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Separation of Magnesium Chloride from Sodium Chloride in Seawater by the Dense-Phase Technique

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Abstract

Experimental results are reported for the solid–solid separation of a mixture of $MgCl_2 \cdot 6H_2O$/NaCl (to be referred to as M/S) using a dense media of such organic solvents as tetrachloromethane, iodomethane, and a combination of these two solvents. The solid M/S mixture to be separated was prepared from two different sources: by evaporating seawater in which the M/S ratio is about 0.14, and by synthesis of the pure salts in which the M/S ratio varied between 0.5 and 1.275. Good separation results are reported for the case of dense-phase separation in which the blend of the two solvents has a specific gravity of 1.9. Recovery was about 95% pure $MgCl_2 \cdot 6H_2O$ from a synthetic mixture having an M/S ratio of 1.0.

INTRODUCTION

The recovery of magnesium chloride from seawater (to be used as a raw material for magnesium) has been a challenging endeavor over the years (*1–4*). This is because magnesium metal is recognized as the world's lightest structural metal and is the eighth element in order of occurrence in the world. Magnesium metal is mainly used in the manufacture of extremely lightweight, strong alloys (particularly Al alloying) which are of great importance in space vehicles and automotive equipment. Magnesium also has nonstructural applications as a reducing agent in

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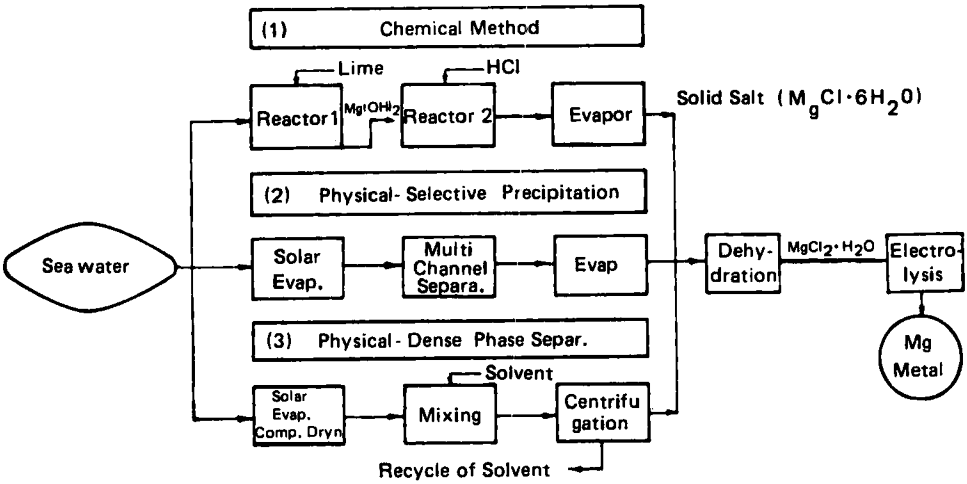

FIG. 1. Physical methods proposed for the recovery of magnesium chloride from seawater.

the production of some metals such as titanium, zirconium, uranium, and beryllium. Magnesium oxide, on the other hand, is finding new uses in air pollution control systems to remove SO_2 from stack gases.

Methods used in separating magnesium chloride from seawater usually follow one of the schemes illustrated in Fig. 1. The physical methods include the one proposed earlier by Kettani and Abdel-Aal (*3*) and the dense-phase technique presented in this paper. In the preferential precipitation method (*3*), seawater is first evaporated by solar energy to bring its specific gravity to a value between 1.20 and 1.25. It is then introduced to a multichannel evaporator for preferential crystallization of the salts. Magnesium chloride separates at the very end in a highly concentrated brine which has an M/S ratio of about 1. It is along this line that the present investigation is pursuing the separation of $MgCl_2 \cdot 6H_2O$ from NaCl either as an additional process tailored to the need of preferential separation or as an innovative process for producing pure magnesium chloride from seawater.

THE APPROACH TO SEPARATION

The difference in specific gravities between the two inorganic salts to be separated ($MgCl_2 \cdot 6H_2O$, $\sigma = 1.56$; NaCl, $\sigma = 2.163$) suggests the possibility of using dense-phase or dense-media separation. Thus the search and selection of the proper solvents in which the solid mixture can be thoroughly mixed and suspended, then subjected to centrifugation for separation, is a very important step in our investigation.

