

Properties of the Impurities in Northern Rock Salt

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ABSTRACT

Impurities from various grades of Northern rock salt were separated in unchanged form from their respective salt matrices. Chemical analysis shows the separated impurities to be principally calcium sulfate. Solubility characteristics of the isolated impurities were examined in saturated and one-half saturated sodium chloride brines. The effect of the following variables on the solubility was determined: (1) Time; (2) Temperature; (3) pH; (4) Impurity particle size; and, (5) Impurity to brine ratio. The possible significance of these data in relation to the quality of brine produced from rock salt is discussed.

INTRODUCTION

Many uses of rock salt require its conversion into brine. In this connection the purity of the brine produced is an important consideration. It is well known that the principal impurity in rock salt is calcium sulfate. It was felt that knowledge of the solubility properties of the impurities might lead to a better understanding of how to produce brine of the highest purity. The purpose of this work was to characterize the solubility properties of the impurities in rock salt.

EXPERIMENTAL

The present study was limited to an examination of the impurities in Northern rock salt. Samples were obtained from the Fairport Harbor, Ohio, mine of the Morton Salt Company.

The technique used was to isolate the impurities from their salt matrix. The properties of the separated impurities were then determined. It was first necessary to devise a method for separating the impurities from the salt without changing their properties. This was accomplished with the aid of the apparatus shown in Fig. 1. A brine half-saturated with salt and saturated with calcium sulfate was prepared. This special brine was allowed to flow through a salt sample in a Buchner Funnel. The salt dissolved, leaving behind the impurities, essentially unchanged. After dissolution of the salt, the impurities were washed free of brine with water saturated with calcium sulfate. This was followed by washes with methanol and acetone, after which the sample was air-dried.

Solubility determinations were carried out in the apparatus shown in Fig. 2. The brine sample was charged into a 500 ml. round-bottom flask equipped with a thermometer, agitator and means of checking pH. The flask was immersed in a constant temperature bath. After temperature and pH were adjusted the impurity sample was added. Samples were withdrawn with a pipette fitted with a filter plug and then immediately and quickly refiltered for analysis. Calciums were determined by EDTA titration method and sulfates by standard gravimetric procedure.

The solubility characteristics of the impurities were determined in sodium chloride brine as a function of time, temperature, brine strength, brine pH, impurity particle size, and impurity

