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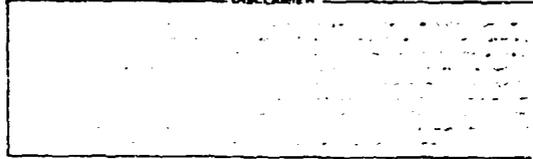
## Consolidation and Permeability of Salt in Brine

- A. J. Shor
- C. F. Baes, Jr.
- C. M. Canonico

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**CONSOLIDATION AND PERMEABILITY OF  
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## CONSOLIDATION AND PERMEABILITY OF SALT IN BRINE

A. J. Shor, C. F. Baes, Jr., and C. M. Canonico

### ABSTRACT

The consolidation and loss of permeability of salt crystal aggregates, important in assessing the effects of water in salt repositories, has been studied as a function of several variables. The kinetic behavior was similar to that often observed in sintering and suggested the following expression for the time dependence of the void fraction:

$$\phi(t) = \phi(0) - (A/B) \ln(1 + Bt/\bar{z}(0)^3),$$

where  $A$  and  $B$  are rate constants and  $\bar{z}(0)$  is initial average particle size. With brine present,  $A$  and  $\phi(0)$  varied linearly with stress. The initial void fraction was also dependent to some extent on the particle size distribution. The rate of consolidation was most rapid in brine and least rapid in the presence of only air as the fluid. A brine containing 5 m  $MgCl_2$  showed an intermediate rate, presumably because of the greatly reduced solubility of  $NaCl$ . A substantial wall effect was indicated by an observed increase in the void fraction of consolidated columns with distance from the top where the stress was applied and by a dependence of consolidation rate on the column height and radius. The distance through which the stress fell by a factor of  $e$  was estimated to change inversely as the fourth power of the column diameter. With increasing temperature (to  $85^\circ C$ ), consolidation proceeded somewhat more rapidly and the wall effect was reduced. The permeability of the columns dropped rapidly with consolidation, decreasing with about the sixth power of the void fraction. In general, extrapolation of the results to repository conditions confirms the self-sealing properties of bedded salt as a storage medium for radioactive waste.

## 1. INTRODUCTION

Although the very presence of a subterranean salt deposit signifies isolation from flowing water over geologic time, somewhat ironically perhaps the suitability of bedded salt for the storage of radioactive waste remains questionable because the consequences of the presence of water (as brine) have not been fully assessed. Water is inevitably present in salt repositories as brine inclusions within salt crystals or as hydrate water in minerals such as gypsum. Water may gain access during the operational period when the repository is open to the surface, during the period of consolidation of backfilled salt, or conceivably during the period of long-term storage. In the temperature gradient around a waste canister, hydrate water could be released and brine could migrate up the thermal gradient.

To assess the consequences of water in a radioactive waste repository, investigators are measuring<sup>1</sup> and modeling<sup>2</sup> movement of brine in a thermal gradient and studying the mechanical properties of salt.<sup>3</sup> We have been studying the consolidation and permeability of granulated salt as a function of the composition of the liquid in which it is immersed, the stress applied, and the temperature.<sup>4</sup>

It has long been known that when the relative humidity is high enough (>75%) to produce water condensation on granulated salt, the crystals cake or stick together and remain caked after the water is removed by evaporation. A mechanism is easily imagined involving dissolution in and reprecipitation from the brine to produce crystals that fit together better and stick together. The driving forces include the enhanced solubility of salt at points of contact between crystals that are under stress from the weight of overlying salt and the energy released from reduction of the interfacial area between crystals and brine.

During deposition and consolidation of salt from evaporating seas to form halite deposits, the crystals quite obviously were not only reshaped to fit more perfectly, but probably grew in size. This suggests processes like those that produce grain growth in the sintering of metal and ceramic powders at temperatures well below their melting points. The mechanism is thought to involve the transfer of ions along or across grain boundaries between adjacent crystals. Here the driving force is reduction of the total area of the grain boundaries.

The consolidation of other mineral crystals has long been of interest to geologists concerned with the processes involved in the formation of rocks. Although the solubilities are lower, the same mechanisms of dissolution and precipitation are thought to be important.<sup>5</sup> The most elegant model appears to be that of Weyl,<sup>6</sup> wherein the rate-determining step is assumed to be the diffusion of excess dissolved material within the film of liquid between the stressed surfaces. This model and similar treatments by Kingery<sup>7</sup> and Rutter<sup>8</sup> lead to the conclusion that, for a given stress, the void fraction should depend on the ratio of the time to the cube of the particle size ( $t/z^3$ ). Unfortunately, the experimental study of the consolidation of various crystalline materials has not progressed far enough to test properly these

models. Our attempts to apply such a model to the present results on the consolidation of salt in brine were not very successful.<sup>4</sup>

The process of sintering is of great technological importance and has received extensive study both experimentally and theoretically. Unfortunately, sintering is too complicated to be treated quantitatively by present theories. Coble<sup>9</sup> concluded from a highly idealized model that the rate at which the void fraction  $\phi$  decreased with time should be inversely proportional to the cube of the particle size  $z$ :

$$\frac{d\phi}{dt} = -A/z^3. \quad (1)$$

The constant  $A$  contains the volume, surface tension, and diffusion coefficient of the crystal vacancies assumed to be responsible for the change in crystal shape. Coble also observed that the cube of the average particle size  $\bar{z}$  grew linearly with time during much of the sintering process:<sup>10</sup>

$$\bar{z}(t)^3 = \bar{z}(0)^3 + Bt. \quad (2)$$

Assuming that  $z$  in Eq. (1) can be replaced by the average particle size  $\bar{z}$ , these equations can be combined and integrated to give

$$\phi(t) = \phi(0) - (A/B) \ln[1 + Bt/\bar{z}(0)^3]. \quad (3)$$

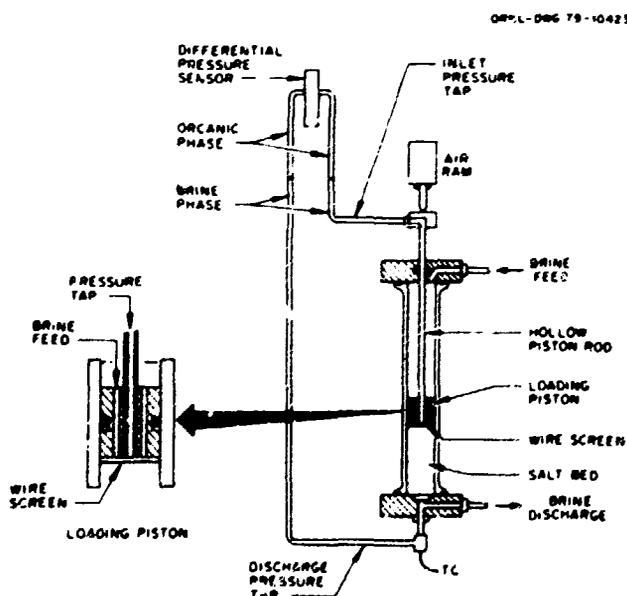
There is a conceptual difficulty, however, in that Eq. (1) was derived for a lattice of crystals of identical size and shape while Eq. (2) must apply to crystals of varying size since it is not possible for some crystals to grow unless others decrease in size. Equation (3) must therefore be regarded as an approximation at best. Experimental studies,<sup>11</sup> however, have indicated that the forms of Eqs. (1) and (2) are approximately correct, with the exponent of  $\bar{z}$  ranging from 2 to 3, and equations of the form of Eq. (3) have been found to be quite useful in representing the dependence of sintering rates on time and particle size. Equation (3) has also proved very useful in treating the present results.

