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Comparative Study of Selective Separation of Magnesium from Brine and Seawater

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ABSTRACT

A highly selective, sensitive, and inexpensive procedure for the separation of magnesium from brine and seawaters is proposed. The method is based on the separation of the harmful major constituent (calcium) of saline water. This is achieved by floating both calcium and magnesium as their oleates at the pH of saline water (7.5–8.5) to avoid the effect of NaCl on the precipitation of Ca as $CaSO_4$. The float is dissolved in HNO_3/methanol, precipitated as $CaSO_4$, and the mother liquor is refloated as pure magnesium oleate. This purity is confirmed by infrared measurements.

INTRODUCTION

Magnesium is the lightest of industrial metals employed on a large scale. It is a very important alloying element. Its uses have been extended to photography, manufacture of machine parts, missiles, corrosion inhibitor, pyroleaching, optical mirrors, and negative electrodes in primary electric cells (1–3). Accordingly, the separation and recovery of pure magnesium from very cheap natural sources is a vital process.

Saline waters account for about 65% of all the magnesium produced in the USA and UK. The American and British methods for selective separation of magnesium from seawater depend on treating the water with lime for precipitation of calcium as calcium carbonate. The remainding seawater is treated with calcined dolomite, the magnesium in which acts as a nuclei upon which magnesium hydroxide is deposited (1–3). However, such a method has the following disadvantages: 1) inevitable partial redissolution of the precipitated $CaCO_3$ due to the solubility of atmospheric CO_2 in water, leading to the formation of soluble calcium bicarbonate (1, 3–5); 2) boron (which exists at about 10 ppm in seawater) decreases the yield of magnesium during electrolysis (3), hence it must be removed or rendered ineffective; 3) the salinity of water hinders complete removing of calcium as carbonate, and hence the residual calcium is coprecipitated with magnesium as hydroxide (5, 6); 4) silica, which may be present in a negative colloid form (5, 6), strongly adsorbs contaminating calcium on $Mg(OH)_2$; 5) iron and nickel, which may coprecipitate with $Mg(OH)_2$, are very objectionable in Al–Mg alloys if present in amounts greater than 0.005%, as they accelerate the attack on the alloys by saline solutions (3); and 6) lime used for selective precipitation of magnesium as $Mg(OH)_2$ must be free from any impurities and is especially prepared by calcining oyster shells and is carefully purified (1, 3).

The aim of this investigation is to study the feasibility and amenability of finding an economic and effective method for selective separation of magnesium from brine and seawaters using the very cheap sodium oleate as collector and Na_2SO_4 as a selective depressant for calcium.

EXPERIMENTAL

Chemical Reagents

All chemical reagents used were of analytical or equivalent grade. Oleic acid used for the preparation of sodium oleate was of technical grade. Sodium oleate stock solution (0.223 mol/L) was prepared by adding 78 mL of 1 mol/L NaOH into 25 mL of oleic acid (3.118 mol/L) and adding this mixture to 350 mL of 10% (v/v) methanolic aqueous solution.

Natural Water Samples and Analyses

Samples of natural waters were taken from the Mediterranean Sea at Ras El-Bar and Alexandria beaches in summer and winter. Samples of brine waters were also taken from El-Manzalah Lake.

The magnesium and calcium contents in the natural water samples used were determined complexometrically and checked, as well as was sodium, using a Perkin-Elmer 2380 atomic absorption spectrometer under the conditions listed in Table 1.

The average concentrations of Mg^{2+} and Ca^{2+}, measured in natural water samples obtained from different locations in either summer or win-

TABLE 1

Parameter	Element Ca	 Mg	 Na
Wavelength (nm)	422.7	285.2	389
Slit width (nm)	0.7	0.7	0.7
Lamp current (mA)	10	4	8
Acetylene flow rate ($L \cdot min^{-1}$)	3	3	3
Air flow rate ($L \cdot min^{-1}$)	21	21	21

ter, were found to be 6000 and 1500 mg/L, respectively. It is worth noting that these values were calculated with respect to calcium carbonate equivalent and taken into consideration in the preparation of synthetic mixtures used throughout our work.

The infrared spectra were recorded on a Perkin-Elmer 1430 ratio spectrophotometer.

