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Floatability of Magnesium Carbonates by Sodium Oleate in the Presence of Modifiers

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Abstract

A laboratory study has been carried out on the anionic flotation behavior of magnesium carbonates in the presence of modifying reagents, followed by experiments of adsorption and zeta-potential measurements aimed at their selective separation. Sodium pyrophosphate and sodium hexametaphosphate were found to be strong depressing agents for dolomite in the alkaline region, presenting only a slight action on magnesite flotation. Carboxymethylcellulose also depressed dolomite in the pH range 7.0–12.0, but it did not affect magnesite. The modifying action was attributed to adsorption on sites where calcium exists.

INTRODUCTION

Magnesite, $MgCO_3$, and dolomite, $(Mg,Ca)(CO_3)_2$, are classified in the group of salt-type minerals; i.e., minerals of the general type M_xA_y, where M denotes some cation (e.g., Ca^{2+}, Mg^{2+}, Ba^{2+}) and A is an anion (e.g., F^-, CO_3^{2-}, SO_4^{2-}, WO_4^{2-}, PO_4^{3-}). Their solubility is greater than oxides and silicates, but less than simple salts (e.g., sylvinite). The crystal structure of magnesite and dolomite is rhombohedral and, like calcite, $CaCO_3$, they belong to the hexagonal system. The bonds between the cations and anions are ionic, while those of the trigonal carbon groups are homopolar (*1*).

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The separation by flotation of salt-type minerals from silicates and oxides is generally possible and is applied at the industrial scale. However, their selective separation from other salt-type minerals is difficult mainly in the case of sedimentary ores, and it is sometimes impossible (*2*). The similar behavior of these minerals during flotation is often attributed to the similar chemical compositions of their surfaces and the great surface activity of the collectors used in flotation. It is due also to solubility, for the different ions existing in pulp possibly react with each other or with the ionic species of the collector and thereby depress separation. Therefore the application of modifying reagents is required. Such reagents are either inorganic salts (e.g., phosphates, dichromates, silicates, fluorides) or organic acids and salts (e.g., starch, tannin, tartaric).

Magnesium carbonate minerals in aqueous dispersions are slightly dissolved and give ions of calcium and magnesium and certainly hydrolysis products. For instance, for dolomite in contact with atmospheric dioxide at equilibrium, a diagram can be constructed, shown in Fig. 1. These ions react with anions of fatty acids to give insoluble salts which can precipitate on particle surfaces. The surface species formed are generally a function of solution composition and pH. This action is not

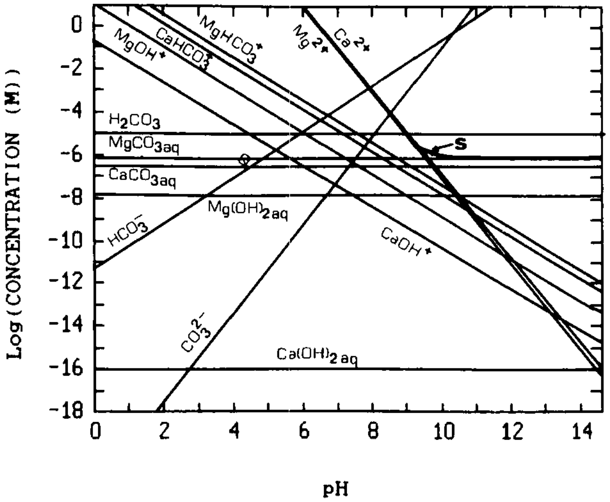

FIG. 1. Equilibrium concentration of different species of dolomite in aqueous solution; curves denote the solubility.

selective and, thus, particles of different minerals yield similar surfaces (*3*, *4*).

