THERMAL GRADIENT MIGRATION OF FLUID INCLUSIONS IN SINGLE CRYSTALS
OF SALT FROM THE WASTE ISOLATION PILOT PLANT SITE (WIPP)*

Edwin Roedder and H. E. Belkin

U. S. Geological Survey
959 National Center
Reston, VA 22092

ABSTRACT

Selected salt single crystals from core samples of bedded salt from the WIPP site have been tested to determine the rate of migration of their liquid-filled (fluid) inclusions in thermal gradients. Gradients of 1.5°C.cm⁻¹, maintained for periods of 3-10 days, at ambient temperatures of 108°-260°C, resulted in rates of movement of 1.2-5.4 cm.yr⁻¹ for cubic inclusions 1 mm on an edge. Inclusions 0.1 mm on an edge moved only ~30% as fast. Increase in ambient temperature and/or gradient increased the rate, in approximately direct proportion. The migration rate for inclusions in different parts of a given sample, however, may vary by a factor of 3, for unknown reasons, and some other interesting observed phenomena are still unexplained.

INTRODUCTION

Most salt beds contain at least some water in the form of liquid inclusions within salt single crystals, on grain boundaries, or in the larger intergranular cavities (i.e., pores). The storage of any heat-generating waste will establish thermal gradients in the salt. An aqueous liquid inclusion within or between crystals of a soluble salt, when placed in a thermal gradient, will continuously dissolve on the hot side and crystallize on the cold side of the cavity, thus causing the cavity, and its included liquid, to move up the thermal gradient toward the heat source. Inclusion movement is of conse-

quence in the design of a waste repository, as the included brines are probably more corrosive to possible canister materials than even a saturated NaCl solution.

Several studies (1, 2, 3) have addressed the problem of the rate of migration of fluid inclusions in salt, experimentally or theoretically. As many variables may affect this rate, and as the interrelations of these variables are not fully understood, experimental determinations are desirable on material from each specific site to be considered. Hence, samples from segments of core from the ERDA no. 9 borehole within the WIPP site in SE New Mexico were subjected to thermal gradients to determine the rate of migration of the fluid inclusions that they are known to contain (4). Salt beds are polycrystalline. In this paper we report measurements only on the movement rates within single crystals. The route taken by the fluid after an inclusion contacts a grain boundary is a much more complex process that is difficult to quantify with meaningful experiments.

PREVIOUS WORK

Wilcox (5) summarized the extensive work (111 references) on the nature and rate of inclusion movement in various substances. Migration of inclusions also causes degradation of laser crystals grown at high temperatures by the Czochralski technique (6). Most liquid inclusions move up the thermal gradient, but if the vapor bubble in the liquid is large relative to the liquid, and particularly if boiling occurs in the inclusion in the gradient, the movement may be in the reverse direction, down the thermal gradient (7, 8, 9). The rate of movement is independent of inclusion size in many systems but is strongly (and directly) dependent on inclusion size in others (5); there may be a threshold size below which no movement occurs (~10 μm in KCl)(10). Large inclusions in several hosts break up during movement (5, 11). Even in a given host, many factors may affect the rate of migration, such as gravity, composition and surface tension of the liquid, inclusion size and shape, host-crystal anisotropy, strain and imperfections, external stress, volume percent of vapor bubble and presence of a foreign gas in it. In salt, the rate of movement in a given gradient can be expected to increase as ambient temperature increases, because the thermal coefficient of solubility, although small at room temperature, increases greatly as temperature increases. Higher ambient temperature also increases the migration rate by increasing the solubility, the diffusion coefficients and the interface kinetics in any host; the increase in rate was found to be particularly striking in NaCl (Ref. 5, p. 20). That the small inclusions in the WIPP site salt have not moved measurably during geological time in the geothermal gradient (4) is perhaps an indication of an exceedingly slow rate under the natural gradient.
It may also be a result of other weak factors, such as gravity, counteracting the thermal gradient effect.

