Research on the mechanism of a mixed collector onto magnesite surface to improve the flotation separation of magnesite from hornblende

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Abstract: Low-grade magnesite is not effectively used mainly due to high silicon content, especially the separation of magnesite and hornblende. In this research, a novel mixture of sodium oleate and dodecyl phosphate collector was used to increase the flotation difference between magnesite and hornblende. Artificially mixed mineral concentrates grade 47.10% (MgO content) concentrate recovery of 84.45% was obtained by micro flotation test, the results showed that the mixed collector of sodium oleate and dodecyl phosphate played a better selective promotion role in the flotation of magnesite. The interaction mechanism of this mixed collector with hornblende and magnesite surfaces was investigated using Fourier transform infrared spectroscopy (FTIR), zeta potential, and X-ray photoelectron spectroscopy (XPS), which showed that the mixed collector in terms of magnesium selection was mainly adsorbed on these magnesium sites of magnesite, and the surface of magnesite thus became hydrophobic, allowing magnesite to float and separate from hornblende.

Keywords: magnesite, hornblende, mixed collector, flotation separation

1. Introduction

Magnesite (MgCO₃) as the most important magnesium raw materials, was extensively employed in numerous fields including alloy preparation, aerospace as well as the manufacturing of basic refractories (Zhang et al., 2018). Generally, magnesite is correlated with these gangue minerals, i.e. quartz, dolomite, etc. (Botero et al., 2007; Chen and Tao, 2004). Hornblende is a common gangue phase in the magnesite reserves. Which contain metallic ions (Fe, Mg, Al, Ca, etc.) in their compositions (Tohry et al., 2021). Many studies show that hornblende to be difficult to separate owing to its structures, chemical compositions, and dissolution behaviors (Chen et al., 2011; Santos and Oliveira, 2007; Enev et al., 2014). With the magnesite developing and utilizing, it is of considerable difficulty to effectively separate magnesite over gangue minerals because of their fine and complex characteristics of gangue minerals particle size, and thus a large amount of inferior low-grade magnesite was accumulated. Plenty of researches with respect to low-grade magnesite ore are conducted by using high-pressure leaching (Amer, 2010), whose cost is too high at present. Brezáni et al. studied the collectorless flotation of talc-magnesite ore concerning particle size (Brezáni, 2013). A concentration plant in Brazil employed an anionic direct flotation circuit to obtain the magnesite with high pure concentration (Santana and Peres, 2001). Some researchers study the application of biotechnology in magnesite flotation (Botero et al., 2008; Bastrzyk et al., 2008). Ozkan has studied the effect of ultrasonic on magnesite flotation (Ozkan, 2002). Brandao et al. studied the anionic flotation of magnesite (Brandão and Poling, 1982). Ivan et al. studied the reverse froth flotation of magnesite ore by using (12-4-12) cationic gemini surfactant (Brezáni et al., 2017). Nermin Gence researched the wettingbehavior of magnesite and dolomite surfaces (Gence, 2006). Aslani et al. have researched that reverseflotation was carried out on Iranian magnesite

(Aslani et al., 2010). At present, the research on low-grade magnesite in China mainly mainly focuses on flotation (Yao et al., 2016; Liu, 2020; Teng, 2018; Ji, 2009; Fu, 2020).

Investigations in terms of flotation separation of magnesite and gangue minerals with varieties of reagents have been carried out. Traditional collectors concerning magnesite separating, for instance, oleate (NaOL) (Yao et al., 2016; Yin, 2019), DDA as well as mixed NaOL and DDA with monohydric alcohol as new collectors (Zhang et al., 2018; Liu, 2018), caused similar flotation performance of two kinds of minerals. Besides, these other collectors, such as an ion-tolerance collector AESNa (Liu et al., 2021), dodecyl phosphate(Chen and Tao, 2004) and DDA (Yao et al., 2016) as well as fatty acid (Matis et al.,2016), have also drawn considerable attention for introducing reverse flotation for magnesite. Flotation with mixed collector, including NaOL (Matis and Gallios, 1989; Sun et al, 2020) and bis(2-hydroxyethyl)dodecylamine (BHDA) (Liu et al., 2018), has not obtained efficient separation as those with the pure minerals. Despite modifiers, including sodium hexametaphosphate (SH), sodium pyrophosphate (Matis et al., 1988; Matis and Gallios, 1989; Sun et al., 2020; Luo et al., 2017), sodium silicate, and calcon (Matis and Gallios, 1989) were introduced, relative to pure mineral flotation, the little floatability distinction still manifested a challenging separation between the two minerals in a lab test. Additionally, among the mineral mixtures recommended in the literature, the recovery ratio of magnesite is still relatively low.