The pHs of the solutions were measured with an electric digital pH-meter, Hanna Instruments 8519. The pH was adjusted with hydrochloric, sulfuric, and nitric acids and/or sodium hydroxide.

The experiments were carried out at room temperature, about 25°C.

Procedure

Ionic coflotation of both Mg^{2+} and Ca^{2+} from their synthetic solutions ($MgSO_4 \cdot 7H_2O$, $CaCl_2 \cdot 2H_2O$) as well as from natural sea or brine waters was achieved in a beaker. This is because magnesium and calcium oleates are self-floatable without air bubbles.

Into a series of 250-mL beakers containing different concentrations of Mg^{2+} and Ca^{2+} up to 6000 and 1500 mg/L (calculated as $CaCO_3$ equivalent), respectively, 30,000 mg/L of NaCl, as a major constituent of natural waters, was added. A fivefold excess of sodium oleate (with respect to Mg^{2+} and Ca^{2+}) was added to these mixtures. Five minutes were sufficient for complete flotation. The floated magnesium and/or calcium oleate(s) were separated from the mother liquors by means of separating funnels. The recovery and effectiveness of selective separation were calculated by quantitative determination of the residual Mg^{2+} and/or Ca^{2+} in solutions. To confirm the above data, the float was dissolved in a mixture of HNO_3 and methanol (1:3) [*Note*: stirring facilitates the solubility], and determined for Mg^{2+} and Ca^{2+} either by EDTA or atomic absorption. In another series of experiments the dissolved (magnesium–calcium) oleates were treated with Na_2SO_4, 30,000 mg/L, for precipitation of Ca^{2+} as $CaSO_4$ after separation of oil drops of oleic acid and adjusting the pH at ~8 with NaOH. Calcium sulfate was separated by filtration. To the remaining filtrate, sodium oleate was added to refloat Mg^{2+} as pure magnesium oleate.

Infrared studies were carried out on magnesium–calcium oleate and the refloated magnesium oleate before and after ignition.

RESULTS AND DISCUSSION

Initial experiments showed that seawater (Mediterranean Sea) and brine water (Manzalah Lake) contain bicarbonate alkalinity of 400 and 480 mg/L as well as magnesium and calcium of 6000 and 1500 mg/L (relative to $CaCO_3$ equivalent), respectively. Consequently, these concentrations of bicarbonate alkalinity, magnesium, and calcium (analogous to natural samples) were used in synthetic mixtures studies during the whole course of this investigation. Also, it has been found that the hydrogen ion and sodium chloride concentrations markedly affect the process of selective separation of magnesium from saline waters. Hence, our attention is focused on studying these factors in some detail.

Precipitation of Magnesium and Calcium

The results of effectiveness of precipitation of magnesium and calcium ions from synthetic solutions of $MgSO_4 \cdot 7H_2O$ and/or $CaCl_2 \cdot 2H_2O$ containing about 6000 and 1500 mg/L of Mg^{2+} and Ca^{2+}, respectively, as a function of pH, using lime as a pH regulator, are graphically illustrated in Figs. 1–3.

Figure 1 shows that magnesium ion is effectively precipitated [as $Mg(OH)_2$] at pH > 11. The presence of NaCl efficiently increases the solubility of $Mg(OH)_2$, i.e., the higher the concentration of NaCl, the greater the solubility of $Mg(OH)_2$, Curves 2, 3, 4. This may be attributed to the salt effect and ionic strength. Data in Fig. 2 indicate that calcium begins to precipitate (as $CaCO_3$) at pH > 8 using lime as a pH regulator. This agrees with the literature data (5, 6) that the precipitation of calcium carbonate requires the conversion of CO_2 and HCO_3^- (already present in natural water) into CO_3^{2-} by the reactive OH^- of lime. Also, NaCl does not favor the precipitation of $CaCO_3$. The separation of Mg^{2+} as hydroxide and Ca^{2+} as carbonate from their synthetic mixtures using lime for adjustment of pH were carried out. The results are presented in Fig. 3. Inspection of the results shows that 1) selective separation of Mg^{2+} from Ca^{2+} is quite impossible, and 2) sodium chloride hinders the precipitation of both Mg^{2+} and Ca^{2+} as hydroxide and carbonate, respectively.