EXPERIMENTAL

The materials used were pure natural minerals of Greek origin. Greek magnesite is of the crypto-crystalline type, with very fine magnesium carbonate crystallites. One of its main admixtures is dolomite. The materials were crushed and ground, and the −180 + 125 μm fraction was taken by wet sieving for the flotation experiments and the −45 μm fraction for adsorption and zeta-potential measurements. The chemical analysis of minerals is given in Table 1, as certified by x-ray diffraction analysis.

Flotation experiments were conducted in a modified Hallimond tube. The zeta potential was measured in an apparatus purchased from Micromeritics, in a manner described elsewhere (*5*). The adsorption experiments are also described elsewhere (*6*). Sodium oleate (technical grade, B.D.H.) was the collector, and the modifying reagents added were sodium pyrophosphate, $Na_4P_2O_7 \cdot 10H_2O$ (pro analysi, Merck), sodium hexametaphosphate, $Na_6P_6O_{16}$ (laboratory reagent, B.D.H.), and the salt with sodium of carboxymethylcellulose (laboratory reagent, Sigma). The latter is water soluble and of low viscosity. Solutions of sodium hydroxide and sulfuric acid (both pro analysi, Merck) were used for pH control.

The way the reagents were added in flotation and their influence were initially tested with pyrophosphate because their activity often depends on the addition sequence. The following methods were tested: 1) Addition of modifier, stirring for 1200 s, addition of collector, stirring for 900 s, and flotation; 2) addition of collector, stirring for 900 s, addition of modifier, stirring for 1200 s, and flotation; and 3) simultaneous addition of

TABLE 1
Chemical Analysis of Materials (in %)

Type	Dolomite	Magnesite
Loss on ignition	46.74	51.58
Silicates and insolubles	0.28	0.26
Total oxides, R_2O_3	0.12	0.20
Calcium oxide	30.50	0.40
Magnesium oxide	21.86	47.52

collector and modifier, stirring for 1200 s, and flotation. The flotation recoveries obtained had a difference of the order of 4%, which was not significant. Method 1) was selected because it resembles industrial conditions. The above stirring periods were previously determined from tests. The flotation time was 120 s.

RESULTS AND DISCUSSION

Phosphate and polyphosphate salts have been widely used for the flotation of sulfide ores. They have recently been examined for the flotation of nonsulfides and salt-type minerals (*7*, *8*). They offer such properties as a dispersion medium for fine mineral particles, precipitation of some metallic ions, stabilization of mineral dispersion, water softening, and depression of gangue flotation. For example, orthophosphate was used in selective flotation of dolomite from apatite (*9*).

In Fig. 2 the influence of pyrophosphate addition on magnesite flotation is shown. The modifier considerably affected flotation in the alkaline region, for it was observed to counteract the effect of pH in the 9.0–12.0 range. With dolomite, presented in Fig. 3, the depressive action of

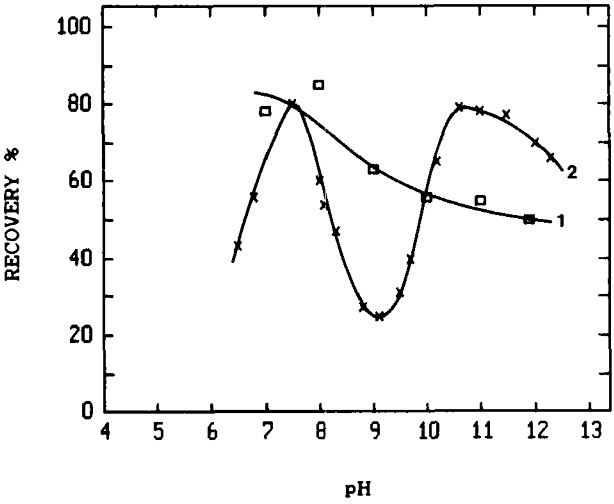

FIG. 2. Effect of pyrophosphate at different pH values on magnesite flotation by 30 ppm sodium oleate: (1) 900 ppm sodium pyrophosphate, (2) without modifier.

