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106/3/CHP/9/12/85

NOTE TO: Walt Kelly

FROM: Charles H. Peterson

SUBJECT: TOPICAL REPORT, "BRINE MIGRATION IN SALT"

This memorandum presents comments on the subject report. In view of the importance of the subject to waste package design, the report has been reviewed in considerable detail. As a general comment, the report presents a useful overview of recent work on brine migration. There appear to be, however, many questions that should be answered before the impact of such migration on waste package design can be assessed. We would welcome further discussion of the subject. Specific comments follow.

Specific Comments

1. Crystal

The text is not clear on precisely what is a crystal and what is an intracrystalline inclusion. One can, for example, say that a crystal is a regular array of unit cells of the particular chemical compound under discussion. A brine inclusion would then simply be a quantity of brine contained in a cavity in that array. This would distinguish the brine inclusion from substances which actually enter the lattice structure.

Some discussion of the nature of grain boundaries would be helpful. In the crystallization of salt from a saturated brine, many nuclei (i.e., unit cells or small aggregates of unit cells) may form. Crystal growth occurs preferentially on the faces of such established nuclei. When the crystals growing from adjacent nuclei meet, their contact defines their grain boundaries, which can be quite irregular in three dimensions. A distinction between halite and polyhalite should also be made.

Put in these terms, one may question precisely what is the conceptual difference between the action of a brine inclusion on some inner face of the crystal containing it and the action on some external face of an adjoining crystal. Is it of importance to brine migration that crystals might be susceptible to movement away from each other at grain boundaries? These locations might thus represent channels through which brine could flow under an appropriate gradient and which are susceptible to changes in physical dimensions.

OFC : WMEG	8601240040	851025			
NAME : CHPeterson:gh	PDR WASTE	PDR			
DATE : 10/24/85	WM-16				

1246

OCT 25 1985

106.3/CHP/9/12/85

- 2 -

2. Brine Inclusions

Similarly, is there a conceptual difference between a brine inclusion and a brine pocket? A $2.7E+06 \text{ m}^3$ quantity of brine surely cannot be within a single crystal. At what size do pockets become inclusions? What fraction of brine is present as inclusions and what fraction is present as pockets in actual salt deposits? Does it matter if the brine is contained in some crystal other than sodium chloride? Is the discussion presented concerned only with brine migration in pure halite?

3. Terminology

Technical terms should be explained so that the information in the paper is more readily available to the reader. Examples are: diagenetic, isochemical, clastic, subgrain boundaries. Ambiguities should be avoided: the term "meteoric" could refer to a meteor or to the atmosphere. It would seem clearer to say "water ... is atmospheric in origin (p. 5)."

In Section III, salt is described as thermally diffusing through (an all-liquid) inclusion and then precipitating at a "cold" face. It appears more appropriate to say the salt recrystallizes at the "cold" face. "Precipitate" implies forming particulate solids that do not necessarily adhere to the cold face or to each other.

4. Laboratory Studies

a. Test materials

What evidence is there that Anthony and Cline did in fact use single crystals? What is the meaning of the statement that "interfacial kinetics control inclusion migration occurrence and velocity"? What interfaces are meant?

b. Findings of other investigators

Several statements are included without comment or evaluation by the writer (page 6):

- 1) Anthony and Cline suggest that there will be no migration below a certain critical inclusion size.
- 2) Surface tension of a grain boundary tended to pull droplets that has passed through a boundary back towards the boundary plane under a temperature gradient. This effect was negated if the temperature gradient was increased.

OFC	:WMEG	:	:	:	:	:	:
NAME	:CHPeterson:gh	:	:	:	:	:	:
DATE	:10/ /85	:	:	:	:	:	:

OCT 25 1985

- 3) If the gas phase is only water vapor, viscous gas flow controls transport of water through the vapor phase.

Does the absence of comment mean that the findings of Anthony and Cline are to be accepted by NRC as completely valid? We think all of the findings should be carefully limited to the experimental context in which they were developed. As to item 1, what is the critical size? Is it the same for other temperatures, temperature gradients, pressures, brine compositions, and phases?