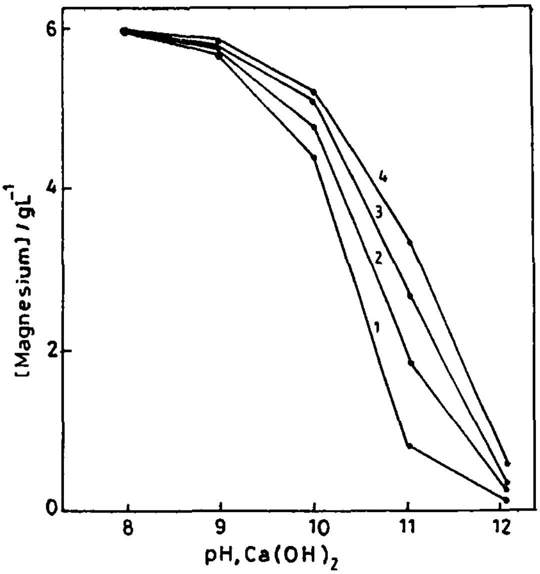

FIG. 1 Precipitation of Mg^{2+} (6000 mg·L^{-1}) as $Mg(OH)_2$ using lime: (1) in the absence of NaCl; (2), (3), and (4) in the presence of 10,000, 20,000 and 30,000 mg·L^{-1} NaCl, respectively. The alkalinity is ~500 mg·L^{-1} HCO_3^-. All concentrations in all illustrations are related to the $CaCO_3$ equivalent.

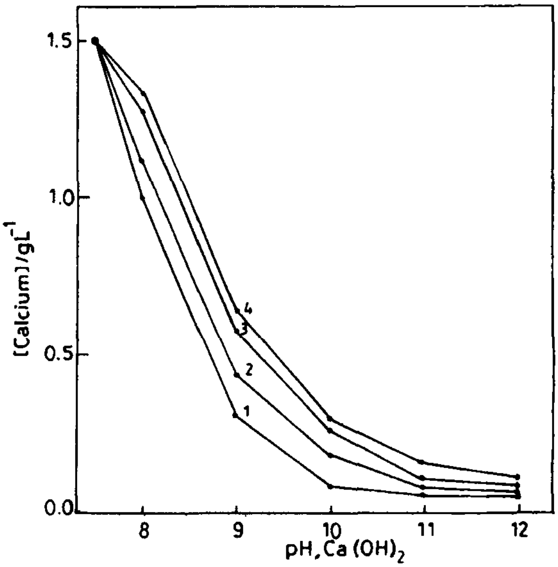

FIG. 2 Precipitation of Ca^{2+} (1500 mg·L^{-1}) as $CaCO_3$ using lime: (1) in the absence of NaCl; (2), (3), and (4) in the presence of 10,000, 20,000, and 30,000 mg·L^{-1} NaCl, respectively. The alkalinity is ~500 mg·L^{-1} HCO_3^-.

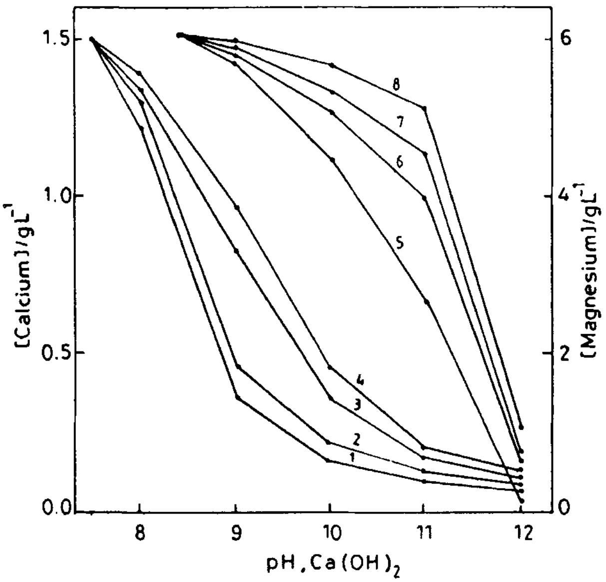

FIG. 3 Precipitation of Mg^{2+} (6000 mg·L^{-1}) and Ca^{2+} (1500 mg·L^{-1}) from their synthetic mixture as a function of pH of lime solution: (1) in the absence and (2), (3), and (4) in the presence of 10,000, 20,000, and 30,000 mg·L^{-1} NaCl, respectively, for Ca^{2+}; (5) in the absence and (6), (7), and (8) in the presence of 10,000, 20,000, and 30,000 mg·L^{-1} NaCl, respectively, for Mg^{2+}. The alkalinity is ~500 mg·L^{-1} HCO_3^-.