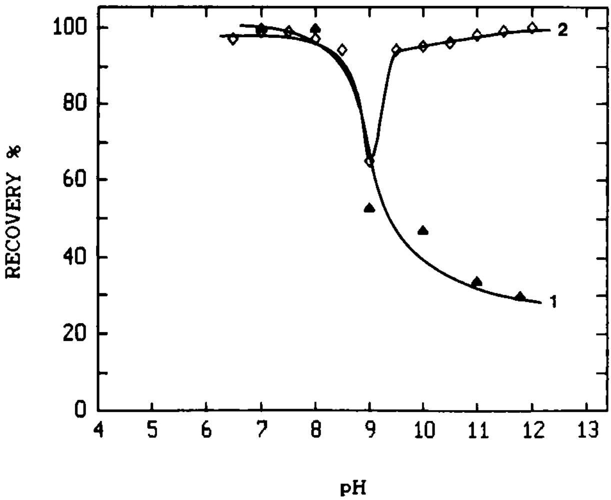

FIG. 3. Effect of pyrophosphate on dolomite flotation by 30 ppm sodium oleate: (1) 900 ppm sodium pyrophosphate, (2) without modifier.

pyrophosphate was more noticeable than that of magnesite at pHs greater than 9.0 because it reduced dolomite recovery up to 60–70%.

In comparing the depressive action of pyrophosphate on the two salt-type minerals, it was observed that magnesite floated more than dolomite in the alkaline region. By using the 30 ppm collector, the greater difference in recoveries when the 900 ppm modifier was added was 20% at pH 12.0. With higher collector concentrations, both recoveries were expected to increase. By adding 50 ppm sodium oleate, as shown in Fig. 4, magnesite was found to float 30% more than dolomite, but dolomite recovery was also significant, of the order of 50%.

The adsorption of collector when studied, as presented in Fig. 5, showed that in the alkaline region there was an appreciable influence, mainly on dolomite, and confirmed the forementioned results. An adsorption study of oleate on dolomite by Prédali (*10*) showed that this was physical in the acidic pH region and chemical in the alkaline pH region. Mention should also be made of the work by Brandao (*11*).

The influence of 20 and 50 ppm sodium hexametaphosphate was then examined. In flotation of magnesite by 20 ppm sodium oleate, it was noticed that recovery increased with increasing modifier concentration in the pH range of approximately 8.0–11.0. The same observation was also

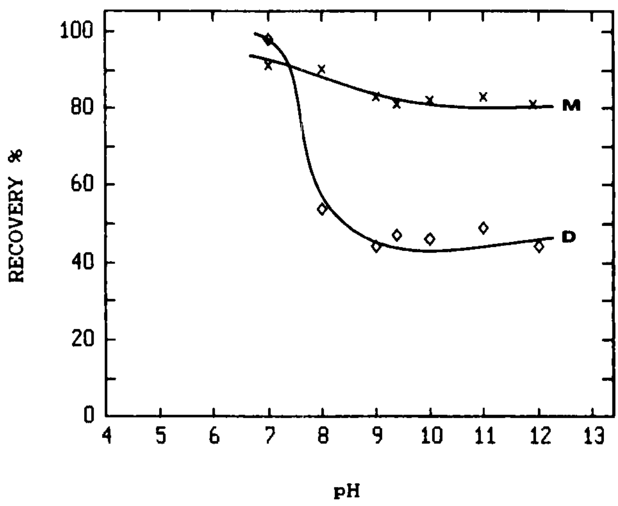

FIG. 4. Comparison of pyrophosphate action (900 ppm) on flotation of two carbonates by 50 ppm sodium oleate; M denotes magnesite and D is dolomite.