Such a phenomenon that the mixed collector plays a more favorable role in collecting performance than a one-fold collector, and two mixed kinds of collectors significantly improve the solution performance is observed (Yao et al., 2016; Zhang et al., 2018; Matis and Gallios, 1989). The mixed collector, combining more than two agents, may not only achieve synergistic effects of various functional groups on the mineral surfacet o obtain a good flotation effect and also enhance this separation index (Zhang et al., 2018). Mixed collector have been used in salt-type mineral flotation separation (Rao and Forssberg, 1997). Oleic acid possesses the powerful collection capacity for magnesite (Yin et al., 2019; Yin et al., 2019; Yao et al., 2020), however, dodecyl phosphate exhibits effective selectivity, while in the pH range of 6-11, $[HPO_4^{2-}]$ is the dominant ingredient in the solution for dodecyl phosphate, and the zeta potential of magnesite is too negative in the pH range of 6-11 to be not conducive for ion adsorption (Chen and Tao, 2004; Liu et al., 2019). A mixed collector of oleic and dodecyl phosphate was employed to separate magnesite from dolomite(Yao et al., 2020), based on these discussions above, both dodecyl phosphate and sodium oleate mixtures were adopted as a novel mixed collector.

In this work, to increase the difference in floatability between magnesite and hornblende, an Mg-ion-selective mixed collector (sodium oleate and dodecyl phosphate) was employed to improve the separation performance of two minerals. In addition, Fourier transform infrared spectroscopy (FTIR), zeta potential, and X-ray photoelectron spectroscopy (XPS) measurements were conducted to investigate the interaction mechanism of the mixed collector with hornblende and magnesite surfaces.

2.   Materials and methods

2.1.   Materials and reagents

In this work, the magnesite sample was used as received from the Dashiqiao, in Liaoning Province, China, and hornblende adopted was provide by the Bajiazi, in Liaoning Province, China. The phase compositions for these samples were identified through X-ray diffraction (XRD) (D8 Advance, BRUKER, Germany) and X-ray fluorescence (XRF) (S8LGER, BRUKER, Germany), as depicted in Fig. 1 and Table 1. Consequently, the purity concerning the magnesite and hornblende is 97.18% and 98.52%, respectively.

The citric acid and anhydrous calcium chloride, used as depressors and activators, respectively, were all purchased from Shenyang Chemical Reagent Co., Ltd. (China), and sodium oleate was purchased from Shenyang Chemical Reagent Co., Ltd. (China) as well. And dodecyl phosphate was purchased from China National Pharmaceutical.

2.2.   AMICS (advance mineral identification and characterization system) tests

5 g Dashiqiao magnesite ore was solidified at 35°C with a mixture of epoxy resin and coagulant (epoxy resin: coagulant = 10:3 wt.%). This original sample surface presents plentiful mineral particles, and
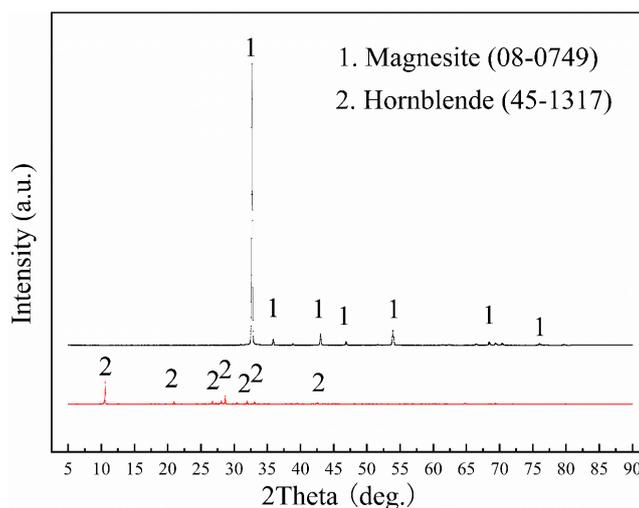
Fig. 1. X-ray diffraction spectrum of magnesite and hornblende