## 2. EXPERIMENTAL

The apparatus used to measure the consolidation and permeability of beds of salt crystals is shown in Fig. 1. The beds were contained in a vertical glass or Monel tube (1.27 or 2.54 cm ID, respectively) and stressed by a perforated piston driven by a Bimba air-actuated ram. Liquid, usually presaturated brine, filled the tube and flowed slowly through the bed during the measurements. The hydrostatic pressure drop across the salt bed was transmitted to a Validyne differential-pressure sensor isolated from the brine by a hydrocarbon liquid to protect the sensor. The height of the bed (determined from the movement of the piston) and the flow rate (determined gravimetrically) were measured as a function of time. The void fraction was calculated from the weight of salt in the bed and the volume it occupied; the permeability was calculated from the hydraulic pressure drop and the flow rate.

Crystals of sodium chloride (CP grade) were sized (usually in the ranges of 75 to 150, 150 to 177, 177 to 250, and 250 to 420  $\mu\text{m}$ ) with standard copper sieves and were thoroughly dispersed in the liquid to be used before forming the settled beds. Grinding was used before sieving in preliminary runs, but this was found to produce fines that were not removed completely by sieving. Photomicrographs of samples in each size range were used to determine the size distribution. The material consisted almost entirely of well-formed cubic crystals.

After most runs the salt columns were sampled and the brine content determined by heating to constant weight at 200°C. Samples were taken from the 1.27-cm glass tubes by excavation with a spatula, a tedious and time-consuming procedure for extensively consolidated salt. In the Monel tubes, consolidated columns could be removed intact by ejection with the piston and sampled by sectioning. A number of sections were polished and etched for examination with optical and scanning electron microscopes.



Salt Bed Column Pressure Consolidation Experiment.

Fig. 1. Apparatus for study of salt consolidation and permeability under a uniaxial stress in brine and other fluids.

### 3. RESULTS

#### 3.1 Consolidation Kinetics

Under constant stress, beds of salt crystals lost volume with the passage of time at a rate that approached linearity with the logarithm of time (Figs. 2 to 4). This dependence was observed to continue to void fractions as low as 0.02. Examination of compacted columns revealed that the void fraction remaining was not uniformly distributed throughout (Fig. 5) but increased with the distance from the top of the specimen where the stress was applied. This indicated a substantial wall effect, causing the stress on the salt to decrease with distance down the column. The effect was confirmed when it was found that under the same conditions consolidation proceeded more rapidly for short columns of salt than for longer ones (Fig. 3a), and more rapidly in the larger (2.54 cm) tubes than in the smaller (1.27 cm) ones (Fig. 3b). There was also some evidence that the consolidation rate depended on the smoothness of the tube wall and the material of which it was made (Fig. 3c).

The principal variables that affected the rate of consolidation in brine were the applied stress and average particle size (Figs. 2a and b)—the smaller the particles and the greater the applied stress, the more rapid the consolidation. Under a given set of conditions, the consolidation increased with temperature (Fig. 4), but the effect was not large. The extent of consolidation was affected by the particle size distribution (Fig. 5). When the fluid medium was varied (Fig. 7), consolidation proceeded most rapidly in brine, less rapidly with  $MgCl_2$  dissolved in the brine (reducing the solubility of  $NaCl$ ), and least rapidly when only air was present. Two runs in dodecane revealed that the consolidation rate was markedly increased by the presence of a small amount of water, wet dodecane being even more effective a medium for consolidation than a brine containing 5 *m*  $MgCl_2$ .

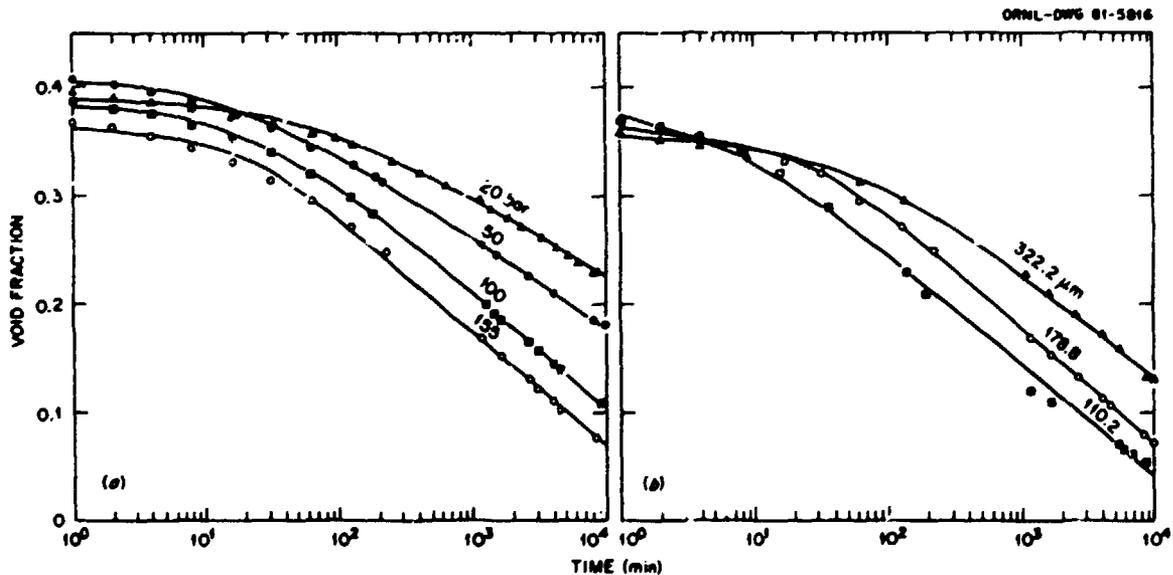


Fig. 2. Consolidation of salt columns (2.54 cm diam) in brine: (a) for various applied stresses and an initial average particle size of 178.8  $\mu m$ ; (b) for various initial average particle sizes at an applied stress of 155 bars.

