EXPERIMENTS ON PRECIPITATION BROUGHT ABOUT BY MIXING BRINES

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The authors describe some experiments in which precipitation of sodium chloride is brought about by the mixing of originally saturated solutions of the materials concerned. Such precipitation might have played a part in the formation of great beds of evaporites which are found in rocks. This possibility is of interest to those who believe in a young Earth, for a Biblical chronology may not leave time for beds of salt to have been formed by slow evaporation.

The Problem

The presence of great beds of rock salt, or of similar minerals such as calcium carbonate, presents a problem to those who believe in a young Earth. But it is by no means true that these deposits are accounted for any better by those who hold uniformitarian views.

These minerals are often called evaporites, since it has been supposed that they arose by the evaporation of sea water, or some similar brine. But it is not easy to find any place where such evaporation is going on to any considerable extent today. So once again the present is *not* the key to the past.

There are other problems. The predominant mineral in sea water, or in the water of salt lakes, is common salt. How, then, did other minerals, such as magnesium chloride, become segregated? Also, if these beds of salt were formed in communication, so to speak, with the sea, it seems strange that they contain so few fossils.

Mixing Proposed as a Mechanism

In view of these difficulties, even for uniformitarians, some other way of depositing these beds was sought. One suggestion was that maybe the mixing of different kinds of brine, say solutions, each originally saturated, of sodium chloride and magnesium chloride, might lead to precipitation of some of the salt. Such a method would avoid the necessity of evaporating a lot of water.

Raup, especially, investigated this mixing.[1] He found that indeed upon mixing much salt might be precipitated. And the precipitation took place without any further evaporation of water, and without any change of temperature.

It is easy to see why those who believe in a world-wide Flood would be interested in his process of mixing, for the Flood surely would have caused mixing on an enormous scale. Thus it seemed worthwhile to repeat some of Raup's work, and to investigate further. This article describes some work along the lines just suggested.

The work was done exclusively with sodium chloride (NaCl) and magnesium chloride ($MgCl_2$). The results agree with Raup's, as will be pointed out in greater detail later. It was found, upon looking a bit further, that the greatest percentage of the NaCl present in the solution is precipitated when the volume percentage of saturated NaCl is about 20%. This fact suggests that precipitation can occur under conditions less vigorous than those proposed by Raup. For the present, however, such conditions for precipitation remain only a suggestion; they have not yet been tested.

Experiments

All work was carried out as close to 25 °C as possible. The saturated solutions of $MgCl_2$ and NaCl were prepared by dissolving the appropriate reagent grade salt in distilled water with a magnetic stirrer in a constant temperature bath (25 ± .1 °C). The solutions were prepared at the beginning of the experiment and used throughout the experiment with no detectable change in the concentration of the salts.

The concentration of the chloride in the solution was determined by the Fajan's method.[2] The silver nitrate was standardized against pure NaCl which had previously been dried at 120° overnight. The concentration of magnesium was determined by titration with a standardized (against pure magnesium metal) EDTA solution. Erio T was used as the indicator.[3]

The densities in this report were determined by weighing 10.00 ml. of the appropriate solution. The volume was measured with a volumetric pipet.

The following general procedure was followed: The appropriate volumes of the saturated solutions were pipetted into a 250 ml no-drip Corning Pyrex beaker. The weight of each solution taken was determined. The exact volume of each solution taken was calculated using the measured densitites of the saturated solutions. The solution was swirled to assure complete mixing, covered with Parafilm and allowed to stand overnight. The next day the solution was filtered using preweighed, predried sintered glass filters—either medium or fine. The liquid removed was saved for further analysis. The precipitate was sucked dry and then washed with ethanol. After drying overnight, the weight of the precipitate was determined. The density, and the concentration of the magnesium and the chloride of the filtered solution were then determined.

Calculations and Results

All data points are the average of three determinations. The data and calculate values can be found in Table 1.

Figure 1 contains a plot of the grams of NaCl precipitated based on a total volume of 100 ml versus the volume percentage of the saturated NaCl solution. The plot also contains Raup's values. It can be seen that Raup's values are consistently lower than ours. The difference can readily be accounted for in the error found in our filter procedure. The filter error was always positive by about .02 grams for a sample of 20 ml, thus making our values high by about 0.1 grams for a 100 ml sample.