SAMPLE MATERIAL USED

Segments of core from the ERDA no. 9 borehole, taken from the Salado Formation at depth intervals 2061.2-2061.6 ft (hereafter designated "2061") and 2618.5-2619.0 ft ("2618") were used in most of the study, but some scoping runs were made on material from 2665.0-2665.1 ft ("2665") and one sample from a core taken from the Vacherie salt dome, Webster Parish, LA, at a depth of 1432.5 ft (12). Only crystals of salt >1 cm were used in these studies, in order to provide test samples that were large enough for our procedure.

EXPERIMENTAL TECHNIQUE

Our test samples were rectangular blocks 1 cm square and ~1-2 cm long, cleaved or cut from portions of single crystals of salt having suitable inclusions, with the final orientation of the block known relative to the crystallographic axes of the salt. In most runs, this orientation was parallel with the cubic (100) cleavage, but several other orientations were also used. To avoid damage to the salt and leakage of inclusions near the surface, cutting was done on a thin-bladed (0.012 in) wafering saw that was slow-speed, lubricated with cutting oil, and charged with very fine diamond grit. The sawn surfaces were smooth enough to permit optical examination and photography using only a cover glass and matching index liquid in lieu of a polish. The positions of the inclusions were photographed through the microscope against a series of fiducial marks (both nearby solid inclusions and fine lines scratched on the surface were used). The block was then placed in a 1x1 cm slot in the center of a cylindrical segmented Teflon (TFE) block (Fig. 1), in tandem with other similar salt blocks, with appropriately placed thermocouple junctions. This assembly was placed in a thermal-gradient furnace which had appropriate controls for both ambient temperature and superimposed gradients. No external stress or pressure was imposed on the sample. The gradient was established (in a horizontal direction) and maintained along the length of the cylinder, perpendicular to the section shown in Fig. 1. The samples were heated to the desired temperature gradient and ambient temperature slowly (<30°C/hr) to avoid thermal stress and held constant under these conditions for several days. After slow cooling, the samples were rephotographed, and the movement of the inclusions relative to the fiducial marks was measured.
Fig. 1. Cross section of thermal-migration-experiment sample holder. The sample (S) consists of a 1x1 cm block of salt, in a closely fitting slot between two hemicylindrical teflon (TFE) blocks (T₁ and T₂), 41 mm in diameter, which fit closely into a closed-end inconel tube (M) of 1.5 mm wall thickness and 18 cm length. Thermocouples (Tc) are placed at known positions along the sample.

RESULTS

Sample 2061

The largest group of data was obtained on sample 2061 and is summarized in Fig. 2. The points on Fig. 2 were derived as follows. For a given run, the observed migration rates in cm.yr⁻¹ for each measured inclusion were plotted (linear scale) against the initial volume of the inclusion in μm³ (logarithmic scale). A best-fit line was drawn through this data set on the basis of visual estimation. The intersections of this line with inclusion volumes were then plotted log-log as in Fig. 2. The original data points from individual inclusions in any given run showed some scatter on the plot of migration rate vs. log initial volume that differed from one sample to another. This scatter was usually <±50% of the migration rate given by the best-fit line for any specific volume inclusion. (Examples are shown in Fig. 3, discussed later). Many reasons for scatter can be suggested, in addition to measurement uncertainties, such as differences in inclusion composition, shape or percent vapor, collisions en route (these were seen to have taken place), and sample strain. Most inclusions had no bubble at the start, but all had a bubble at the end of a volume percent proportional to the ambient temperature used. The inclusions expanded by deformation of the host salt during the slow heat-up period and were presumably liquid-filled during the runs.