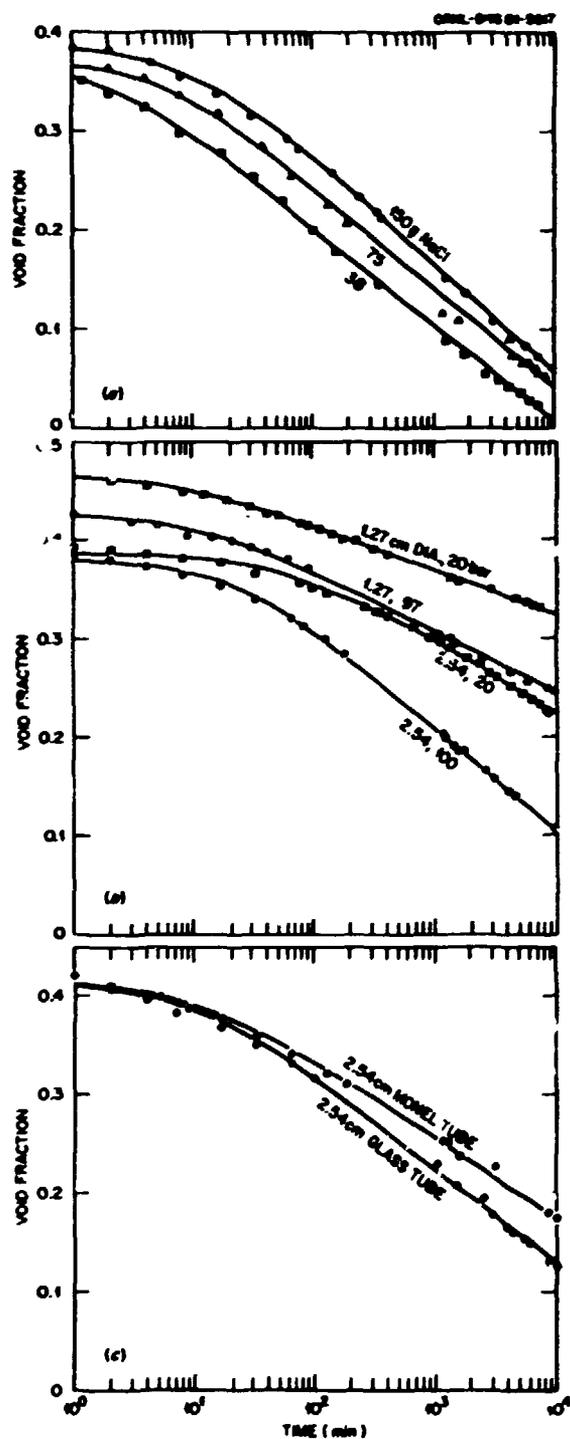


Fig. 3. Consolidation of salt in brine: (a) for various weights of salt in 2.54-cm-ID Monel tubes at an applied stress of 155 bars and initial average particle size of 110.2  $\mu\text{m}$ ; (b) for two tube diameters (the larger of Monel and the smaller of glass) with columns of similar height and applied stresses; (c) for Monel and glass tubes of 2.54 cm ID with a stress of 20 bars and an initial average particle size of 110.2  $\mu\text{m}$ .

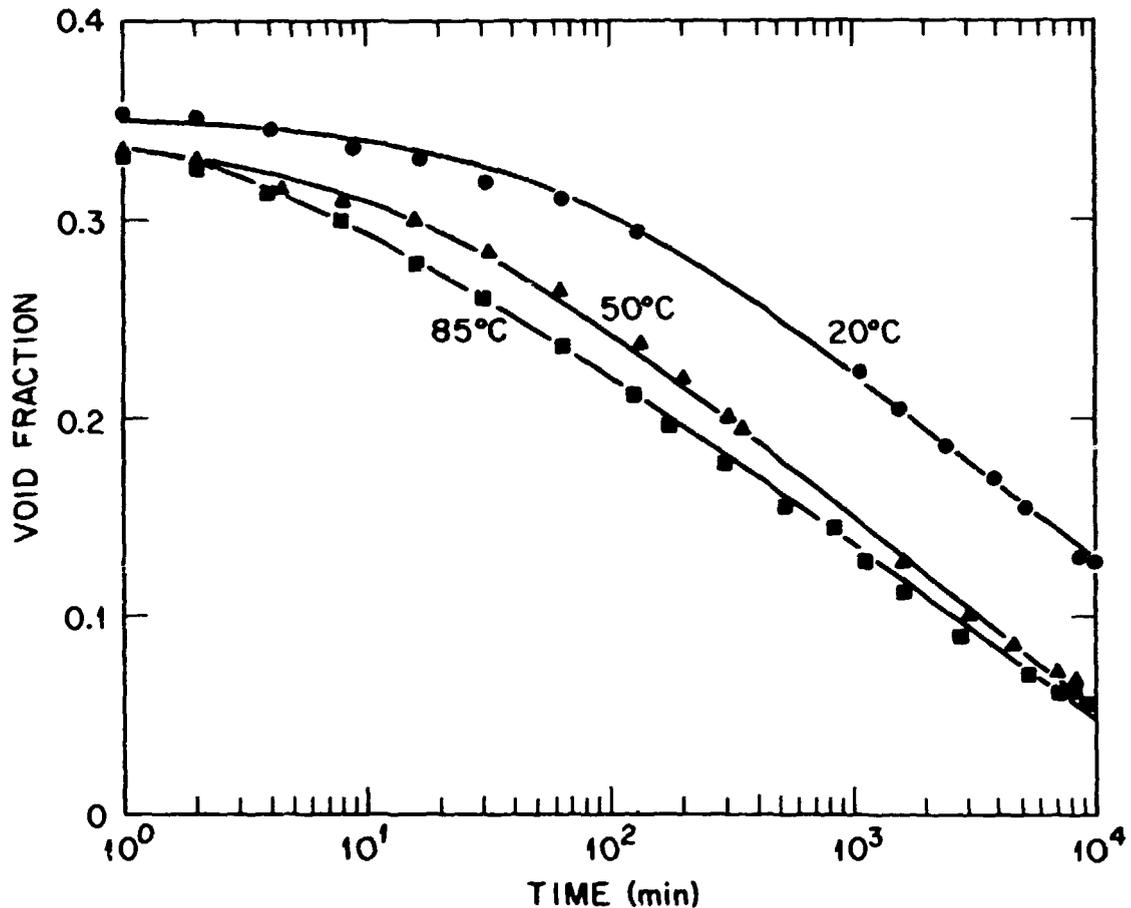


Fig. 4. Consolidation of salt columns (2.54 cm diam) in brine at various temperatures, with 155 bars applied stress and an initial average particle size of 322.2  $\mu\text{m}$ .

The decrease in the observed void fraction  $\phi$  during the isothermal consolidation of salt can be represented quite well by an equation of the form

$$\phi(t) = a - b \ln(c + t), \quad (4)$$

which is strikingly similar to the one suggested by Coble [Eq.(3)]. When the parameters  $a$ ,  $b$ , and  $c$  were adjusted by least squares to obtain the best fit to each run (Table 1), the agreement between the observed and calculated void fraction was usually within experimental error, as may be seen from the curves in Figs. 2 to 4, 6, and 7, generated by use of Eq. (4). While the values of  $a$ ,  $b$ , and  $c$  obviously reflect the effect of such variables as particle size, stress, and temperature, they are so strongly covariant with one another that it is not possible to assign these dependencies with much certainty.