More interesting results can be obtained if one plots the percentage of the total NaCl initially present that is precipitated as a function of the volume percentage of

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Table 1. This shows the experimental results. Where appropriate, concentrations are shown in molarity units; and this is indicated in the text, where necessary, by brackets around the formula, in the usual way.

Columns 1 and 2 show the volumes of saturated solution, found by weighing and dividing by the density of the solution. Column 3 gives the concentration of $MgCl_2$ in the filtrate, as calculated from the EDTA titration. In column 4 is the concentration of NaCl in the filtrate. It was found by getting the concentration of Cl^- by Fajan chloride titrations, and subtracting twice the concentration of $MgCl_2$.

Column 5 gives the per cent of NaCl precipitated. This was found by dividing the amount of NaCl collected by the total amount present. The latter amount was found as the product of the initial concentration of NaCl, the volume of solution used, and the factor 58.5.

Column 6 shows the amount precipitated per 100 ml. of solution. In the actual experiments, the amount used was usually close to 20 ml.

Column 7, giving the density, based on 10 ml. of solution, and column 8, giving the percent decrease in volume, are self-explanatory.

Volume of saturated NaCl	Volume of saturated $MgCl_2$	$[MgCl_2]_f$	$[NaCl]_f$	% NaCl Precipitated	gram, NaCl precipitated based on 100 ml total volume	Density final	% Volume change
1.00 ± .01	19.19 ± .03	4.74 ± .02	0.03 ± .02	73 ± 3	1.17 ± .03	1.301 ± .003	0.8 ± 0.1
2.00 ± .00	18.14 ± .03	4.51 ± .02	0.06 ± .06	80.8 ± .5	2.56 ± .01	1.291 ± .001	1.19 ± .01
2.99 ± .01	17.04 ± .01	4.30 ± .01	0.08 ± .03	83.7 ± .5	3.97 ± .04	1.280 ± .001	2.17 ± .01
4.98 ± .02	15.05 ± .03	3.85 ± .01	0.19 ± .04	80 ± 1	6.3 ± .1	1.258 ± .004	3.44 ± .08
6.99 ± .01	13.05 ± .03	3.39 ± .02	0.409 ± .006	72.9 ± .3	8.08 ± .04	1.239 ± .004	4.9 ± .1
9.01 ± .01	11.02 ± .03	2.851 ± .009	0.85 ± .03	62.6 ± .2	8.94 ± .02	1.220 ± .001	4.54 ± .05
10.01 ± .01	10.02 ± .02	2.590 ± .005	1.11 ± .01	57.1 ± .3	9.07 ± .06	1.213 ± .001	4.44 ± .03
10.01 ± .02	10.06 ± .02	2.58 ± .02	1.36 ± .02	54.9 ± .2	8.72 ± .03	1.215 ± .001	3.49 ± .07
11.01 ± .01	9.02 ± .05	2.30 ± .02	1.490 ± .008	49 ± 1	8.5 ± .2	1.206 ± .002	3.42 ± .08
12.99 ± .02	7.00 ± .01	1.785 ± .009	2.26 ± .01	37.2 ± .3	7.70 ± .05	1.200 ± .001	2.90 ± .08
15.00 ± .04	5.03 ± .02	1.272 ± .009	3.06 ± .05	25.7 ± .2	6.11 ± .04	1.193 ± .001	0
16.98 ± .03	2.97 ± .01	0.752 ± .004	3.33 ± .02	14.6 ± .3	3.93 ± .06	1.192 ± .001	2.00 ± .09
19.03 ± .11	1.0 ± .1	0.250 ± .004	4.99 ± .02	5.1 ± .3	1.52 ± .09	1.189 ± .001	0.8 ± .2