Table 1. Pure mineral XRF analysis results (wt.%)

sample	Chemical composition				
	MgO	CaO	Fe2O3	Al2O3	SiO2
magnesite	46.46	0.20	0.31	0.02	0.1
hornblende	6.97	11.39	14.65	13.00	48.96

and subsequently, the mirror surface appears after grinding and polishing procedures. The polished sample sprayed with gold was then placed in an ion sputtering apparatus (ETD-2000C, Beijing Elaborate Technology Development Ltd., China) sputtering carbon for 1 min (control current: 10-20 mA; vacuum: 0.1-2mbar). Scanning electron microscope (SEM) (Sigma 500, ZEISS, Germany) coupled with backscatter probe, using the high-pressure 20 KV high-speed flow and 60 μm aperture parameters, is performed to obtain clear images. Opening the energy dispersive spectrometry (EDS) (XFash 6I100, BRUKER, Germany) and testing these samples in AMICS.

2.3. Micro-flotation tests

Microflotation of hornblende and magnesite was carried out. In a laboratory flotation unit (mechanical agitation) with a 40 mL sorting cell with a stirring speed of 2200 rpm. Flotation the slurry was prepared by adding a single mineral (2 g) or an artificial mixture of minerals (1.93 g magnesite and 0.07 g hornblende) to 30 mL deionized water to the flotation cell. The resulting slurry is stirred for 1 min to achieve uniform mixing. Then the different reagents were added to the cell in sequence according to the flotation flowsheet (see Fig. 2). The concentrate and tailings are collected separately. The sequence of single mineral flotation process is scraping, filtering, drying and weighing. The mineral recovery can be quantified based on the percent dry mass of the concentrate product. In contrast, for the flotation of artificially mixed minerals, the concentrate and tailings products were assayed for MgO grades via X-Ray Fluorescence Spectroscopy (S8TLGER, Bruker, Germany), to calculate the hornblende and magnesite recoveries in the concentrate. Each flotation experiment is repeated at least three tests under the same test conditions to obtain the mean value, and the recovery and taste for magnesite were thus evaluated. The mean values with a variation of ±2.5% for three independent tests were obtained (Liu et al., 2018; Liu et al., 2019; Yang et al., 2020) .

2.4. Zeta-potential measurements

Zeta potential measurements were conducted by utilizing a Nano-ZS90 zeta potential analyzer (Zetasizer Nano ZSE, Malvern, Britain). Magnesite and hornblende were triturated with a particle size below 5 μm, 20 mg various minerals were separately introduced into 50 mL aqueous potassium chloride solution (1×10^{-3} mol/L) as the background electrolyte (Liu et al., 2018; Liu et al., 2019), and subsequently
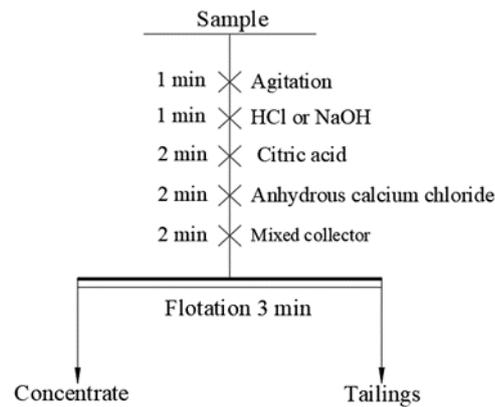
Fig. 2. Flowsheet of the micro-flotation test

stirring for 2 min. Then, the pulp pH was regulated with hydrochloric acid and sodium hydroxide solutions within 2 min, followed by adding the corresponding agent as necessary. Eventually, enabling this pulp to be stirred for 10 min to ensure particle dispersion. The pulp was a static settlement for 5 min, and then the supernatant was extracted to test the zeta potential. There is a mean value derived from three independent measurements, within the variation of ±0.2 mV (Deng et al., 2017; Deng et al., 2017).

2.5. FTIR spectroscopy

2 g mixtures consisted of magnesite and hornblende, as well as 20 mL distilled water were introduced into the flotation cell with 2 min stirring, and meanwhile this pH was adjusted to be 10 during stirring 2 min. And then there is an appropriate amount of mixed collector added into the slurry as desired with 3 min stirring. Ultimately, such solid phase was first cleared via utilizing filtration, subsequently washed through deionized water, and finally placed in a vacuum oven at 313 K for 36 h. Such kind of Vertex 80 FTIR (VERTEX 80v, BRUKER, Germany) spectrometer detected within 25 ± 2 °C and 4000-500 cm^{-1} was carried out to collect the sample infrared spectra.