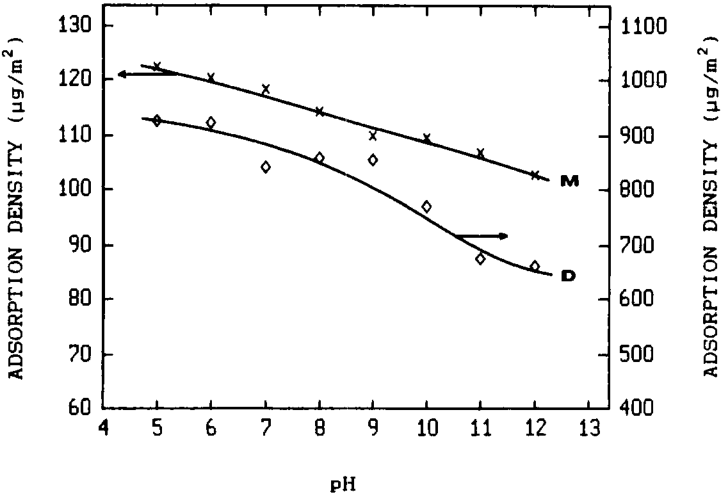

FIG. 5. Adsorption experiments of 50 ppm sodium oleate on dolomite and magnesite in the presence of 900 ppm sodium pyrophosphate.

made when an oleate concentration of 10 ppm was tried. Figure 6 presents the results obtained for dolomite. It was shown that sodium hexametaphosphate, which possesses a higher negative charge than pyrophosphate, is a strong depression agent for dolomite in the pH range of 7.5–12.0, where the mineral was only slightly floated (around 15%). No influence was found at pH 7. The same observation was also made with a lower collector concentration.

The points of zero charge of magnesite and dolomite were found at pH 6.0–6.5 (*4*). Therefore, in the range studied, both carbonates were negatively charged. Adsorption of oleate on mineral surfaces, which is not encouraged due to electrostatic repulsions, was possible by chemisorption because oleate has a great chemical affinity for the ions of calcium and magnesium. The same conclusion was reached for the system calcite/oleate (*12*).

Zeta-potential measurements, shown in Fig. 7, show that sodium hexametaphosphate shifted the dolomite zeta-potential to more negative values in the pH range 8.5–12.0, with the greater difference of −110 mV at pH 12.0. On the contrary, the zeta potential of magnesite is not changed by hexametaphosphate (*4*).

By comparing the effect of sodium hexametaphosphate on flotation recovery of the two salt-type minerals against pH, shown in Fig. 8, it is

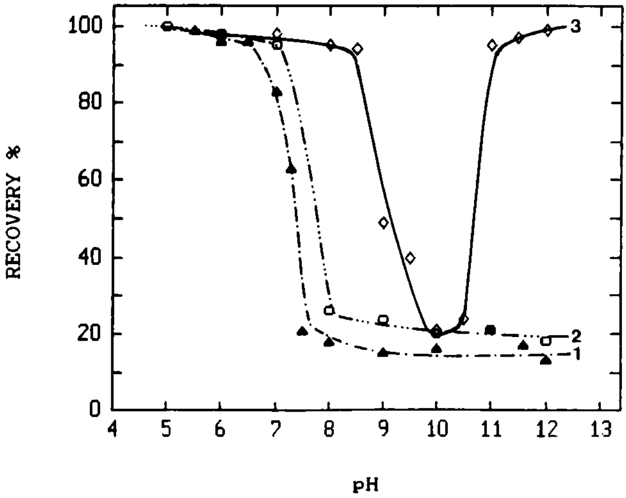

FIG. 6. Effect of sodium hexametaphosphate on dolomite flotation by 20 ppm sodium oleate: (1) 20 ppm modifier, (2) 50 ppm modifier, (3) without modifier.