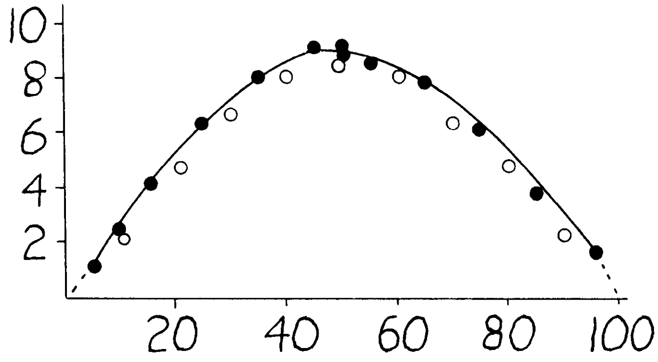

Figure 1. This shows the amount of NaCl precipitated, in grams (plotted vertically) based on a total of 100 ml solution, vs. the volume per cent of the saturated NaCl solution (plotted horizontally). "Volume per cent" is to be understood as follows: a mixture of 40 ml of NaCl solution, for instance, with 60 ml of $MgCl_2$ solution would be called 40 volume per cent of saturated NaCl solution. The solid points show results from the present experiments; the open circles are from Raup's work.

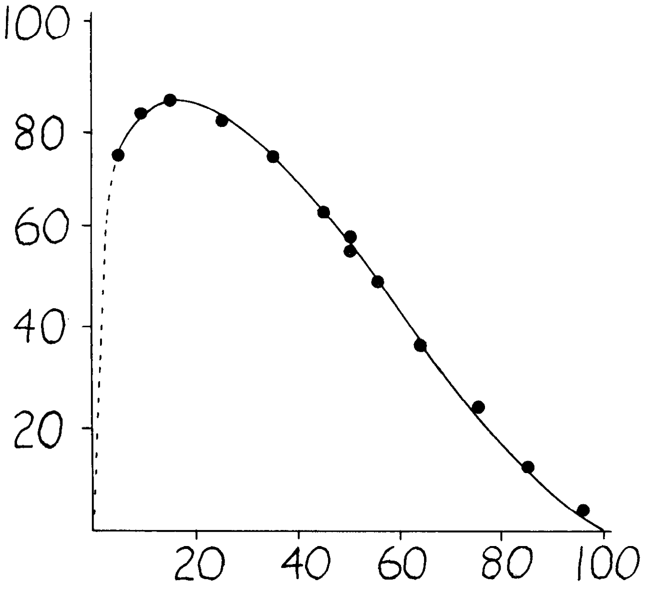

Figure 2. This shows the per cent of the total NaCl which was initially present actually precipitated vs. the volume per cent of the saturated NaCl solution.

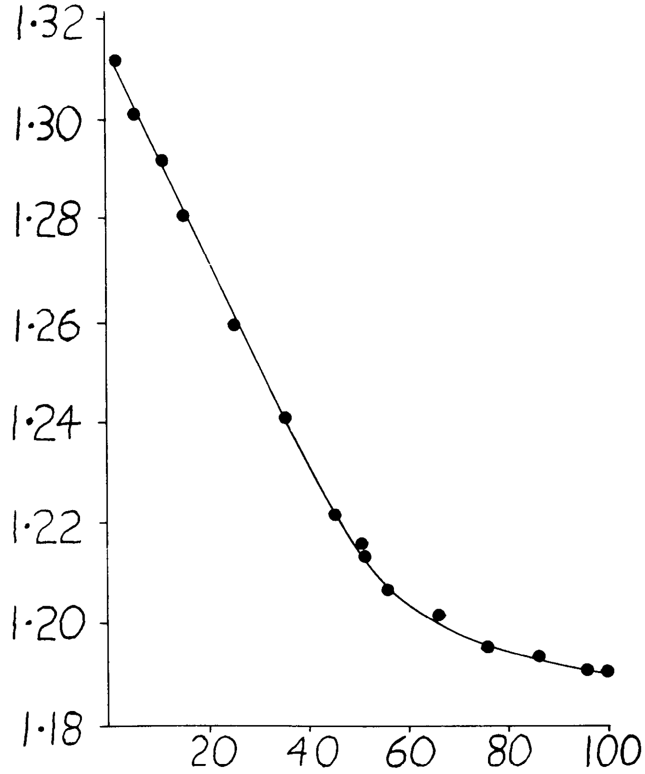

Figure 3. This shows the density of the final solution plotted vs. the volume per cent of NaCl solution.

the saturated NaCl solution. This plot can be found in Figure 2. It can be seen that the greatest percentage of the NaCl is precipitated at a very low volume percentage of the saturated NaCl solution.