2.6. XPS measurements

Handling of sample and procedures in terms of XPS (XPS, Thermo VG ESCALAB 250Xi spectrometer, America) was the same as described for FTIR measurements, whilst this discrepancy is the amount for mixed collector in XPS measurement is 5 times for that in FTIR measurement. Besides, X-ray photoelectron spectroscopy was employed to detect sample spectra with/without the mixed collector. Based on such C1s peak corresponding to contamination at around 284.8 eV, this binding energy scale was calibrated according to the internal binding energy standard (Liu et al.,2019) [34].

3. Results and discussion

3.1. AMICS (advance mineral identification and characterization system) tests

AMICS is performed to confirm the relative content of main minerals, as shown in Table 2 and Fig. 3. In the light of these results of the AMICS measurement, we can get that the main gangue mineral is hornblende. The hornblende is associated with magnesite and other minerals, whose particle size is not only fine and also inhomogeneous distribution, and is thus difficult to take advantage of low-grade magnesite ore.

Table 2. The content of main minerals in Dashiqiao magnesite ore samples (wt.%)

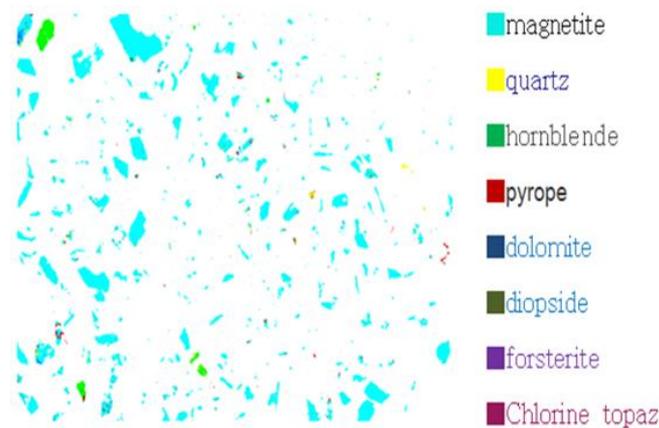| Sample	Magnesite	pyrope	hornblende	Hornblende	Quartz	forsterite	Chlorine topaz	Diopside	Chlorite
Content	91.05	1.77	3.4	1.04	0.93	0.66	0.08	0.06	0.03

Fig. 3. Mineral decomposition map of Dashiqiao magnesite

3.2. Micro-flotation test results

3.2.1. Single mineral micro-flotation tests

Sodium oleate plays an effective collection-capacity role concerning magnesite and hornblende, and yet dodecyl phosphate exhibits good selectivity concerning magnesite flotation. Consequently, two kinds of reagents were combined as mixed collector. Fig. 4 displays the influence derived from the dosage of sodium oleate to dodecyl phosphate within mixed collector on the flotation recoveries of magnesite and hornblende at pH 10, with the molar ratio of sodium oleate to dodecyl phosphate being 5:1.
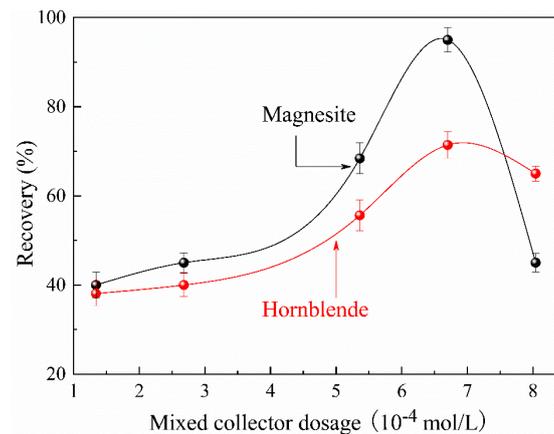

Fig. 4. Effect of mixed collector dosage on recovery of a single mineral

Generally, the recovery of flotation for hornblende gradually increased with a mixed collector dosage increasing, and the highest flotation recovery was obtained at 6.70×10^{-4} mol/L, after that, the flotation recovery of hornblende decreased slightly. Therefore, the largest flotation recovery gap was the highest in the magnesite recovery.

The flotation test results concerning the single minerals as a function of the mixed collector dosage, based on the molar ratio of sodium oleate to dodecyl phosphate of 5:1, the dosage of 6.70×10^{-4} mol/L and the mixed collector dosage at pH 7-11, are illustrated in Fig. 5.