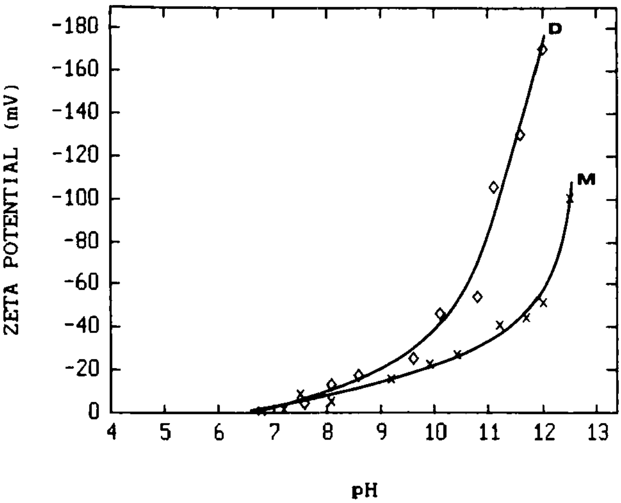

FIG. 7. Zeta potential of carbonates against pH in the presence of 100 ppm sodium hexametaphosphate.

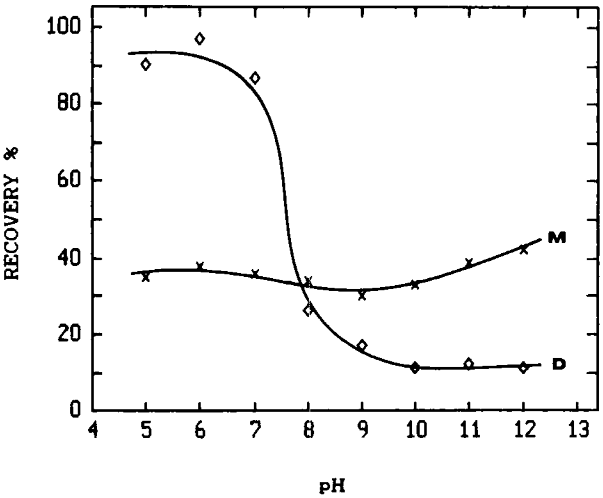

FIG. 8. Influence of 50 ppm sodium hexametaphosphate on flotation of carbonates by 10 ppm sodium oleate.

seen that in the alkaline region magnesite floats more than dolomite, but the differences are not significant (of the order of 15–30%, depending on the collector concentration). However, in the acidic region the modifier has no influence. An increase of modifier concentration, shown in Fig. 9, was observed to reduce the difference obtained in recoveries.

The nonaction of pyrophosphate and hexametaphosphate in the acidic pH region is attributed to the change in solution composition with pH and the hydrolysis of phosphates, which is favored by the presence of metallic cations (calcium and magnesium). The final hydrolysis product is the orthophosphate ion, which possesses a much lower negative charge than polyphosphates. Also, a decrease in pH favors the formation of insoluble oleic acid in fine dispersion, and adsorption of it on the minerals is different than that of the anionic species.

It seemed that the mechanism of action of phosphate ions could be explained by accepting that they are adsorbed on mineral surfaces and increase their negative charge due to their high negative charge. Thus, they depress the adsorption of anionic collectors since the electrostatic repulsions were increased and they antagonize the collector ions. It was also shown for the chemical adsorption of tripolyphosphate on calcite (*13*), where the modifier was found to be antagonistic with oleate ions. From the zeta-potential measurements (Fig. 7) it was observed that

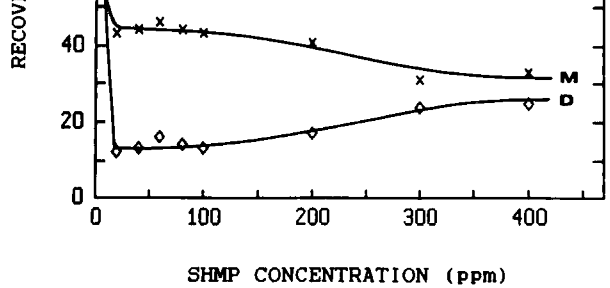

FIG. 9. Influence of sodium hexametaphosphate addition on carbonates flotation by 20 ppm sodium oleate at pH 12.0.

phosphates significantly increase the negative charge of dolomite, as was also found for scheelite (*7*).