Several features of Fig. 2 should be noted. First, a rather uniform decrease in migration rate takes place as inclusion volume decreases, so that the rates for inclusions of 10⁹ μm³ volume (i.e.,
Fig. 2. Migration rates of various sizes of fluid inclusions in salt sample 2061, after 72-252 hours at 1.5°C cm⁻¹ gradient and the ambient temperatures indicated. Each curve is based on smoothed data for a group (17 to 44) of inclusions.

cubes 1 mm on an edge) are about three times those for inclusions of 10⁶ μm³ volume (i.e., cubes 0.1 mm on an edge). The relatively few inclusions that were flattened perpendicular to, or elongated parallel to, the direction of motion were checked particularly for deviations in rate; most of these that did deviate appreciably did so in the direction of higher rates for the flattened and lower rates for the elongated inclusions, but the amount of deviation and the numbers of such inclusions were too small for any meaningful quantification of the differences. The rates for the run at 260°C ambient are ~3.5 times those found for the other temperature runs for a given volume inclusion. The rate for runs at 108°, 160° and 260°C ambient show a consistent pattern, but that for the run at 201°C does not. In view of the differences we found between this sample and sample 2618 (see below), we suspect that the anomalously low rate for the 201°C run on sample 2061 may be a result of similar differences within parts of the same sample.

Effects of Crystallographic Orientation

Several runs were made to check the possible effects of the crystallographic orientation of the host relative to the direction of migration. Thirteen inclusions in a piece of sample 2061 cut to obtain movement perpendicular to the dodecahedron (110) yielded a rate identical with that of 27 inclusions cut to move perpendicular to the cube (100), within the precision of the measurements (Fig. 3).
The two pieces were run at 201°C ambient simultaneously, and the inclusions covered the same size range (1x10^5–5x10^8 μm^3). Another run, at 157°C ambient, again using two pieces of sample 2061, showed a rate for 44 inclusions moving perpendicular to (100) that was less than one third of that for 19 inclusions moving perpendicular to the octahedron (111). This difference may not be solely the result of the crystallographic orientation, however, as the rate for movement perpendicular to (100) was well under (and that for movement perpendicular to (111) was well over) the rates for other runs perpendicular to (100) on this same sample in this ambient temperature range, as given in Fig. 2.
Behavior of Small Inclusions

Small inclusions (10^4-10^5 \mu m^3) move so little that many are below the threshold for reliable detection of movement with our method (\sim 10 \mu m). With runs of the durations used here, this threshold corresponded to rates in the range 0.01-0.1 cm yr^{-1}. Determinations on such small inclusions are of little practical interest, as usually very little of the total water content in any given salt is present as inclusions in this size range (4). Their movement, however, does have some theoretical interest. The best-fit line through the bulk of the data on a plot of movement vs. log initial inclusion volume, such as Fig. 3, was generally a straight line that appeared to intersect the ordinate at a threshold volume, below which no movement could be detected, and some inclusions of \sim 10^5-10^6 \mu m^3 volume were found not to have moved measurably. However, on some of the runs, some inclusions as small as 2 \times 10^4 \mu m^3 and hence, well below the various apparent intercepts at "zero movement", were found to have migrated small but finite amounts. The sensitivity of the method used was too poor to permit quantification, but these points suggest that perhaps the best-fit line should not intersect the ordinate but should approach it asymptotically.

Intra- and Intersample Comparisons

Several runs were also made on sample 2618 to determine whether there were differences between samples, even though other studies of the fluid inclusions in these various samples had shown that intra-sample variation was apparently as large as intersample variation (4). The results of one of these runs (Fig. 3) show that 15 inclusions in a sample of 2618 moved at rates more than three times those for sample 2061 run at the same time. Actually, the 2618 sample was run between the two pieces of 2061. No larger inclusions were present in the sample of 2618 shown in Fig. 3, so another run was made on 42 inclusions in sample 2618 at 202°C ambient and 1.5°C cm^{-1}. Most of these were larger than 10^7 \mu m^3. This run yielded a line that had the same slope as that shown for 2618 on Fig. 3, but even greater movement rates. Thus, at 10^8 \mu m^3, the rate was 2.9 cm yr^{-1} rather than 2.4 cm yr^{-1} as shown in Fig. 3.