Selection of the Proper Organic Solvent

Organic liquids needed for our experiments should satisfy the following criterion with respect to the value of the specific gravity σ:

$$2.163 > \sigma_{\text{solvent}} > 1.56$$

In addition, they should be nontoxic, nonexpensive, and easy to recover for recycle usage. The fact that some of these solvents were not available for immediate use in the laboratory led to the proposal of blending two solvents in different ratios to meet the above criterion. Tetrachloromethane and iodomethane were selected for this type of experiment.

Experimental Technique

Once we have selected the right solvent, we move next to accomplish the separation using what we call "Sedimentation Centrifuges." It is well known that the gravitional forces acting on a particle are proportional to its mass. The buoyant forces, on the other hand, are proportional to its volume, while the surface forces are proportional to the surface area. Careful adjustment of these forces in proper equipment can lead to an economic separation of solids that differ in size and density.

In our case a test-tube sedimentation centrifuge is used in which the centrifugal and the gravitional forces are utilized to separate materials that differ in density. Accordingly, materials that are more dense than the organic solvent will sink, and those less dense will float. After being thoroughly mixed in the solvent, the dry salt M/S mixture is poured into the test tubes, which are then placed in the centrifuge. Gravitional forces cause separation which is accentuated by the swirling and rotation of the fluid. The heavier sodium salt settles at the bottom of the tube, while the lighter magnesium salt stays at the top.

RESULTS AND DISCUSSION

In this investigation the M/S solid mixture to be separated into pure salts was prepared by two different ways:

(a) By evaporation of seawater in which the M/S ratio is 0.14.
(b) By synthetic preparation of a mixture of the pure salts in which the M/S ratio varies between 0.5 and 1.275.

Thus two sets of experiments were carried out, depending on the type of feed to be separated.

Separation of Magnesium Chloride from Seawater

The first experiments carried out to separate magnesium chloride from seawater by using tetrachloromethane as the dense-phase media were not successful. This is attributed to two reasons. First, the very low M/S ratio makes it rather difficult for the magnesium salt to separate. Second, the solvent selected for the separation has a σ very close in value to that of magnesium chloride (1.595 and 1.56, respectively).

For these reasons a blend was formulated using tetrachloromethane and iodomethane. Different blends were prepared by using different ratios in which the specific gravity of the product varied between 1.7 and 2.0.

For example, to prepare 100 cm^3 of a blend having σ = 1.9,

$$(100)(1.9) = (100 - V_1)(1.595) + (V_1)(2.265)$$

from which V_1, the volume of iodomethane, is found to be = 45.5 cm^3.

Four experimental runs were performed in which a sample of 2.5 g of the solid M/S mixture (obtained by evaporating seawater which has 9.44% by weight magnesium chloride) was used. For each experiment, the M/S ratio was not changed (1:7) while the specific gravity of the dense-phase solvent was varied. After centrifugation, separation, and drying, the weight of separated magnesium chloride was determined. As shown in Fig. 2, a specific gravity of 2.0 of the blend is the upper limit for NaCl to separate along with the magnesium salt. A specific gravity of 1.9, on the other hand, gave the best recovery of pure magnesium salt (92% yield).

Separation of Magnesium Chloride from Synthetic Mixture

Similar to the previous set of experiments, tetrachloromethane was tested as a dense-phase medium in four runs. For each run a sample of

