LETTERS TO THE EDITOR

REMARKS ON "MIGRATION OF BRINE INCLUSIONS IN SALT"

In a recent paper, Pigford[1] calculated the threshold temperature gradients $\nabla T_{s,min}$, below which, according to theory, brine in salt should not migrate. His calculations were restricted to 25°C (his Tables II, III, and IV), and the change of $\nabla T_{s,min}$ as a function of ambient temperature in salt was not explored. Unfortunately, he used these $\nabla T_{s,min}$ values at 25°C to compare with the temperature gradients expected at salt repositories, ignoring the fact that the ambient temperature at such repositories will probably be much higher than 25°C. In fact, he cited a maximum salt temperature of 176°C as a typical repository condition. Consequently, in his conclusions, he overestimated the effects of the interfacial kinetics and grain-boundary surface tension on the amount of brine that can migrate into the cavity around a waste canister. The following discussions indicate that the migration resistances in the crystal lattice and at grain boundaries are small and should be ignored rather than being taken into account in a conservative estimation of the total brine in-flow in the cavity around a waste canister.

The theoretical equation for zero migration of a cubic inclusion within a salt crystal,

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

shows that $\nabla T_{s,min}$ is temperature dependent, because all parameters in this equation are functions of temperature. However, the term $(2 + K_l/K_s)/3L$ is not very sensitive to temperature change and can be treated as a constant. Even though no data are available at higher temperatures for the critical concentration difference required for the surface distortion accompanying dissolution at the hot surface and crystallization at the cold surface ΔC^*, the magnitude of ΔC^* tends to become smaller as temperature increases because higher temperatures promote equilibration. The numerical values for C_l, $(1/C_l)(dC_e/dT)$, and $(-\sigma)$ increase as temperature increases. As a result, $\nabla T_{s,min}$ calculated from Eq. (1) should become smaller as temperature increases. For example, values of $\nabla T_{s,min}$ at 25 (horizontally ruled area) and 50°C (vertically ruled area) are compared in Fig. 1. Pigford's Eq. (30) is inconsistent with his Eqs. (26), (27), and (29). In this calculation, Eq. (1), which is consistent, was used. Also, the numerical values for $(1/C_l)(dC_e/dT)$ listed in Table I were used because those given by Pigford (his Table I) are incorrect, as shown by Jenks and Claiborne.[4] The value 2×10^{-5} adopted by Pigford for $\Delta C^*/C_l$ was used at both temperatures. The values for $(-\sigma)$ were assumed to be 0.002 ± 0.001 (°C^{-1}) at 25°C and 0.004 ± 0.001 (°C^{-1}) at 50°C. No reported experimental or theoretical values of $(-\sigma)$ are available for $MgCl_2$-rich solutions, but the claim made by Jenks and Claiborne[4] that $(-\sigma)$ values for the natural inclusions in bedded salt range from 0.004 to 0.005°C^{-1} in the temperature range from 50 to 200°C is not valid,[5] and $(-\sigma)$ values could be as much as an order of magnitude higher.[5,6] The $(-\sigma)$ values assumed at 25 and 50°C in the present calculations (Fig. 1) are considered to be reasonable. Even though accurate threshold temperature gradients at higher temperatures cannot be calculated because of insufficient data, they should become smaller as temperature increases, as demonstrated in Fig. 1. Also shown in Fig. 1 (solid circles) are the 25°C values given by Pigford (his Table II).

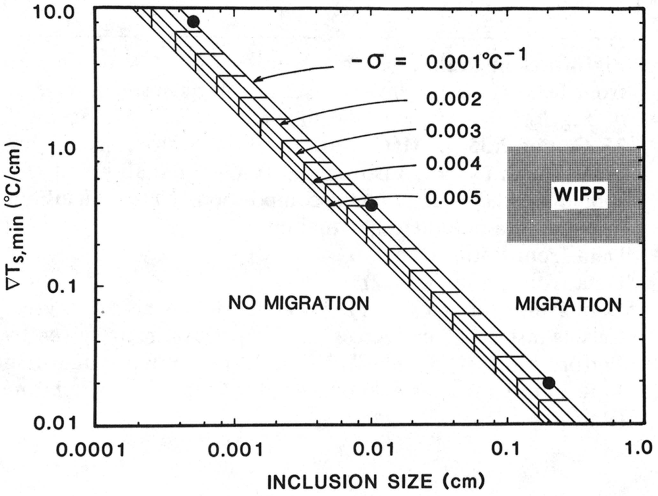

Fig. 1. Calculated threshold temperature gradients for 2.41 *m* $MgCl_2$ brine inclusions in NaCl single crystals as a function of inclusion size and Soret coefficient (σ) of NaCl at 25 (horizontally ruled area with $\sigma = -0.002 \pm 0.001$°C^{-1}) and 50°C (vertically ruled area with $\sigma = -0.004 \pm 0.001$). The value for $\Delta C^*/C_l$ was assumed to be 2×10^{-5} at both temperatures. Data given by Pigford (Ref. 1) are shown as solid circles. Most of the liquid in WIPP halite (stippled area) is predicted to migrate. Note that the vertical axis for the stippled area is temperature gradient (∇T_s) instead of $\nabla T_{s,min}$.