Another piece of sample 2618 was cut for movement perpendicular to (110) and run at 157°C ambient together with the two pieces of sample 2061, one perpendicular to (100) and the other to (111), referred to above. In this run, inclusions in sample 2618 migrated at a rate intermediate between those for the two pieces of 2061 (e.g., at 10^8 \mu m^3, the rates were 0.5 cm yr^{-1} [2061, (100)]; 1.3 cm yr^{-1} [2618, (100)]; and 1.7 cm yr^{-1} [2061, (111)].
From the above data, three-fold differences are readily apparent in the migration rates for inclusions in different pieces of a given WIPP sample and for different WIPP samples; differences due to crystal orientation alone may be of this same order of magnitude or may be negligible, as we have not eliminated the intra-sample variation. We have not recognized any differences between the parts of a given sample that yield different migration rates. Additional runs and tests are being planned in an attempt to isolate the several effects.

Comparison with a Sample from a Louisiana Salt Dome

Inclusions in some salt from cores in the Rayburn and Vacherie salt domes in Louisiana have been found to contain solutions that were close to simple NaCl-H₂O brines, i.e., they contain relatively small amounts of other ions (12), rather than the bitterns present in the WIPP samples (4). As the presence of ions other than Na and Cl affects the solubility of NaCl, and as this solubility value enters into any theoretical calculation of the rate of migration (R. W. Potter II, pers. comm., 1979), we made a comparison run using a block of salt from the Vacherie dome, at 1432.5 ft depth, and WIPP samples 2061 and 2618, at 157°C ambient and 1.5°C.cm⁻¹ gradient. The Vacherie sample was cut parallel to (100) and contained 16 small inclusions (2.0x10⁴⁻2.7x10⁶ μm³). Only 3 of these were >5x10⁵ μm³, so the amount of movement was generally small, and some showed no detectable movement, but the apparent slope and migration rate on a plot like Fig. 3 were about the same as the WIPP sample 2061.

Migration Rates at Other Ambient Temperatures and Gradients

At the start of this work, some rough scoping experiments were set up to provide guidance for the experimental design of the migration runs. The temperature control and measurement were both much inferior to those used in the runs described above, but the values obtained (Table 1) provide at least some rough indications of the magnitude of the effects of these higher ambient temperatures resulting in faster migration.

Changes in Inclusion Shape with Movement

Most inclusions studied in this work were cubic or nearly cubic as found. At the end of the run, after the inclusions had moved tens or hundreds of micrometers, they were still nearly cubic if the original volume was ≤ 2.7x10⁶ μm³. Larger inclusions were quite different in shape at the end of the run regardless of the ambient temperature used, from 108° to 260°C. The advancing front surface
Table 1. Migration Rates Found in First Rough Scoping Experiments.

<table>
<thead>
<tr>
<th>ERDA-9 Core Sample</th>
<th>Ambient temp (°C)</th>
<th>Gradient (°C.cm⁻¹)</th>
<th>Time (hrs)</th>
<th>Inclusion size (μm³)</th>
<th>Migration rate (cm.yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2665.0-2665.1'</td>
<td>250</td>
<td>4</td>
<td>4</td>
<td>5.5x10⁹</td>
<td>109</td>
</tr>
<tr>
<td>2606.5-2609.9'</td>
<td>278</td>
<td>20</td>
<td>34-60</td>
<td>2.4x10⁷</td>
<td>1.8</td>
</tr>
<tr>
<td>2606.5-2609.9'</td>
<td>340</td>
<td>20</td>
<td>31</td>
<td>1.0x10⁶</td>
<td>10</td>
</tr>
<tr>
<td>2606.5-2609.9'</td>
<td>320</td>
<td>20</td>
<td>23</td>
<td>3.8x10⁵</td>
<td>11</td>
</tr>
<tr>
<td>2606.5-2609.9'</td>
<td>320</td>
<td>20</td>
<td>23</td>
<td>6.4x10⁴</td>
<td>8.8</td>
</tr>
<tr>
<td>2606.5-2609.9'</td>
<td>330</td>
<td>20</td>
<td>26</td>
<td>8.0x10³</td>
<td>0.8</td>
</tr>
<tr>
<td>ERDA No. 7</td>
<td>248</td>
<td>1.0</td>
<td>84</td>
<td>4.3x10⁵</td>
<td>6.7</td>
</tr>
<tr>
<td>ERDA No. 7</td>
<td>248</td>
<td>1.0</td>
<td>84</td>
<td>1.0x10⁶</td>
<td>3.3*</td>
</tr>
</tbody>
</table>

