

Dissolving of Compressed Salt Blocks

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ABSTRACT

Although grid-plate dissolvers using compressed salt blocks have been in use for a considerable length of time, there appear to be no references in the literature as to the actual rates of brine formation which may be expected of dissolvers with varying configurations.

A preliminary study was made to determine the factors that influence the brine-forming rate and an equation developed for the estimation of brine concentration at any elapsed time.

INTRODUCTION

Although grid-plate dissolvers using compressed salt blocks have been in use for a considerable length of time, there appear to be no references in the literature as to the actual rates of brine formation which may be expected from such dissolvers with varying configurations.

Attempts to correlate experimental data obtained under different conditions were unsuccessful, initially, since the available theoretical equations could not be applied because of the many variables encountered. Therefore, a preliminary study was made to determine the factors that influence the brine-forming rate. From the results, a simplified equation was developed for the estimation of brine concentration at any elapsed time.

THE PROBLEM

The immediate problem was to determine the time required to produce specific quantities of brine of a particular concentration using 50-pound evaporated salt blocks, known as brine blocks. Two of the basic theoretical equations applying to solubility are as follows:

1. Fick's Law (1855)

$$\frac{dw}{dt} = - DA \frac{dC}{dx} \quad (1)$$

where dw = quantity of solute diffusing at right angles to the surface being dissolved

A = surface area

dC = rate of change of concentration in a distance dx from the surface

x = distance

t = time

D = diffusion constant

2. Noyes and Whitney equation (1897)

$$\frac{dw}{dt} = -K'S(C_s - C) \quad (2)$$

where dw = loss in weight of the particle in a given time

t = time

S = surface of the particle

C_s = concentration of a saturated solution (at the particle surface)

C = concentration existing in the solution

K' = rate constant for the particular conditions

As pointed out by Dallavalle (1951, p. 246) Pick's law applies only for linear diffusion where there is no motion of the medium or particle. This was not true of the practical situation being studied: As soon as a salt block begins to dissolve convection currents are set up because of the different densities of water and brine and the nature of these convection currents affects the rate of brine formation.

The Noyes and Whitney equation appeared to present an easier approach to the solution of the problem since all the parameters except one are easily measurable. The one exception is S , the surface area. Garner and Hoffman (1961, p. 148) while engaged in a theoretical study of a similar problem determined both surface area and weight by compressing their solid into spheres, weighing and then photographing the spheres at fixed time intervals while the solid spheres were dissolving in containers with plane glass windows in two opposite sides. Simple calculations gave them the required figures.

Anyone who has ever observed a salt block dissolving will readily see why the Garner and Hoffman method was completely inapplicable to the work being discussed. A 50-pound salt block is roughly square in cross section, about $8\frac{1}{8}" \times 8\frac{1}{8}"$ at the smaller end and $8\frac{1}{2}" \times 8\frac{1}{2}"$ at the larger, and with all four corners beveled. The block is 11" long and hand and/or stake holes are provided at each end. Considerable figuring would be required to determine the surface area of a block before it begins to dissolve; determination of surface area after dissolution had commenced would be barely possible even if the block dissolved uniformly over its entire surface.

The actual dissolution of a block is anything but uniform. It varies with the depth of immersion and the method of immersion. The extent of the problem becomes apparent when we place a block on the bottom of a container with the liquid level about $\frac{2}{3}$ of the way up. As soon as the block begins to dissolve convection currents are set up. These are illustrated in Fig. 1.

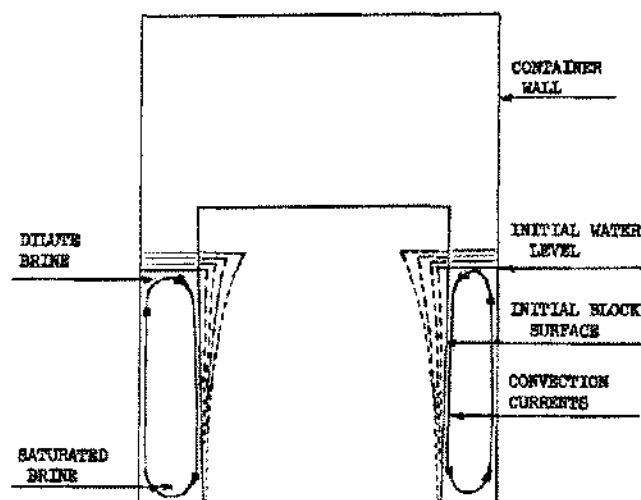


Figure 1. Convection Currents under Deep Immersion Conditions.