The recovery of flotation for a single mineral raised as the pH value increased, as indicated in Fig. 5. With the pH exceeding 10, recovery of flotation for a single mineral started to decrease. The recovery of flotation for magnesite was higher than that for hornblende during the same circumstances. In the pH range of 7-11, such flotation recovery for magnesite ascended from 52.00% to 89.47%, whereas that for hornblende merely ascended from 15.00% to 52.38%. Under these various circumstances, this greatest difference in flotation recovery between magnesite and hornblende was obtained when the flotation recovery for magnesite and hornblende was 89.47% and 31.58%, respectively. Therefore, the flotation test was implemented at pH 10.
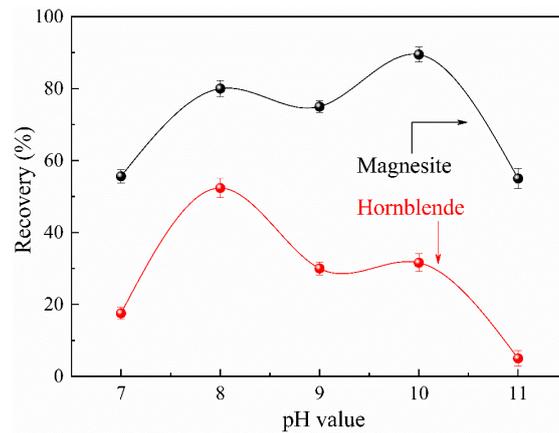
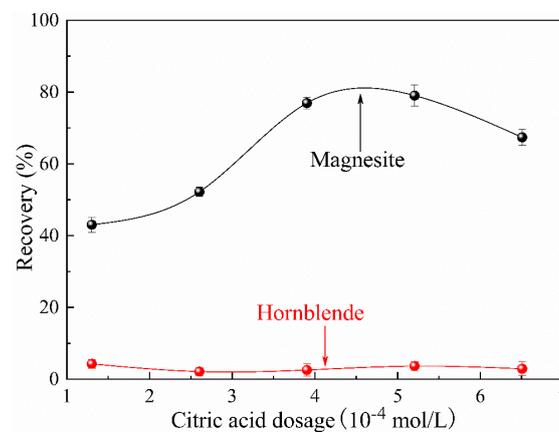Fig. 5. Effect of pulp pH on recovery of single mineral

Fig. 6. Effect of citric acid dosage on recovery of single mineral

Under the conditions of the molar ratio of sodium oleate to dodecyl phosphate of 5:1, 6.70×10^{-4} mol/L mixed collector dosage, and pH 10, the influence of citric acid dosage on flotation recovery of the single mineral is demonstrated in Fig. 6.

Fig. 6 expresses the evolution of flotation recovery in terms of the magnesite and hornblende. The recovery in terms of magnesite initially enhanced and subsequently decreased within the recovery ratio range of 43.04% and 79.04%, while the flotation recovery for hornblende stably fluctuated in such range of 2.92% and 4.27%. When the citric acid dosage was 5.21×10^{-4} mol/L, this difference in flotation recovery between magnesite and hornblende was greatest and flotation recovery for the magnesite and hornblende was 79.04% and 3.66%, respectively. Hence, the optimum value for citric acid dosage was 5.21×10^{-4} mol/L.

Under the conditions of the molar ratio of sodium oleate to dodecyl phosphate of 5:1, 6.70×10^{-4} mol/L mixed collector dosage, 5.21×10^{-4} mol/L citric acid dosage, and pH 10, the influence of anhydrous calcium chloride dosage on flotation recovery of single mineral is implied in Fig. 7.

With anhydrous calcium chloride dosage raising, the recovery of flotation for the single magnesite or hornblende exhibited an initially increased and then decreased trend, as revealed in Fig. 7. And under the same circumstance, the recovery for magnesite was greater than that for hornblende. When adopting an anhydrous calcium chloride dosage of 2.25×10^{-4} mol/L, this greatest difference in flotation recovery between magnesite and hornblende was detected, and the flotation recovery for magnesite and hornblende was 89.47% and 60.01%, respectively. The flotation test was thus implemented with anhydrous calcium chloride dosage of 2.25×10^{-4} mol/L.