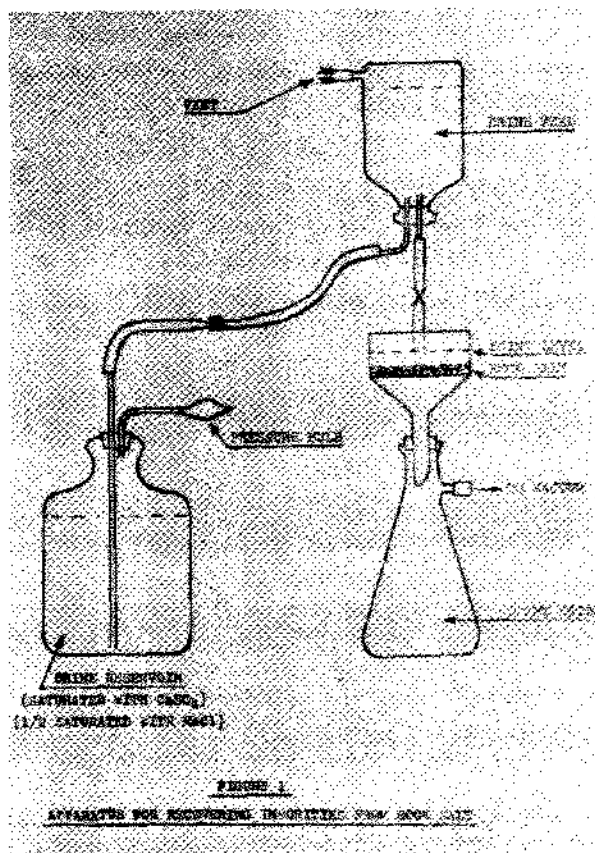


Figure 1

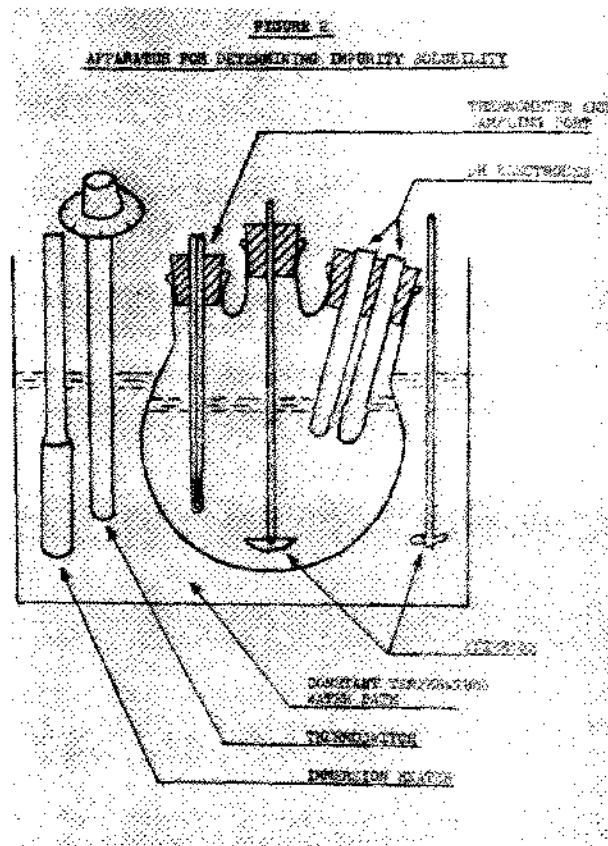


Figure 2

exposure ratio. (This term is defined below.) Two brine strengths were used. In this work saturated brine contains 351 grams of sodium chloride per liter of water and half-saturated brine contains 164 grams of sodium chloride per liter of water. Reagent grade sodium chloride was used to prepare these brines.

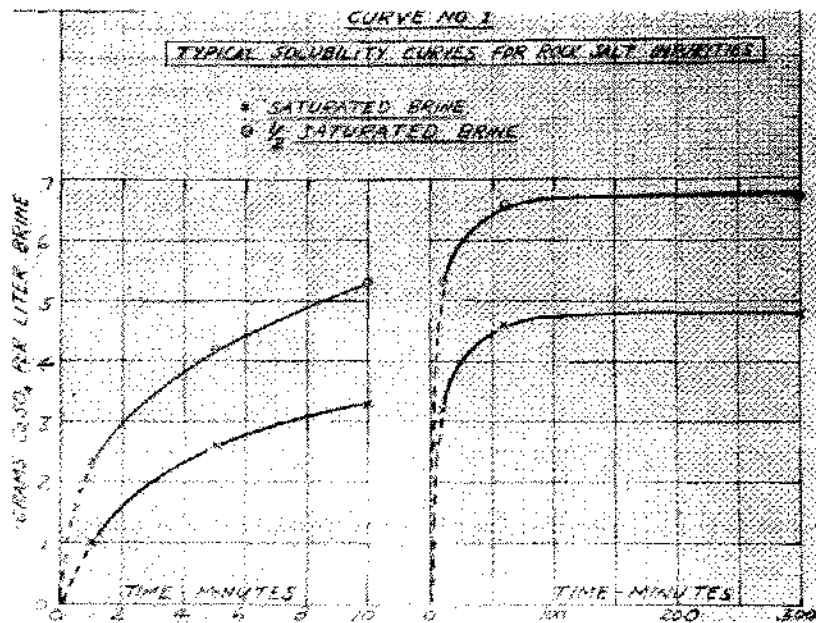
DATA AND RESULTS

Chemical analyses on the isolated impurities showed them to be 98.1 weight percent calcium sulfate. From X-ray diffraction analysis it was determined that the impurities were almost entirely anhydrite, with very small amounts of gypsum and dolomite, and a trace of α -quartz.

