

Natural Convection Controlled Dissolution of KCl in H₂O-KCl Solutions Saturated and Unsaturated with NaCl

John Walden

FMC Corporation
Princeton, New Jersey

Allen P. McCue

FMC Corporation,
New York, New York

Hung Tsung Chen

Newark College of Engineering,
Newark, New Jersey

ABSTRACT

The natural convection controlled dissolution of KCl crystals was studied in H₂O-KCl solutions saturated and unsaturated with respect to NaCl. The dissolution was followed by continuous recorded weighings and time lapse photography. Single and multiple KCl crystal arrangements were run at 70°C.

When a NaCl saturated solvent was used, NaCl crystallized from solution in the vicinity of the dissolving KCl face. Although lower rates were obtained with such solvents, the dissolution process continued for run times up to 90 hours under a 43g/l KCl unsaturation. Dissolution is faster at the top of a crystal situated between top and bottom inert boundaries and only exposed to solvent at one vertical face. The rate of advance at the top boundary is 0.26 cm/hr (0.21 ft/day) in a solvent unsaturated with NaCl and 0.11 cm/hr (0.069 ft/day) for the case where NaCl crystallizes from solution.

Knee shaped profiles develop in solvents unsaturated with NaCl. Dissolution takes place across the entire crystal height including the bottom. Nearly linear profiles develop when NaCl crystallizes from solution. In this case there is no dissolution at the bottom edge of the crystal in contact with the inert boundary.

INTRODUCTION

The natural convection controlled dissolution process has been studied by Durie and Jessen (1964, p. 183) using salt blocks in water, by Husband and Ozsahin (1967, p. 234) using synthetic

potash ore blocks in water and by others, (Wagner, 1949, p. 1030; Wilke, 1953, p. 663; Dommers, 1963). The general mathematical approach is to use the heat transfer analogy.

The objective of this work was to study the dissolution of KCl crystals in H₂O-KCl solutions saturated and unsaturated with respect to NaCl. When NaCl saturated solutions are used, NaCl crystallizes from solution as the KCl dissolves. Particular attention was given to the affect the crystallized NaCl had on the continuing dissolution of the KCl. This paper is primarily intended to present some typical dissolution data together with a word and picture description of the dissolution process.

The KCl crystals were usually sandwiched between inert top and bottom glass boundaries and sealed so that only one vertical face dissolved. The affect of these boundaries is described. In some cases there was no top boundary so dissolution took place from one vertical face and the top of the crystal. The dissolution of arrays of KCl crystals is also described. This work extends the time variable beyond the first eight minutes of dissolution as presented by Husband and Ozsahin (1967, p. 234). Their work showed good agreement between theory and experiment in the comparison of initial rates. In the present work experiments were continued to about 90 hours. Theoretical work in progress will attempt to develop an equation that can describe the extended time data for dissolution with and without crystallization of NaCl.

THEORY

Natural convection and molecular diffusion control the mass transfer assuming negligible forced

convection. Equation 1 describes the dissolution of a vertical KCl crystal face with no crystallization of NaCl. This equation is based on a semi-infinitely tall dissolving face with no end effects but it adequately describes early time dissolution of finite crystals lying between top and bottom inert boundaries.

$$N_{\text{avg}} = \frac{0.123 C_s^{5/4} D^{3/4}}{\nu^{1/4} H^{1/4}}, \text{ g/sec/cm}^2 \quad (1)$$

where total rate = $(N_{\text{avg}}) (\text{Height} \times \text{width}) = \text{g/sec}$

and $(N_{\text{avg}}) (\text{Height}) = \text{g/sec/cm width}$

N_{avg} = average dissolution rate over entire height, g/sec/cm².

C_s = concentration difference between bulk concentration and the salt surface, g moles/l.

D = diffusivity, cm²/sec.

ν = kinematic viscosity, cm²/sec.

H = total height of the vertical dissolving surface, cm.

EXPERIMENTAL

Optical grade KCl crystals measuring 0.63 × 2.54 × 5.08 cm were obtained from the Harshaw Chemical Co. The crystals were either used as received for the single crystal experiments or were cleaved to size for the multiple crystal experiments. Preparation for the single crystal experiments involved sealing four sides between microscope glass slides using epoxy cement. The fifth side (the back of the crystal) was sealed with just epoxy cement, see Figure 1. Note the channel in front of the exposed crystal face. This served to catch the crystallized NaCl. The mounted crystal was suspended in a battery jar of quiescent (unstirred) solvent from an automatic recording balance according to the following procedure:

The inside surface of the preheated dry battery jar was swabbed with hot mineral oil at the level where the top of the solvent surface would be to prevent salt from creeping up the glass walls. About 2.1 of the heated solvent was added to the battery jar and the jar was placed into a thermostated bath. The sample previously heated to slightly above the experimental temperature was