It is known (*14*) that phosphate and polyphosphate ions bound from solution calcium and magnesium form complexes or insoluble salts. Their complexation ability is often great, and they are able to redissolve calcium salts with other anions which had precipitated. The formation of a complex or precipitate depends on the concentration of free calcium ions which exist in dynamic equilibrium with the complex (or precipitate). If the free calcium concentration is less in the complex than in the precipitate, the latter is redissolved. The above thoughts can be described by the following reactions:

$$Ca^{2+} + \text{phosphate ion} \rightleftharpoons \text{calcium phosphate complex}$$

$$Ca^{2+} + \text{precipitation ion} \rightleftharpoons \text{insoluble salt (precipitate)}$$

where the precipitation ion could be the same phosphate or some other ion.

The solubility of these complexes is high, and calcium is rapidly dissolved from dolomite surface, resulting in a negative surface charge. The solubility rate of calcium is a function of the crystal structure of the mineral. In relatively high concentrations, it was found (*15*) that precipitates between the phosphate and calcium ions in solution were formed and then adsorbed on the mineral surface. Either or both of the aforementioned two mechanisms could happen in this case.

An organic modifying reagent, the sodium salt of carboxymethylcellulose, was tested. The flotation experiments with 20 ppm oleate on magnesite gave only a slight activation action of 100 pm carboxymethylcellulose. However, with dolomite in the pH range from 7.0–12.0, it acted as a strong depressing agent, as presented in Fig. 10. The modifier completely hindered dolomite flotation, since recovery was only around 10%, but no influence was observed at a pH of less than 7.0 and dolomite recovery was greater than 95%.

In comparing flotation results in the presence of carboxymethylcellulose at varying pH, as shown in Fig. 11, different behaviors were noticed. In the acidic region, dolomite was floating quantitatively, about 50% more than magnesite. In the alkaline region, both recoveries were small (less than 50%), and magnesite's was greater.

An adsorption study with varying cellulose additions, presented in Fig. 12, showed a significant decrease of oleate adsorption on dolomite for 100 ppm concentration and no influence at all on magnesite. Upon increas-

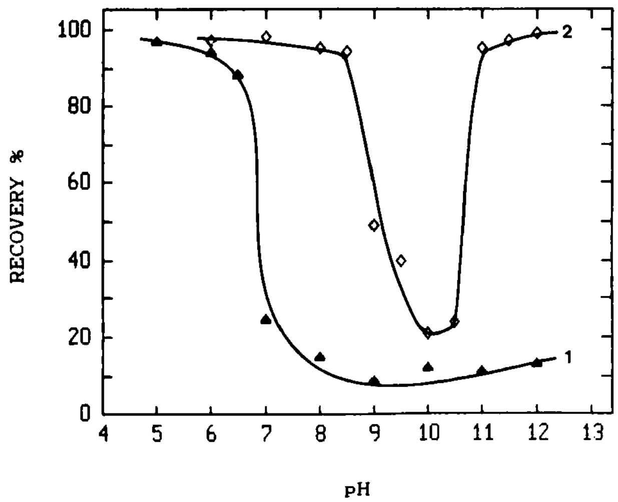

FIG. 10. Effect of carboxymethylcellulose on dolomite flotation by 20 ppm sodium oleate: (1) 100 ppm cellulose, (2) without modifier.

