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MODELING OF BRINE MIGRATION IN HALITE

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ABSTRACT

When canisters containing radwastes are emplaced in a repository the heat produced by the decaying radwaste will cause elevated temperatures and moderate thermal gradients to develop in the adjacent medium. The thermal effect will cause the brine present in a halite medium (salt deposits) to accumulate around the canister. A mathematical model which adequately describes the migration under conditions applicable to storage of such radwastes is needed.

Four different models of the migration process have been reviewed to determine their suitability as a working model. While there are several common factors in the models additional factors are included to account for several possible effects. The detail of each model leads to a certain degree of difficulty in applying the model to the problem at hand. One model predicts that inclusions smaller than 0.1 mm dimension probably will not migrate. The other models do not consider size as a factor. Thermal diffusion (Soret effect) is considered insignificant in three models, while in the fourth model it is added to the concentration diffusion term.

The following conclusions can be made as a result of this study. Appropriate values of the parameters used were taken from the literature, or estimated on the basis of "best available approximation."

1. Temperature is the most significant parameter in all models and must be known as a function of time, and distance from the canister.
2. All four models predict about the same migration velocity for a given set of conditions. For 100°C and 1°C/cm thermal gradient, the individual values are 3.0, 4.8, 5.6 and 6.4 mm/yr.
3. The diffusion of ions through the brine inclusions is the rate controlling mechanism.
4. The difference between the thermal gradients in the liquid and in the solid should always be considered, and is a function of droplet shape.
5. The model based upon work by Nernst is easiest to use since all necessary parameters are readily available in the literature. However, of the four models it predicts the lowest migration rate.
6. The maximum volume of pure brine accumulated at the canister surface would be less than 20-40 liters in 50 years, for a canister initial thermal power of 3.5 kW. Bitterns would migrate proportionately less volume.

A computer code, BRINE, was developed to make these calculations by means of any of the four models. The choice is dictated by the user, and by values available for the parameters.

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MODELING OF BRINE MIGRATION IN HALITE

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INTRODUCTION

When canisters filled with radwastes are emplaced in a deep bedded salt repository the heat produced by the decaying waste will cause high temperatures and moderate thermal gradients to develop in the salt. The temperature and thermal gradient may be sufficient to cause the brine inclusions present to migrate towards the canister. The larger inclusions of SALT VAULT, [1] were shown to migrate readily toward the emplacement hole while the very small ones were either unable to migrate or migrated very small distances [2].

The rate of droplet migration can be limited either by ion diffusion through the liquid droplet or by the kinetics of ion removal from or deposition on the facets of the droplets. When the diffusivity and solubility of the solid in the liquid are large, the kinetic processes at the solid-liquid interface control the overall droplet velocity.

MODELS AVAILABLE

Four different models have been studied to determine their suitability as a working model for brine migration. All four models have several common factors, however, the remaining factors are present to account for several possible effects. The detail of each model leads to a certain degree of difficulty in applying it to the problem at hand.

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Nernst Model

The first model considered was based upon the linear rate of growth of a crystal surface in a saturated solution [3]. This model describes a plane crystal surface growing uniformly in a supersaturated solution. The growth rate is limited by the diffusion across a solute boundary layer at the surface. The rate of transport of solute is given by Fick's Law and the solute concentration at the interface is assumed to be the equilibrium value. The latter is true provided that the kinetic process is extremely rapid compared with the volume diffusion. The resulting equation is:

$$v = \frac{D}{\rho_s - C_l} \cdot \frac{\partial C_l}{\partial T} \cdot G_l \quad (1)$$

where,

v = linear rate of growth of crystal
 D = diffusion coefficient
 ρ_s = density of the crystal, $= C_s$
 C_l = solute concentration at interface, $x = 0$

$\frac{\partial C_l}{\partial T}$ = slope of liquidus curve, at $x = 0$

$\frac{\partial T}{\partial x} = G_l$ = thermal gradient in the liquid, at $x = 0$

Equation (1) is dependent upon the values of the diffusion coefficient and the thermal gradient in the liquid. The diffusion coefficient can be estimated from viscosity data by using the Stokes-Einstein relationship [4]:

$$D = \frac{kT}{6\pi r\eta} \quad (2)$$

where,

k = Boltzman constant
 T = absolute temperature
 η = viscosity
 r = average ionic radius, $\left[\frac{(r_{Na^+} + r_{Cl^-})}{2} \right]$

This method of estimation is subject to an error of less than an order of magnitude, but is considered to be the best available [5]. Reliable data at elevated temperatures are badly needed. It is difficult to measure the thermal gradient in the liquid, G_l , although it is very easy to measure the thermal gradient in the solid -- see Equation (4), below.