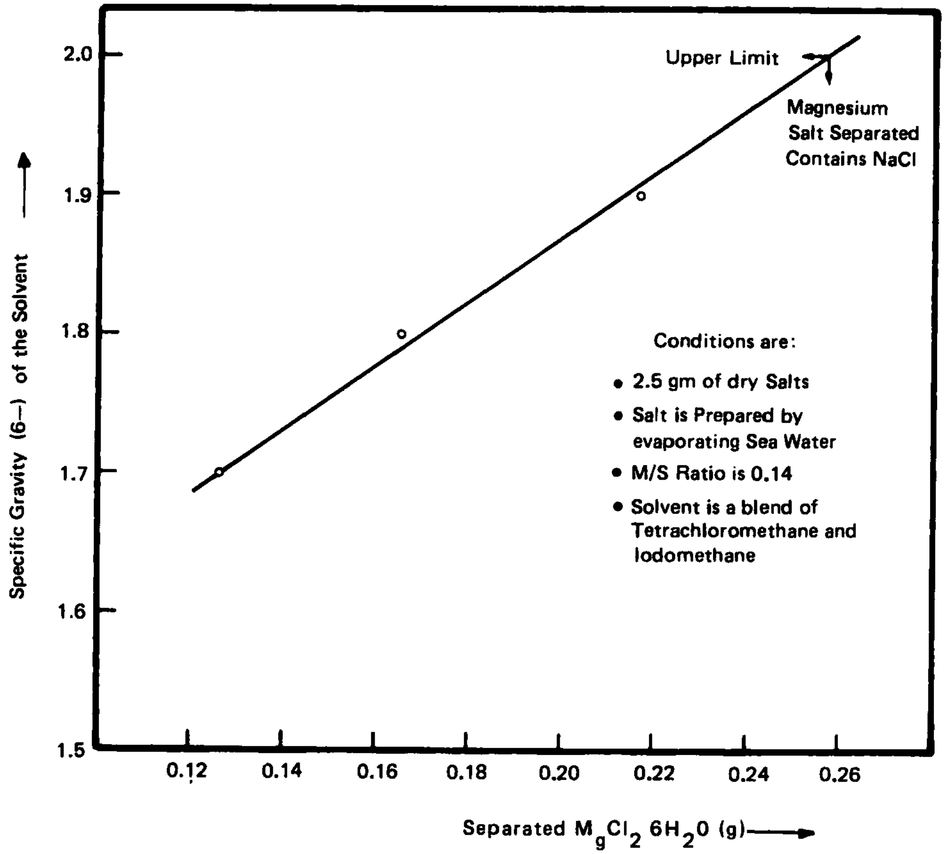

FIG. 2. Effect of specific gravity of solvent on the separation of magnesium chloride.

the solid mixture containing 2 g NaCl with a variable M/S ratio over the range 0.5–1.275 was used. Figure 3 shows the effect of the amount of magnesium chloride to be separated on the amount actually recovered, while Fig. 4 presents the relationship between the ratio of M/S in the salt to be separated and the ratio of magnesium salt recovered to that lost. It is evident from these plots that the recovery of magnesium chloride increases with an increase in the ratio of M/S in the salt to be separated. In general, the efficiency of separation of magnesium chloride using tetrachloromethane was rather poor (about 30%). This is again due to the low specific gravity of this solvent.