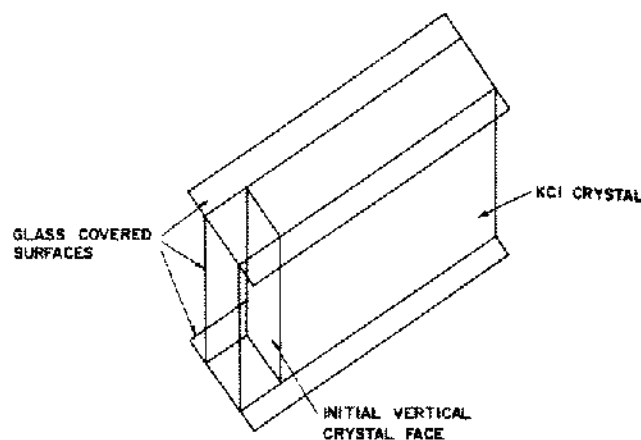


Figure 1. Single KCl crystal enclosed on five sides, leaving one vertical face open to solvent contact. Note the open glass channel in front of the exposed crystal face.

immersed in the solvent and attached to the balance using wire hangers. Hot mineral oil was carefully poured onto the top solvent surface to form a layer about one-half inch thick to minimize evaporation. Illuminating lamps directed at the top solution surface reduced surface cooling. The recording balance was placed in operation to continuously record sample weight changes. Time-lapse photographs were taken of the sample at right angles to the dissolving face through above five inches of water and salt solution. The crystal remained essentially motionless throughout the experiment.

Solvents were prepared with reagent grade sodium and potassium chloride. When NaCl saturated solutions were prepared approximately 2 additional grams per liter NaCl were added above that required for NaCl saturation to be certain the solution was saturated. The solvent compositions are given in Table I.

The KCl crystals were obtained measuring 0.63 × 2.54 × 5.80 cm. By orienting and sealing the crystals in three different ways three different vertical face heights were exposed to the solvent. Dissolution rates were calculated to a common sample width of one cm.

The observed balance weight loss in g/sec was corrected for solution buoyancy and crystallized NaCl, which was able to be weighed because it was kept within the glass rectangular channel at the front of the crystal (Fig. 1). After applying the buoyancy correction the corrected g/sec was divided by the sample width to obtain g/sec/cm width.

TABLE 1. Solvent Compositions

Run No.		
17	175 g/l KCl	unsaturated with
20	228 g/l NaCl	respect to NaCl
22		
15		
16		
23	175 g/l KCl	saturated with
18	242 g/l NaCl	respect to NaCl
28		
26		

All solvents had 43 g/l KCl unsaturation at 70°C.

If it is desired to make measurements on the photographs or photographic tracings the scale may be determined from the crystal height stated in the accompanying description. Each frame should be scaled separately because of non-uniform dimensional changes occurring in the photographic processes.

RESULTS AND DISCUSSION

The following is a general description of the dissolution process:

KCl crystals dissolve when placed in a water solution unsaturated with respect to KCl and either unsaturated or saturated with respect to NaCl. As the crystal dissolves a thin boundary layer forms which is denser than the bulk solvent. Consequently, the boundary film falls down the face of the dissolving crystal under the influence of gravity. If the solvent is saturated with respect to NaCl, NaCl crystallizes from solution, probably at the solution-crystal interface in the vicinity of the moving boundary layer. The crystals of NaCl grow to some size as they fall down the face coming to rest on accumulations of NaCl or on the bottom ledge of the glass enclosure. Approximately 0.4 cm³ of NaCl crystallizes for 1 cm³ of dissolved KCl at 70°C. The net effect is to form a cavity in front of the dissolving face that is only partially filled with crystallized NaCl.

The KCl crystal dissolves faster at the top than at the bottom because the dissolution is a mass transfer process partially controlled by the boundary film thickness which is thicker at lower lying positions. Because of the difference in the top and bottom dissolution rates a dissolving KCl crystal develops a characteristic knee profile in solvents unsaturated with NaCl. A nearly linear profile develops in the presence of crystallized NaCl.

More detailed discussions of the dissolution process are given in the explanatory comments accompanying the following Figures:

Figure 2 - Run 16

This is a 2.54 cm tall crystal in a solvent saturated with NaCl. Only the left vertical face is exposed to solvent. The white or light colored area is the field of crystallized NaCl crystals. The dark areas within the NaCl field are solvent filled voids.

There is no dissolution from the bottom front of the crystal. The rate of advance at the top inert boundary averages 0.11 cm/hr.

Prior to 40 hours the profile is irregular and slightly concave up. At 40 hours the profile is nearly linear. Once the top of the dissolving face reaches the back of the enclosure (vertical inert

Elapsed Time, Hours

0



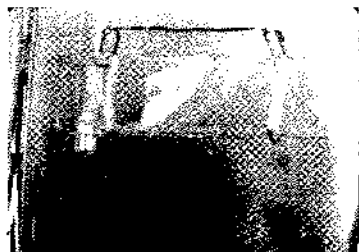
5



10



15



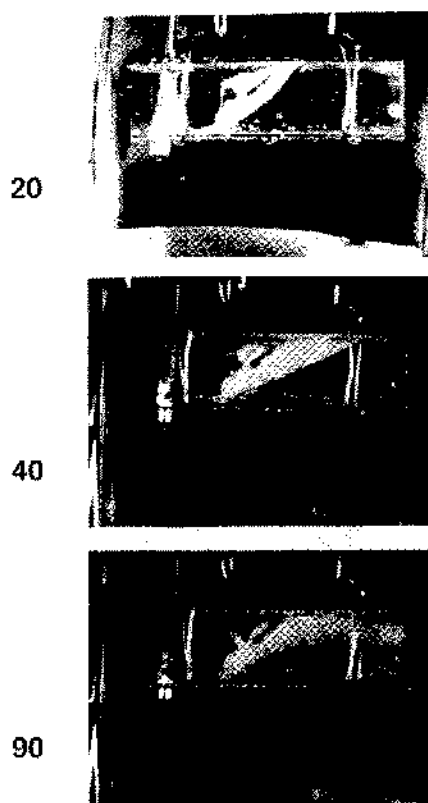


Figure 2. Run 16.

boundary) the right most part of the dissolving face starts to approach the horizontal. The dissolving face generally remains slightly irregular. Run 16 dissolution data are given in Figure 13.