Moreover, the data reveal that the expected suitable pH range for ionic flotation of Mg^{2+} and Ca^{2+} must be 7.5–8.5 to avoid any contamination from the formation of $Mg(OH)_2$ and $CaCO_3$.

To confirm the precipitation of Ca^{2+} and Mg^{2+} as carbonate and hydroxide, as previously mentioned, tests were run in soda medium. The results obtained are graphically illustrated in Figs. 4–6. Comparison of Figs. 1–3 with 4–6 reveals that, bicarbonate and carbonate alkalinities have a depression effect on both Ca^{2+} and Mg^{2+} which begin to precipitate noticeably at $pH > 8$ and $pH > 9$, respectively. Accordingly, lime is more suitable than soda as a pH regulator. Also, the American and British method for separation of Mg^{2+} from natural waters using lime as a precipitating agent is not quite selective.

Selective Ionic Flotation

Since our goal is the selective separation of Mg^{2+} from brine waters, so the feasibility and amenability of coflotation of both Mg^{2+} and Ca^{2+},

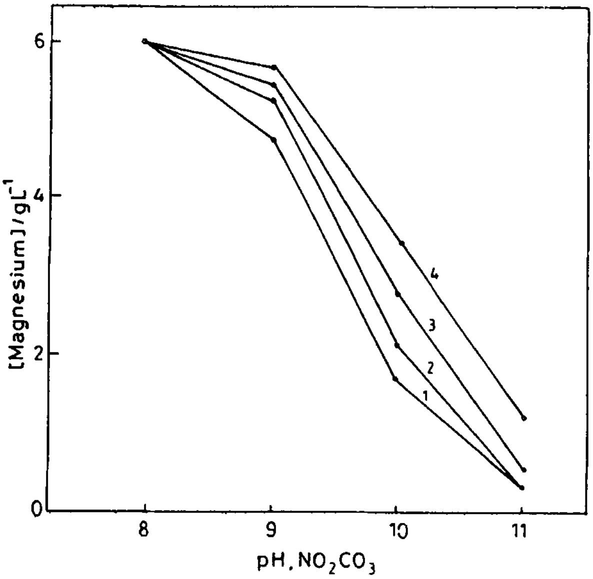

FIG. 4 The legend as for Fig. 1 but with Na_2CO_3 used as the pH regulator instead of lime.

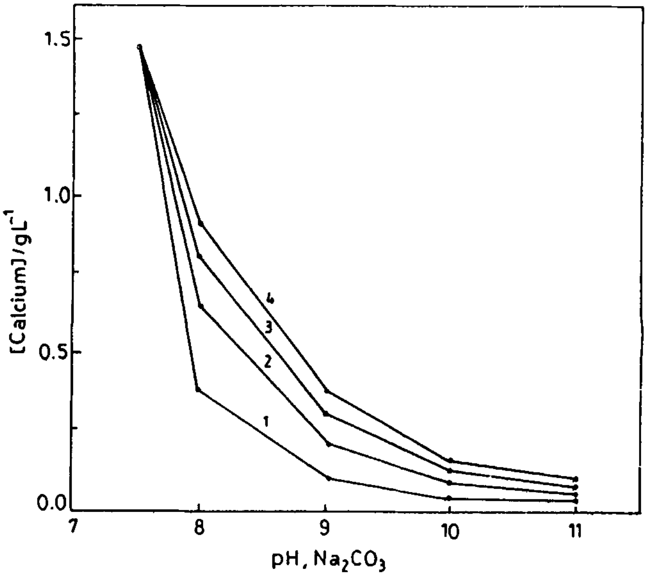

FIG. 5 The legend as for Fig. 2 but with Na_2CO_3 used as the pH regulator instead of lime.