Three runs using the blend solvent (mixture of tetrachloromethane and

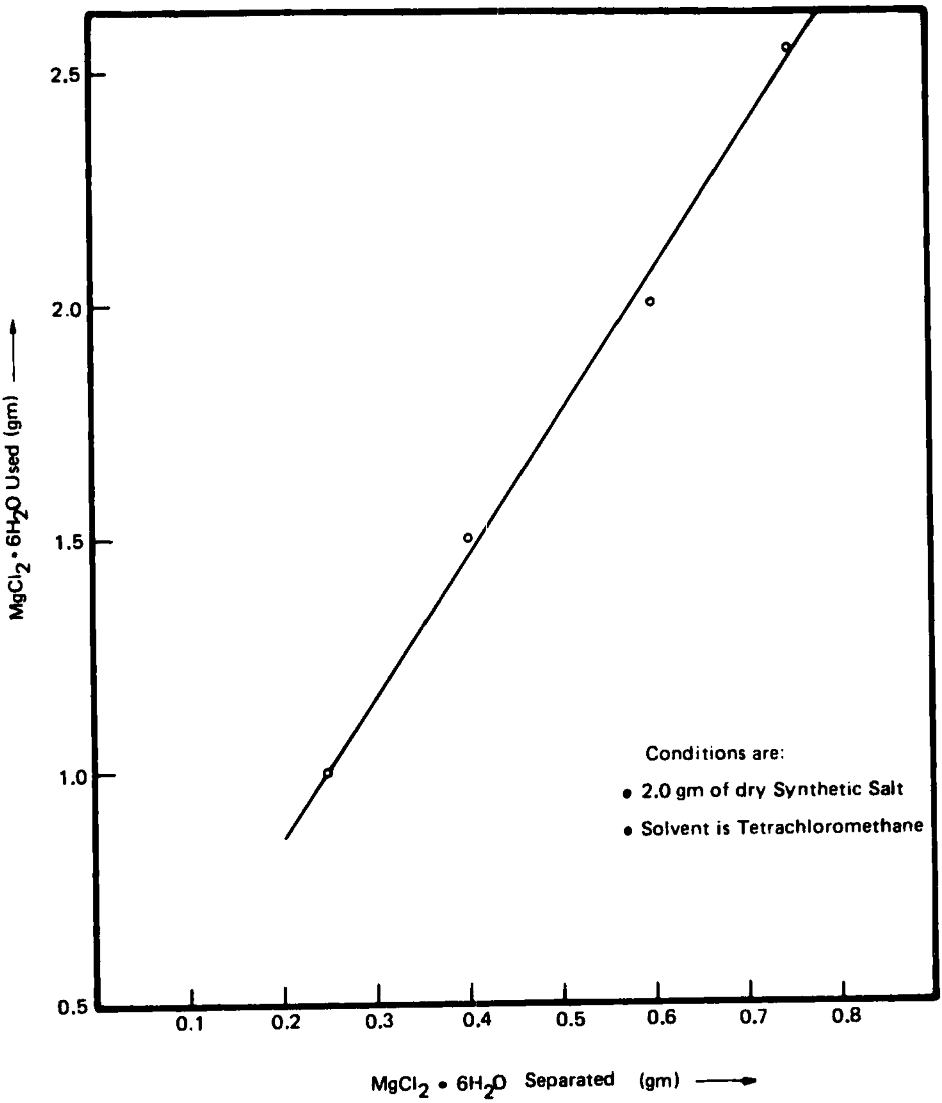

FIG. 3. Relationship between amount of magnesium chloride to be separated and the amount recovered.