3.2.2. Mixed mineral micro-flotation test

Single magnesite/hornblende flotation test presented a great discrepancy at pH 10, 5:1 molar ratio about sodium oleate to dodecyl phosphate, as well as mixed collector and inhibitors and activators dosage
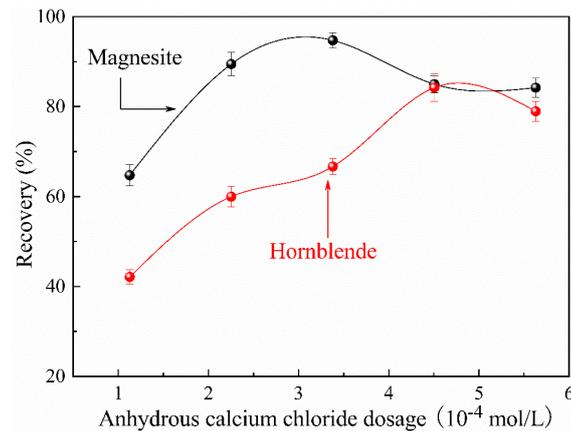
Fig. 7. Effect of anhydrous calcium chloride dosage on recovery of single mineral

of 6.70×10^{-4} mol/L, 5.21×10^{-4} mol/L, and 2.25×10^{-4} mol/L, respectively. For the sake of confirming these results, relevant tests concerning mixed collectors of both the magnesite and hornblende were conducted.

For each test, the 2 g mixed mineral of both the magnesite and hornblende (193:7 wt.%) was utilized. And according to the single mineral test procedure and flotation reagent system, the effect of the mixed collector on the flotation separation of magnesite from hornblende was evaluated by employing the flotation test for mixed collector. Relevant results of the mineral flotation test with the mixed collector were shown in Table 3.

Table 3. Mixed mineral flotation test results

Magnesite: Hornblende	Product	Yield (%)	Grade (%)		Recovery (wt.%)	
			MgO	SiO$_2$	Magnesite	hornblende
	Concentrate	83.21	47.10	0.74	84.45	35.71
193:7	Tailings	16.79	41.57	6.39	15.55	64.29
	Raw ore	100	46.14	1.71	100	100

At the magnesite and hornblende of 193:7 (wt.%), the recoveries of magnesite and hornblende are 84.45% and 35.71%, respectively, which manifests magnesite floats up and separates from hornblende with using mixed sodium oleate and dodecyl phosphate as the mixed collector, citric acid as the depressant and anhydrous calcium chloride as the activator.

3.3. Zeta potential measurements

Based on these above results, the mixed collector of both sodium oleate and dodecyl phosphate played an effective role in flotation measurements. The surface zeta potential alters when an agent adsorbing on the mineral and further produces a great influence on the flotation capacity of minerals. Zeta potential tests were therefore conducted to identify the adsorbed discrepancy between sodium oleate and dodecyl phosphate on surfaces of both hornblende and magnesite.

The zeta potential relationship in terms of the minerals and the pulp pH values in deionized water is depicted in Fig. 7, and the isoelectric points for hornblende and magnesite are about pH 5, almost coinciding with these literature results (Dittrich and Sibler,2005; Zhu et al.,2020; Gao et al.,2014; Henjes-Kunst et al.,2014).

To demonstrate what adsorption influence of pH on mixed collector on the surfaces of both magnesite and hornblende, the zeta potential values under various pH values were obtained with sodium oleate to dodecyl phosphate of 5:1 (mol.%) and 6.70×10^{-4} mol/L mixed collector dosage, as presented in Fig. 9.

The zeta potential for magnesite was -16.37 mV with pH being 2 and negatively altered by 34.84 to -51.21 mV when pH was 10, which is because the mixed collector is adsorbed on the magnesium sites of
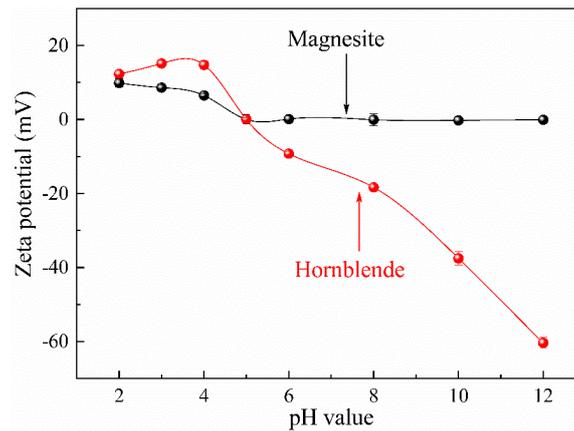
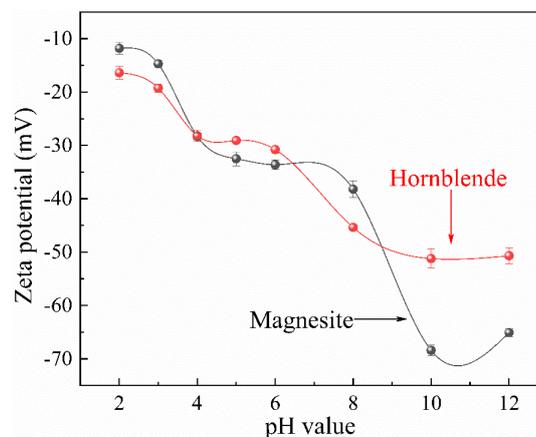Fig. 8. Effect of pH value on mineral dynamic potential in deionized water