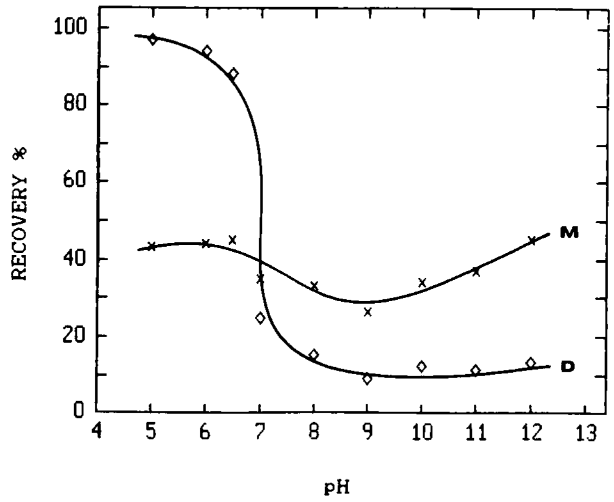

FIG. 11. Effect of 100 ppm carboxymethylcellulose on flotation of carbonates by 20 ppm sodium oleate.

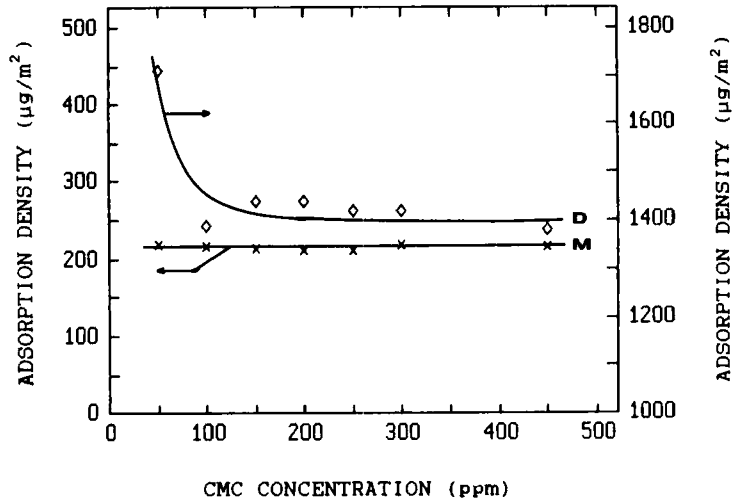

FIG. 12. Adsorption experiments of 20 ppm sodium oleate on the carbonates in the presence of carboxymethylcellulose at pH 7.0.

ing the modifier addition, the behavior of dolomite was also unchanged. This agreed with flotation experiments.

The change of carboxymethylcellulose concentration in pulp from 100 to 600 ppm at pH 6.0 did not produce any change in the recovery of salt-type minerals by 10 ppm oleate (shown in Fig. 13) or by 20 ppm oleate. The recovery difference was 50 and 65%, respectively. It was considered that selective separation of a mixture of magnesite and dolomite was possible in these conditions.

At pH 12.0 this modifier, with 50 ppm, hindered dolomite flotation but did not affect magnesite recovery which was constant at 40%, even with 300 ppm cellulose. The depression of dolomite was reduced by an increase in the collector concentration, as shown in Fig. 14; with 50 ppm, dolomite was found quantitatively in the froth.

At alkaline pH, carboxymethylcellulose is known (*16*) to be ionized completely and possesses a high negative charge. It adsorbs electrostatically on positive charged sites on surfaces and replaces these by hydroxyls that are strongly hydrophilic. As a result, its adsorption on mineral surfaces gives a more negative charge to the surfaces.

The results of zeta-potential measurements in this case, presented in Fig. 15, showed that in the presence of cellulose the zeta potential of dolomite was shifted to more negative values in the alkaline region, while

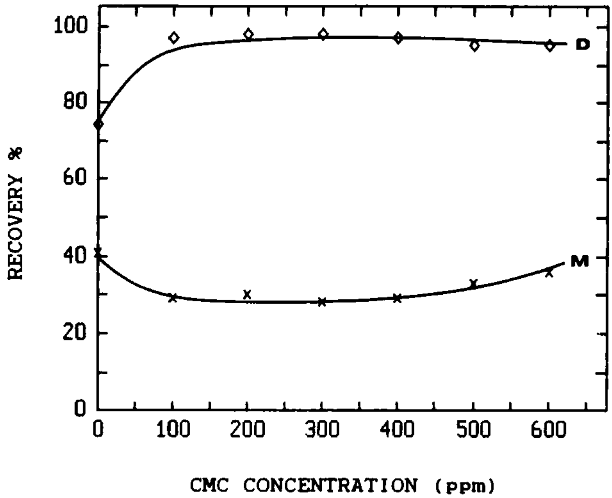

FIG. 13. Influence of carboxymethylcellulose addition on the flotation of minerals by 10 ppm sodium oleate at pH 6.0.