Figure 3—Run 17

This is a 2.54 cm tall crystal in a solvent unsaturated with respect to NaCl. The left vertical face is the only one exposed to solvent.

The typical knee profile develops almost immediately. An enlarged sketch of the knee profile is given in Figure 4.

Dissolution rates are greater than for the case where NaCl crystallizes from solution. They also hold steadier (Fig. 13). The rate of advance at the top boundary averages 0.26 cm/hr. Smooth dissolving faces are usually observed.

Figure 4

This is a sketch of a typical knee profile of a KCl crystal dissolving from only the left side and situated between top and bottom inert boundaries. The crystal had an initial vertical face. This profile occurs when NaCl does not crystallize from solution. Note the short vertical portion of the

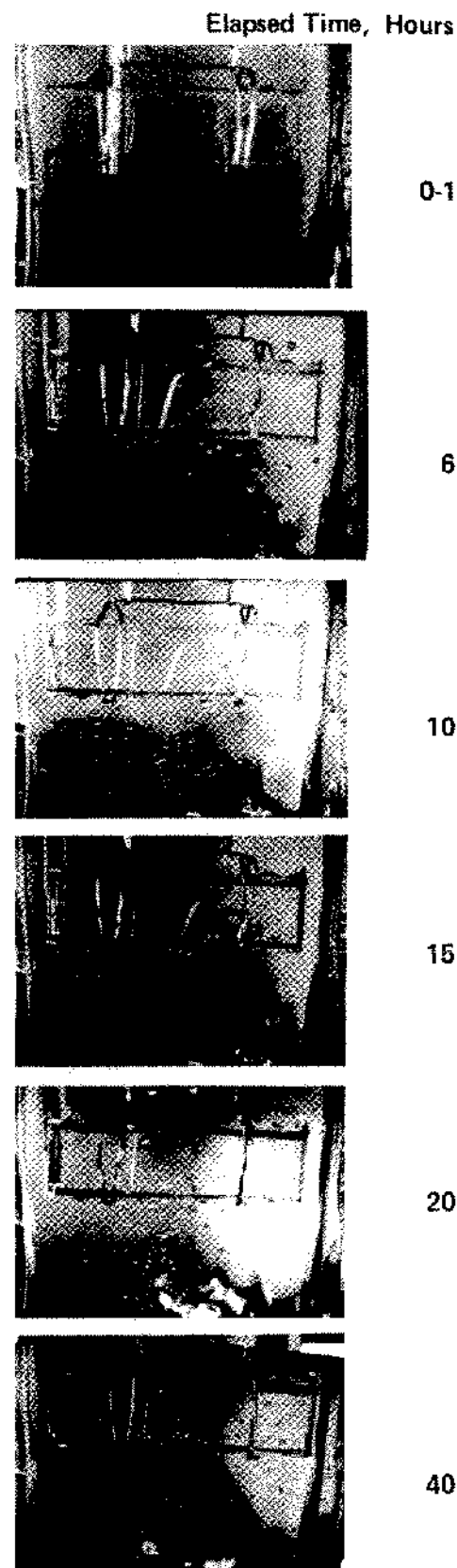


Figure 3. Run 17.

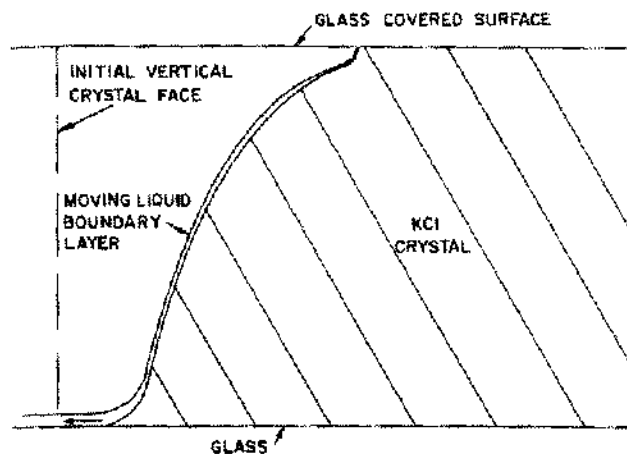


Figure 4. Sketch of typical knee profile of a KCl crystal dissolving in a solution unsaturated with respect to NaCl. Note the crystal profiles near the top and bottom inert boundaries.

dissolving face at the top boundary and the tail at the bottom boundary. The short vertical section is due to an end effect of the top inert boundary. This is where the boundary layer is first established. The tail results from the limited diffusion of fresh solvent through the nearly horizontal boundary layer flowing on the flat bottom boundary.

