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Reverse Flotation of Magnesite by Dodecyl Phosphate from Dolomite in the Presence of Sodium Silicate

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ABSTRACT

Magnesite and dolomite are two salt-type minerals. They show similar flotation behavior due to the same crystal structure, similar chemical composition, and high solubility. It is difficult to achieve effective flotation of magnesite from dolomite in a single stage. The present study was performed to develop a new and better flotation scheme for magnesite from dolomite. The flotation tests show that there exists a significant difference in flotability between magnesite and dolomite when dodecyl phosphate synthesized with dodecanol, phosphorus oxychloride, and other chemicals is used as collector. Modifiers are necessary to improve flotation selectivity. It was found that sodium silicate selectively depressed magnesite at a pH of 4.5 to 7.5. The flotation mechanism was

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investigated by characterizing surface electrical properties and measuring the adsorption density of the reagents on magnesite and dolomite.

Key Words: Dodecyl phosphate; Dolomite; Flotation; Magnesite; Sodium silicate.

INTRODUCTION

Magnesite ($MgCO_3$) is one of major sources of magnesium oxide. When magnesite is heated up to 1400 to 1800°C, the carbonates are removed as carbon dioxide and magnesium oxide is produced. Magnesium oxide is an important refractory material that can be used to produce fire-resistant products widely used in metallurgy, chemical, and ceramic industries. When magnesite mineral is heated up to 700 to 1000°C, the resulting product can be used to produce soundproof materials, wear-resisting materials, insulating materials, as well as pharmaceutical products. It also has a high absorption property, which can be used as adsorbent for removal of harmful gases from the air.[1] The absorption characteristics of magnesium oxide are directly related to the purity of magnesite ores. The demand for high purity magnesium oxide increased considerably in recent years. It becomes necessary to develop more efficient flotation process for magnesite separation from associated gangue minerals to obtain higher grade magnesite.

Gravity and flotation separations are two major methods used for magnesite ore beneficiation. Gravity separation is employed in coarse size (>1 mm) magnesite separation. Flotation is used for fine magnesite, particularly when a high grade of magnesite concentrate is needed.[2–4]

Froth flotation was used in magnesite mineral processing as early as in 1930s by Doerner and Dwight.[2] Their work showed that it was quite easy to separate silicate minerals from magnesite in neutral pulps using alkyl sulfonate as collector and caustic soda as depressant. The effects of sodium dihydrogen phosphate and dodecylamine acetate as collectors for magnesite and dolomite flotation were studied by Li and Salatic.[5] Their results indicated that the reagents could not separate magnesite mineral from gangue minerals effectively. In magnesite flotation carried out by Hanna and Somasundaran,[6] fatty acids were used as collector to float magnesite and hexametaphosphate and carbomethoxycellulose as depressants to depress dolomite and calcite. The results showed that hexametaphosphate and carbomethoxycellulose were effective for depressing calcite, but they also depressed magnesite.

Predali[7] studied fatty acids with hydrocarbon chains of different structures to separate magnesite from dolomite by flotation. The results showed that the magnesite recovery was higher at low pH than in neutral and

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high pH ranges. Matis and Gallios[8] used sodium fluoride silicate as depressant in magnesite and dolomite flotation. Their results showed that the reagent depressed dolomite effectively, but not magnesite. The effect of combined modifiers in magnesite and dolomite flotation was studied by Mao et al.[9] Their results suggested that when dodecyl amine was used as collector in magnesite mineral flotation, HCl and sodium phosphate could be added as modifiers to depress gangue minerals and remove SiO_2.

In magnesite mineral processing, a reverse flotation is often used to remove silicate, followed by a regular flotation to remove calcium and iron minerals.[10–12] In reverse flotation, cationic collectors such as amines are used. In some cases, pH modifiers might become necessary.[9] In regular flotation, fatty acids, alkyl sulphonate, and alkyl sulfates are used as collectors, and various depressants are used to depress gangue minerals.[7,8,13] Although silicate can be effectively removed from magnesite minerals by flotation, the removal of calcite from magnesite minerals remains a challenge. Moreover, calcite removal is often accompanied by considerable reduction of concentrate recovery. As a result, there is a need for a more selective collector for magnesite and dolomite ($CaCO_3 \cdot MgCO_3$) flotation and better understanding of the mechanisms of the separation.