For item 2, what is the surface tension of a grain boundary? There may be different surface energies at different boundaries, but it would seem more accurate to discuss surface tension at a boundary inasmuch as physical dimensions are relevant to the magnitude of the effect. Also, the grain boundary is probably not planar.

For item 3, since there seems to be no net flow of gas or vapor through an inclusion, the transport mechanism in the case of a pure water vapor phase is probably self diffusion. The slower migration velocity of water vapor through a gas phase can therefore be attributed to differences in molecular properties of the non-diffusing gas.

c. Thermal fracture of salt

The text notes that Bradshaw and McClain showed that Hutchinson salt fractured with considerable violence at 280°C. Perhaps exploded is a better term. It would be of interest to any reader to note that the vapor pressure of pure water at 280°C is about 63 atmospheres. This may incidentally provide an indication of the tensile strength of crystalline salt. The basis Bradshaw and McClain used for calculating the migration rate of brine released by fracturing (heat fracturing?) should be briefly stated and compared to the Jenks equation. Similarly, the Soviet work is noted as substantial in quantity but no conclusions or comparisons are offered.

The Hohlfelder tests of 1980 used salt block containing total volatiles (mainly water) of between 0.1 and 0.5 percent. What was the balance? At what percent gas does the transport mechanism become significantly affected? What "thermomechanical response of the salt" is meant as a determinant of water release rates? Given an extensive salt deposit, how does water release rate differ from brine migration?

OFC :WMEG	:	:	:	:	:	:
NAME :CHPeterson:gh	:	:	:	:	:	:
DATE :10/ /85	:	:	:	:	:	:

OCT 25 1985

106.3/CHP/9/12/85

- 4 -

d. Limits on migration

Some comment should be provided on the findings that only the larger inclusions crossed grain boundaries in thermal migration and that these inclusions stopped at least 7 cm from the heater hole. The presence of small inclusions closer to the heat source would be consistent with the known fact that the vapor pressure of a pure liquid is inversely proportional to the droplet radius. However, were these grain boundaries inside the test specimens? If so, then the migration was not intracrystalline. Boiling is suggested, but was any water vapor detected exiting the hole? On page 8, the text notes that smaller inclusions would not cross grain boundaries if the boundaries were tight. The meaning is not clear. The physical dimensions of $10^9 \mu\text{m}^3$ are better understood if expressed as 1 mm^3 .

Is there a rationale for the Olander observation that large inclusions tended to break up into smaller ones when a thermal gradient was present? How was it established that migration velocities were affected by dislocations present in the salt crystal? Do the presence of dislocations mean that the test specimen was not a single crystal? The statement that interfacial kinetics (i.e., the processes affecting movement at the grain boundaries) were rate controlling for inclusion migration velocity except for large inclusions seems circular. Previously it was noted that small inclusions apparently could not cross grain boundaries. How are rates measured when there was no observable process? In any case the above statement that the processes affecting movement at the grain boundaries controlled movement at those boundaries does not appear to be a new finding.

What is the basis for stating that the reason large inclusions can cross grain boundaries is that they intersect enough dislocations?

The effect of stress noted calls for more discussion. One wonders whether the brine migration under load is akin to extrusion. What was the direction of migration for the case of axial loading?

e. Gas-liquid inclusions

The meaning of the following is not clear: "Inclusions migrated up or down the temperature gradient in an indirect, two-dimensional manner." Yagnik apparently attributes this effect to a distortion in the solid lattice at the grain boundary, and the grain boundary is an area of minimum energy which would promote inclusion migration along

OFC :WMEG	:	:	:	:	:	:
NAME :CHPeterson:gh	:	:	:	:	:	:
DATE :10/ /85	:	:	:	:	:	:

OCT 25 1985

106.3/CHP/9/12/85

- 5 -

the grain boundary. "Minimum energy" would suggest rather that any molecule arriving at such a location would remain there.

f. Polycrystalline salt

Biggers and Dayton hot pressed polycrystalline salt samples to control microstructures. What kind of control was achieved? What microstructures are affected? Why were not macrostructures affected? What were the hot pressing conditions?