*This value determined by the line-intercept method described in text, based on the largest inclusion (above) and 11 others.

became smaller though still flat and square in outline, and the sides became curved, forming a tapered, bullet shape. The rear face remained approximately the same size and shape as originally, but a thin sheetlike peripheral fringe of liquid had developed on all four edges, tapering off to the rear (Fig. 4). We do not know whether this shape developed early in the run and represents a dynamic equilibrium shape or whether it was still in the process of evolving at the end of the runs. Inclusions forced to migrate perpendicular to (110) and (111) formed similar fringes trailing off the outer edges. Somewhat similar trailing "veils" formed at the edges of migrating flat disk-like inclusions in synthetic KCl (10).

Reverse Motion (Down the Gradient) for Gas-Rich Inclusions

Only five gas-rich inclusions were found in the samples used in these runs. All five were in sample 2061 material and moved down the gradient, toward the cold end, at the following rates:

<table>
<thead>
<tr>
<th>Ambient temp (°C)</th>
<th>Gradient (°C.cm⁻¹)</th>
<th>Time (hrs)</th>
<th>Initial size (μm³)</th>
<th>Vol gas (%)</th>
<th>Migration rate (down)(cm.yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>108</td>
<td>1.5</td>
<td>252</td>
<td>9.8x10³</td>
<td>28</td>
<td>0.42</td>
</tr>
<tr>
<td>108</td>
<td>1.5</td>
<td>252</td>
<td>9.8x10³</td>
<td>28</td>
<td>0.45</td>
</tr>
<tr>
<td>108</td>
<td>1.5</td>
<td>252</td>
<td>4.0x10⁶</td>
<td>14</td>
<td>1.67</td>
</tr>
<tr>
<td>160</td>
<td>1.5</td>
<td>183</td>
<td>1.6x10⁶</td>
<td>28</td>
<td>0.69</td>
</tr>
<tr>
<td>160</td>
<td>1.5</td>
<td>183</td>
<td>5.5x10⁶</td>
<td>25</td>
<td>3.10</td>
</tr>
</tbody>
</table>

This movement was not only in the reverse direction from that for liquid inclusions, but was considerably faster than that for liquid inclusions of the same size (from 1.25 to 10 times greater).
Fig. 4. Inclusions in salt sample 2618 before (above) and after (below) a 156-hour run at 202°C ambient and 1.5°C.cm⁻¹ gradient. The large inclusion has split into gas-rich and liquid-rich parts that moved in opposite directions relative to the thermal gradient, which increased to the left. The original position of the inclusion can still be seen, outlined by minute specks of unidentified solids (see arrows). The fiduciary mark (a vertical scratch) is visible to the left of the inclusion in the upper photo; it is almost invisible in the lower photo, because of the illumination needed to see the (much larger) bubble, but a series of small specks to the right act as internal reference points. Scale bar = 500 μm.