Fig. 9. Effect of pH value on zeta potential of single mineral

magnesite, resulting in a large negative charge on the magnesite surface. The dodecyl phosphate and sodium oleate are both anionic collectors, as pH value is greater than 5, there is a negatively charged existing on the surface of magnesite, exhibiting chemical adsorption concerning the magnesite and agent occurs. Also, in the 2-6 pH range, the zeta potential for hornblende alters and fluctuates in the potential range of -11.81 mV to -33.62 mV; on the other hand, the zeta potential for hornblende gradually decreases from -33.62 mV to -68.43 mV in 6-10 pH range. When the pH value is 10, the greatest discrepancy in the zeta potential between hornblende and magnesite was obtained, and the zeta potential for magnesite and hornblende is -51.21 mV and -68.43 mV, respectively.

The zeta potentials for both magnesite and hornblende as a function of the collector mixture dosage are illustrated in Fig. 10, with these conditions of collector mixture dosage ranging from 5.36×10^{-4} mol/L to 11.99×10^{-4} mol/L. With the increase of mixed collector from 5.36×10^{-4} mol/L to 6.70×10^{-4} mol/L, the zeta potential for magnesite gradually reduced from -44.73 mV to -68.43 mV, and subsequently altered little. In the meanwhile, the zeta potential in terms of hornblende gradually lowered from -45.42 mV to -55.83 mV and subsequently altered little as well, which indicated the mixed collector occupied the Mg^{2+} adsorption sites on the surface of magnesite and possessed better selectivity for magnesium from calcium. Especially, this greatest discrepancy in the zeta potential of the hornblende and magnesite was obtained with the collector mixture dos-age being 6.70×10^{-4} mol/L, which agreed well with the micro-flotation results.

3.4. FTIR measurement

As reflected in Figs. 11 and 12, FTIR technology was utilized to study the adsorption mechanism of the mixed collector on these surfaces of hornblende and magnesite under the conditions of 10 pH, sodium oleate to dodecyl phosphate of 5:1 in molar ratio, 6.70×10^{-4} mol/L mixed collector dosage. For untreated magnesite, these peaks, centered at around 1451.36, 887.24, and 748.21 cm^{-1}, are generated from the
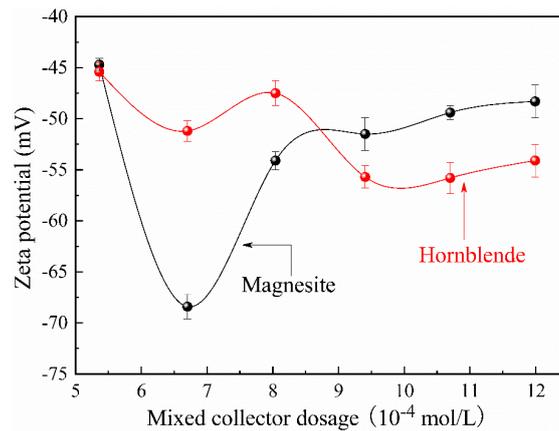
Fig. 10. Effect of the mixed collector dosage on zeta potential for single minerals

vibration of CO_3^{2-} (Yin et al., 2019; Yin et al., 2019; Zhang et al., 2019), as implied in