HOWS Model

The model developed by Hoekstra, Osterkamp and Weeks, as modified by Seidensticker, [6], is based upon a study of brine pockets

in glacial ice migrating under a thermal gradient. This model assumes that the shape of the inclusion does not change, therefore, the velocity of migration is independent of the aspect ratio of the inclusion and the direction of movement with respect to crystal orientation. Their consideration of thermal diffusion (Soret effect) indicated that it was less than 1% of the diffusion caused by concentration; subsequently, they neglected this effect.

Thus, they calculated velocities, from the equation:

$$v = D \frac{1}{C_L} \cdot \frac{\partial C_L}{\partial T} \cdot G_s \cdot \frac{3K_s}{2K_s + K_L} \cdot \frac{\rho_L}{\rho_s} \quad (3)$$

where,

K_s = thermal conductivity of solid
 K_L = thermal conductivity of brine solution
 ρ_L = density of the brine
 G_s = thermal gradient in the solid

and other symbols as previously defined, are within 1% of observed values for KCl and within 20% for NaCl.

The product of thermal conductivity factor and G_s in Equation (3) approximates G_L as indicated by the relationship [7]:

$$G_L = \frac{K_s}{(1-F) \cdot K_s + F \cdot K_L} \cdot G_s \quad (4)$$

where for salt K_s and K_L change with temperature and are given by (T in °C):

$$\log K_s = 0.7618 - 1.37 \times 10^{-3} T \quad (5a)$$

$$K_L = 0.5402 + 1.711 \times 10^{-3} T - 5.866 \times 10^{-6} T^2 \quad (5b)$$

The factor F depends only on the aspect ratio of the droplet, and its value is 0.333 at $X/L = 1.0$ (cube and sphere) and increases to a value of 1.0 at $X/L \gg 1.0$. L is the dimension in direction of migration and X is dimension perpendicular to direction of migration. Intermediate values of F are 0.53, 0.64, and 0.70 at $X/L = 2.0, 3.0$, and 4.0, respectively.

The parameters of Equation (3) are known or can be evaluated to some degree of reliability at the conditions expected in a repository. The thermal conductivity data are available for a wide range of temperatures, 0° - 340°C, as well as density data for a range of concentration and temperature [8,9].

Wilcox Model

Another model for impurity migration has been presented by Wilcox [10] to describe removing inclusions from crystals by gradient techniques (zone refining). He was especially concerned with inclusions formed during crystallization from solution. He assumed that diffusion through the zone is rate controlling, that the process is at steady state, there is no solubility of the solvent in solid, no convective mixing, constant properties, and no thermal diffusion (Soret effect). His derivation results in the equation:

$$v = D \cdot \frac{1}{m(1-w_o)} \cdot \frac{\rho_l}{\rho_s} \cdot G_l \quad (6)$$

where v , D , G_l , ρ_l and ρ_s are as previously defined, and

w_o = weight fraction of crystallizing material at the cold side of inclusion

$$\frac{\partial T}{\partial w} = m = \frac{\text{change in freezing point}}{\text{change in weight fraction}}, \text{ i.e., the slope of}$$

the liquidus curve on the crystal-solvent phase diagram

A closer look at the factor $1/m$ allows it to be recognized as $\partial C_l / \partial T$ expressed in units of weight fraction rather than molarity. If $(1-w)$ were similarly expressed, we would have the molarity of the solvent.^o

Anthony-Cline Model

The most complete model has been presented by Anthony and Cline [11-18] and is expressed by:

$$v = D \frac{C_l}{C_o} \left[\left(\frac{1}{C_l} \cdot \frac{\partial C_l}{\partial T} + \sigma \right) G_l - \frac{1}{RT} \left(\frac{K}{L} + \frac{4 \gamma \bar{V}_s}{XL} \right) \right] \quad (7)$$

where, R = gas constant
 σ = Soret coefficient
 K = kinetics potential at interface
 γ = surface tension of liquid
 $\bar{V}_s$ = partial molar volume of solid
 T = absolute temperature, °K

and other symbols as previously defined. The four component terms can be represented as:

$$v = v_T + v_\sigma - v_K - v_\gamma \quad (7a)$$

where, v_T = velocity due to ordinary diffusion
 v_T^S = velocity due to thermal diffusion (Soret effect)
 v_K = velocity due to kinetics at interface
 v_Y = velocity due to surface tension at grain boundaries

Because of the completeness of Equation (7), it is interesting to study the significance of each term. v_T is essentially the same as Equations (1), (3) and (6). The effects of interface kinetics and grain boundaries are found in the third and fourth terms in Equation (7), i.e., v_K and v_Y . When a steady state for brine migration has been established within a crystal, there is no surface tension effect and v is equal to zero. In this region, Anthony and Cline [18] quote values for K of 0.1 to 1.4 J/mole, depending upon approximate geometry of droplet.