This implies that the salting-out of the NaCl is much more efficient under the condition of low volume percentage of the saturated NaCl and therefore should occur under much less rigorous conditions. Raup mixed equal volumes of solutions that were not saturated. It is suggested from this data that the subsaturated solutions be tried with the volume percentage of the NaCl rich solution being about 25%.

The density of the final solution was measured in each case. Figure 3 contains a plot of the density data. It can be seen that the function is not linear. The majority of the decrease (90%) in density from a pure saturated $MgCl_2$ solution occurs in the first 50 volume percentage. This is also the area where the highest percentage of the NaCl is precipitated.

One indication of what may be happening in this area is shown on Figure 4. This figure contains a plot of the percentage volume change in the solution as a function of the volume percentage of saturated NaCl solution. It can be seen that the greatest percentage volume change occurs in the lower volume percentage of saturated NaCl solutions.

One can speculate as follows. The magnesium ion has a high charge density and as such it tends to orient the water molecules to a large extent. Experiments indicate that the solvation number for magnesium chloride is about 15. The comparable value[4] for NaCl is 7. A saturated $MgCl_2$ solution is about 5 M, and has a density of about 1.3 g/ml. Thus there are about 9 water molecules per $MgCl_2$ unit. For a saturated NaCl solution, the comparable value would be 10. This means that on the average each of the $MgCl_2$ units can combine with more water, while each of the molecules in the NaCl solutions is complete.

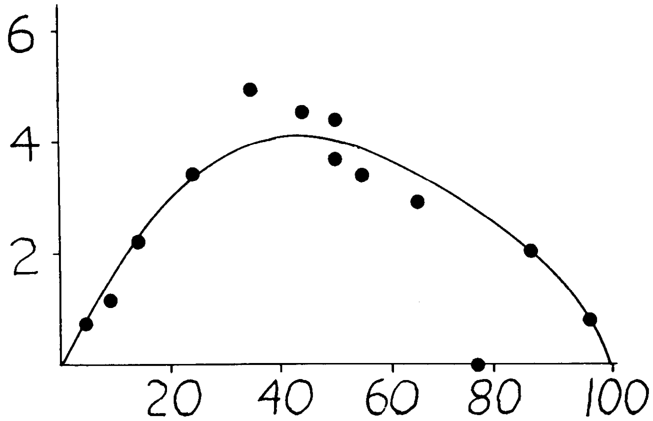

Figure 4. This shows the per cent change in volume of the solution vs. the volume per cent of NaCl solution.

When the two solutions are mixed, the magnesium chloride tends to attract the water molecules from the NaCl. As the number of water molecules available to the NaCl decreases, it begins to precipitate from the solution. In essence the NaCl is being crowded out of the solution. It is granted that the above is speculative and could stand much more study.

Possibilities for Future Research

1) It appears that less vigorous conditions than those used by Raup might still achieve the precipitation of NaCl. Therefore the project needs to be conducted at about 25 volume percentage NaCl solution using subsaturated concentrations.

2) It might be valuable to investigate the effect of temperature on these precipitations. If some of the flood water in Noah's flood came from within the earth,[5] it was probably much hotter than that which fell as rain or was already in the sea. Being hotter, it seems that it would have more chemicals in it and that as it moved over the land it would extract more chemicals. Upon mixing with cooler water, a precipitate might form. This is speculative but is an area for research.

Acknowledgement

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References

[1] Raup, Omer B. 1970. Brine mixing: an additional mechanism for formation of basin evaporites, *Bulletin of the American Association of Petroleum Geologists* 54(12):2246-2259.

[2] Skoog, D. A., and D. M. West 1969. Fundamentals of analytical chemistry. Holt, Rinehart, and Winston, New York. Second Edition, pages 234 *et seq.*

[3] *Ibid.*, pages 355 *et seq.*

[4] Robinson, R. A., and R. H. Stokes 1959. Electrolyte solutions. Butterworths, London. Chapter 3.

[5] Many believe that the breaking up of the fountains of the great deep, mentioned in Genesis 7:11, could have caused something of the sort.