The solubility of calcium phosphate is 3.2×10^{-4} mol/L, but magnesium phosphate is an easily dissolvable salt. These two species have notable differences in solubility. It is clear that the affinity between PO_4^{3-} and Ca^{2+} is stronger than that between PO_4^{3-} and Mg^{2+}. Thus, the adsorption density of phosphate on the surface of magnesite and dolomite can be different. The longer the hydrocarbon chain of a collector, the higher the hydrophobicity. However, if the hydrocarbon chain becomes too long, its solubility may suffer, which will have adverse effects on the collectivity of a collector.

The surface properties of magnesite mineral, silicate, quartz, and various iron minerals are known to be different. They can be readily separated by flotation. Magnesite and dolomite have the same crystal structure, similar surface property, and high solubility. Figures 1 and 2 show the structure of crystal lattice of magnesite and dolomite, respectively. As can be seen, the structure is exactly the same. The parameters of magnesite and dolomite are shown in Table 1.[5] Their separation by flotation is difficult and it is difficult to obtain effective recovery of magnesite in a single stage. The associated gangue minerals of magnesite often consist of silicate, quartz, dolomite, calcite, and various iron minerals. Thus, the specific objectives of this study were:

1. Development of a new collector for recovery of magnesite from dolomitic ores using a single-stage flotation process.
2. Removal of dolomite from magnesite mineral by selective flotation.

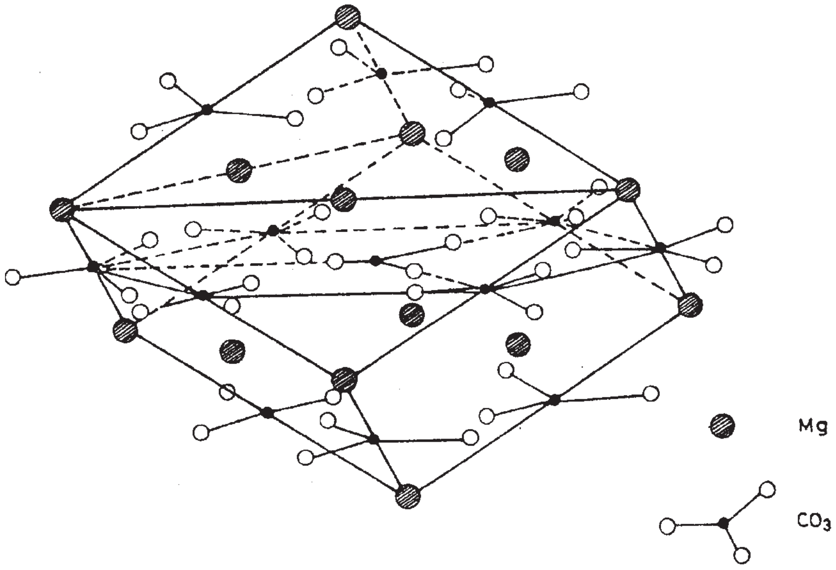

Figure 1. Structure of crystal lattice of magnesite.

3. Study of the collector chemistry and mechanisms for magnesite flotation.

EXPERIMENTAL

Pure dodecyl phosphate was not readily available as collector for flotation tests. Therefore, dodecyl phosphate was synthesized in the laboratory following the reaction scheme shown in Eq. (1) and Eq. (2).[14]

$$C_{12}H_{25}OH + POCl_3 \longrightarrow C_{12}H_{25}OPOCl_2 + HCl\uparrow \quad (1)$$

$$C_{12}H_{25}OPOCl_2 + 2H_2O \longrightarrow C_{12}H_{25}OPO(OH)_2 + 2HCl\uparrow \quad (2)$$