Pigford assumed a gradient of 0.2 to 1°C/cm for the Waste Isolation Pilot Plant (WIPP) wastes on the basis of the reports by Hunter[7] and George.[8] He also indicated that, according to Jenks,[9] most of the liquid in WIPP halite is contained in the few relatively large inclusions, with diameters of ~0.1 cm and greater (shown as the

TABLE I

Solubility-Related Parameters for Halite-Saturated 2.41 m $MgCl_2$ Brine*

T (°C)	C_l[a]	C_l[b]	$(1/C_l)(dC_e/dT) \times 10^{3}$[c]
25	1.934	1.91	2.493
50	2.057	2.02	2.646
100	2.364	2.32	2.829
150	2.725	2.66	2.910
200	3.152	3.02	2.911

*Pigford claimed that data given in his Table I were adopted from Jenks (Ref. 2). However, Jenks only gave values for 2.41 m $MgCl_2$ brine, which is equivalent to 2.12 M $MgCl_2$ at 25°C, not 2.35 M $MgCl_2$, as stated by Pigford. Note that even though C_l $(= C_e)$ is in molarity (M), molality unit (m) should be used to describe the composition of brine inclusions in halite in a polythermal situation.

[a] Data from Potter (Ref. 3).

[b] Data from Jenks (Ref. 2).

[c] Data from Potter (Ref. 3). The unit should be per degrees Celsius instead of in degrees Celsius per centimetre given by Pigford (Ref. 1) in his Table I. Data given by Jenks in Ref. 2 are wrong, as acknowledged by Jenks and Claiborne (Ref. 4).

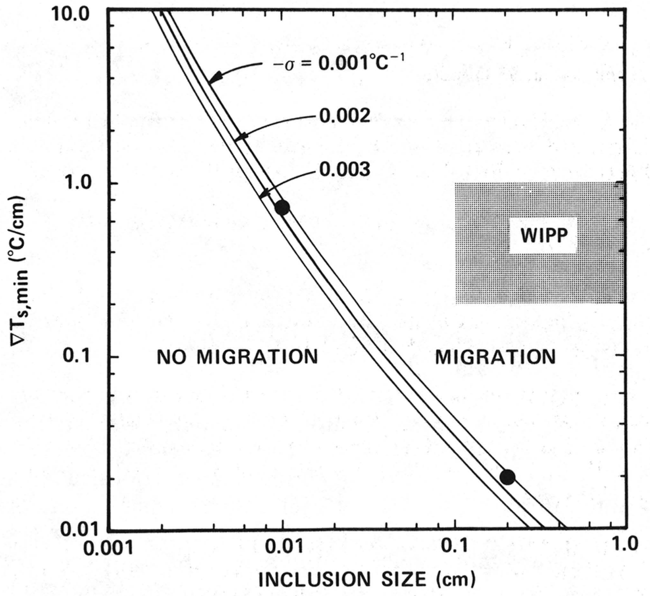

Fig. 2. Calculated threshold temperature gradients for 2.41 m $MgCl_2$ brine inclusions for migration across grain boundaries of halite as a function of inclusion size and σ at 25°C. Most of the liquid in WIPP halite (stippled area) is predicted to migrate across the grain boundaries. Note that the vertical axis for the stippled area is temperature gradient (∇T_s) instead of $\nabla T_{s,min}$.

stippled area in Fig. 1). Figure 1 shows that most of the liquid in WIPP halite will migrate even though the ambient salt temperature is assumed to be as low as 25°C. This conclusion remains valid even when the values reported by Pigford[1] (solid circles in Fig. 1 and his Table II) are used. Of course, migration of inclusions may terminate if the inclusions fission into smaller inclusions in the process of migration. On the other hand, the fluids contained in the smaller stationary inclusions may migrate after coalescing with those in bigger migrating inclusions through collision.[10,11] At present, the net effect of fissioning and coalescence of inclusions on the quantity of migrating fluid is not known.

The theoretical equation given by Pigford [his Eq. (35)] for the threshold temperature gradient for no migration across grain boundaries is inconsistent with his Eqs. (27), (33), and (34) and should be replaced by the following equation:

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

By using this equation and the numerical values given by Pigford for its parameters, except those for $(1/C_l)$ (dC_e/dT) and $(-\sigma)$, as discussed above, $\nabla T_{s,\,min}$ values were calculated for no migration across halite grain boundaries at 25°C as a function of σ and inclusion size. Results are shown in Fig. 2 together with Pigford's data (solid circles). Again, $\nabla T_{s,\,min}$ values at higher temperatures are difficult to estimate because of insufficient data. However, $\nabla T_{s,\,min}$ values undoubtedly tend to decrease as temperature increases. Most of the liquid in WIPP halite (stippled area in Fig. 2) is predicted to migrate across the grain boundaries.