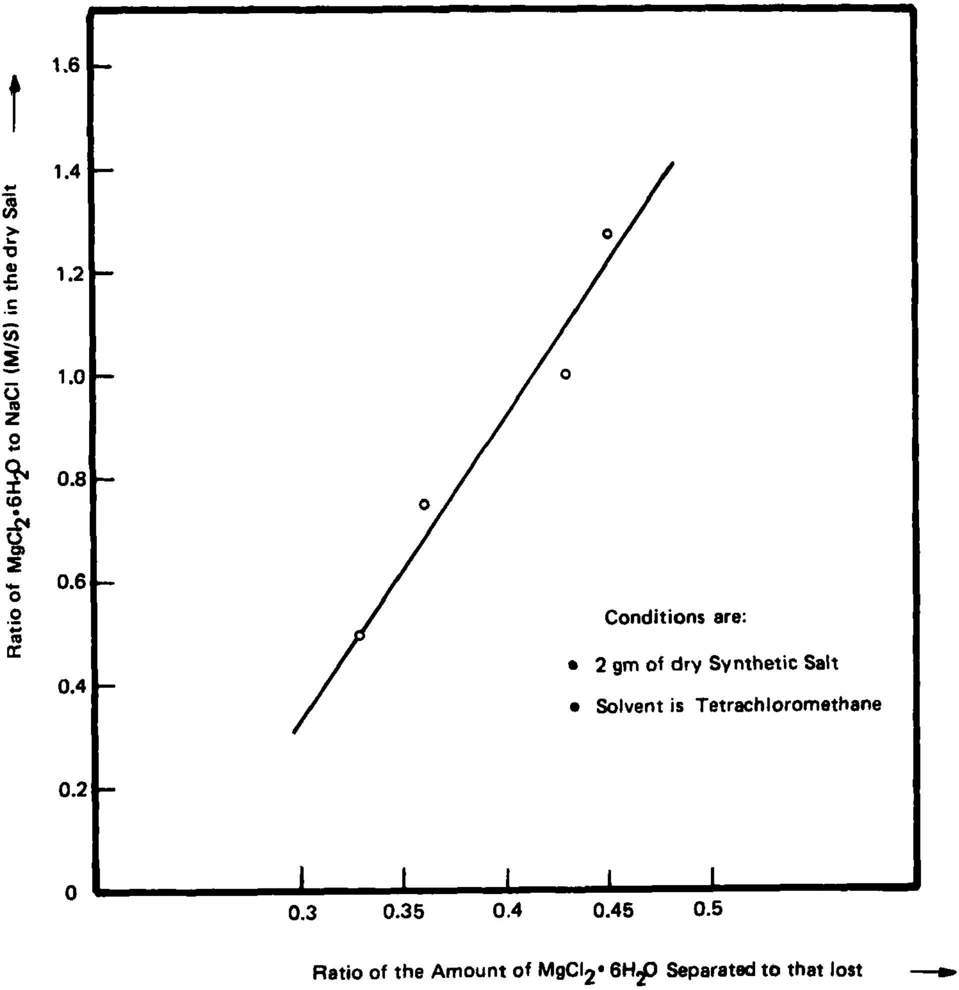

FIG. 4. Relationship between M/S ratio in dry salt and ratio of M separated/lost.

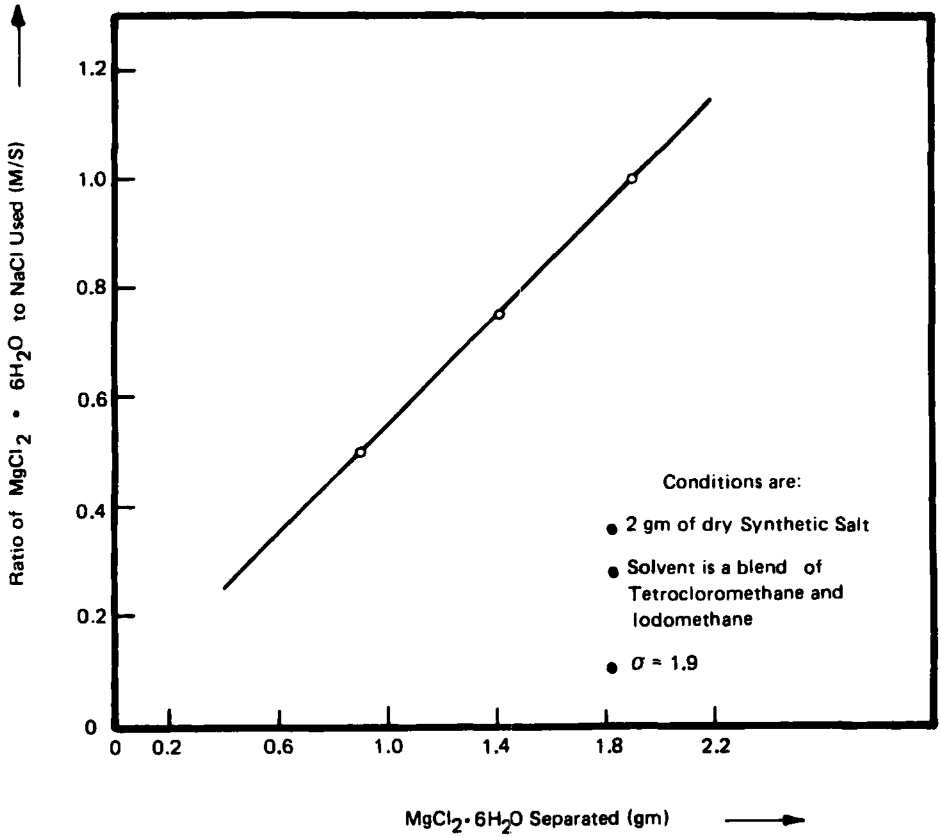

FIG. 5. Effect of ratio of M/S in feed on amount of magnesium chloride separated.

iodomethane) for the separation of magnesium chloride were carried out in which the value of σ of the blend solvent was fixed at 1.9, which is the optimum value used in the previous runs. A sample of the salt containing 2 g NaCl was used, and the M/S ratio was varied over the range 0.5–1.0. Contrary to tetrachloromethane, the blend solvent of 1.9 specific gravity gave very promising results in which the efficiency of separation was 95%. The results are shown in Fig. 5.