One mole (83 mL) of phosphorus oxychloride was placed in a 300-mL three-neck round bottom flask (reactor) and stirred at 25°C. One mole (186 mL) of dodecanol solution was then added drop by drop from a constant pressure funnel into the reactor. The mixture was stirred for 1 hour, and then heated up to 50°C. After 5 hours of reaction, the solution was filtered. The filtrate was transferred to a constant pressure funnel and dripped into a 300-mL reactor filled with 100-mL distilled water at 30°C. This reaction was maintained for

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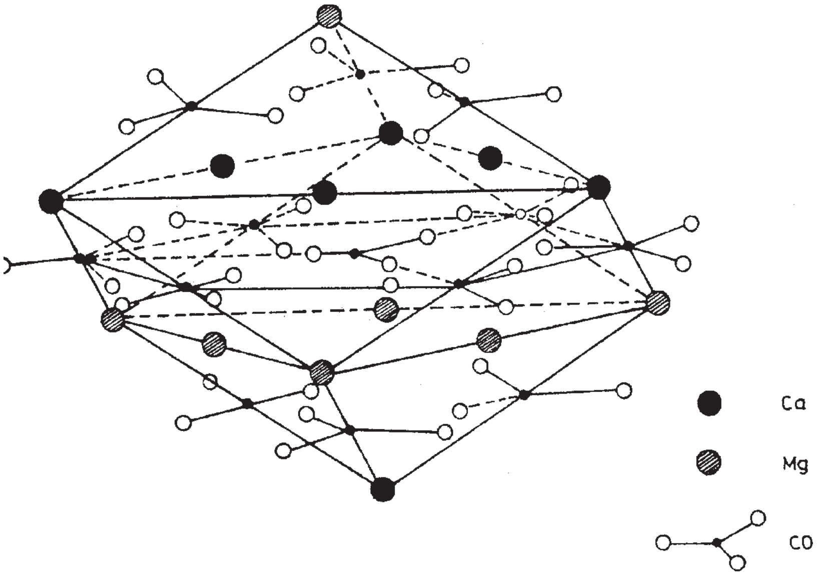

Figure 2. Structure of crystal lattice of dolomite.

5 hours. The solution was dodecyl phosphate. The elemental analysis indicated that the purity of the synthesized dodecyl phosphate was 91.3% and the byproducts mainly included didodecyl phosphate and tridodecyl phosphate.

In the preparation of dodecyl phosphate, the main factors that affect the final product were the amount of water, the stoichiometric ratio of reactants, and the stirring intensity. Various reactant stoichiometric ratios were investigated in the experiment. Lower amount of phosphorus oxychloride required less

Table 1. Parameters of magnesite and dolomite.

Parameter	Magnesite	Dolomite
Chemical formula	$MgCO_3$	$CaCO_3 \cdot MgCO_3$
Chemical composition	48.9% MgO	30.4% CaO 21.9% MgO
	51.1% CO_2	47.7% CO_2
Density (g/cm^3)	2.9–3.1	2.85–2.95
Surface tension (erg/cm^2)	1362	1032
Crystal lattice energy (kJ/mol)	237.01	206.49–232.41
Decomposition temperature (°C)	400	650

dodecanol. An excess of phosphorus oxychloride may result in an acid solution that is unfavorable for the hydrolysis and decreases the product yield. A 1 : 1 stoichiometric ratio of dodecanol to phosphorus oxychloride was considered the best. The agitation intensity was another important factor. The product yield increased with increasing agitation intensity. Higher intensity was more favorable to hydrolysis. The rotational speed of 1000 rpm was used in the present study.

To study the selective flotation of magnesite and dolomite, the flotation experiments were carried out for individual minerals and mineral mixtures in a 125-mL Hallimond microflotation cell. The pulp containing a 500-mg mineral sample and 125-mL distilled water was conditioned for 3 minutes. The flotation was then initiated and lasted for 3 minutes.

The magnesite sample and dolomite sample used in the experiment were mined in Haicheng Magnesite Mine and Dashiqiao Dolomite Mine, respectively. The particle size used in flotation of both magnesite and dolomite minerals was $-0.104\,\text{mm}+0.074\,\text{mm}$ (-140 and $+200$ mesh). The grade of MgO is 47.35% in magnesite mineral and 21.63% in dolomite mineral.