The heavy lines indicate the initial water and block surfaces. Lighter lines indicate subsequent stages. It will be noted that the block dissolves fastest near the surface of the water because the convection currents keep bringing up the unsaturated brine to the top. As it contacts the block the salinity increases and the brine flowing down along the block surface dissolves less and less salt. At the very bottom of the container a layer of saturated brine reduces solubility to zero.

It can be readily seen that under these conditions there is a great difference between exposed surface area and effective surface area and that this method of dissolution is not particularly useful for the determination of solubility rates although it is one of the most effective methods for making brine from blocks.

THE APPROACH TO A SOLUTION

It was found that placing the salt block on a grid plate in a container just a little larger in cross section than the block, and keeping the immersion to a minimum (about 1/4") gave a more effective method for the determination of solubility rates. As Fig. 2 shows, a precaution had to be taken to keep the immersion from increasing as brine was formed. An overflow was provided at the proper height to keep the liquid level constant. At the required time intervals the brine in the dissolver was drained into a separate container, brine in the beaker was added to it and the salinity was determined. The brine was then replaced in the dissolver through the funnel shown, any excess immediately overflowing into the beaker.

A large number of runs was made using the equipment illustrated, with the grid plate set at varying heights. Considering the variability which is inherently present in individual blocks, curves drawn through the plotted data points gave reasonably accurate predictions of brine concentration versus time, but difficulty was still experienced in arriving at a reasonably constant dissolving rate constant. Since this was a practical problem rather than a theoretical one, it was decided to consider the surface area as constant for the duration of any particular run. Furthermore, if the surface area were calculated in terms of block units, S would become one for a single block and could be eliminated from the Noyes and Whitney equation. In addition, the minus sign before K was dropped because we were more interested in the increase of solute in the solution than in the decrease in weight of the solid. The resulting equation was:

$$\frac{dw}{dt} = K (C_s - C) \quad (3)$$

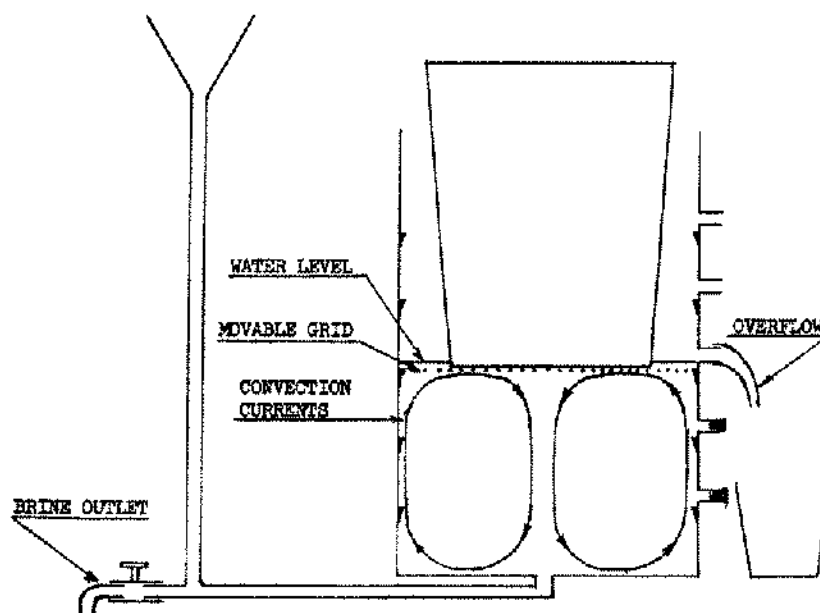


Figure 2. Equipment used to Determine Solubility Rates.

Attempts to derive K using the experimental data and equation (3) were not too successful chiefly because of errors in determining $(C_s - C)$ or ΔC . For small ranges of concentration these errors were negligible. Thus, it could be said with reasonable accuracy that between an initial salinity of 0° and a final salinity of 1° the mean ΔC was:

$$\frac{(100 - 0) + (100 - 1)}{2} = 99.5$$

Similarly between an initial salinity of 90° and a final one of 91° the mean ΔC was:

$$\frac{(100 - 90) + (100 - 91)}{2} = 9.5$$

The actual experimental results covered considerably greater salinity ranges than this, and it was quite incorrect to say, for example, that between an initial salinity of 0° and a final one of 90° that the mean ΔC for the time period was the arithmetic average.

$$\frac{(100 - 0) + (100 - 90)}{2} = 55$$

DEVELOPMENT OF TABLE OF CONCENTRATION-TIME FACTORS

What was needed at this point was an integrated mean concentration. This figure could have been calculated for each experimental determination, but such calculations would be subject to the error that usually creeps in when a tedious calculation has to be performed a large number of times. In addition, if similar experiments were again carried out after a period of time, the calculations would have to be repeated. A table was therefore prepared so that, knowing the final salinity, the integrated mean salinity difference could be immediately read off from the table. The development of the table was as follows:

If we express our concentration in degrees of salinity and let M equal the maximum weight of solute that the solution can hold at saturation we obtain the relationship

$$C = \frac{100w}{M} \quad (4)$$

Since the concentration at saturation is 100°, substituting (4) in (3) gives

$$\frac{dw}{dt} = K \left(100 - \frac{100w}{M} \right) \quad (5)$$

On grouping the variables,

$$\frac{dw}{M-w} = \frac{100 K}{M} dt \quad (6)$$

Integrating (6) and letting $w = 0$ at $t = 0$ and transposing,

$$t = \frac{M}{100K} \ln \left(\frac{M}{M-w_t} \right) \quad (7)$$

Substituting $\frac{100w_t}{C}$ for M inside the bracket gives

$$t = \frac{M}{100K} \ln \left(\frac{100}{100-C} \right) \quad (8)$$

Now if we let T_f (time factor) = $\ln \left(\frac{100}{100-C} \right)$, and substitute in equation (8),

$$t = \left(\frac{M}{100K} \right) T_f \quad (9)$$

Letting C (Integrated average concentration) = $\frac{C}{T_f}$ (10)

We derive our other final equation: $K = \frac{w_t}{t C_i}$ (11)

In determining the time factor T_f it was assumed that the dissolving rate would depend primarily on the difference between the salinity at the surface of the block and the salinity of the entire solution, and that the rate at which convection currents brought unsaturated brine to the dissolving surface would be relatively constant. Experiments indicate that this is not so, for K values calculated in this fashion decrease as the salinity increases and the time required to reach saturation is considerably greater than that indicated by equation 9. Apparently viscosity and density affect the velocity of the convection currents, so T_f must be compensated for these effects. An empirical compensated time factor T_{fc} was derived using the equation. . . .

$$T_{fc} = T_f \left(1 + \frac{C^A}{10,000} \right) \quad (12)$$

. . . . and successively assigning the values 1.8, 1.9, 2.0, 2.1 to A. The time factor T_f in equation 9 was then replaced by T_{fc} giving

$$t = \left(\frac{M}{100K} \right) T_{fc} \quad (13)$$

A FORTRAN program was set up for an IBM 7070 computer and a table giving T_f , C_i , T_{fc} for 0.5 degree increments of C from C = 0.5 to C = 99.5 was generated. The results are given in condensed form in Table 1 which contains seven columns.

Column 1 is C -- Concentration at time t

Column 2 is T_f -- Time factor

Column 3 is C_i -- Integrated average concentration over the time span 0 to t

Columns 4, 5,

6, 7 are T_{fc} -- Compensated time factors for the successive values of A

Columns 2 and 3 are given to four decimal places because they are independent of experimental conditions. The others have three significant figures which is more in accord with the accuracy associated with practical work.

A comparison between theoretical curves and actual experimental values indicated that the best correlation was obtained using 1.9 as the value of A, so that was the figure used in subsequent calculations. The compensated time factors for other values of A were included in the table because they may more nearly approximate the actual results when other dissolver configurations are used.

Now let us consider a practical application of these equations using actual experimental data to first determine the "K" factor.

Hours	Degrees Salinity	Pounds Salt Dissolved	K
0.5	19	1.55	0.0344
1.0	32	2.71	0.0327
2.0	50	4.47	0.0311
4.0	70	6.66	0.0286

The K values in pounds/(hr.) ($^{\circ}\Delta C$) were determined using equation 11 and C_i from Table 1. For example, for a final salinity of 70 degrees,

$$K = \frac{w_t}{t C_i} = \frac{6.66}{4 \times 58.14} = 0.0286 \text{ lb. / (hr.) } (^{\circ}\Delta C)$$

The K values were graphically extrapolated to zero concentration giving an approximate value of 0.036 for K. Using the compensated time factor, T_{fc} , this K value at zero concentration can be used as a constant over the entire range of concentration, when we use equation 13 and Table 1 to determine t. Thus, if we wanted to determine the time it would take to make five gallons of 80° brine, using a 50-pound brine block in a grid-plate dissolver slightly larger in C.S.A. than the

Table 1. Concentration and Time Factors

Concentration, C (Degrees salinity)	Time Factor, T_f	Integrated Concentration Difference, C_i	Compensated Time Factor, T_{fc}			
			A=1.8	A=1.9	A=2.0	A=2.1
2	0.0202	98.9957	0.02	0.02	0.02	0.02
4	0.0408	97.9864	0.04	0.04	0.04	0.04
6	0.0619	96.9691	0.06	0.06	0.06	0.06
8	0.0834	95.9443	0.08	0.08	0.08	0.08
10	0.1054	94.9120	0.11	0.11	0.11	0.11
12	0.1278	93.8720	0.13	0.13	0.13	0.13
14	0.1508	92.8239	0.15	0.15	0.15	0.15
16	0.1744	91.7674	0.18	0.18	0.18	0.18
18	0.1985	90.7023	0.20	0.20	0.20	0.21
20	0.2231	89.6282	0.23	0.23	0.23	0.24
22	0.2485	88.5448	0.25	0.26	0.26	0.26
24	0.2744	87.4517	0.28	0.29	0.29	0.30
26	0.3011	86.3485	0.31	0.32	0.32	0.33
28	0.3285	85.2348	0.34	0.35	0.36	0.36
30	0.3567	84.1102	0.37	0.38	0.39	0.40
32	0.3857	82.9741	0.41	0.41	0.42	0.44
34	0.4155	81.8261	0.44	0.45	0.46	0.48
36	0.4463	80.6656	0.47	0.49	0.50	0.53
38	0.4780	79.4920	0.51	0.53	0.54	0.58
40	0.5108	78.3046	0.55	0.57	0.59	0.63
42	0.5447	77.1028	0.59	0.61	0.64	0.68
44	0.5798	75.8858	0.63	0.66	0.69	0.74
46	0.6162	74.6527	0.68	0.71	0.75	0.81
48	0.6539	73.4027	0.72	0.76	0.81	0.88
50	0.6931	72.1347	0.77	0.81	0.87	0.95
52	0.7340	70.8476	0.82	0.87	0.93	1.03
54	0.7765	69.5402	0.88	0.93	1.00	1.11
56	0.8210	68.2111	0.94	0.99	1.08	1.21
58	0.8675	66.8587	1.00	1.06	1.16	1.31
60	0.9163	65.4814	1.06	1.14	1.25	1.41
62	0.9676	64.0771	1.13	1.21	1.34	1.53
64	1.0217	62.6437	1.20	1.30	1.44	1.66
66	1.0788	61.1785	1.28	1.39	1.55	1.79
68	1.1394	59.6787	1.37	1.48	1.67	1.94
70	1.2040	58.1408	1.46	1.59	1.80	2.11
72	1.2730	56.5608	1.55	1.70	1.94	2.29
74	1.3471	54.9339	1.66	1.83	2.09	2.48
76	1.4271	53.2542	1.77	1.96	2.26	2.70
78	1.5141	51.5148	1.90	2.11	2.44	2.94
80	1.6094	49.7068	2.04	2.27	2.64	3.21
82	1.7148	47.8190	2.19	2.46	2.87	3.51
84	1.8326	45.8370	2.37	2.66	3.13	3.85
86	1.9661	43.7411	2.56	2.90	3.42	4.24
88	2.1203	41.5043	2.79	3.17	3.76	4.69
90	2.3026	39.0865	3.06	3.49	4.17	5.23
92	2.5257	36.4251	3.39	3.89	4.67	5.89
94	2.8134	34.4114	3.82	4.39	5.30	6.73
96	3.2189	29.8241	4.41	5.10	6.18	7.90
98	3.9120	29.0510	5.41	6.29	7.59	9.85
99	4.6052	21.4976	6.41	7.46	9.12	11.75

block, we would first determine M the weight of salt required to make five gallons of saturated brine. This would be 13.25 pounds. For a final concentration of 80°, T_{fc} is equal to 2.27 at an A value of 1.9. Then,

$$t = \frac{13.25 \times 2.27}{3.6} = 8.4 \text{ hrs.}$$

As long as the dissolver configuration is kept relatively constant the results obtained by the method shown are reasonably accurate though the solubility rate constant appears to be greater at greater grid heights. This can be explained on the assumption that the velocity of the convection current is higher at greater elevations. Experimental results with the grid plate set at 2.5, 5.0, and 10.0 inches are shown in Fig. 3. In each case the curve represented by equation (13) fits the points fairly well, though the K values vary from one curve to another. A height of grid factor should therefore be incorporated into equation (13) in order to make it more general.