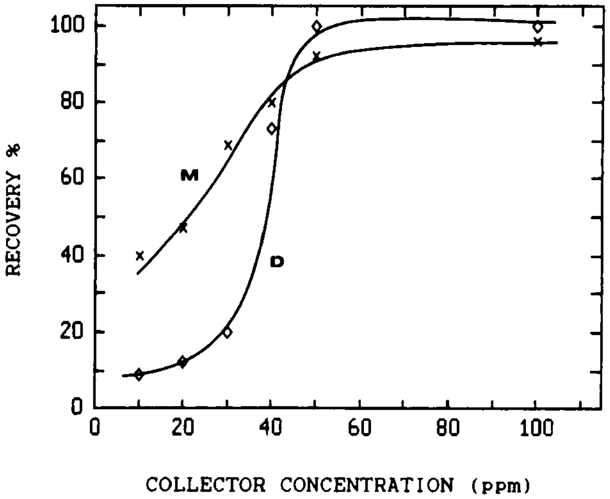

FIG. 14. Effect of sodium oleate concentration on flotation at pH 12.0 in the presence of 100 ppm carboxymethylcellulose.

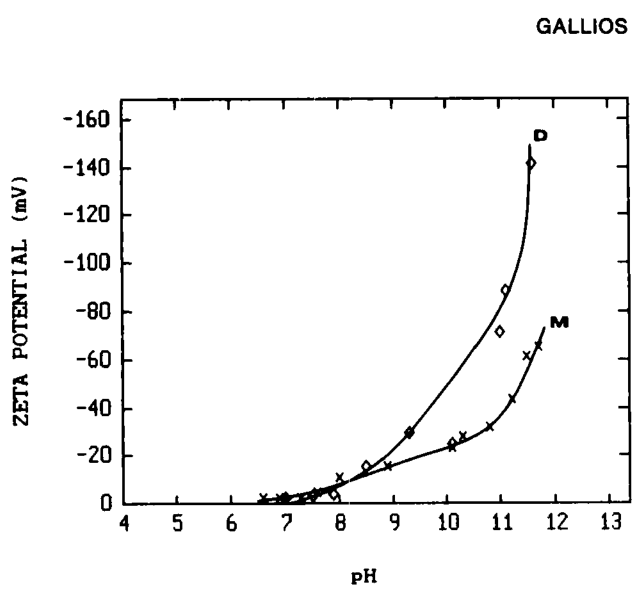

FIG. 15. Zeta potential of carbonates against pH in the presence of 100 ppm carboxymethylcellulose.

that of magnesite was essentially unchanged. Hence, this modifier was adsorbed only on dolomite. Another study (*17*) noted the action of starch during oleate adsorption on calcite. Starch has the same basic structure as carboxymethylcellulose, although the latter is a linear polymer.

At pH 7.0–11.0, magnesite and dolomite had the same charge and similar crystal structures. If carboxymethylcellulose adsorption is due only to electrostatic forces, it should adsorb on both minerals. However, its nonadsorption on magnesite is an indication of chemisorption in relation to the existence of calcium ions on the surface. Adsorption of the modifier on a dolomite surface, in preference to sites where calcium was present, reduced the available sites for collector adsorption, with the result that there is a reduction of flotation recovery in the alkaline pH region. In the acidic region, where carboxymethylcellulose is not charged, its adsorption is rather small and does not influence carbonate flotation.

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