RESULTS AND DISCUSSION

Effects of pH and Dodecyl Phosphate Concentration

For various minerals, the flotation response is significantly affected by solution pH and collector dosage.[15] Figures 3 and 4 show effects of pH and collector dosage on flotation yield of magnesite and dolomite, respectively. It is clear that dodecyl phosphate was an effective collector for both magnesite

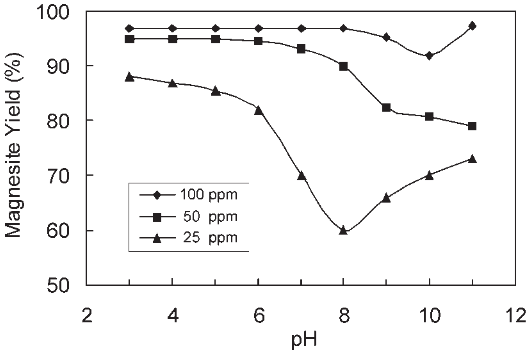

Figure 3. Effects of pH and dodecyl phosphate concentration on magnesite yield.

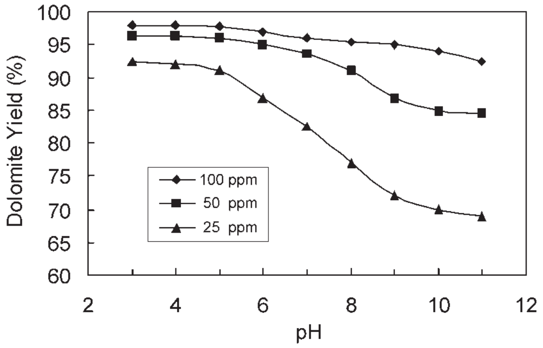

Figure 4. Effects of pH and dodecyl phosphate concentration on dolomite yield.

and dolomite. Both magnesite and dolomite yields increased with increasing dodecyl phosphate concentration. In acidic solutions (pH < 6), the flotation yield could be as high as 88% for magnesite and 92% for dolomite with 25 ppm dodecyl phosphate. However, dodecyl phosphate concentration affected magnesite and dolomite yields more significantly at a higher pH (>7) than at a lower pH. Figure 3 indicates that in alkaline solutions, the magnesite yield varied more significantly as the collector dosage changed. For example, the magnesite yield was less than 60% with 25 ppm dodecyl phosphate, but the flotation yield was nearly 90% with 50 ppm dodecyl phosphate at pH 8.0. Figure 4 shows that at a low pH (<6), the dolomite yield could be as high as 93 to 98%, but the flotation yield reduced to 65% with 25 ppm dodecyl phosphate at pH 10.0. These results demonstrated that the collecting ability of dodecyl phosphate for magnesite mineral and dolomite mineral was different. This conclusion is in good agreement with previous results reported by Chen and Li.[16] Typical flotation rates of individual magnesite and dolomite at pH 5.5 and collector dosage 100 ppm are given in Fig. 5. The flotation rate was much faster for dolomite than for magnesite under the same operating conditions. The flotation rate constant was 1.611 min^{-1} for dolomite and 0.938 min^{-1} for magnesite with 75 ppm dodecyl phosphate at pH 5.5.

Effect of Depressant

Since the dodecyl phosphate adsorbed on both magnesite and dolomite minerals, modifiers are invariably needed to achieve good selectivity. Li and Salatic[5] have shown that sodium dihydrogen phosphate selectively depressed magnesite when dodecylamine acetate was used as collector for

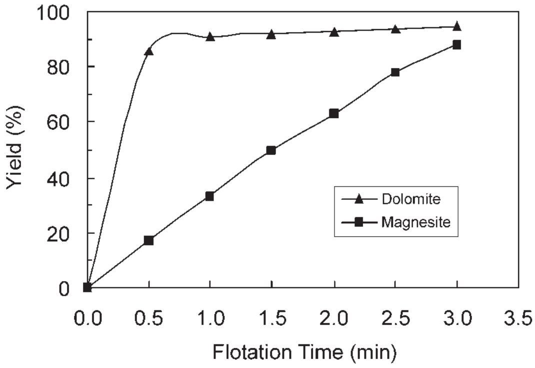

Figure 5. Flotation rates of individual magnesite and dolomite minerals at pH 5.5.