Figure 5—Run 20

This is a 5.08 cm tall crystal in a solvent unsaturated with respect to NaCl. The left vertical face is the only one exposed to solvent.

The typical knee profile develops almost immediately. Smooth dissolving faces are usually observed.

The top of the dissolving face reaches the back (right) wall of the enclosure in 10 hours for an average rate of advance of 0.25 cm/hr. The average rate over the first hour was about 390×10^{-6} g/sec/cm width which was followed by a 13% decline in 7 hours. Equation 1 predicts 351×10^{-6} g/sec/cm width.

Figure 6—Run 22

This is a 2.54 cm tall crystal in a solvent unsaturated with NaCl. Both the left vertical and top horizontal faces are exposed to solvent. (There is no top inert boundary).

Dissolution is greater in from the left than down from the top. The left dissolving face is nearly linear and inclined slightly. A nearly horizontal top dissolving face is maintained throughout the run. Both the faces are smooth. Note that the bottom of the left face is dissolving. Compare this with

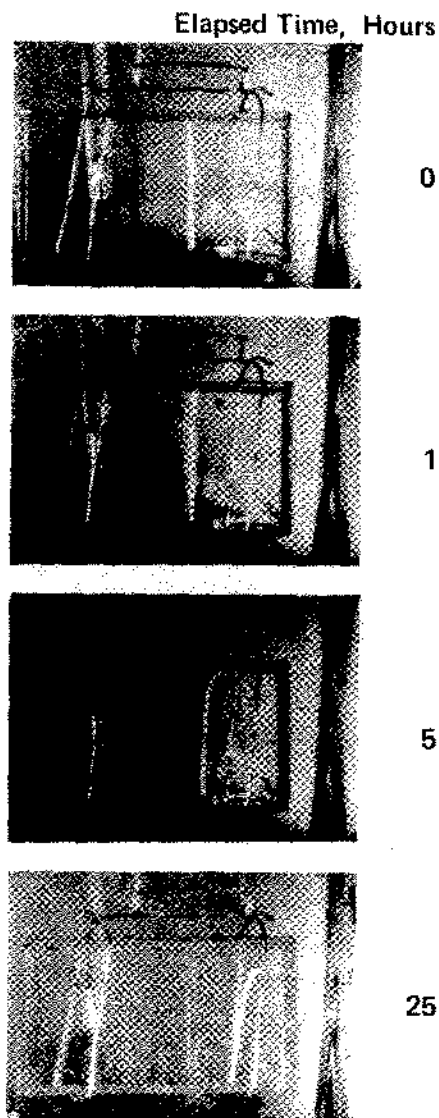


Figure 5. Run 20.

Figure 7, Run 23. The remaining KCl is shown as the cross-hatched areas in the 0 and 10th hour frame tracings.

Figure 7—Run 23

This is a 2.54 cm tall crystal in a solvent saturated with NaCl. Both the left vertical and top horizontal faces are exposed to solvent.

The dissolution rate is slower than the case where solvent is unsaturated with NaCl, see Figure 6, Run 22. As soon as solvent contacts the top crystal face NaCl crystallizes and settles on the top surface. This reduces the rate of access of fresh solvent to the top face. No dissolution takes place

Elapsed Time, Hours

0



5



10



15



20



Figure 6. Run 22.

at the bottom of the left face. This also occurs when only one vertical face has access to solvent as shown by Run 16 (Fig. 2). Part of the crystallized NaCl is lying on the bottom of the glass channel in the 5th and 10th hour frames. In the 30th through 60th hour frames it can be seen resting on the crystal itself.