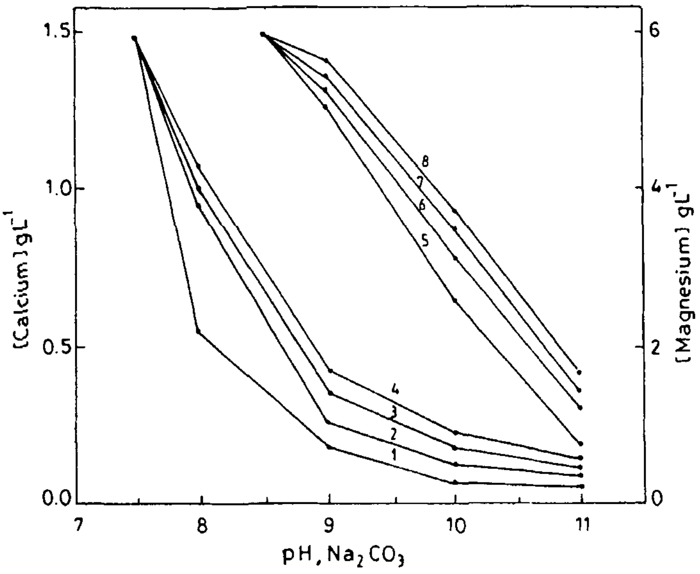

FIG. 6 The legend as for Fig. 3 but with Na_2CO_3 used as the pH regulator instead of lime.

precipitation of Ca^{2+} as $CaSO_4$, and reflotation of pure Mg^{2+} have been investigated. Figure 7 indicates the effective precipitation action of sulfate on Ca^{2+} from the dissolved float of both calcium and magnesium oleates. Examination of the results shows that H_2SO_4 is inferior to Na_2SO_4 in precipitating Ca^{2+} as $CaSO_4$. In addition, the effectiveness of precipitation of Ca^{2+} as $CaSO_4$ increases with the pH of the solution. Thus, the percentage of Ca^{2+} precipitated in a solution of H_2SO_4 of pH ≤ 2 is much less than that precipitated at pH ≥ 2, e.g., pH 3.

It is also noted that a sulfate concentration of 30,000 mg/L (as $CaCO_3$ equivalent) led to precipitation of about 97% of Ca^{2+} ions at a pH ranging between 7.5 and 8.5 in the absence of NaCl (Fig. 7, Curve 1). It is worthy to note that sodium chloride hinders the efficiency of precipitation of Ca^{2+} as $CaSO_4$ to 83% (Curve 2). Consequently, to compensate for the effect of NaCl, coflotation of both Mg^{2+} and Ca^{2+} as their oleates should first be carried out. The collective ionic flotation of both Mg^{2+} and Ca^{2+} from synthetic mixtures or natural sea and brine waters has been performed. The results in Fig. 8 show that the maximum flotation efficiencies of both Ca^{2+} and Mg^{2+} have been achieved in the pH range 7.5–8.5. Recovery of Mg^{2+} and Ca^{2+} decreases at pH < 7.5, probably due to the relatively

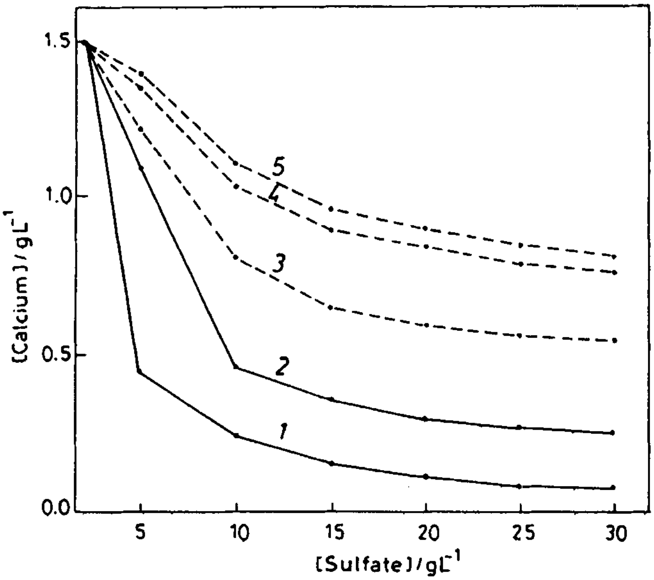

FIG. 7 Precipitation of Ca^{2+} as $CaSO_4$ from synthetic mixtures containing 6000 mg·L^{-1} Mg^{2+} plus 1500 mg·L^{-1} Ca^{2+} using SO_4^{2-}. (1) and (2): By Na_2SO_4 at pH ≈ 8 in the absence and the presence of 30,000 mg·L^{-1}NaCl. (3) and (4): By H_2SO_4 at pH ≈ 3 in the absence and the presence of 30,000 mg·L^{-1} NaCl. (5): By H_2SO_4 at pH ≈ 2 in the absence and the presence of 30,000 mg·L^{-1} NaCl.