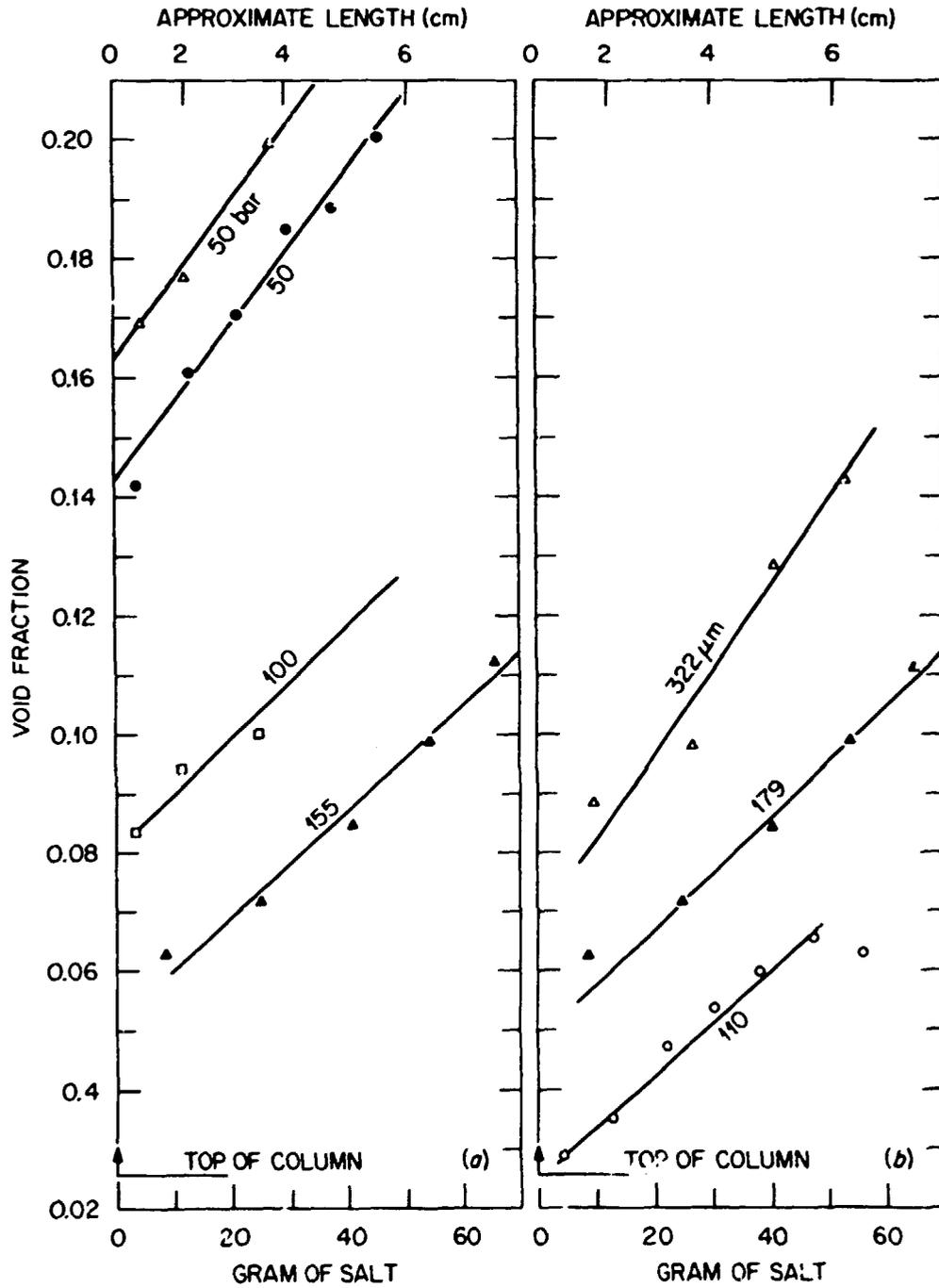


Fig. 5. Void fraction in consolidated salt columns vs. distance (weight of salt) from piston: (a) for various applied stress and an initial average particle size of 178.8  $\mu\text{m}$ ; (b) for various particle sizes at an applied stress of 155 bars.

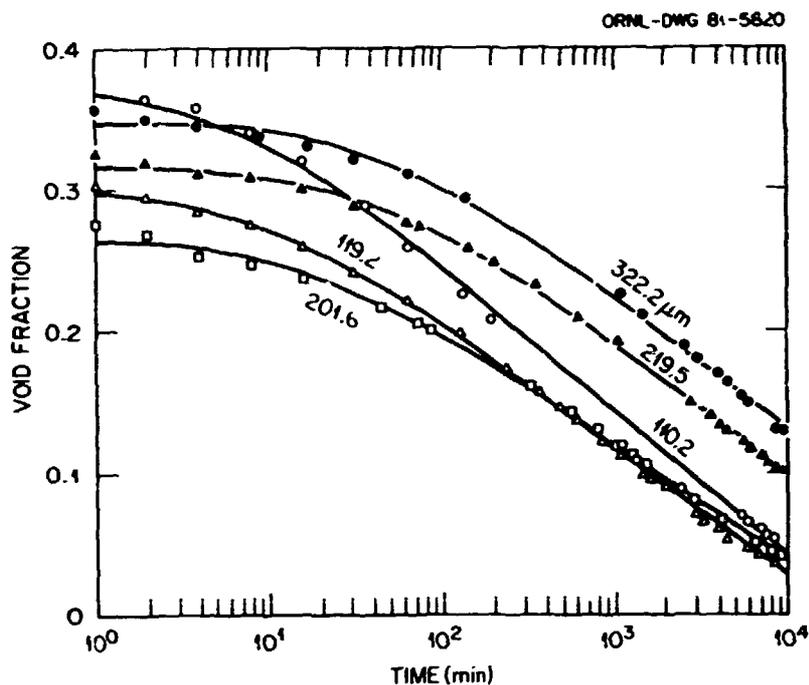


Fig. 6. Consolidation of salt columns (2.54 cm diam) in brine with various initial average particle sizes and distributions, at an applied stress of 155 bars.

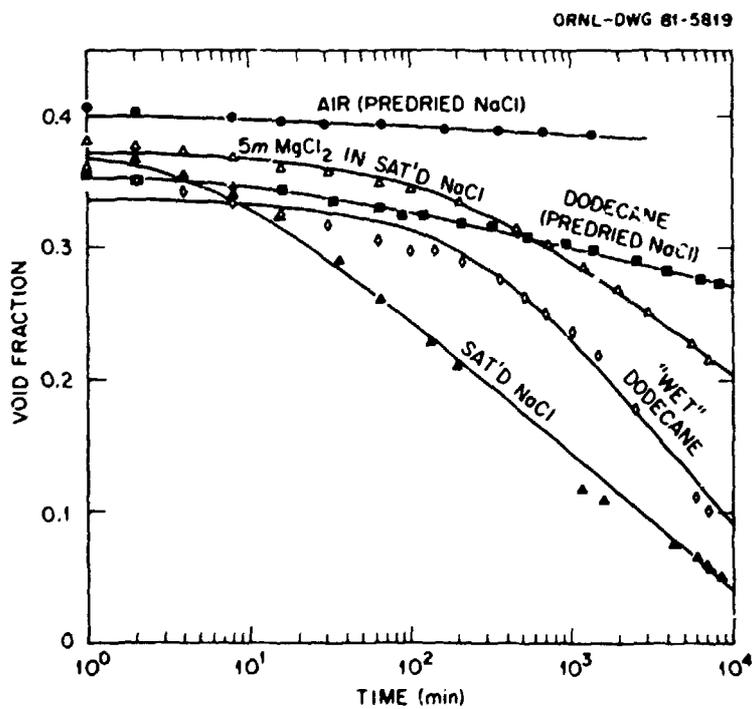


Fig. 7. Consolidation of salt columns (2.54 cm diam) in various fluids with an applied stress of 155 bars and an initial average particle size of 110.2 μm.