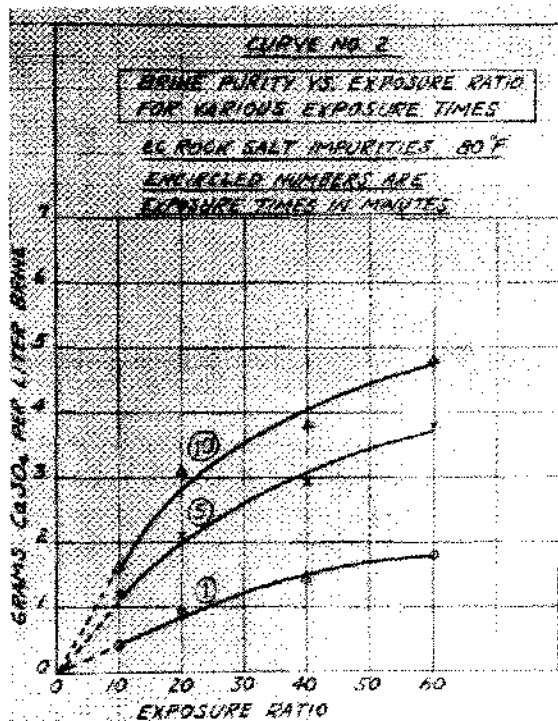
Curve No. 1 shows typical solubility curves. The amount of calcium sulfate dissolved is plotted versus time. The curves on the left are shown on an expanded scale for a ten-minute period. As is to be expected, the solubility is higher in half-saturated brine. The noteworthy point here is the very rapid solubility rate in the first few minutes. After a ten-minute period 70-80 percent of the total dissolution has occurred.

Curve No. 2 shows the brine purity as a function of exposure ratio for various exposure times. (In this paper brine purity and grams of calcium sulfate per liter of brine are used as interchangeable terms.) Exposure ratio is defined as the grams of impurity taken per liter of brine. It is an indicator of the amount of impurity exposed to the brine. These data show the strong effect of exposure ratio on impurity solubility. For example, at ten minutes the impurity increases from 1.6 grams CaSO_4 per liter at an exposure ratio of 10 to 4.8 grams per liter at a ratio of 60 -- a threefold increase.

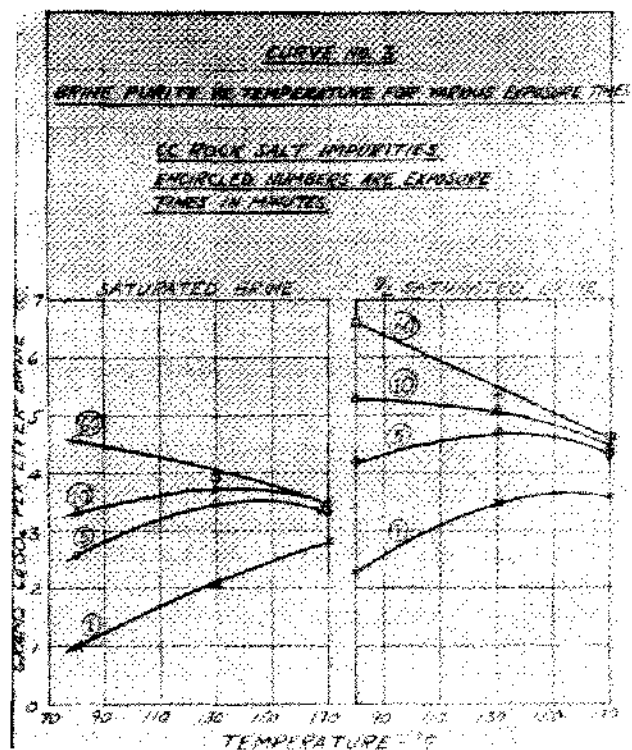
Curve No. 3 shows the effect of temperature. These data show that, generally, increasing temperature wipes out the effect of time, and that the brine purities tend to come to a common