high pK_a of oleic acid (7). On the other hand, at pH > 8.5, the recovery of Mg^{2+} in the collective Mg^{2+}, Ca^{2+} oleate decreases markedly due to the precipitation of Mg^{2+} as $Mg(OH)_2$, whereas that of Ca^{2+} remains almost constant on raising the pH even up to 11. This may be attributed to the existence of Ca^{2+} ions in strong alkaline solutions due to the high solubility of $Ca(OH)_2$.

The data in Fig. 9 indicate the selective separation by reflotation of Mg^{2+} from Mg-Ca oleate after its dissolution in a HNO_3/CH_3OH mixture and precipitation of Ca as $CaSO_4$ at different pHs. The maximum separation efficiency of Mg^{2+} (97%) is achieved with a minimum Ca^{2+} content (3%) in the pH range 7.5–8.5. Sodium sulfate (used for calcium separation) and other ions (commonly associated with Mg in saline waters) do not float at all. Thus, a quite selective and effective method of separation of Mg^{2+} from sea (Mediterranean Sea) and brine (Manzalah Lake) waters was achieved. Ionic flotation is superior to the American-British method.

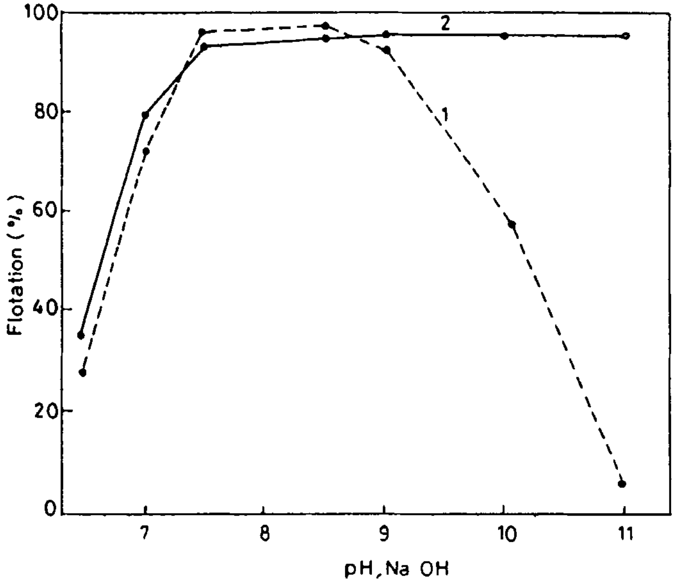

FIG. 8 Coflotation of Mg^{2+} and Ca^{2+} as a function of pH from their synthetic mixture (6000 mg·L^{-1} Mg^{2+} + 1500 mg·L^{-1} Ca^{2+}) in presence of 30,000 mg·L^{-1} NaCl or natural water using a fivefold excess of sodium oleate surfactant: (1) Mg^{2+} and (2) Ca^{2+}.

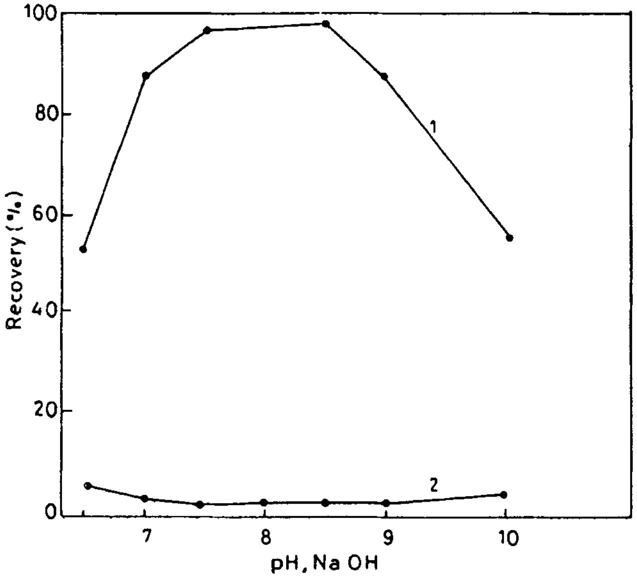

FIG. 9 Selective ionic reflotation of Mg^{2+} from dissolved Mg-Ca concentrate after removing Ca^{2+} as $CaSO_4$ as a function of pH: (1) Mg^{2+} and (2) Ca^{2+}.