Splitting of Inclusions into Vapor and Liquid

One run yielded a strange result that has yet to be duplicated. As far as we are aware, nothing was peculiar in the material used or the operation of the run. The material was sample 2618, cut to yield movement perpendicular to (100). The gradient was 1.5°C.cm⁻¹ and the ambient temperature was 202°C, for 156 hours, a combination that had been used in other runs as well. At the end of the run, however, many of the measured inclusions were found to consist of two separate parts, a small, asymmetric, dumbbell-shaped, vapor-rich inclusion (>5 vol % of original inclusion) that was now on the cold side of the original inclusion location, i.e., it had moved down the gradient, and a larger liquid inclusion, with a vapor bubble, that had moved up the gradient (Fig. 4). The actual migration distance of the two individual parts ranged widely from 15 to 725 μm; all inclusions >10³ μm³ in volume (12 total) had liquid moving farther than gas: liquid moved 437 to 725 μm up the
gradient, and gas moved 15 to 475 \( \mu m \) down the gradient. Four of the seven inclusions having \(<10^7 \mu m^3\) volume (down to \(1.5 \times 10^7\)) had gas movements down the gradient that were greater than the corresponding liquid inclusions up the gradient. We cannot convert these movements to rates because we do not know at what stage during the run the splitting occurred; if it occurred at the start of the run, the liquid movements up the gradient yield rates in the same range as that found in other runs that did not exhibit splitting. A very few of the inclusions in some other runs showed similar splitting, but no other run yielded such a consistent splitting. We do not understand this phenomenon at present, but are investigating several possible explanations. We also do not understand the shape of the gas-rich part. Fig. 4 shows a typical example at the conclusion of the run; the vapor-rich inclusion consisted of two connected parts, a smaller, flattened, somewhat cubic mass of liquid at the front (in the direction of the movement), and a larger, almost spherical mass of gas (trailing), with a narrower neck between. A similar geometry of liquid and vapor parts of a vapor-rich inclusion moving down gradient has been seen in ADP crystals (5), but with quite different shapes.

DISCUSSION AND CONCLUSIONS

The rates of migration of fluid inclusions measured in these experiments are mostly well below those determined by Bradshaw and Sanchez (1) for inclusions in salt from Hutchinson, Kansas, but because the inclusions they used were much larger, the data would not be expected to be comparable. The volumes of the smallest inclusions they used (\(8 \times 10^9 \mu m^3\)) were approximately an order of magnitude larger than our largest inclusions, and their largest were three orders of magnitude larger (\(1 \times 10^{12} \mu m^3\)). Although they do not specify the sizes of the individual inclusions they measured, a rough extrapolation of their data to the smaller size inclusions we ran (using Fig. 2), at \(1.5^\circ C.cm^{-1}\), yielded a migration rate only 34% higher than we found. Jenks (3) reviewed migration rate data for inclusions in KCl and in Kansas salt. He derived an empirical equation for the maximum migration velocity per unit temperature gradient for such salt as a function of temperature only that yields migration rates greater than we found for \(1 \text{ mm}^3\) inclusions.

The application of these data to engineering design of the WIPP site is not simple. The bulk of the water in these beds is probably present in a relatively few large (\(>>1 \text{ mm}\)) inclusions (4) whose rates of migration could not be measured by the procedures used. Even in the necessarily biased samples that were used, the bulk of the water was present in the relatively few inclusions \(\sim 1 \text{ mm}\) on an edge. Hence, the maximum migration rates found here (i.e., those for \(1 \text{ mm}\) inclusions) are the most nearly appropriate for calculating a minimum total rate of influx into a canister chamber.
Perhaps the most important aspect of the present work is the discovery that different samples from the same core, and even different parts from the same piece of core, can yield migration rates differing by a factor of 3. As differences of this magnitude exist between the otherwise apparently identical large crystals of salt selected for this study, it would be hazardous to extrapolate these rates to the inclusions in the major part of the salt beds, which consists of smaller crystals than we used. Hence, it would be equally hazardous to extrapolate these rates to a calculation of expected brine inflow in a given storage scenario.

REFERENCES