Table 1

## KINETICS OF CONSOLIDATION OF SALT UNDER VARIOUS CONDITIONS

$$\phi(t) = a - b \ln(c + t)^a$$

Run No.	Crystal Size z(0) <sup>b</sup> cm	Appl. Stress bar	Wt. of Salt g	a	b	c min	Std. Err. of Fit <sup>c</sup>
<u>In NaCl Brine, 1.27 cm ID Glass Tubes, ~20°C</u>							
26	0.0100	57.4	7.00	0.4877	0.02960	9.0	0.0031
15	"	57.4	17.4	0.5394	0.02815	5.1	0.0035
21	"	57.4	17.4	0.6732	0.04725	133.4	0.0064
18	"	96.5	17.8	0.4704	0.02961	0.6	0.0020
12	0.0165	20.1	17.8	0.5030	0.01930	7.1	0.0012
17	"	96.5	17.8	0.4947	0.02709	17.8	0.0026
20	0.0333	20.1	17.3	0.4866	0.01336	48.7	0.0014
24	"	57.4	7.06	0.4732	0.02017	67.9	0.0028
16	"	57.4	17.4	0.4694	0.01132	27.6	0.0021
13	"	57.4	17.4	0.5314	0.02620	97.7	0.0084
19	"	57.4	17.8	0.4883	0.01714	51.3	0.0034
<u>2.54 cm ID Monel Tubes, ~20°C</u>							
115	0.01102	20	38	0.4745	0.025741	3.7	0.001
102	"	20	75	0.4965	0.034934	10.2	0.009
119	"	20	75	0.5047	0.032051	11.0	0.003
111	"	155	38	0.4039	0.043011	2.0	0.005
104	"	155	75	0.4501	0.044408	5.4	0.009
109	"	155	75	0.4386	0.044613	3.9	0.008
110	"	155	150	0.5010	0.048093	10.2	0.002
122	0.01192	155	75	0.3889	0.029485	8.8	0.002
108	0.01788	20	75	0.5126	0.031142	56.7	0.004
118	"	50	38	0.4868	0.035266	12.4	0.002
117	"	50	75	0.5039	0.035119	16.1	0.002
107	"	100	75	0.5226	0.045306	21.6	0.002
106	"	155	75	0.4978	0.046460	17.0	0.003
121	0.01877	50	75	0.4924	0.034544	41.4	0.003
120	"	100	75	0.4808	0.036193	22.5	0.002
132	0.02016	155	75	0.3643	0.035421	15.3	0.004
123	0.02195	155	75	0.4686	0.040131	43.2	0.004
116	0.03222	20	38	0.4740	0.021195	51.1	0.002
114	"	155	38	0.4151	0.031918	18.5	0.002
105	"	155	75	0.5037	0.040568	44.2	0.005
101 <sup>d</sup>	0.01102	20	75	0.5062	0.040780	9.2	0.006
103 <sup>d</sup>	0.01788	20	75	0.5006	0.034101	22.7	0.002
100 <sup>d</sup>	0.03222	20	75	0.4304	0.020305	38.4	0.003

Table 1 (contd.)

Run No.	Crystal Size $z(0)^b$ cm	Appl. Stress bar	Wt. of Salt g	a	b	c min	Std. Err. of Fit <sup>c</sup>
<u>50°C</u>							
127	0.01102	155	75	0.3950	0.043555	0.8	0.007
128	"	155	150	0.4676	0.049057	4.4	0.005
129	0.03222	155	75	0.4402	0.042143	12.1	0.008
<u>85°C</u>							
131	0.01102	155	75	0.3720	0.043760	0.2	0.010
130	"	155	75	0.3896	0.036913	3.4	0.003
<u>In Other Fluids at ~20°C<sup>e</sup></u>							
124	0.01102	155	75	0.5480	0.037301	113.7	0.004
125	"	155	74	0.7173	0.068266	263.2	0.011
126	"	155	75	0.3798	0.011706	10.4	0.003
113	0.01788	155	75	0.4025	0.023010	-----	0.001

<sup>a</sup>  $\phi(t)$  is the void fraction at time  $t$  (min).

<sup>b</sup> The average crystal size: Information about the size distribution is given in Table 3.

<sup>c</sup> Standard deviation of the calculated from the observed void fraction.

<sup>d</sup> These runs were carried out in 2.54 cm i.d. glass rather than monel tubes and were not included in determination of the parameters in Table 2.

<sup>e</sup> Run 113, in air; run 124, in a brine 6 m in  $MgCl_2$ ; run 125, undried salt in dodecane; run 126, dried salt in dodecane (see Table 4). These runs were not included in determination of the parameters in Table 2.

### 3.2 Consolidation Model

Accordingly, we turn to the model suggested by Coble.<sup>9,10</sup> A comparison of Eqs. (3) and (4) show that they are equivalent if

$$\phi(0) = a - b \ln c. \quad (5a)$$

$$A = b \bar{z}(0)^3 / C. \quad (5b)$$

$$B = \bar{z}(0)^3 / C. \quad (5c)$$

We then examined the effect of conditions on the values of  $\phi(0)$ ,  $A$ , and  $B$  given by these relationships. As might be expected, the initial void fraction  $\phi(0)$  seemed to decrease with increasing applied stress. A linear decrease with stress seemed to be an adequate approximation, though  $\phi(0)$  was obviously affected by particle size and size distribution as well. We will consider these effects presently. The quantity  $A$  was found to increase approximately linearly with increasing applied stress.

These correlations were obscured by the wall effect, which causes the local stress  $\sigma$  in a column to be less than the applied stress  $\sigma(0)$  and the local void fraction to differ from the observed or integrated void fraction. These correlations did suggest, however, that for the consolidation of salt in brine, a good representation of the time dependence of the local void fraction would be given by Eq. (3) if we assume that the local void fraction and  $A$  vary linearly with the local stress:

$$\phi(w,0) = P_0 - P_1 \sigma. \quad (6a)$$

$$A = A_0 + A_1 \sigma. \quad (6b)$$

Here we assume the local void fraction to be a function of the distance down the column expressed in terms of the weight of salt  $w$  as well as the time. (In view of the limited information we have on the wall effect, it was deemed appropriate not to consider explicitly the dependence of the local void fraction on the distance from the wall.) The wall effect was dealt with by assuming that the stress decreased exponentially with  $w$ :

$$\sigma(w) = \sigma(0) \exp(-w/C), \quad (7)$$

where  $C$  is the weight of salt through which the stress falls by a factor of  $e$ . An expression for the observed void fraction is then derived by performing the integration

$$\phi(t) = \left( \frac{1}{W} \right) \int_0^W \phi(w,t) dw. \quad (8)$$

where  $W$  is the total weight of salt in the column. The resulting expression for the observed void fraction is

$$\phi(t) = (P_0 - P_1 \bar{v}) - [(A_0 + A_1 \bar{v})/B] \ln[1 + Bt/\bar{z}(0)^2]. \quad (9)$$

In which  $\bar{v}$  is given by

$$\bar{v} = \frac{1}{W} \int_0^W v \, dw = v(0) \frac{C}{W} [1 - \exp(-W/C)]. \quad (9a)$$

### 3.3 Consolidation in Brine at Room Temperature

All the consolidation data on room-temperature brine from the 2.54-cm Monel tube were fitted by least squares to Eq. (9). Included were the profiles of void fraction vs  $w$  from direct sectioning of consolidated columns (Fig. 5). The latter data were fitted by replacing  $\bar{v}$  in Eq. (9) with  $v(w)$  from Eq. (7). In making these fits, values of  $A_0$ ,  $A_1$ ,  $B$ , and  $C$  were adjusted for all the data simultaneously. The parameters  $P_0$  and  $P_1$  presented a problem because, as noted above, these were not the only quantities that determined the initial void fraction  $\phi(0)$ ; therefore,  $P_0$  was adjusted for each run so that it could include the effects being neglected in Eqs.(6). Even so, the overall fit to the data was so insensitive to the choice of  $P_1$  that this parameter could not be freely adjusted simultaneously with  $A_0$ ,  $A_1$ ,  $B$ , and  $C$ . By inspection,  $P_1$  seemed to be in the range 0.0007 to 0.0015 bar<sup>-1</sup>. The parameter values obtained are summarized in Table 2. Values of  $P_0$  were in the range 0.41 to 0.51, and the average deviation calculated from observed void fraction was 0.011.