Elapsed Time, Hours

0



5



10

No frame at
15th hour

20



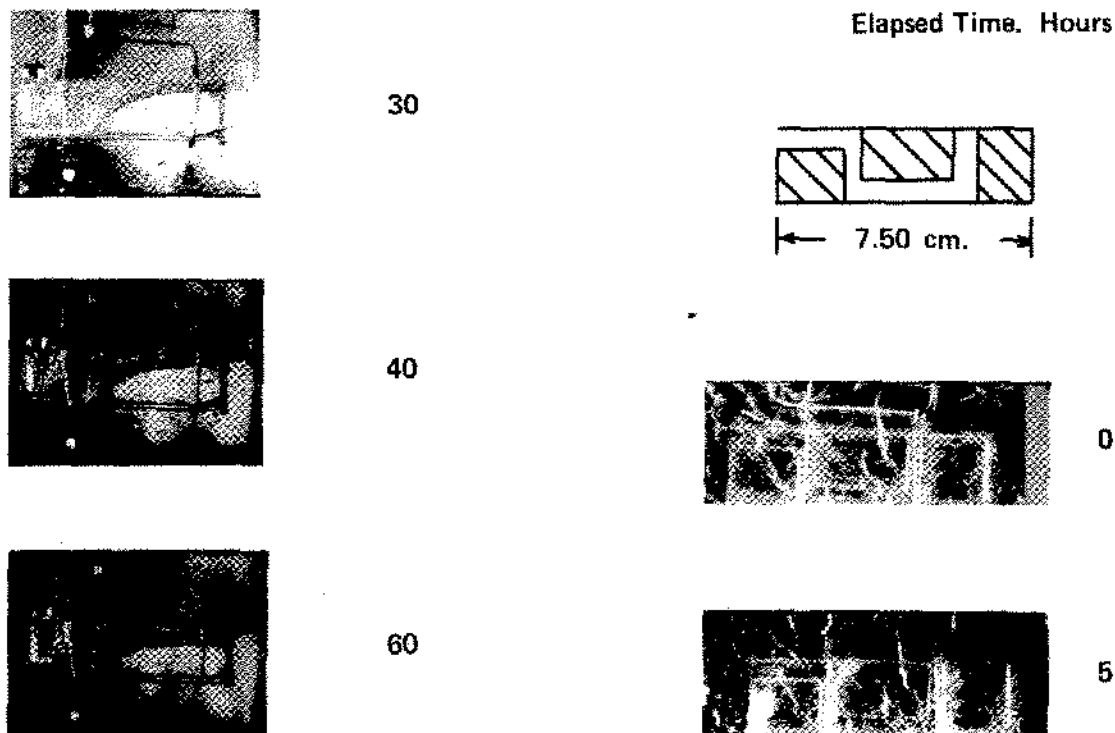


Figure 7. No frame at 15th hour. Run 23.

Figure 8—Run 28

This is a sketch of an array of three KCl crystals of different sizes arranged with solvent filled channels between them. Solvent access is only from the left side. At the start of the run the channels become filled with bulk solvent. The progress of the dissolution is shown in Figure 9.

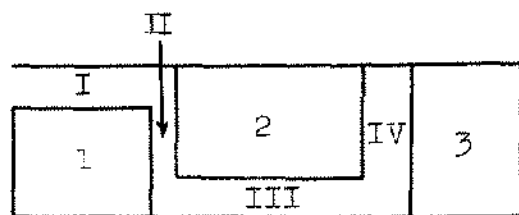


Figure 8. Run 28. KCl crystals are numbered 1, 2, 3. Solvent channels are numbered I, II, III, IV. Solvent access is from the left.

Figure 9—Run 28 continued

Initial dissolution starts at the left and top of crystal 1 and top left of crystal 2. The crystallized

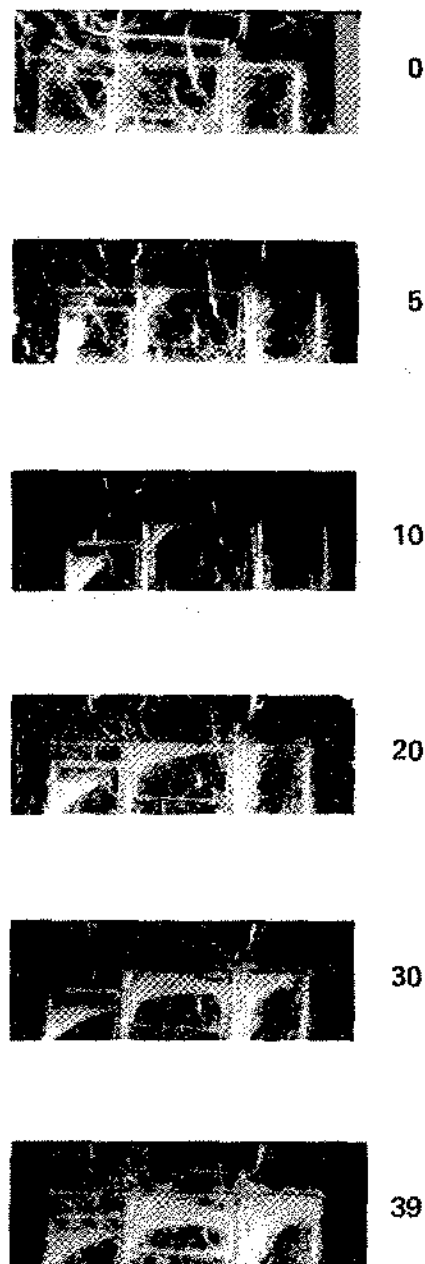


Figure 9. Run 28.

NaCl appears as a solid white or light colored area. The initial dissolution pattern continues for about 18 hours at which time a connection is made between channels I and IV across the top of crystal 2. The 20th hour shows this breakthrough is complete. At this time noticeable dissolution has taken place on the right side of crystal 2 and the left side of crystal 3. The latter two surfaces continue to dissolve extensively as shown in the 30th and 39th hour frames.

Throughout the 39 hours there is negligible dissolution at the bottom of crystal 2 or the bottom right of 1. This may be explained by the saturation of channel III with KCl. Only 0.1 mm of KCl needs to dissolve, say from the bottom of 2, to saturate channel III.

There is also negligible dissolution from the vertical KCl surfaces forming channel IV up until the time the connection is made between channels I and IV. When this connection is made fresh bulk solvent can reach channel IV allowing saturated solution to make its way from channel IV to II and then down the left dissolving face of crystal 1. Unless saturated solution and fresh solvent have exit and access routes, respectively, dissolution is severely limited.