Curve No. 1



Curve No. 2

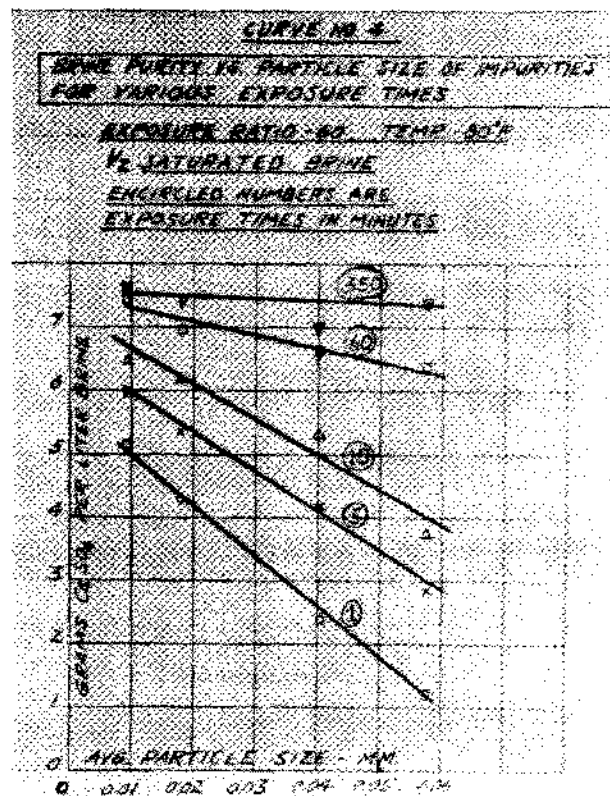


Curve No. 3

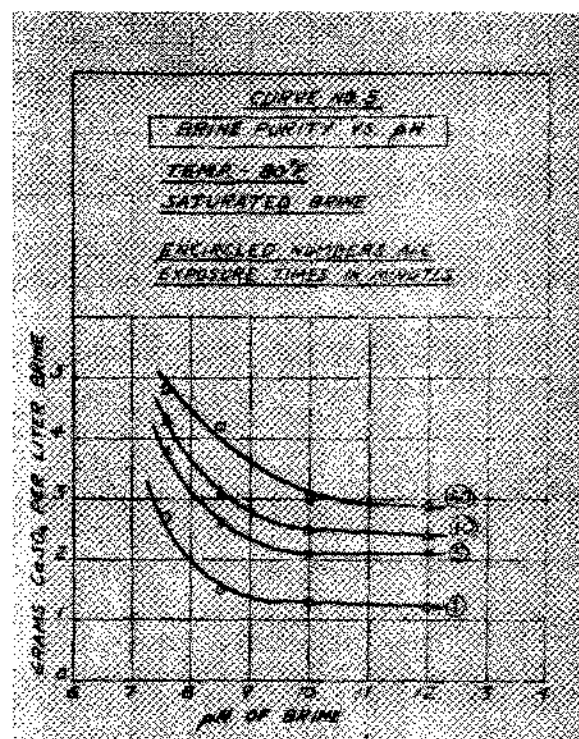
level as the temperature rises. For example, at 170°F. the difference in brine purities is not particularly significant. For long exposure times an increase in temperature does give some improvement in brine purity, especially with the half-saturated brine. This is shown by the negative slope of the 60-minute curves.

Curve No. 4 shows brine purity versus impurity particle size for various exposure times. This shows that particle size is very important for low exposure times, but that its effect vanishes with long exposure time. For example, at five minutes the solubility of a sample with 0.01 mm. particle size is 6.0 G.P.L., or twice that of a sample with 0.06 mm. particle size. At 60 minutes the difference in solubility is small, and at 350 minutes there is no appreciable difference.

Curve No. 5 demonstrates the effect of pH. There is a sharp beneficial effect of pH up to pH 10. Above pH 10 no further improvement in brine purity results. The relative effect of pH is not affected by time since the curves are roughly parallel. Of course, the position of each curve is influenced by time since the amount of dissolved CaSO_4 does increase with time.



Curve No. 4



Curve No. 5

DISCUSSION

The data above clearly show that the brine purity which can be expected when dissolving rock salt is influenced by many factors. The following are conditions favoring highest brine purity: (1) Attainment of brine saturation as rapidly as possible, (2) Reduction of contact time between impurities and brine to a minimum, (3) Prevention of impurities from accumulating in the system and staying in contact with brine, (4) adjustment of pH to about 10.

CONCLUSIONS

This work has shown that the properties of the impurities in rock salt can be studied by isolating the impurities and examining their solubility in brine under various conditions. The solubility of the impurities is increased by: (1) contact time, (2) reduced particle size, (3) increasing impurity to brine ratio (exposure ratio). The solubility is decreased by raising pH up to a value of about 10. Temperature does influence the solubility, but for the range studied its effect is not as strong as the other variables examined.