The more limited data from 1.27-cm ID tubes for consolidation in brine were insufficient to provide an independent set of  $P_1$ ,  $A_0$ ,  $A_1$ , and  $B$  values, but they were consistent with the above values. With these values fixed, the parameter  $C$ , which is the measure of the wall effect, was adjusted for all the smaller tube data (Table 2). Again  $P_0$  was adjusted for each run. The values were in the same range as for the 2.54-cm columns. The average deviation calculated from observed void fraction in this case was 0.014.

The much smaller value of  $C$  for the 1.27-cm-diam columns suggests that the wall effect decreases rapidly with increasing diameter. If there were no effect of diameter, we would expect  $C$  for the smaller columns to be one-fourth of the value for the larger columns. In fact, the ratio seems to be about 1 to 38, suggesting that  $C$  increases with about the sixth power of the diameter. Thus, when viewed in terms of the distance down the column through which the applied stress is reduced by a factor of  $e$ , the wall effect appears to decrease as about the fourth power of the column diameter.

The magnitude of  $B$  should be the rate of growth in volume of the average salt particle during consolidation. Thus, after a week (10,000 min) the average size should be about 0.15 cm, which is much greater than any value that might be estimated from a section of a consolidated column shown in Fig. 8. It may be more appropriate, however, to take the effective particle size as that of an aggregate from which the brine has been excluded. As may be seen from the figure, such aggregates are roughly of this size.

Table 2

AN EXPRESSION FOR THE CONSOLIDATION OF SALT IN BRINE<sup>a</sup>

$$\phi(t) = \phi(0) - (A/B) \ln [1 + Bt/z(0)^3]$$

$$\phi(0) = P_0 - 0.001 \bar{\sigma}$$

$$A(293 \text{ K}) = (8.63 \pm 0.59) \times 10^{-9} + (3.93 \pm 0.29) \times 10^{-11} \bar{\sigma}$$

$$B(293 \text{ K}) = (3.18 \pm 0.23) \times 10^{-7}$$

$$A(T \text{ K}) = A(293 \text{ K}) \exp [D (1/T - 1/293)]$$

$$B(T \text{ K}) = B(293 \text{ K}) \exp [D (1/T - 1/293)]$$

$$D = - 5130 \pm 320$$

$$\bar{\sigma} = \sigma(0) (C/W) [1 - \exp (-W/C)]$$

$$C = 213 \pm 22 \text{ (in 2.54 cm ID columns)}$$

$$C = 3.1 \pm 0.8 \text{ (in 1.27 cm ID columns)}$$

Run No., $P_0$									
12	0.481	21	0.476	107	0.447	116	0.415	123	0.465
13	0.433	24	0.424	108	0.425	117	0.435	127	0.524
15	0.508	26	0.467	109	0.501	118	0.427	128	0.521
17	0.447	102	0.434	110	0.509	119	0.457	129	0.445
18	0.451	104	0.510	111	0.495	120	0.462	130	0.486
19	0.440	105	0.460	114	0.448	121	0.417	131	0.524
20	0.461	106	0.485	115	0.472	122	0.468	132	0.409

<sup>a</sup> Fitted by least squares to the consolidation runs in NaCl brine summarized in Table 1, and to the data showing the wall effect in Fig. 5 (see text):  $\phi(t)$  is the void fraction at time  $t$  (min);  $\sigma(0)$  is the applied stress (bars);  $z(0)$  is the initial mean particle size (cm);  $W$  is the weight of salt in the column (g);  $\bar{\sigma}$  is the stress after correction for the wall effect. In the absence of a wall effect,  $\sigma(0)$  replaces  $\bar{\sigma}$  in the expressions for  $\phi(0)$  and  $A$ .



Fig. 8. Section of salt column (2.54 cm diam) consolidated at an applied stress of 165 bars and an initial average particle size of 322.2  $\mu$ m.

#### 3.4 Effect of Temperature

The results at 50 and 85°C could be adequately accounted for by assuming that  $A_0$ ,  $A_1$ , and  $B$  in Eq. (9) all had the same exponential dependence on the absolute temperature  $T$ , for example,

$$B(T) = B(293) \exp[D(1/T - 1/293)]. \quad (10)$$

The parameter  $D$  was assumed to be the same for all three quantities (Table 2) because (1) the coefficient of the log term in Eq. (9) —  $(A_0 + A_1 \bar{v})/B$  — was found to

have an inappreciable temperature dependence and (2) the temperature dependence of  $A_0$  and  $A_1$  could not be distinguished because the applied stress was not varied in these runs. The average deviation of the calculated from the observed void fraction in the five runs at elevated temperature was 0.012. Since one of the runs (128) involved twice the usual amount of salt, it was possible to test for a temperature dependence of the parameter  $C$ , related to the wall effect. It appeared that the wall effect decreases ( $C$  increases) rapidly with temperature, but the data are insufficient to define the magnitude of this dependence.

### 3.5 Initial Void Fraction

As already noted, while the initial void fraction seemed to decrease about linearly with the stress, it was also dependent on the particle size and size distribution. This effect is indicated by seven runs, all with the same amount of salt in brine under the same applied stress (Table 3). In four of these, the usual narrow size distributions (cuts) were used. The average crystal size increased from 0.0110 to 0.0322 cm, whereas  $\phi(0)$  decreased from 0.38 to 0.33. In three runs, mixtures of cuts gave  $\phi(0)$  values less than 0.34. Of this series, the run (132) that gave the lowest value of  $\phi(0)$  (0.28) involved a mixture with a fairly uniform distribution of particle sizes across the full range from 75 to 420  $\mu\text{m}$ . A mixture (Run 122) of a large number of the smallest particles with a small number of the largest particles and a mixture (Run 123) of equal numbers of the smallest and the largest particles gave higher  $\phi(0)$  values (0.34 and 0.33). Such behavior is not surprising: for particles with a narrow size distribution, the initial void fraction should be relatively high. For a wider size distribution, the void fraction should be less because of more efficient packing; but if the size distribution is wide and bimodal (as in Run 123), the packing will be determined by the larger particles and the void fraction will be higher. The results in Table 3 suggest that the average fractional deviation from the mean particle size might be a better measure of this effect than the fractional root-mean-square deviation.

### 3.6 Effect of the Fluid Phase

Values of the parameters  $\phi(0)$ ,  $A$ , and  $B$  calculated from Eqs. (4) and (5) are compared in Table 4 for a series of runs in which the fluid phase was varied. The value of  $\phi(0)$  is in the range 0.34 to 0.38 for all fluids except air which gave a value of 0.41. The parameters  $A$  and  $B$  are highest for pure NaCl brine, and both decrease in the same order (NaCl brine > dry dodecane > NaCl-MgCl<sub>2</sub> brine > wet dodecane); however,  $B$  shows a wider variation than  $A$ . The resulting consolidation

