

The Solubilization of Rock Salt Anhydrite

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ABSTRACT

Rock salt deposits in the United States are characterized by 1 to 5 percent impurities, the principal impurity being anhydrite, CaSO_4 , partially soluble in brine.

This paper describes the solubilization of this anhydrite by heat treatment of the rock salt. Results are discussed for rock salt from mines in New York, Ohio, Michigan and Louisiana.

Laboratory and pilot plant studies were made, resulting in average reduction of rock salt insolubles from the level of 1 to 2 percent down to less than 0.1 percent.

The technical literature abounds in references to a variety of forms of the mineral anhydrite—anhydrous CaSO_4 . Cameron and Bell (1906, p. 8) reported "Artificial anhydrite . . . differs from the natural anhydrite mainly in having a greater solubility and possessing only metastability."

Further, they state (p. 24) "By long contact of the soluble anhydrite with boiling water—the solubility decreases—(with)—no change in the solid phase, as the natural anhydrite is more stable than either the soluble anhydrite or the hemihydrate."

"There exists but two forms of this salt which are stable in the presence of any solution—gypsum and natural anhydrite—and the conditions under which one or the other form is stable depend on the temperature and the nature of the solution with which it is in contact—the other two forms—soluble anhydrite and the hemihydrate—are always metastable, and the conditions under which gypsum changes to either one will be determined from the intersection of the proper vapor pressure curves." (Cameron and Bell, 1906, p. 25)

"The only two modifications of calcium sulfate found in nature are, as might be expected, natural anhydrite and gypsum, the stable forms." (Cameron and Bell, 1906, p. 26)

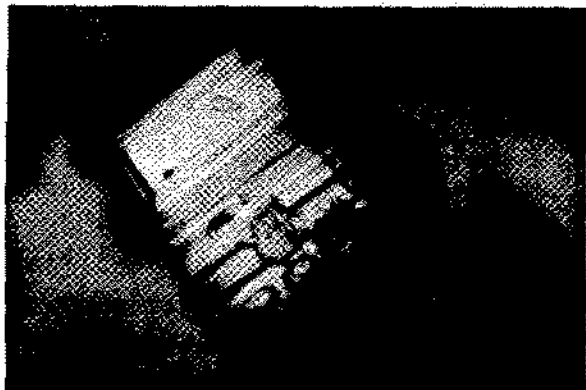
Kelley, Southard, and Anderson (1941, p. 6) reported:

"Two forms of anhydrous calcium sulfate have been generally recognized, namely insoluble (or natural) anhydrite and soluble anhydrite. There is now considerable evidence showing that soluble anhydrite exists in two forms depending on whether alpha—or beta—hemihydrate was used in its preparation. The two varieties accordingly have been called alpha-soluble and beta-soluble anhydrite."

Further, they state (p. 6) "Insoluble anhydrite—may be prepared by heating either of the soluble anhydrites for an hour at about 900°C."

Lawton (1892), McTear (1909) and Webster (1914), obtained U.S. patents on systems to purify rock salt by melting it and allowing the impurities to settle out. The purification of ores and minerals by melting and separation of impurities is widely practiced.

The calcium sulfate content of brine prepared from rock salt varies in accordance with such factors as solvent pH, temperature, and concentrations of sodium chloride and common ions. Another significant factor is the geographical source of the rock salt or, in other words, the nature of the anhydrite which contaminates rock salt from that locality. The following figures illustrate the appearance of the anhydrite grains in samples of rock salt from Louisiana, New York, Ohio and Michigan. Of particular interest is the similarity in appearance of the anhydrite in New



Courtesy: Avery Island, Louisiana

Figure 1.



Courtesy: Retsof, New York

Figure 2.



Courtesy: Cleveland, Ohio

Figure 3.



Courtesy: Detroit, Michigan

Figure 4.

York and Louisiana specimens, and the similarity in appearance of the anhydrite in Ohio and Michigan specimens. These factors are the subject of a separate paper being presented at this symposium. However, the existence in nature of anhydrite with varying degrees of solubility suggests the possibility of conversion of rock salt which is contaminated with anhydrite into a form which will produce a brine of enhanced purity.

It seems possible then that rock salt could be upgraded by melting and refreezing during which process the impurities would either separate by gravity from the molten salt or, according to Kelley, Southard and Anderson (1941), convert from a relatively soluble anhydrite to a relatively insoluble form. Accordingly, a program was established to investigate the extent to which a gravity separation could be made from molten rock salt or

a conversion of anhydrite from a semisoluble to a less soluble state. This program started with initial experiments at the Battelle Memorial Institute under the direction of Dr. William M. Goldberger, Chief of Minerals and Metallurgical Processing. The test involved melting a sample of salt in a vertical 1 1/2" ID vycor tube sealed at the bottom and held vertically in a graphite resistance tube furnace. Experiments were conducted wherein the salt sample was melted and then gradually frozen either from the bottom upward or from the top downward in an attempt to facilitate the separation of impurities from the salt. Analysis of the frozen billets indicated no significant migration of anhydrite in the vertical direction. However, the melts did result in a reduction of water insolubles from an average of 0.4%–0.5% to below 0.1% and in some cases as low as 0.03%. The samples in this first series were

contaminated by silica from the vycor tubes. The results are shown on Table 1.