Figure 10—Run 26

This is a sketch of an array of three KCl crystals of different sizes arranged with solvent filled channels between them. Solvent access is only from the right side. At the start of the run the channels become filled with bulk solvent. The progress of the dissolution is shown in Figure 11.

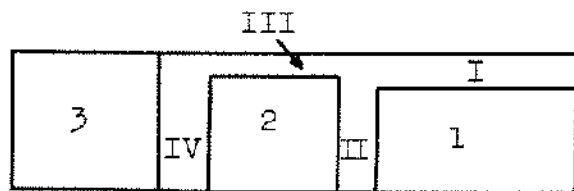


Figure 10. Run 26. KCl crystals are numbered 1, 2, 3. Solution channels are numbered I, II, III, IV. Solution access is from the right.

Figure 11—Run 26 continued

Initial dissolution starts at the top and right of crystal, at the top of 2 and top right of 3. There is negligible dissolution from the left side of 1, from the bottom right and left of 2 and the bottom right of 3. This continues through the 80th hour.

Dissolution probably does occur initially from the vertical crystal walls forming channels II and IV but these channels rapidly become saturated. Once saturated dissolution stops because the

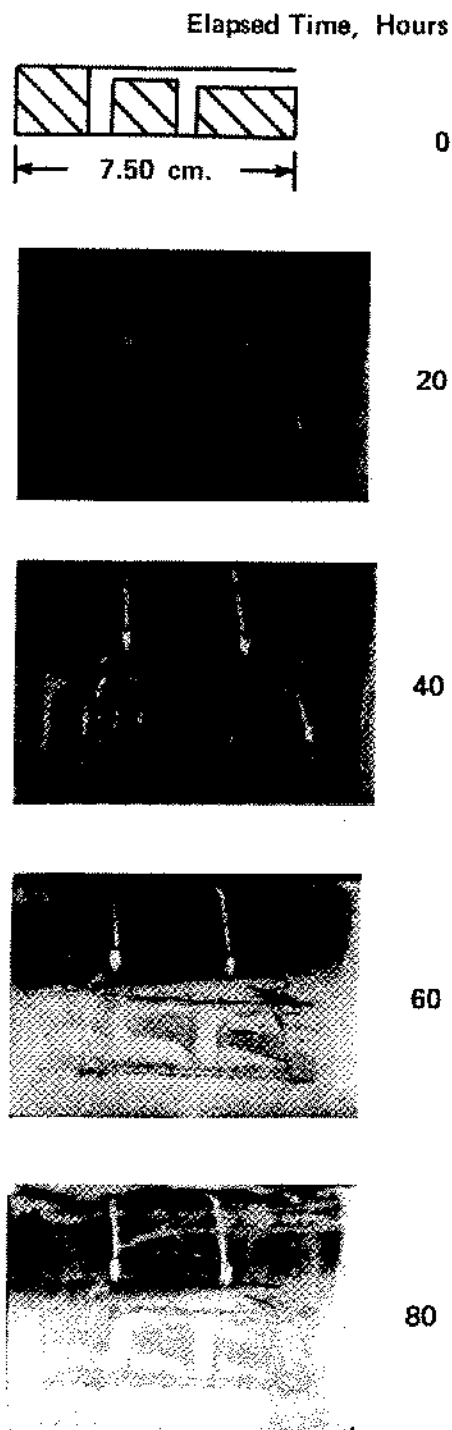


Figure 11. Run 26.

saturated solvent has no exit and the fresh bulk solvent no access route.

Note the nearly continuous profile extending across the tops of crystals 1, 2 and 3. The crystallized NaCl remains resting on top of the crystals. It appears as a white or lighter colored area.

Figure 12—Run 18

This is a 2.54 cm tall crystal inclined in solvent saturated with respect to NaCl. The left face is the only one exposed to solvent.

At the 1st hour the dissolving face is slightly irregular but essentially parallel to the initial face. A slight knee profile develops by the 5th hour. From about this time on there is negligible dissolution from the bottom of the dissolving face. The crystallized NaCl can be seen in the 5th hour frame lying on the bottom of the glass channel and in front of the dissolving face.

At the 6th hour an undercutting occurs about $1/3$ the way up the crystal. By the 10th hour the undercutting is more severe. By the 15th hour the undercut has enlarged by extending upward. Dissolution occurs upward in the pocket of the undercut. The 20th hour shows the undercut has continued to dissolve upward and is close to the top of the remaining crystal.

The 6th through 20th hours shows the crystallized NaCl has fallen away from the dissolving face with more lying on the bottom of the glass channel.

A change may be noticed in the top right corner of the crystal. There was a pin hole leak in the epoxy cement allowing solvent to dissolve some KCl.

Typical dissolution rates

Figure 13 presents some typical dissolution data for runs saturated and unsaturated with respect to NaCl. Average hourly rates are plotted. The data were not otherwise smoothed. The more pronounced variations in the Run 16 data cannot be attributed to the movement or settling of the field of crystallized NaCl because equally wide variations were observed in other NaCl unsaturated runs.

The affect of crystallized NaCl on the dissolution is apparent in the lower Run 16 rates. The crystallized NaCl forms a field which hinders the flow of bulk solvent to the dissolving face as well as possibly hindering the flow of the boundary layer.