Infrared Studies

Infrared spectra were used for qualitative analyses, molecular structure studies, and determination whether a product is a new compound or physical mixture of reactants. The infrared spectra of the compounds formed on the addition of Na_2SO_4 to the synthetic mixture (6000 mg/L Mg^{2+} + 1500 mg/L Ca^{2+}) or saline waters are recorded in Fig. 10. The spectra prove the formation of $CaSO_4{\cdot}2H_2O$. This confirmation is supported by the appearance of the following: 1) medium and shoulder bands at 290 and 400 cm^{-1}, respectively, characteristic for ν(Ca—O) vibrations (8, 9); and 2) a strong band centered at 1140 cm^{-1} with a very broad band at 3430 cm^{-1} characteristic for the bending and stretching O—H vibrations of the water of crystallization in $CaSO_4{\cdot}2H_2O$ (10).

It has been found that the solubility of calcium sulfate is decreased by the addition of sulfates but is quite considerably increased by other salts and acids. The previous experiment was conducted under the same conditions except for using H_2SO_4 instead of Na_2SO_4 (Fig. 11). The appearance of new absorption bands at 980, 1060, and 1140 cm^{-1}, which are characteristic for ν(S—O), $\nu_s(SO_2)$, and $\nu_{as}(SO_2)$ vibrations, respectively, is noted, indicating the presence of H_2SO_4 molecules. Accordingly, it is quite reasonable to assume the formation of new compounds of the type $CaSO_4{\cdot}H_2SO_4$ and/or $CaSO_4{\cdot}3H_2SO_4$ which are fairly soluble and can be isolated. Hence, Na_2SO_4 is more suitable for our purpose in isolating Ca than is H_2SO_4.

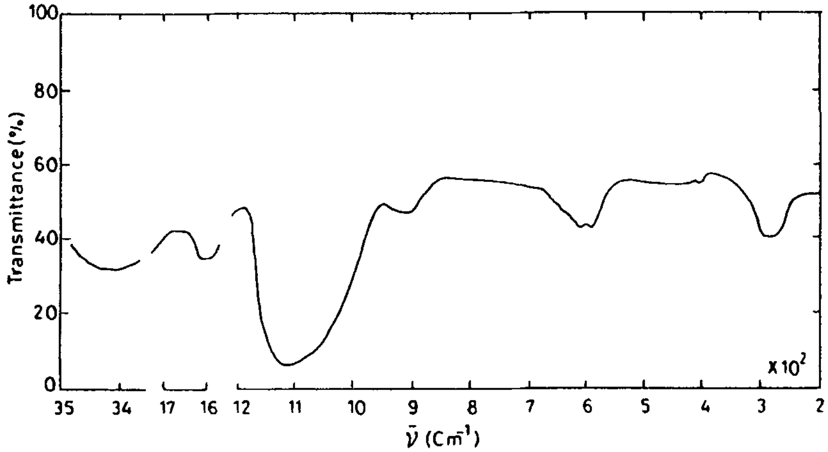

FIG. 10 Infrared spectra of calcium sulfate precipitated from a synthetic mixture (6000 and 1500 mg·L^{-1} of Mg^{2+} and Ca^{2+}, respectively) by Na_2SO_4 (1500 mg·L^{-1}).