When migration across grain boundaries occurs the surface tension must be considered and surface kinetics can become significant since most droplets change shape during migration; the surface tension is a function of the surface area exposed. When the droplet has reached a steady shape Anthony and Cline [11] calculate a value of 0.13 J/mole for K for a particular size droplet, $38 \times 38 \times 10$ microns. These are the only values for K available in the literature and they are for KCl.

Anthony and Cline reported that during migration larger droplets tended to lose fragments, and thereby become an 'optimum' size for migration. Also, migrating droplets changed shape until their thickness (L) approached 8-10 microns, and attained an optimum aspect ratio, $X/L = <3$. Consequently, the following conclusions can be made:

(1) As X approaches L , the surface tension effect goes to zero. The surface tension effect is only significant when crossing grain boundaries.

(2) As L decreases, K increases but there is a limiting value for K as L approaches 10 microns.

(3) The magnitude of the surface tension effect is about 10% of the magnitude of the kinetic interface effect.

(4) The total volume of brine contained in droplets of $L < 1$ mm, $X < 1$ mm, would be rather small, so the contribution from surface effects toward total volume migration can be insignificant.

A COMPARISON

The comparison cases use the TRUMP computer code to generate the thermal fields around the buried canisters as functions of time and position. The power output of the canister (at the time of emplacement) is 3.5 kW for the HLW case and 0.55 kW for the spent fuel (10-yr old) case. The details of the TRUMP calculations are found in

the work of Altenbach [19]. The canister is assumed to be 1 ft. in diameter and 8 feet long for the HLW case and 16 feet long for spent fuel. Further, there is assumed to be no ventilation for heat removal from the repository itself and perfect thermal contact is assumed to exist between the waste canister and the salt.

A computer code, BRINE, was written [20] in FORTRAN and, with appropriate values in the input file, or the code itself, the output gives the brine accumulation as a function of time. With various output controls operating, such quantities as temperature, temperature gradient, diffusion coefficients, velocity, etc., can be printed for values of time and position desired.

The thermal effects calculated for these two waste forms indicated that for the spent fuel the temperature remained below 60°C at the canister surface (maximum at 43 years) and the gradient in the salt was always less than 0.25°C/cm. With the HLW, however, canister surface temperatures were rising to above 500°C after 50 years (limit of TRUMP calculations), but the thermal gradient peaked at 32 years at 5.9°C/cm. The Anthony-Cline model predicts that droplet migration becomes effectively zero below some critical thermal gradient, and they observed this trend experimentally at about 1°C/cm [18].

A comparison of the results of each model will be informative. The results of the BRINE calculations are given for each model in Table 1. Notice that all of the above models give results which are within a factor of two of each other.

CONCLUSIONS

Conclusion 1: Equation (7) requires data which are not currently available in the literature.

In particular, Equation (7) is the most complete model because it accounts for most known phenomena occurring in the migration process.

Table 1: Results of Four Models Which Describe Brine Migration

Model	Volume of Brine Accumulated, at 0.5% water, liters		
	HLW (3.5 kW) 50 years	Spent Fuel (0.55 kW) 50 years	1000 years
Nernst	50.2	0.04	0.16
HOWS	89.4	0.17	0.78
Wilcox	63.8	0.06	0.23
Anthony-Cline (X=1, L=1 mm)	79.7	0.00	0.00

However, two of the terms are droplet size dependent and one needs data on the distribution of these sizes and number of droplets of each size. Such data are not available in the literature. The smaller of these droplets make very little contribution to the total volume of brine present. Also, Soret coefficients are available only for temperatures below 45°C and almost no data are available for NaCl [21, 22]. Similarly, the value for the kinetic potential is available only for KCl. However, these surface effect terms make less than 10% contribution to the velocity. (See Conclusion II).

Conclusion II: The diffusion phenomenon is rate controlling, for all practical purposes.

Equations (1), (3) and (6) had an original assumption that the migration process was concentration diffusion controlled, i.e., kinetic effects and Soret effects were considered not significant. Consequently, it is surprising that these three models predict results in such close agreement with Equation (7).

Conclusion III: Neglecting the difference between the thermal gradients in the liquid and in the solid could affect the results by a factor of 2.

All equations have the factor for thermal gradient in the liquid droplet. This is not easy to measure, but the thermal gradient in the solid can be measured quite readily.

Conclusion IV: The models may be ranked according to the difficulty of obtaining needed data: (1) < (6) < (3) < (7), or, the Nernst model is easier to apply than the Wilcox model, which is easier than the HOWS model, which is significantly easier than the Anthony-Cline model.

Existing data are inadequate to determine the relative accuracy of the various models. Because Equation (3) has been successfully applied to the Project SALT VAULT experiment [23] it is tempting to use it as the model for brine migration, however, Equations (1) and (6) should also be considered. The Anthony-Cline model requires the greatest amount of estimation for the parameters needed, although the additional details may contribute little to the final result (see Conclusion II).

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