Table 2 presents average rate of advance data at the top of the dissolving face. Rate of advance is independent of face height for the same conditions

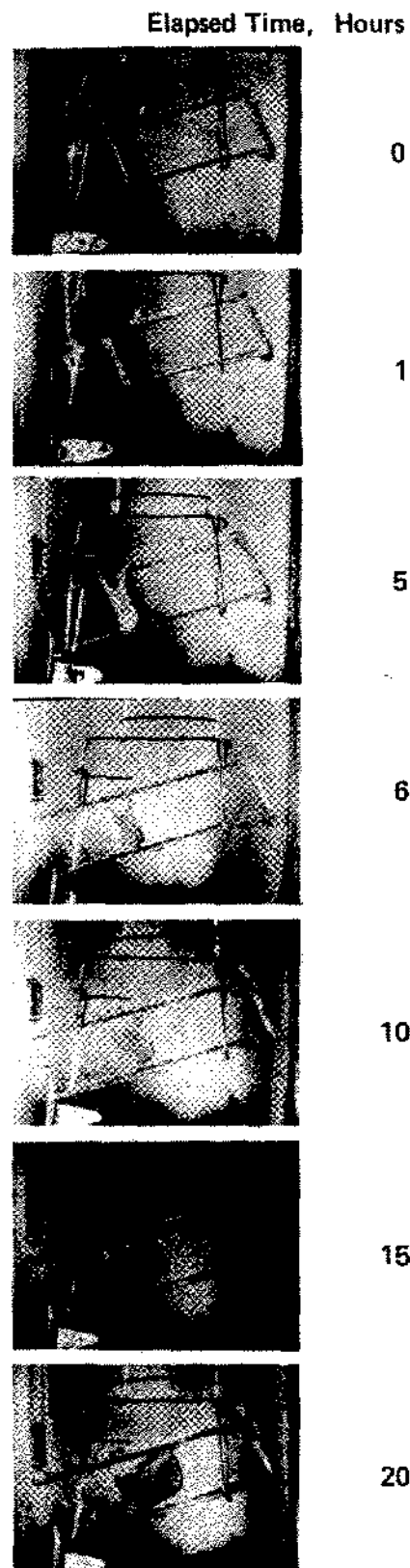


Figure 12. Run 18.