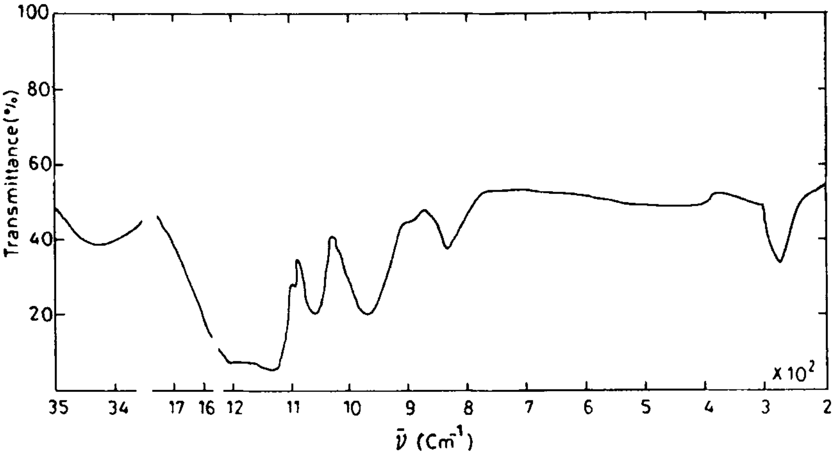

FIG. 11 Infrared spectra of calcium sulfate precipitated from a synthetic mixture (6000 and 1500 mg·L^{-1} of Mg^{2+} and Ca^{2+}, respectively) by H_2SO_4 (1500 mg·L^{-1}) at pH 3.

To study the selectivity of the proposed procedure, the purity of the final magnesium oleate separated in the refloated concentrate was investigated by infrared spectra. By comparing the spectra of magnesium-calcium concentrate before (Fig. 12a) and after (Fig. 12b) ignition, one sees the disappearance of the oleate bands. The spectra show absorption bands only at 290, 400, and 445, characteristic of ν(Ca—O) and ν(Mg—O) (9). Also, the infrared spectra of the refloated Mg-oleate (after dissolving Mg-Ca oleates in HNO_3/CH_3OH, precipitation of Ca as $CaSO_4 \cdot 2H_2O$, and refloating of Mg-oleate at pH 8–8.5) are shown in Fig. 12c. The spectrum of the ignited refloated Mg-oleate (Fig. 12d) shows an absorption band only at 445 cm^{-1}, characteristic of ν(Mg—O) (9). Close inspection of the spectra in Fig. 12 seems to indicate the effectiveness and selectivity of separation of Mg^{2+} from Ca^{2+} by ionic flotation using sodium oleate as a collector in the pH range 8–8.5. Furthermore, the disappearance of the absorption bands due to magnesium oelate after ignition is in agreement with the mechanism of combustion of hydrocarbon compounds:

$$\text{Mg-oleate} \xrightarrow{\text{combustion}} MgO + CO_2 + H_2O$$

It is possible to obtain MgO as the end product selectively, effectively, and quite economically from brine and seawaters. This method is superior to the classical old method (American-British method) of extraction of

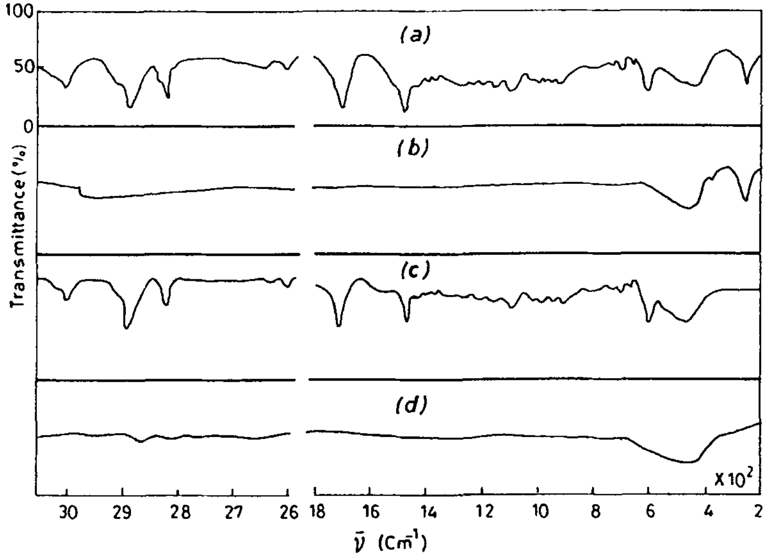

FIG. 12 Infrared spectra of collective Mg-Ca concentrate (oleate): (a) before ignition and (b) after ignition; (c) and (d) of magnesium selectively separated from collective Mg-Ca concentrate by reflotation before and after ignition, respectively.

Mg^{2+} from seawaters by precipitation using lime as $Mg(OH)_2$ due to its drawbacks as explained earlier.

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