Migration velocities (of presumably liquid inclusions) were at least an order of magnitude higher than those observed in experiments on single crystals. This suggests that intercrystalline migration is faster than intracrystalline. B&D conclude that brine prefers to migrate along paths of high crystalline activity, i.e., grain and subgrain boundaries and crystal defects. This finding should be reconciled with the Yagnik one on "minimum energy."

g. In situ studies

The text, page 9, states brine was collected as condensate. Was it really condensed from a vapor state, or was it rather an exudate? It is of interest that substantially more moisture was collected when "considerable" shale was present. The Avery Island tests are not reviewed in the context of the proposed salt repository design. Details are incomplete. What is the meaning of "effective" moisture content? From what quantity of salt was the brine collected? Was the migration complete or did other brine migrate into vacated sites? Was any gas phase present? Again, brine movement was along microcracks or grain boundaries since no salt dissolution and no migration of brine into salt crystals were observed.

The Asse tests showed that increasing pressure in the borehole decreased brine collection, suggesting that pressure gradients significantly affect migration. What was the range of gradients used? Is the flow due to the pressure gradients used greater than the flow under a thermal gradient in the absence of a pressure gradient?

h. Models

All of the terms in equation (1) are defined but it would be a further help to understanding to provide dimensions. Only temperature is dimensioned, and that as °K. SI practice is simply K.

OFC	:WMEG	:	:	:	:	:	:
NAME	:CHPeterson:gh	:	:	:	:	:	:
DATE	:10/ /85	:	:	:	:	:	:

OCT 25 1985

106.3/CHP/9/12/85

- 6 -

Droplet velocity presumably is in m/s. The first term on the right side of the equation is dimensionally D/T , which works out to $m^2/s-K$ if the usual units apply. This is clearly inconsistent.

Reading further, Anthony and Cline found that the last term had relatively little effect on the calculated velocity. These two terms were intended to allow for interface kinetics and surface tension at the grain boundaries. However, on page 6, it was reported that the same authors suggested that interfacial kinetics controls both inclusion migration occurrence and inclusion velocity. Olander and Yagnik were also referenced for migration velocity of small inclusions (page 81). Clarification of these apparently conflicting statements is needed.

Equation 1, attributed to Anthony and Cline, includes these two terms. Yet on Page 11 the writer notes that researchers at Blakeley expanded on their work by including variables for these two effects. While the work of Chou cited as tending to support the Anthony and Cline conclusion on the lack of importance of interface kinetics and surface tension is noteworthy, it seems more important to include the basis for his conclusion that the migration velocity might be several orders of magnitude larger. However, later in the text (page 12) it appears that there are five reasons for the Chou conclusion, none of which involve interface kinetics or surface tension. The order of presentation should be revised to show the logic more clearly.

i. Uncertainties in Prediction

Considering the above critique, we cannot agree that intracrystalline migration is a fairly well understood process. The migration mechanisms for all-liquid and gas-liquid inclusion appear plausible but incomplete. For example,

- 1) Why do large inclusions breakup?
- 2) What is the role of defects and foreign bodies?
- 3) Why cannot small inclusions cross grain boundaries?
- 4) What fraction of the migration is accounted for by large inclusions?
- 5) Why were tests not done by injecting a nearly saturated brine into the test specimens rather than deionized water?

OFC :WMEG	:	:	:	:	:	:
NAME :CHPeterson:gh	:	:	:	:	:	:
DATE :10/ /85	:	:	:	:	:	:

OCT 25 1985

106.3/CHP/9/12/85

- 7 -

The brief citations on other effects (construction damage and radiation) serve to emphasize the importance of not transferring laboratory based models directly to field settings.

j. Conclusions

The overall conclusion appears to be that the state-of-the-art thus far does not permit dismissing the effect of brine migration on the isolation capacity of a salt repository. We wonder whether some guidance to further research could be provided by estimations of limiting conditions.



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cc: JTGreeves
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OFC	:WMEG	:	:	:	:	:	:
NAME	:CHPeterson:gh	:	:	:	:	:	:
DATE	:10/ /85	:	:	:	:	:	:
