

Higher Raw Brine Purity From Rock Salt

Richard R. Mitchell

Project Engineer
International Salt Company
Clarks Summit, Pa.

ABSTRACT

Brine prepared from rock salt is known to contain as impurities calcium, magnesium, and sulfate ions. The relative concentrations of these ions affects not only the out-of-pocket chemical treating costs, but also the capital cost for sizing of settling tanks and filters for chlor-alkali applications.

A key to higher raw brine purity is the differential in dissolving rates between the sodium chloride and the non-salt impurities. An aqueous solvent in contact with rock salt will become saturated with sodium chloride in a few minutes whereas hours may be required to reach saturation levels of the impurities. A simple laboratory test has been devised to determine the effects of various factors on the purity of raw brine from rock salt. Included among these factors are contact time, salt-to-solvent ratio, solvent pH, solvent temperature and common ion retardation.

The effect of geographical source of the rock salt was also studied under various environmental dissolving conditions.

INTRODUCTION

Brine prepared from rock salt is known to contain as impurities calcium, magnesium, and sulfate ions. Before it is suitable for use in chlor-alkali cells, brine must be purified by chemical precipitation, settling, and filtration. The cost of treating chemicals and, to a certain extent, the size of treating equipment depends on the raw brine purity, i.e., for brines containing larger amounts of dissolved impurities, more treating chemicals are required, more floc must be taken from the settling tanks, and more entrained solids must be removed

by the filters. If the purity of raw brine could be substantially improved, equipment and chemical treating costs could be reduced considerably, or possibly, the need for brine treatment could be eliminated altogether.

It is the purpose of this work to determine the potential optimum raw brine purities which can be achieved under various operating conditions and with rock salt from various sources. Whereas inhibitors such as the polyphosphates have been used to improve brine purity, these will not be covered here. Also, the work will not cover the many types of dissolving equipment which are available.

A key to higher raw brine purity lies in the fact that the sodium chloride fraction of rock salt dissolves many times faster than the non-salt impurities. An aqueous solvent in contact with rock salt will become saturated with sodium chloride in a matter of minutes, whereas hours are required to reach saturation levels of the impurities. The point is illustrated in Figure 1.

The slope of the curves may be interpreted as the rate of dissolution. The difference in dissolving rates is apparent.

By means of a simple laboratory dissolving test, various factors have been studied which are known to influence the dissolving rate of rock salt impurities.

DISSOLVING TESTS— ANALYTICAL PROCEDURES

One liter of distilled water, adjusted to the desired pH and temperature, was placed in a vigorously agitated vessel. Temperatures were monitored throughout the test, and when

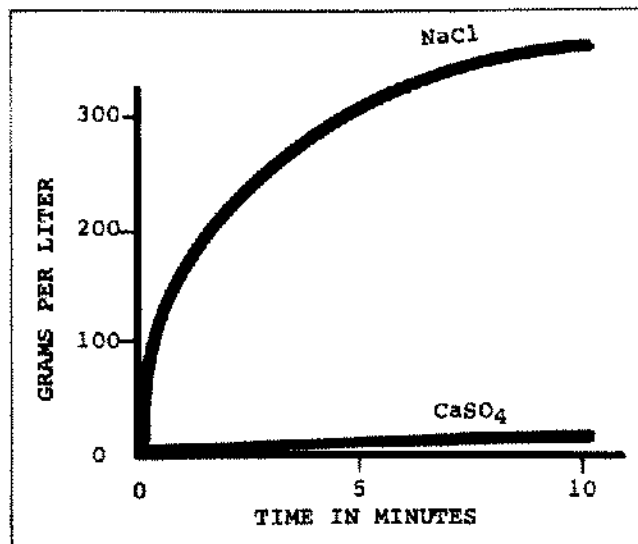


Figure 1.

necessary, heat was applied by means of a hot plate. As the start of a stopwatch, rock salt was added to the water, and, at intervals of 2, 10 and 60 minutes, 40 ml samples of brine were removed from the system. These were filtered in a Buchner funnel and were subsequently analyzed for hardness by the Schwarzenbach method, and for sulfate by a turbidimetric method. The next three figures will show the type of data which was taken. The source of the rock salt was a mine in New York State.

In Figure 2 the dissolving water was at pH 7 and 70°F. "S = 1" refers to the salt-solvent ratio, i.e., the ratio of salt weight per solvent weight. For convenience, the value of unity is meant to imply that only that weight of salt required to produce a saturated brine has been added to the solvent. At a value of "S = ," a 100% excess of salt is indicated. Figure 3 shows the effect of pH variation. pH levels of 3, 7 and 10 were selected as being inclusive of conditions found in most chemical plant brine operations. Note that the rock salt impurities dissolve faster in acidic solvents. In Figure 4, the effect of temperature variation is shown. Again, the range of 70°F to 160°F was selected to be inclusive of most chemical plant brine operations. As might be expected, the dissolution rates of rock salt impurities are found to increase at higher temperatures.

The next four graphs show data taken on rock salt from Ohio. Note now, the horizontal axis represents solvent pH and the individual curves show

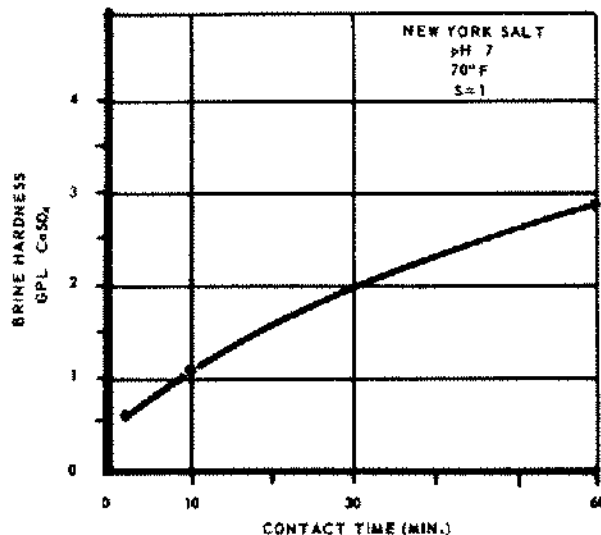


Figure 2.

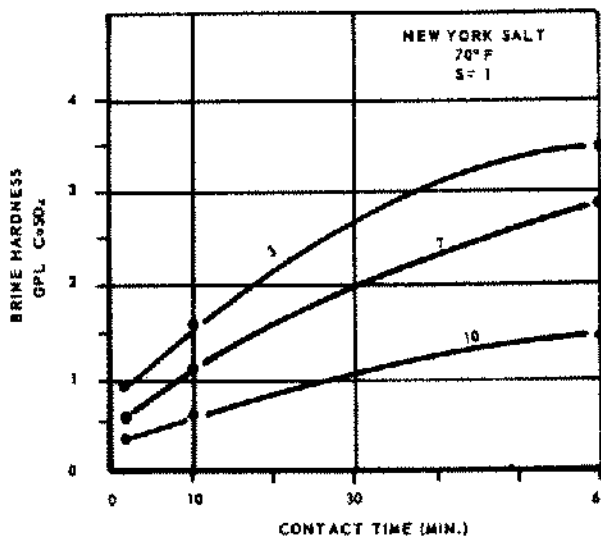


Figure 3.

purity variation due to contact time (2, 10 and 60 minutes). In Figure 5 the temperature is at 70°F with no excess rock salt exposed to the solvent over that required for sodium chloride saturation. Note the higher CaSO₄ levels for the acidic brine and for the extended contact times. Figure 6 shows the effect of increased temperature (160°F).

In Figures 7 and 8 a 100% excess of rock salt is added to the solvent. Because there is more impurity present, the rate of dissolution is increased.

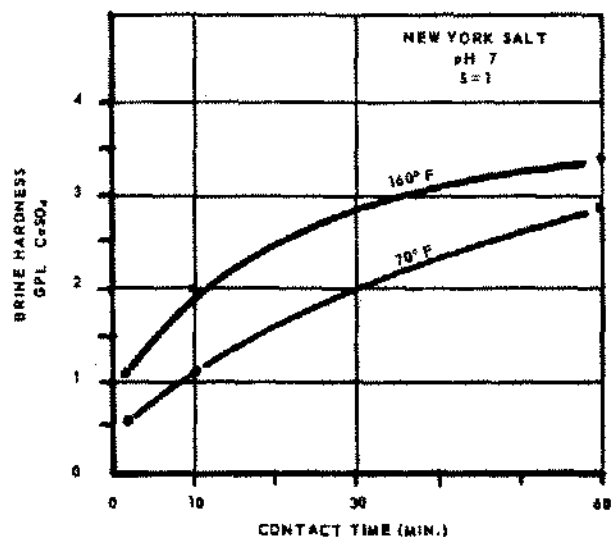


Figure 4.

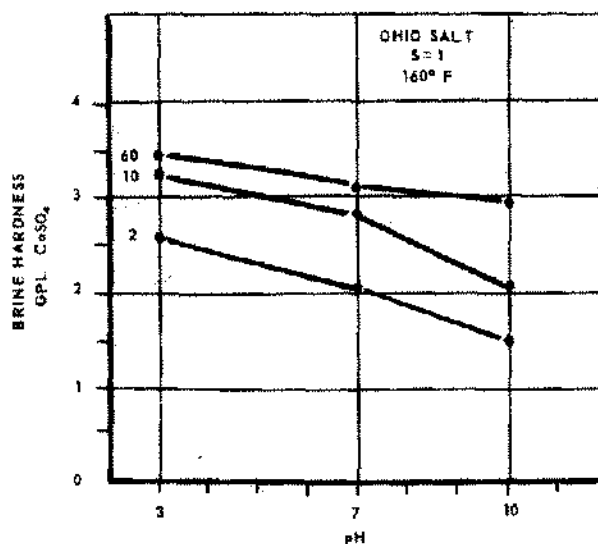


Figure 6.

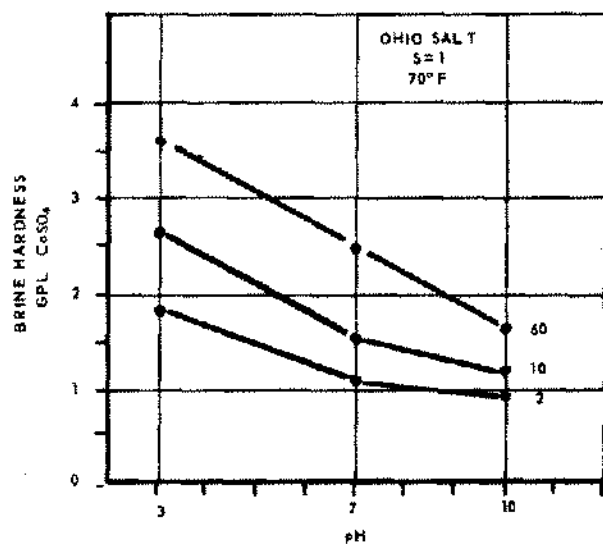


Figure 5.

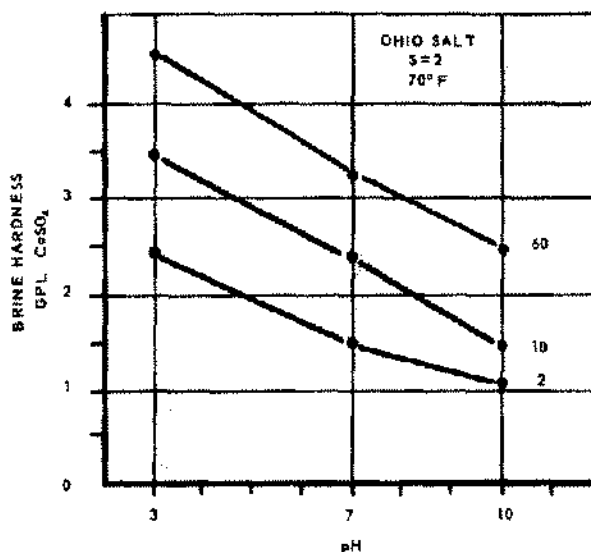


Figure 7.

In all, the study included rock salt samples from five different deposits in the United States. The chemical analyses are shown in Table 1.

It is important to note that the material reported as calcium sulfate is only that quantity of CaSO_4 which would dissolve in 5 minutes under standard laboratory conditions. Actually, the material reported as water insolubles contains much CaSO_4 which would dissolve if given longer contact time. The salts are placed on the table with the

salt having the highest level of CaSO_4 on the left—the lowest on the right.

Particle size of rock salt is known to be a factor in the dissolving rate of the salt. Accordingly, the salt samples used were of similar particle size distribution as indicated by the screen analyses in Table 2.

Figures 9 and 10, at 70°F, show brine purity levels at 2 and 10 minutes contact time respectively. In Figures 11 and 12, similar data is shown

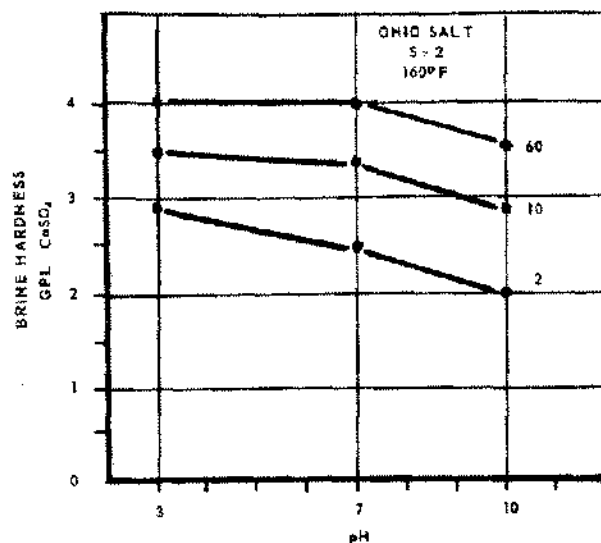


Figure 8.

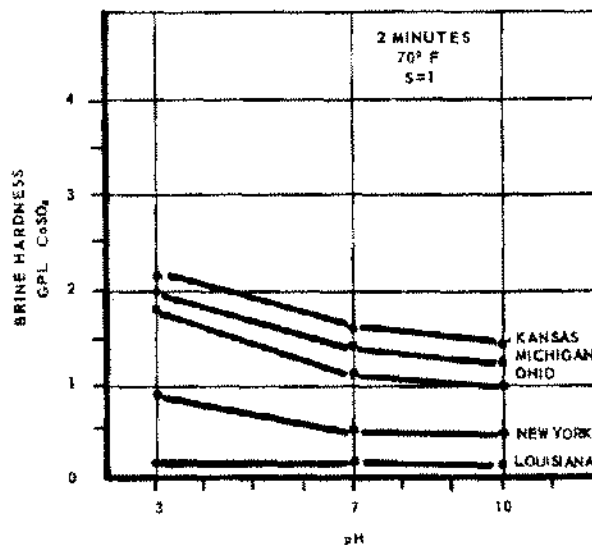


Figure 9.

TABLE 1
CHEMICAL ANALYSES

	Kansas	Michigan	Ohio	New York	Louisiana
Moisture	0.42	0.26	0.13	0.03	0.01
H ₂ O Insol.	2.10	0.63	1.16	1.22	0.72
CaSO ₄	1.33	0.82	0.60	0.59	0.27
CaCl ₂	0.01	0.07	0.02	—	—
MgCl ₂	0.13	0.10	0.06	—	—
NaCl (Wet)	96.01	98.13	98.02	98.16	99.01
NaCl (Dry)	96.43	98.39	98.15	98.19	99.01

TABLE 2
SCREEN ANALYSES

U. S. Sieve No.	Kansas	Michigan	Ohio	New York	Louisiana
4	0.0	0.0	0.0	0.0	0.0
8	0.2	0.0	1.3	0.2	1.6
12	1.8	0.8	22.7	13.5	10.1
20	30.0	41.2	36.5	39.7	47.7
40	28.3	25.5	19.9	22.2	22.4
70	20.8	16.5	—	13.1	8.9
80	3.5	3.2	11.6	2.1	1.2
Pan	15.4	12.8	8.0	9.2	8.0

at 160°F. A summary of all the data taken is given in Tables 3 and 4.

It is recognized that the dissolving rates of rock salt impurities are strongly affected by common ion retardation, i.e., presence of calcium and/or sulfate ions in the solvent will reduce the rate of rock salt impurity dissolution. This is illustrated in Figure 13.

In conclusion, a summary is made of observations derived from the data.

1. Even when commercial sources of rock salt contain similar levels of sodium chloride, they will not necessarily produce brine of the same purity under the same dissolving conditions. The difference in brine purity is not simply a matter of more calcium sulfate in the salt, but rather is due to the dissolving character of the particular calcium sulfate which is present.

2. Reduction of contact time between rock salt and solvent is by far the greatest means available

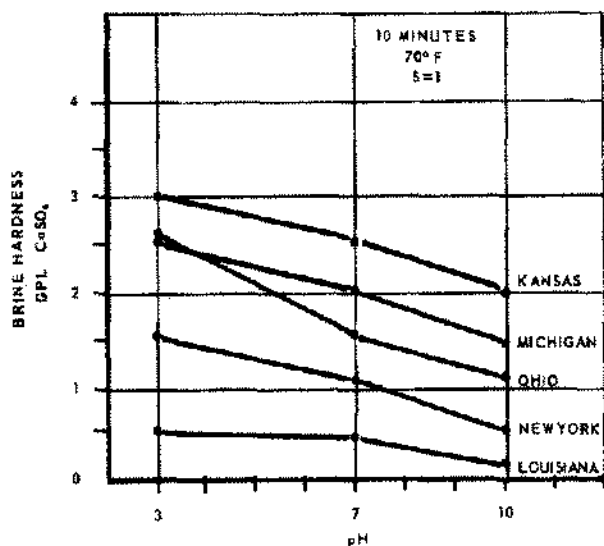


Figure 10.

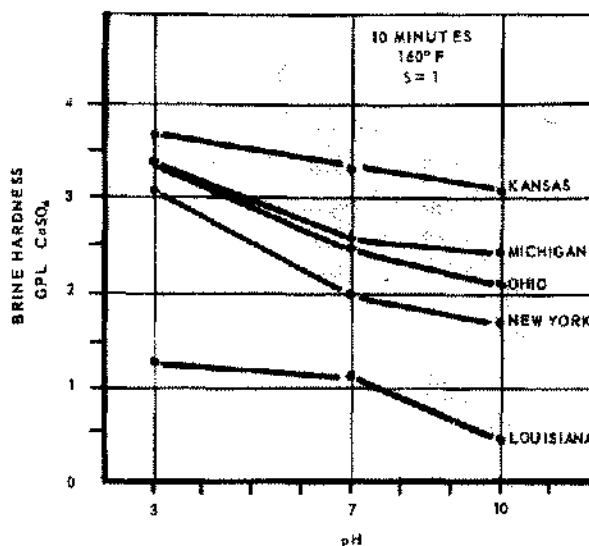


Figure 12.

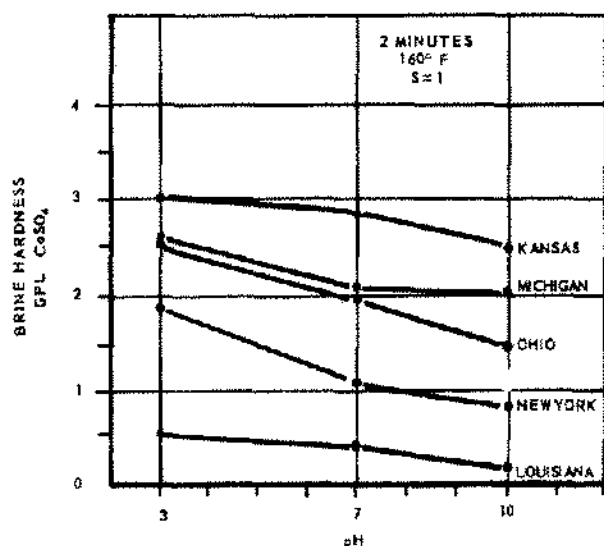


Figure 11.

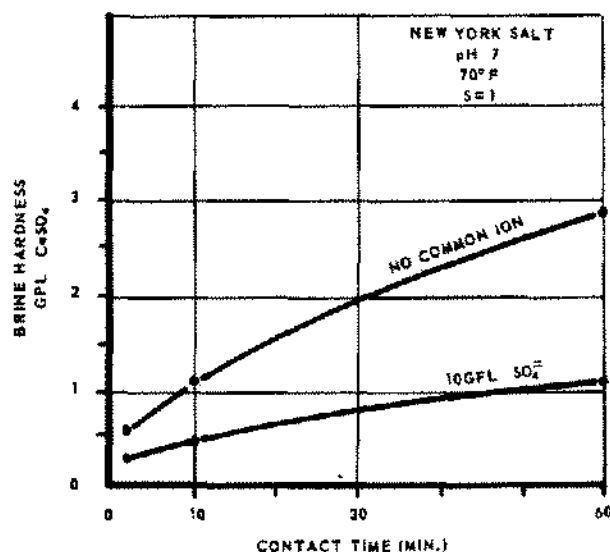


Figure 13.

4. Control of the salt-solvent ratio can improve v brine quality. Situations should be avoided ere large quantities of salt are maintained under ne. Ideally, the salt should be stored and han- d dry, and then introduced into a dissolving item at the rate of dissolution. Only that amount salt should be present in the dissolving zone

which is required to provide saturation. To this same end, undissolved impurities should not be al- lowed to accumulate in the dissolving zone. Means should be provided for continuous, or, at the very least, frequent removal of rock salt impurities from the dissolver.

TABLE 4

BRINE HARDNESS - GPL CaSO_4 (160° F)

NEW YORK STATE											
S=1				S=2							
pH	3	7	10	pH	3	7	10				
(Min) 2	1.9	1.2	0.8	(Min) 2	2.3	1.6	1.0				
10	3.1	2.0	1.8	10	3.0	2.6	2.0				
60	3.7	3.3	3.0	60	4.0	3.8	3.0				

MICHIGAN											
S=1				S=2							
pH	3	7	10	pH	3	7	10				
(Min) 2	2.7	2.1	2.1	(Min) 2	3.8	2.8	3.0				
10	3.3	2.7	2.7	10	4.2	3.6	3.4				
60	3.6	3.2	3.4	60	4.9	4.4	4.3				

OHIO											
S=1				S=2							
pH	3	7	10	pH	3	7	10				
(Min) 2	2.7	2.1	1.5	(Min) 2	2.9	2.5	2.0				
10	3.3	2.8	2.2	10	3.5	3.3	2.8				
60	3.4	3.2	2.9	60	4.0	4.0	3.7				

LOUISIANA											
S=1				S=2							
pH	3	7	10	pH	3	7	10				
(Min) 2	0.5	0.4	0.2	(Min) 2	0.7	0.5	0.5				
10	1.3	1.2	0.5	10	1.2	1.0	0.8				
60	2.0	2.1	1.0	60	3.3	2.7	1.4				

KANSAS											
S=1				No data taken at S=2							
pH	3	7	10								
(Min) 2	3.0	2.8	2.4								
10	3.7	3.3	3.1								
60	3.9	3.4	3.4								