Table 3  
 PARTICLE SIZE DISTRIBUTION IN SALT BATCHES AND EFFECT ON  
 INITIAL VOID FRACTION

Cryst. Batch <sup>a</sup>	Ave. Part. Size (cm) z(0)	Standard Dev. (cm) <sup>b</sup> $\sigma/z$	Ave. Dev. (cm) $\sigma/z$	Fractional Deviations $\frac{\sigma/z}{\bar{z}(0)}$ $\frac{\sigma/z}{\bar{z}(0)}$		Run No.	Init. Void Fraction <sup>c</sup> $\phi(0)$
Cut 1	0.01102	0.00290	0.00246	0.263	0.223	104 109	0.379 0.370
Mix 1	0.01192	0.00523	0.00320	0.439	0.269	122	0.337
Cut 2	0.01788	0.00195	0.00166	0.109	0.093	106	0.354
Cut 3	0.01877	0.00256	0.00220	0.137	0.117		
Mix 2	0.02016	0.00832	0.00750	0.413	0.372	132	0.278
Mix 3	0.02195	0.01149	0.01067	0.523	0.486	123	0.334
Cut 4	0.03222	0.00553	0.00469	0.172	0.145	105	0.329

<sup>a</sup>The nominal size ranges were: cut 1, 75-150 $\mu$ m; cut 2, 150-177 $\mu$ m; cut 3 177-250 $\mu$ m; cut 4, 250-420 $\mu$ m. The mixtures were made as follows: mixture 1, 37.5 g each of cut 1 and cut 4; mixture 2, 2.12 g, 8.98 g, 10.74 g, and 53.16 g of cuts 1, 2, 3, and 4, respectively; mixture 3, 3 g of cut 1 and 73 g of cut 4. These batches were used in runs in the 2.54 cm i.d. monel tube. In the 1.27 cm i.d. glass tubes, the size ranges used were: 75-125 $\mu$ m, 150-180 $\mu$ m, and 250-425 $\mu$ m. The size distributions were not determined.

<sup>b</sup>The root mean square deviation from the mean particle size.

<sup>c</sup>With 75 g of salt in NaCl brine at about 20°C, in the 2.54 cm monel tube, and under an applied stress of 155 bars:  $\phi(0)$  is calculated from the parameters in Table 2.

Table 4  
 EFFECT OF FLUID PHASE ON CONSOLIDATION<sup>a</sup>

Run No.	Fluid Phase	a	b	c (min)	Std. Err. of Fit $\phi(0)$	A (cm <sup>3</sup> /sec)	B
104	6.1 m NaCl	0.4501	0.044408	5.4	0.009	0.375	1.10 25
109	6.1 m NaCl	0.4386	0.044613	3.9	0.008	0.378	1.53 34
124	0.14 m NaCl 5 m MgCl <sub>2</sub>	0.5480	0.037301	113.7	0.004	0.371	0.044 1.18
125	Wet Dodecane	0.7173	0.068266	263.2	0.011	0.337	0.035 0.508
126	Dry Dodecane	0.3798	0.011706	10.4	0.003	0.352	0.151 12.9
113	Air	0.4025	0.023010	0	0.001		

<sup>a</sup>All runs were made with 75 g of salt cut 1 (cf. Table 3) in the 2.54 cm i.d. monel tube, with an applied stress of 155 bars, and at ~20°C. The parameters a, b, c (Eq. 4) were fitted by least squares with the indicated standard deviation. The parameters  $\phi(0)$ , A and B (Eq. 3) are derived from a, b, and c using Eq. 5.

Curves in Fig. 7 have the order NaCl > wet dodecane > 5 m MgCl<sub>2</sub> > dry dodecane > air. This result is the expected one with the exception of wet dodecane, that is, dodecane in contact with undried salt. The small amount of NaCl brine present evidently greatly enhances the rate of consolidation. The 5 m MgCl<sub>2</sub> brine, involving much lower NaCl concentrations, considerably retards consolidation. The low consolidation rate in air indicates that mechanical deformation does not play a large role in consolidation.

### 3.7 Permeability of Consolidating Salt

The permeability  $P_m$  of a consolidating column of salt varied approximately as the square of the average particle size and decreased rapidly as consolidation proceeded. The results are summarized in Fig. 9, where the log of the ratio  $P_m/\bar{z}(0)^2$  is plotted vs. the log of the void fraction. Though there is considerable scatter, a good correlation is obtained with a straight line corresponding to the expression

$$\ln P_m(t)/\bar{z}(0)^2 = 21 + 6 \ln \phi(t), \quad (11)$$

where the permeability is defined as the brine flow (g/min) through a 1-cm<sup>2</sup> area under a hydrostatic pressure gradient of 1 bar/cm; that is, the units are g-cm<sup>-1</sup> min<sup>-1</sup> bar<sup>-1</sup>. The right-hand scale in Fig. 9 shows the specific permeability  $P_s$  in darcy units, which is the flow (cm<sup>3</sup>/s) of a liquid with a viscosity of 1 cP through 1-cm<sup>2</sup> area under a hydrostatic pressure gradient of 1 atm/cm. The specific permeability predicted from the Blake-Kozeny equation,<sup>12</sup> a good empirical correlation for porous media, is given by

$$P_s(\text{darcy}) = 6.76 \cdot 10^6 z^2 \phi^3 / (1 - \phi)^2. \quad (12)$$

For saturated brine at room temperature, with a density of 1.205 g/cm<sup>3</sup> and a viscosity of 1.27 cP, the predicted permeability is

$$P_m(\text{g-cm}^{-1} \text{min}^{-1} \text{bar}^{-1}) = 2.72 \cdot 10^7 z^2 \phi^3 / (1 - \phi)^2. \quad (13)$$

This equation was used to construct the dashed curve in Fig. 9.

The Blake-Kozeny equation gives a good estimate of the initial permeability of an unconsolidated bed of salt crystals. As consolidation proceeds, the expected dependence of permeability on the square of the initial particle size remains a good approximation; however, the permeability falls much more rapidly with the void fraction than this equation predicts, showing about a sixth power dependence. If this dependence continues below  $\phi = 0.06$  (the lower limit of our measurements), then at void fractions of 0.02 in a bed of consolidated 100- $\mu$ m crystals (which could be reached after only one week under some of our experimental conditions), the specific permeability would be about 0.2  $\mu$ darcy. Thus, consolidation of salt crystals may ultimately permit achievement of a permeability comparable to that of intact salt.