magnesite and dolomite proceedings. In this study, various depressants were tested to modify the magnesite and dolomite surface prior to the addition of dodecyl phosphate as a collector. Hexametaphosphate, starch, sodium silicate, and carbomethoxycellulose were tested individually and in combinations to evaluate the effects on the flotability of magnesite and dolomite. Figure 6 shows the flotation results obtained using 100 ppm dodecyl phosphate as collector and 75 ppm sodium silicate as depressant. At pH 4.5 to 7.5, sodium silicate selectively depressed magnesite mineral. More interestingly, at pH 5 to 6, a greater difference in flotation yield, i.e., 80 to 98% for dolomite and 12 to 28% for magnesite, was obtained. Other modifiers used individually or in combinations can also improve the difference in flotability between magnesite

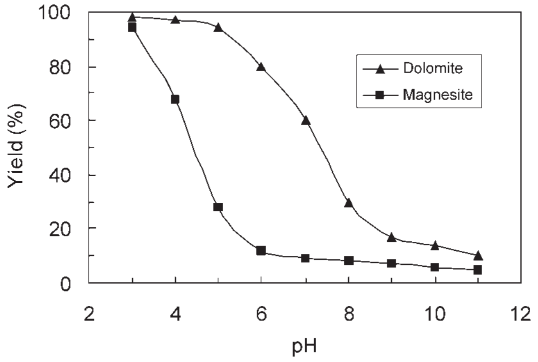

Figure 6. Effect of pH on magnesite and dolomite yield with 100 ppm dodecyl phosphate as collector and 75 ppm sodium silicate as depressant.

and dolomite minerals. However, the result is not as good as that obtained using sodium silicate.

Effect of Depressant on Flotation of Mineral Mixtures

Effects of depressant (i.e., sodium silicate) on flotation of mineral mixtures were studied using magnesite and dolomite minerals mixed at a weight ratio of 39 : 1, which gives 1.22% CaO and 46.71% MgO. This mineral mixture is similar to the magnesite ore mined in industry. In this test, reverse flotation was used to remove dolomite. The flotation tests were conducted at pH 5.5 with 100 ppm dodecyl phosphate and the results obtained at different dosages of sodium silicate are shown in Table 2. As sodium silicate concentration increased, the tailings yield increased sharply, but MgO grade remained almost unchanged. At 50 ppm sodium silicate, the tailings yield, MgO grade, and CaO grade were 58.47%, 47.67%, and 0.41%, respectively. At 100 ppm sodium silicate, they were 82.53%, 47.30%, and 0.69%, respectively. Meanwhile, MgO recovery increased from 58.95% to 82.97%. Sodium silicate appeared to be an effective depressant for magnesite.

Effect of pH and Sodium Silicate on Zeta Potential

Zeta potential affects the adsorption of reagents and thus the flotability of minerals. Zeta potentials of magnesite and dolomite minerals were measured as a function of pH and are given in Fig. 7. The zeta potentials of both minerals showed a similar trend, which is consistent with previous studies.[5,16] The point of zero charge of magnesite mineral was at pH 6.8 while that of dolomite mineral was at pH 7.6. Figure 8 shows zeta potentials of both minerals as a function of sodium silicate dosage at pH 5.5. As the sodium silicate concentration increased, the difference in zeta potential between two minerals

Table 2. Magnesite and dolomite mixture flotation results with 100 ppm dodecyl phosphate at pH 5.5.