Two other factors appear to have an important bearing on the time required for the solution to reach the desired concentration. It has been observed that, when compressed salt is dissolved on a grid plate in the manner shown, there is an apparent increase in K values (based on actual surface) when the surface decreases, and a decrease in K when surface increases. K appears to be more uniform when it is considered in relation to the periphery of the exposed surface, than it is in relation to the surface itself. Figure 2 shows the nature of the observed convection currents. Upwardly flowing brine of low saturation contacts the surface of the block near its periphery much more than it does the surface near the middle of the block. This would have to be taken into consideration if equation 13 were to be applied to a wider range of practical situations.

The third factor appears to be related to the ratio of the cross-sectional area of the block to the cross-sectional area of the dissolver. The work discussed was done with the dissolver only

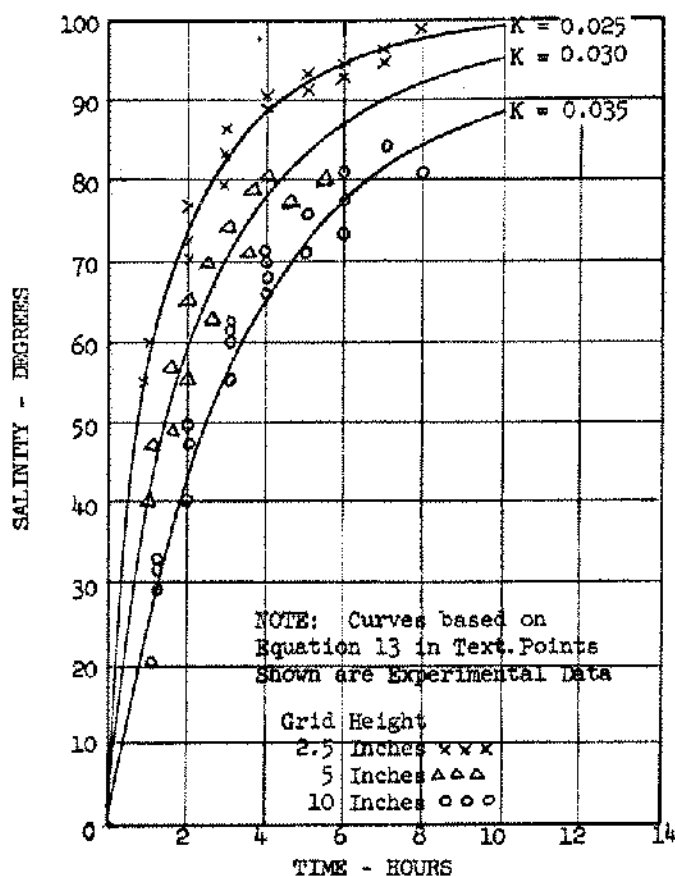


Figure 3. Variation of Salinity with Time at Different Grid Heights.

slightly larger in cross section than the salt block. This would probably be the ideal situation insofar as convection currents are concerned. As the area of the dissolver increases in relation to the area of the salt block, convection, as a means of mass transfer, becomes less and less important and diffusion increases in importance. Under these conditions we would expect that the time required for the brine to reach a particular concentration would increase over that calculated by equation 13. There are indications that this is indeed so, but no work has been done which would permit us to express the amount of this increase quantitatively.

SUMMARY

Mass transfer coefficient, K , was determined for compressed salt in a one-block, grid-plate dissolver. It was observed that considerable variation in K from that predicted by a first order solubility equation occurred because of the variation of convection current velocities with concentration. A method was developed by which the maximum K value could be determined by graphically plotting K values at various concentrations and extrapolating to zero concentration. Using this K value, and a compensated time factor, T_{fc} , the time required to produce a given volume of brine of a specified concentration in a one-block grid-plate dissolver can be simply calculated. It is believed that the method developed here can be used as a guide in the design of dissolvers of different configuration.

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Appendix A. Fortran Program for Calculating Table 1

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DIMENSION CN(200), T(200), CA(200), TA(200), TB(200), TC(200), TD(200)
Y = LOGF (100.)
DO 10 I = 1,199
X = 1
CN(I) = X/2.
T(I) = Y - LOGF (100.-CN(I))
A = (CN(I)**1.8)/10000.
TA(I) = T(I)*(1.+A)
B = (CN(I)**1.9)/10000.
TB(I) = T(I)*(1.+B)
C = (CN(I)**2.0)/10000.
TC(I) = T(I)*(1.+C)
D = (CN(I)**2.1)/10000.
10 TD(I) = T(I)*(1.+D)
PRINT 20, (CN(I), T(I), CA(I), TA(I), TB(I), TC(I), TD(I), I = 1,199)
20 FORMAT (
```