Comparison between the Solvents

In order to compare tetrachloromethane and the blend with σ = 1.9, Fig. 6 was prepared using the data obtained for the separation of

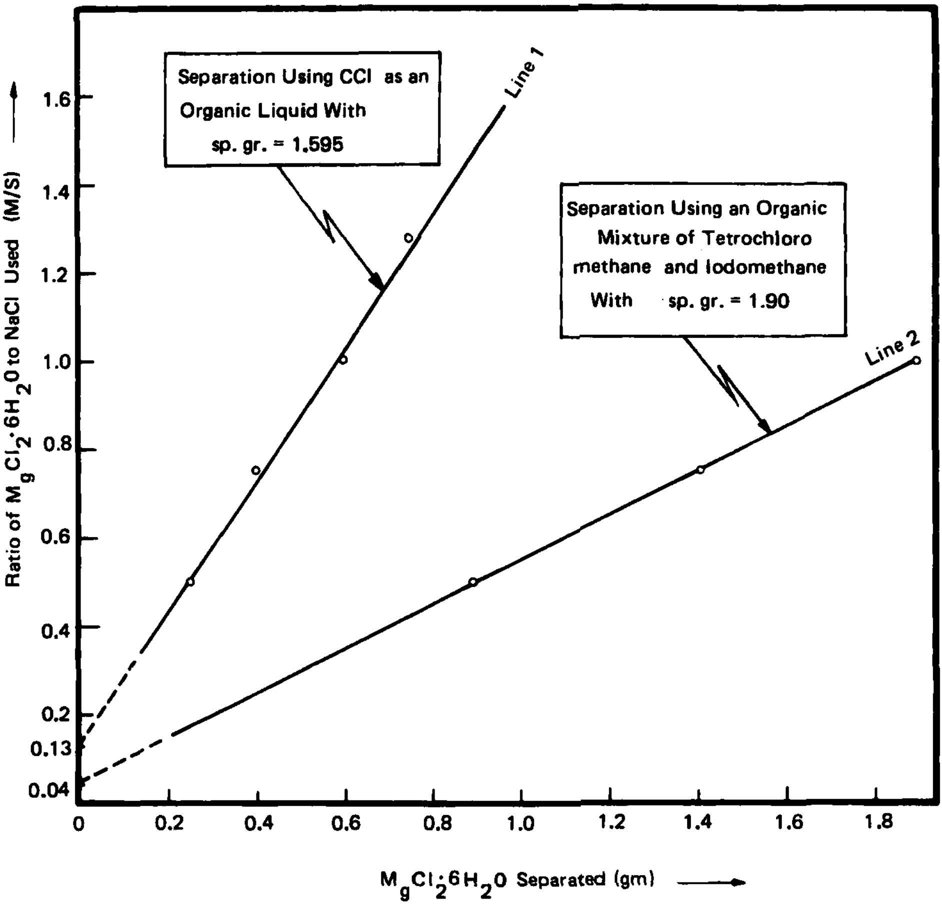

FIG. 6. Comparison between the solvents for the separation of magnesium chloride in synthetic feed mixtures.

magnesium chloride from the synthetic M/S mixture. It is evident from this plot that for a given ratio of M/S mixture to be separated, a higher recovery of magnesium chloride is obtained using the blend. Quantitatively speaking, the amount of magnesium chloride separated by using the blend is almost three times the amount separated when using tetrachloromethane. This value is consistent with the ratios of the slopes of the two lines, i.e.,

$$(\text{slope of Line 1})/(\text{slope of Line 2}) = 3.0$$

CONCLUSIONS

The experimental technique proposed in this paper for the solid–solid separation of $MgCl_2 \cdot 6H_2O$ from NaCl offers a very promising approach to obtain pure magnesium chloride from seawater. However, the economics of this method have to be established and then compared with the chemical method currently used on an industrial scale.

Note the values obtained by extending the lines in Fig. 6 to the Y-axis. For Line 1, the value of 0.13 means that no magnesium salt will separate out if the M/S ratio in the feed is < 0.13 when using tetrachloromethane as a solvent. This is comparable with the ratio of M/S in seawater, which is about 0.142. Similarly for Line 2, the value of 0.04 indicates that no separation of the magnesium salt occurs if the M/S ratio in the feed is $<$ 0.04 when a blend of the two solvents having a specific gravity of 1.9 is used.

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