Sodium silicate (ppm)	Tailings yield (%)	Grade (%)		Recovery of MgO (%)
		MgO	CaO	
50	58.47	47.67	0.41	58.95
75	76.10	47.34	0.52	76.64
100	82.53	47.30	0.69	82.97

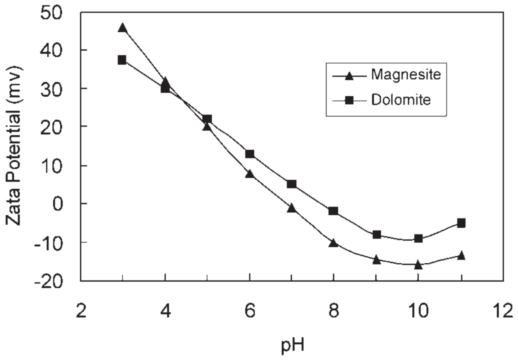

Figure 7. Effect of pH on zeta potential of magnesite and dolomite minerals.

increased slightly. At 75 ppm sodium silicate, the difference was 30 mV. This compares to about 22 mV at 5 ppm sodium silicate dosage.

The adsorption density of dodecyl phosphate on magnesite and dolomite was determined by inductively coupled plasma atomic emission spectrometer (ICP AES). Figure 9 shows the effect of pH on dodecyl phosphate adsorption density on magnesite and dolomite. Figure 10 demonstrates the effect of sodium silicate concentration on dodecyl phosphate adsorption. These two figures reveal that pH and sodium silicate significantly affected dodecyl phosphate adsorption. At pH 5.5 and 75 ppm sodium silicate concentration, the adsorption of dodecyl phosphate on magnesite was $0.75\times10^{-6}\,\mathrm{mol/m^2}$ and the adsorption on dolomite was $2.1\times10^{-6}\,\mathrm{mol/m^2}$. Obviously, preferential adsorption of dodecyl phosphate took place on dolomite surface

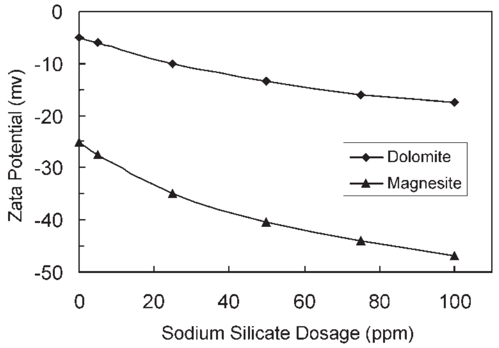

Figure 8. Effect of sodium silicate dosage on magnesite and dolomite zeta potential at pH 5.5.

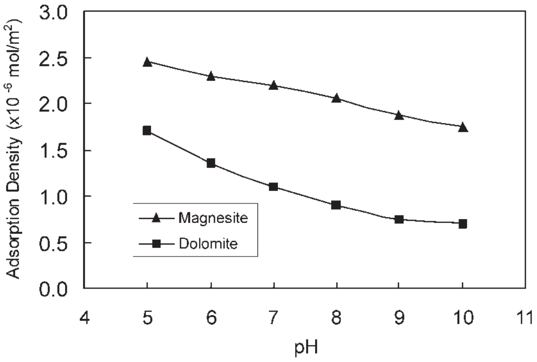

Figure 9. Effect of pH on dodecyl phosphate adsorption.

when sodium silicate was used as depressant which selectively depressed magnesite.

The adsorption of dodecyl phosphate on magnesite and dolomite was also measured by infrared spectroscopy, as shown in Figs. 11 and 12, respectively. These infrared spectra show that dolomite had a much stronger adsorption spectrum at 2950 cm^{-1} and 2850 cm^{-1} after dodecyl phosphate adsorbed on it. But magnesite only had a weak adsorption spectrum at 2950 cm^{-1}. This result proved that the interaction between dodecyl phosphate and dolomite was stronger than that between dodecyl phosphate and magnesite.

Since the zeta potential of untreated magnesite and dolomite was almost identical but flotation recovery was significantly different, chemical adsorption of dodecyl phosphate took place. In fact, the solubility constant (Ksp) of calcium phosphate (2.0×10^{-29}) is much less than that of magnesium

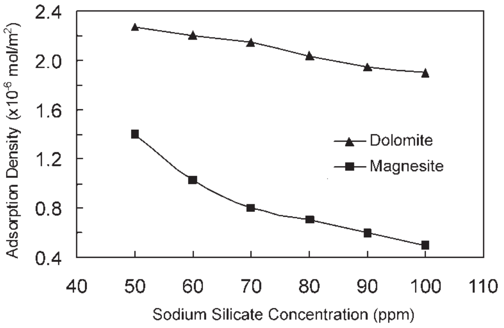

Figure 10. Effect of sodium silicate concentration on dodecyl phosphate adsorption.