Table 1

	Water Insolubles Detroit-Cleveland		Soluble CaSO ₄ Detroit-Cleveland	
Original Sample	0.40	0.60	1.30	1.40
Bottom Section	0.94*	0.55*	1.70	1.60
Intermediate	0.39*	0.47*	1.73	1.49
Intermediate	0.25*	0.48*	1.93	1.49
Intermediate	0.097	0.33*	1.81	1.57
Top	0.51*	0.60*	0.70	1.54

Table 2. Spectrographic Analysis of Insolubles, Percent

Original Sample	Cleveland	Detroit
Ca	15-30	15-30
Si	1-3	1-3
Mg	3-5	3-5
Top Section	Cleveland	Detroit
Ca	0.3	0.05
Si	15-30	20-40
Mg	0.5	0.2

Additional melts were then made using graphite crucibles. Tests run on samples of salt from mines in New York, Ohio, Michigan, and Louisiana confirmed that the anhydrite in each case was being converted to a virtually completely soluble state. The results are shown in Table 3.

The following photomicrographs illustrate the appearance of fragments of salt from various sources which have been melted and refrozen. Of particular interest is the change which has taken place in the anhydrite structure.

Table 3

	Water Insolubles Detroit-Cleveland		Soluble CaSO ₄ Detroit-Cleveland	
Original Sample	0.40	0.60	1.30	1.40
Bottom 1/4	0.08	0.36	1.32	1.53
Second 1/4	0.07	0.11	1.33	1.50
Third 1/4	0.07	0.11	1.36	1.47
Top 1/4	0.07	0.09	1.33	1.42



Courtesy: Avery Island, Louisiana

Figure 5.



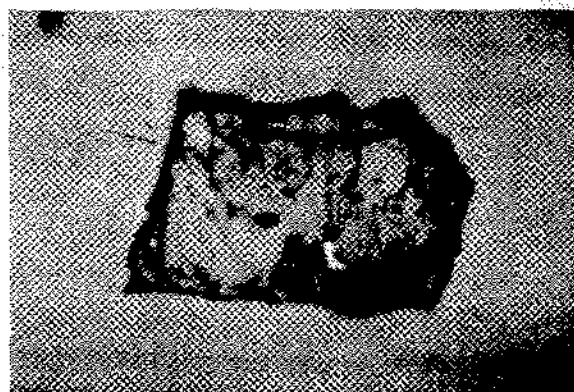
Courtesy: Retsof, New York

Figure 6.



Courtesy: Cleveland, Ohio

Figure 7.



Courtesy: Detroit, Michigan

Figure 8.

The next phase of this program was to check the results on a semi-commercial scale. Results of one-ton melts in an electric furnace confirmed that the anhydrite was being converted irrespective of the geographic sources of the salt. Contamination from the electrodes of the electric furnace caused discoloration of the product but with negligible contribution to the insoluble content. Analysis of the product indicated complete conversion to a soluble form of calcium sulfate. Results of these tests are shown in Table 4.

A series of laboratory scale tests were conducted to determine whether the anhydrite conversion would take place at a temperature below the melting point of the rock salt. These tests showed no conversion while the rock salt was in the solid state. Further tests are under way to determine the effects of small concentrations of additives to the

salt to improve the physical appearance of the product after melting and refreezing. With no additives the appearance of the melted and refrozen salt ranges from an offwhite to a light creamy tan. For obvious reasons a white or transparent product would be more commercially attractive.

In summary, we have demonstrated two significant points. First, that the native anhydrite in rock salt possesses differing solubility characteristics according to the geographical source of the salt. This difference is evident in the photomicrographs of the salt samples. Second, irrespective of geographic source the anhydrite can be converted from a semi-soluble state to a completely soluble state by melting the rock salt.

At a recent American Management Association course on research management L.H. Kilian, in his

Table 4

	Cleveland		Detroit	Retsof	Avery	
	Melt 1	Melt 2	Melt 1	Melt 1	Melt 1	Melt 2
Insolubles Top	.054	.010	.047	.038	.017	.011
Insolubles Middle	.036	.014	.039	.041	.010	.006
Insolubles Bottom	.034	.014	.072	.466	.056	.056
Calcium ⁺⁺	.504	.512	.424	.424	.176	.180
Sulfate ⁻	1.129	1.123	.856	.953	.379	.360
Calcium Sulfate (Soluble)	1.633	1.635	1.280	1.377	.555	.540
Insolubles Feed	2.200		0.949	1.120		.467

talk "Organizing and Staffing the Research Program," commented on serendipity in research. "Whereas many discoveries have been made by serendipity," he said, "serendipity usually turns out to be the result of carefully planned and executed research." From our experience in this project we certainly agree with Kilian.

REFERENCES

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