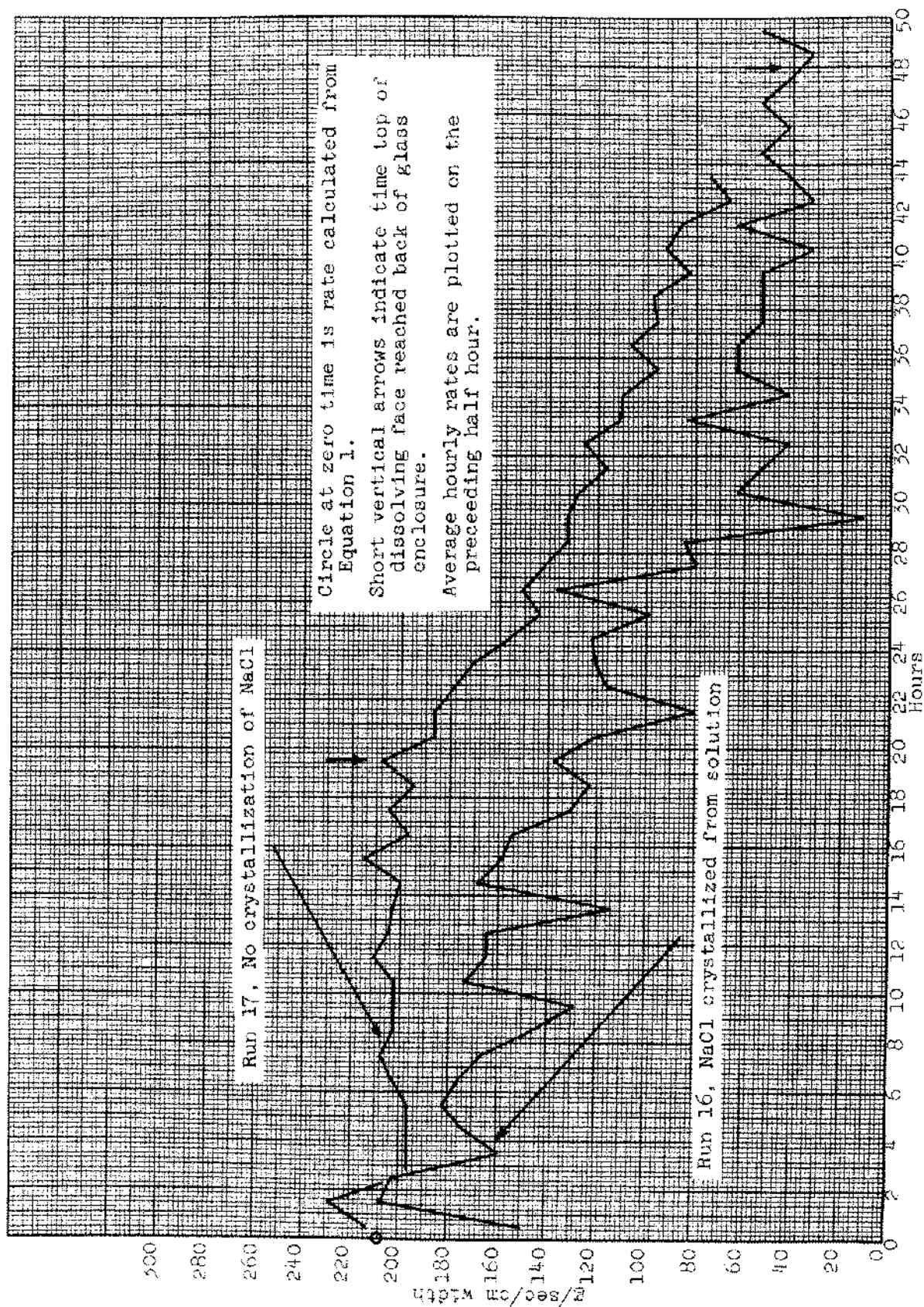


Figure 13. Typical KCl dissolution rates with and without crystallization of NaCl 2.54 cm tall crystals sandwiched between top and bottom inert boundaries.

TABLE 2. Rate of Advance at Top of Dissolving Face

Run No.	Face Height cm	Is Solvent Saturated with NaCl?	Average Rate of Advance	
			cm/hr	Interval over Which Average Taken, Hours
16	2.54	Yes	0.11	20
17	2.54	No	0.26	20
15	5.08	Yes	0.11	20
20	5.08	No	0.25	10

of NaCl crystallization. Rate of advance with NaCl crystallization is 43% of that without crystallization.

The dissolution rates were probably not significantly affected by changes in bulk concentration caused by dissolving KCl as evidenced by the following: The boundary layer of denser liquid flows down the dissolving face and across the bottom of the glass channel. A denser filament of liquid can be seen falling from the front edge of the glass channel down toward the bottom of the battery jar where it tends to accumulate. Several checks of the bulk solution concentration several centimeters in front of the glass enclosure showed no significant difference between the start and end KCl concentration. The sample was suspended in the upper part of the battery jar to keep the bulk solvent in front of the crystal as far as possible from the build-up of denser solution at the bottom.

OBSERVATIONS AND CONCLUSIONS

1. KCl crystals dissolve faster in solutions unsaturated with respect to NaCl.
2. The presence of a field of crystallized NaCl crystals does not prevent a properly oriented KCl crystal from dissolving extensively. This was observed in experiments lasting about 90 hours.
3. Close-up view of the crystallized NaCl field shows it to be full of solvent voids.
4. The crystallized NaCl field is not static. As time passes and more KCl dissolves, the field tends to settle and compact. In doing so a clear solvent channel opens up across the top of the KCl crystal.
5. The rate of advance at the top of the dissolving face is relatively constant for each case. It

is about 0.26 cm/hr. for unsaturated NaCl solutions and 0.11 cm/hr. for saturated solutions, both at 70°C. The rate of advance at the top boundary is independent of face height for 2.54 and 5.03 cm tall crystals.

6. A knee shaped profile develops in solvents unsaturated with NaCl for crystals lying between top and bottom inert boundaries. Close examination of the face profile at the top boundary shows a short, nearly vertical section. The face profile close to the bottom boundary shows a tail. The bottom front of the crystal does dissolve. Smooth dissolving faces are usually observed.
7. A nearly linear dissolving face develops in solvents saturated with respect to NaCl for KCl crystals lying between top and bottom inert boundaries. The bottom front of the crystal does not dissolve. The dissolving face is usually slightly irregular.
8. A knee profile also develops when solvent access is from both a side and the top. Dissolution is faster in from the side regardless whether NaCl crystallizes or not.
9. In multiple crystal arrangements with liquid filled channels between crystals, only those portions of the crystals will dissolve that are continually contacted by fresh solvent, i.e., a circulation pattern must be set up.

WORK IN PROGRESS

Equation 1 applies to steady state dissolution from semi-infinite vertical surfaces without end effects. Once the dissolving face assumes the characteristic knee profile in solvents unsaturated with NaCl, equation 1 becomes inapplicable. Work is in progress to derive an equation for finite crystals heights with allowance for end effects and the

changing profile shape. The new equation attempts to account for the presence of crystallized NaCl.

REFERENCES

- Dommers, O.B., et al., 1963, Feasibility of Creating Spherical Cavities in Underground Salt Domes: Univ. of Texas, Dept. of Petroleum Eng., June 30, 186 p.
- Durie, R.W., and Jessen, F.W., 1964, Mechanism of the Dissolution of Salt in the Formation of Underground Salt Cavities: Society of Petroleum Engineers Journal, June, p. 183-190.
- Husband, W.H.W., and Ozsahin, Selim, 1967, Rates of Dissolution of Potash Ore: The Canadian Journal of Chemical Engineering, v. 45, p. 234-237.
- Wagner, C., 1949, The Dissolution Rate of Sodium Chloride With Diffusion and Natural Convection as Rate-Determining Factors: The Journal of Physical and Colloid Chemistry, v. 53, p. 1030-1033.
- Wilke, C.R., Tobias, C.W., and Eisenberg, Morris, 1953, Free-Convection Mass Transfer at Vertical Plates: Chemical Engineering Progress, v. 49, no. 12, p. 663-674.