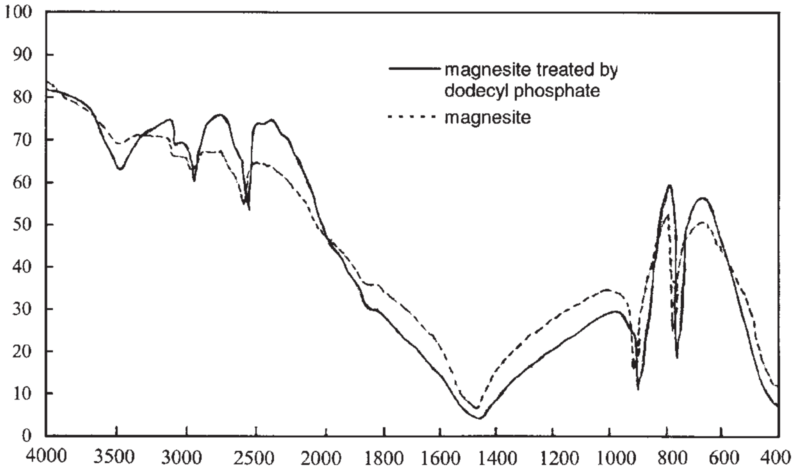

Figure 11. Infrared spectrum of magnesite.

phosphate (6.35 × 10^{-26}).[17] According to the Targgart principle, a chemical reaction theory, the lower the *K*sp value of chemical compound of an ion and a mineral lattice ion, the stronger the affinity between the ion and the mineral surface. This confirms that the adsorption of dodecyl phosphate on magnesite and dolomite is of chemical nature.

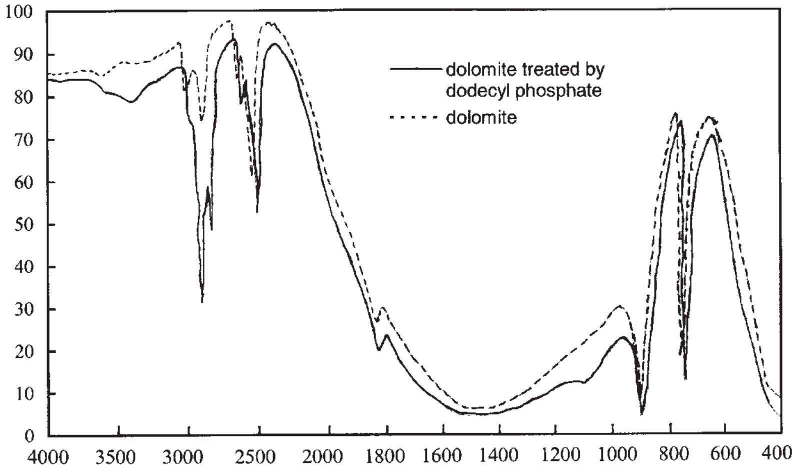

Figure 12. Infrared spectrum of dolomite.

CONCLUSION

Based on the above results, the following conclusions can be drawn:

1. Magnesite and dolomite showed almost the same zeta potential at a given pH.
2. Dodecyl phosphate was an effective collector for both magnesite and dolomite. However, the flotation rate constant was much greater for dolomite than for magnesite. It was 1.611 min^{-1} for dolomite and 0.938 min^{-1} for magnesite at pH 5.5.
3. Chemical adsorption of dodecyl phosphate took place on magnesite and dolomite minerals.
4. Using dodecyl phosphate at 100 ppm as a collector for dolomite and sodium silicate at 75 ppm as a depressant for magnesite at pH 5.5, the best separation of magnesite from dolomite was achieved in a reverse flotation, which resulted in a 76.10% yield of magnesite with a grade of 47.34%.

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