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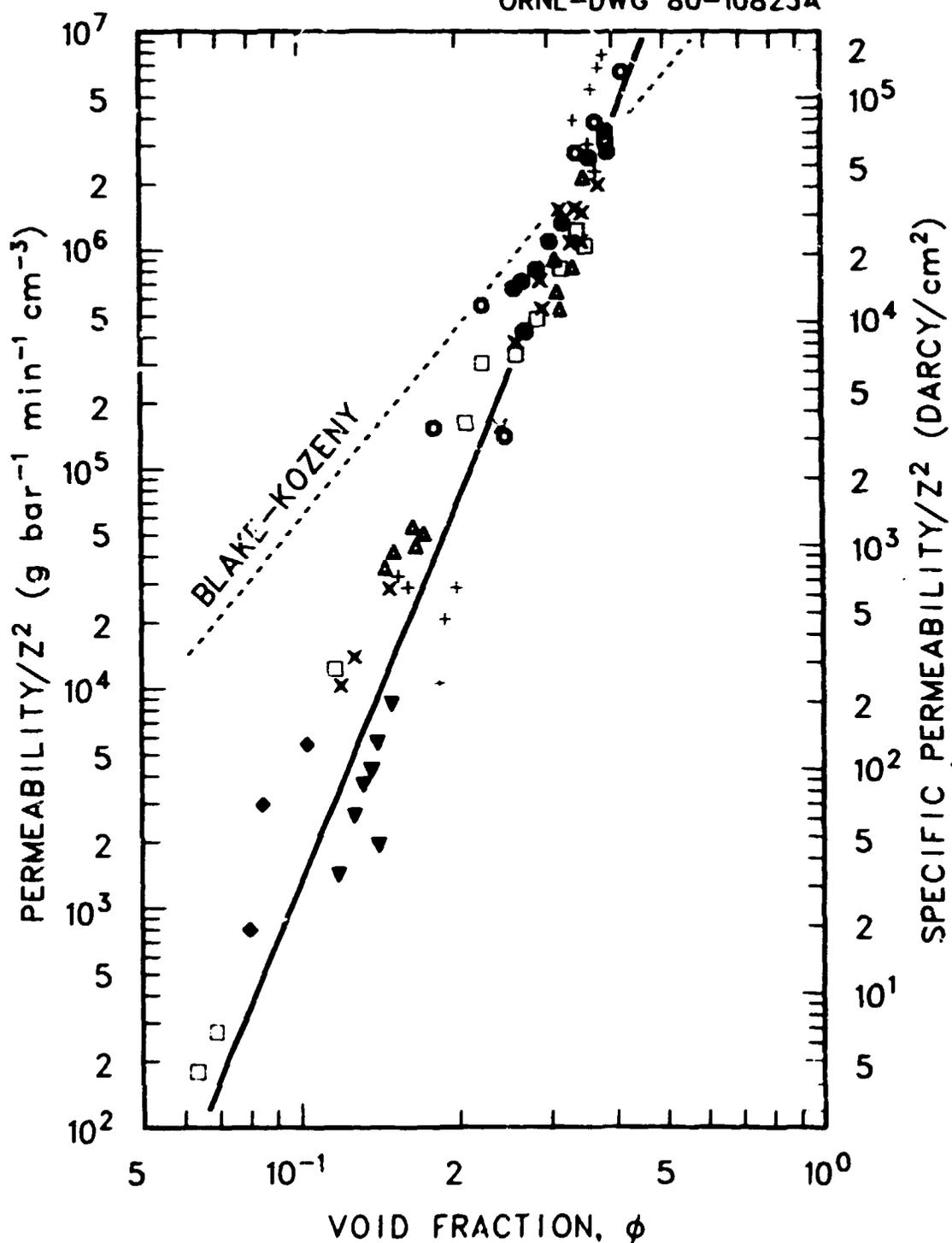


Fig. 9. Permeability of salt columns in which the void fraction is reduced by consolidation. The various symbols denote different runs. The solid line has been drawn with a slope of 8, and the dashed line represents permeability predicted by the Blake-Kozeny equation.

#### 4. SUMMARY AND CONCLUSIONS

Beds of salt crystals in brine and other fluids subjected to a constant applied stress consolidated in an approximately linear fashion with the logarithm of time. The rate increased with increasing stress and decreased with increasing particle size. The decrease of the void fraction  $\phi$  with time  $t$  could usually be described almost within experimental error (Figs. 2-6, 7, Table 1) by a simple three-parameter equation [Eq. (4)].

This equation can be transformed [Eqs. (5)] into one [Eq. (3)] suggested by Coble<sup>8,10</sup> to describe the kinetics of sintering in terms of three parameters—the initial average particle size  $\bar{z}(0)$ , a rate constant  $A$  for the loss of void volume, and a rate constant  $B$  for the growth of the average particle size. It was found that the initial void fraction  $\phi(0)$  and  $A$  varied approximately linearly with the applied stress  $\sigma$ .

A substantial wall effect was indicated by an observed decrease of the void fraction with distance from the top of the consolidating column where the stress was applied (Fig. 5) and by the observation that shorter columns consolidated faster than taller ones of the same diameter (Fig. 3a). This effect was represented by an exponential decrease in the local stress with distance from the top of the column expressed as the weight of intervening salt  $w$  [Eq. (7)].

This correction for the wall effect and an assumed linear dependence of  $\phi(0)$  and  $A$  on the local stress gave a general expression [Eq. (9) and Table 2] that could be fitted to all the consolidation data obtained in NaCl brine for both 2.54-cm-diam columns in Monel tubes and 1.27-cm columns in glass tubes and at temperatures from 20 to 85°C. The parameter  $C$ , the weight of salt through which the local stress is assumed to drop by a factor of  $e$ , was found to increase as about the sixth power of the column diameter. Thus, the distance down the column through which the local stress decreases by a given amount due to the wall effect appears to increase as about the fourth power of the diameter. The limited data at elevated temperatures (to 85°C) suggested that  $A$  and  $B$  increased with about the same exponential dependence on the absolute temperature (Table 3) and that the wall effect decreased with increasing temperature.

In fitting the data, it was necessary to adjust the initial void fraction  $\phi(0)$  for each run (Table 2), evidently because this quantity depended to some extent on the particle size and the size distribution (Table 3) as well as the stress.

The rate of consolidation was found to decrease markedly when large amounts of  $MgCl_2$  were added to the brine (Fig. 7), presumably because of the resulting decrease in the solubility of NaCl (Table 4). Even undred salt in dodecane consolidated more rapidly than salt in the magnesium-rich brine, suggesting that the concentration of NaCl in the brine is more important than the amount in determining the rate of consolidation. Dried salt in air showed the lowest consolidation rate, suggesting that mechanical deformation was not an important mechanism in consolidation.

The permeability of salt columns decreased with the second power of the initial particle size [Eq. (12)], as expected from the Blake-Kozeny equation;<sup>12</sup> but as consolidation proceeded the permeability decreased with the sixth power of the void fraction [Eq. (11)], much more rapidly than would be expected from the Blake-Kozeny correlation (Fig. 9).

Several important implications may be drawn from these studies regarding the suitability of bedded halite as a storage medium for radioactive waste. Perhaps most

important are (1) the rapidity with which consolidation can take place and (2) the low permeabilities that can result. Thus, from the general expression fitted to our data in NaCl brine, at a lithostatic stress of about 100 bars and a temperature of 30°C, we have

$$\phi(t) = \phi(0) - 0.04 \ln \left( 1 + 0.3t/z(0)^3 \right), \quad (14)$$

when  $t$  is expressed in years and  $z(0)$  in centimeters. Extrapolating this expression to larger crystals and longer times suggests that a medium of 1-cm crystals would consolidate and, from Eq. (11), lose its permeability to flowing NaCl brine about as follows:

	Time (y)						
	0	10	100	1000	10,000	27,000	34,700
$\phi$	0.37	0.31	0.23	0.14	0.05	0.01	0.00
$P_m$ (darcy)	86,000	30,000	5000	250	0.5	$3 \times 10^{-6}$	

If the initial size of the crystals were reduced to 1 mm, these times would be reduced a thousand-fold; that is, consolidation would be complete in about 35 years. The permeability at a given void fraction would be reduced a factor of 100 and at 27 years would have fallen to 0.3  $\mu$ darcy. Thus, the self-sealing properties of bedded salt which originally attracted attention to this material as a storage medium are supported by the present measurements.

Another important implication is the fact that the present consolidation results can be rationalized in terms of an expression developed to treat sintering kinetics. If, as appears to be the case, salt consolidation is indeed analogous to sintering, then it involves the growth of crystals by the movement of grain boundaries. This would provide a means of including foreign ions within crystals. While NaCl is a poor sorber for all radionuclide ions except possibly  $\text{Cs}^+$  and  $\text{I}^-$  in very small amounts, it is quite possible that other minerals and barrier materials could consolidate by a similar mechanism and thus provide a possibly important mechanism for the immobilization of radionuclide ions.

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