The seemingly uniform distribution of brine inclusions in natural salt was cited by Pigford as evidence for the existence of finite values for ΔC^*. His arguments are not valid because he failed to incorporate the effect of the gravitational force as discussed by Anthony and Cline,[12] Roedder and Belkin,[13] and Jenks and Claiborne.[4] Even if we confirm $\Delta C^* \neq 0$ at 28°C, there is still no warranty that ΔC^* will not vanish at higher temperatures. Furthermore, as indicated by Jenks and Claiborne,[4] the radiation damage of the salt adjacent to the waste package in a repository conceivably can promote equilibrium conditions at the solution/salt interfaces. Jenks and Claiborne also indicated that thermal stresses in the salt might produce effects similar to those of radiation damage. These effects were totally ignored in Pigford's discussion.

Clearly, *most* of the liquid in WIPP halite is predicted to migrate not only through the lattice but also across the grain boundaries, even when the most favorable numerical values for the threshold temperature gradients are used. Contrary to Pigford's conclusions, the effects of interfacial kinetics and grain-boundary surface tension on the predicted migration rates of brine inclusions in the designed conditions of salt repositories are small, especially at higher temperatures, and should be ignored in a conservative migration rate estimation.

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REPLY TO "REMARKS ON 'MIGRATION OF BRINE INCLUSIONS IN SALT'"

The author is grateful that Chou's[1] remarks about Ref. 2 provide the opportunity to correct typographical errors and to update the evidence for a critical concentration difference, i.e., "critical supersaturation," for brine migration.

Equations (30) and (35) should be corrected as shown in Chou's[1] Eqs. (1) and (2), and the dimension of the second column of Table I should read "$^\circ C^{-1}$."

Chou adopts what is evidently newer solubility and Soret data, though unreferenced, to calculate the threshold temperature gradients at two different temperatures. His results, indicate by lines in his Figs. 1 and 2, differ little from the threshold gradients that this author calculated, shown by the solid circles in these same figures. It is good to learn that the new parameters adopted by Chou have so little effect on the predicted threshold gradients.

The remainder of Chou's comments seems to question that existence of the critical supersaturation ΔC^*. Before responding specifically to his comments, it is more constructive to summarize additional evidence not available when Ref. 2 was first submitted for publication. Olander et al.[3] show experimentally that the aspect ratio of a migrating inclusion in KCl depends on the critical supersaturation ΔC^*, as theoretically predicted by their Eqs. (1) and (A12). From their plots of the variation in inclusion size with applied temperature gradient (Fig. 7 of Ref. 3) at 63°C, Olander et al. deduce finite values of the critical ΔC^* shown in their Table 4. Also, by fitting their migration velocity data to the theoretical nonlinear kinetic model [their Eq. (18)], they deduce values of ΔC^* that generally agree with those deduced from aspect ratio.

Critical supersaturations derived for synthetic single crystals are not necessarily those for natural salt, where impurity cations in the crystals can account for most of the critical supersaturation[4,5] and can be expected to yield higher values of ΔC^* than for pure single crystals. Yagnik[6] observed that inclusions in rock salt were stationary for temperature gradients of 10°C/cm, whereas similar size inclusions in synthetic NaCl single crystals exhibited small but measurable migration at 10°C/cm. Yagnik's data show migration velocity as a function of $L \nabla T$ and indicate the existence of a threshold gradient for migration.

Within the range of these experiments, which were limited to very small inclusions, critical supersaturation is nonzero. Chou's statement that critical supersaturation disappears at high temperature is probably correct at some temperature, because the solid state finally disappears. It is speculative to conclude that critical supersaturation disappears within the temperature range of repository salt, and it is incorrect to infer that critical supersaturation does not exist in the lower temperature regions of a salt repository where it is important.

The theory of inclusion migration summarized in Ref. 2 assumes linear interfacial kinetics [see Eqs. (1) and (2), Ref. 2]. Olander et al.[3] have included a more general description of the interfacial kinetics to encompass the theory of Burton et al.,[7] who conclude that interfacial kinetics are linear when the critical supersaturation is large and are nonlinear when the critical supersaturation is small.

Reference 2 and Chou's comments speak of the migration of brine inclusions *across* grain boundaries, implying that migration proceeds from one halite crystal, across the grain boundary, and into an adjacent crystal. More recent data[6] on brine release from polycrystalline halite suggest that inclusions reaching a grain boundary then migrate along grain boundaries rather than across adjacent crystals. Mobility along these grain boundary pathways can be affected by stress concentrations, including thermal stress, and must be considered in more detailed calculations of the migration of brine inclusions in repositories.

The author agrees with Chou that his calculations show that the 0.1-cm brine inclusions in Waste Isolation Pilot Plant (WIPP) salt will migrate if exposed to the maximum temperature gradients quoted for the WIPP repository, but this