predicting the extent of brine migration in geologic repositories. The resulting amount of brine migration will be less than that heretofore predicted.

The development herein of the theory of brine migration shows that the Russian (Geguzin-Dzyuba) and American (Anthony-Cline) theories are, in fact, similar expressions of the same phenomena.

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