Figs. 10(a) and 11(a). As the mixed collector act on magnesite, Fig. 11(b) elucidates two characteristic peaks located at 2974.04 cm^{-1} and 2923.90 cm^{-1}, stemmed from the symmetric and asymmetric tensile vibration of -CH$_3$ and -CH$_2$, respectively. On the other hand, one new peak emerging at 1051.14 cm^{-1} is correlated with the tensile vibration absorption peak of the trans-P-O bond, manifesting the chemical adsorption originated from mixed collector on magnesite surface occurs. When the mixed collector act on the hornblende, Fig. 12(b) illustrates one peak corresponding to 1413.73 cm^{-1}, implying there is sodium oleate/dodecyl phosphate on the hornblende surface due to chemical adsorption. Moreover, at 1413.73 cm^{-1}, the peak intensity for hornblende treated with mixed collector is weaker than that for magnesite treated with mixed collector, which suggests such selective adsorption of collectors mixtures on the surface of magnesite. However, there is a small number of adsorption capacity on hornblende surface.
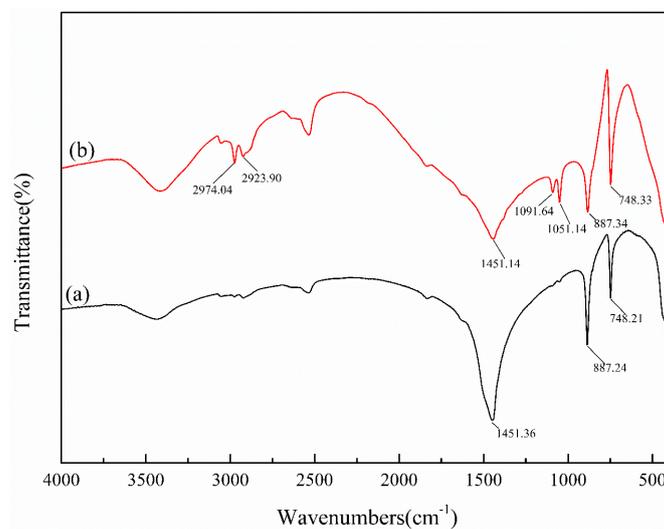

Fig. 11. Magnesite infrared spectrum analysis: (a) magnesite, (b) magnesite + mixed collector

3.5. XPS measurement

For further proving such selectivity in terms of mixed collector, XPS tests treated with/without mixed collector were carried out under the conditions of 10 pH, and a molar ratio of sodium oleate to dodecyl phosphate of 5:1 as well as 6.70×10^{-4} mol/L mixed collector dosage, as suggested in Table 4 and Figs. 13 and 14.

In comparison to these samples without using a mixed collector, a shift occurs in terms of binding energy for Mg2p arising from treated samples, as shown in Table 4, and the binding energy shifts for Mg2p in hornblende and magnesite are 0.57 eV and 0.64 eV, respectively. In contrast, the binding energy
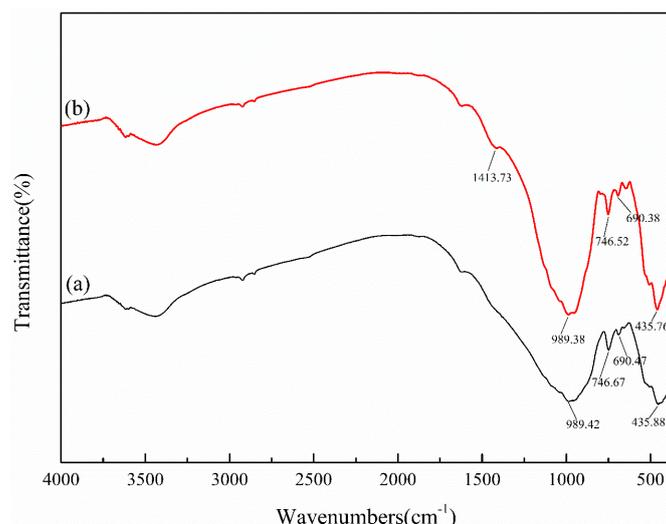
Fig. 12. Hornblende infrared spectrum analysis: (a) hornblende, (b) hornblende + mixed collector

shift for Ca2p in hornblende was not obvious, which represents this mixed collector was mainly adsorbed on these sites of magnesium on the sample surface. As depicted in Fig. 13, these peaks that are located at 49.37 eV and 51.70 eV and caused by Mg2p in untreated magnesite, moved to 50.05 eV and 52.31 eV for treated magnesite, manifesting that the mixed collector adsorption on the surface of magnesite might be because of the chemical bond on the magnesium site rather than static electricity (Zhang et al., 2018; Luo et al., 2017; Yao et al., 2020), and such similar phenomenon was detected on the surface of hornblende as well.

Table 4. XPS characterization of samples with and without mixed collector treatment

Sample	Binding energy, eV				
	C	O	Mg	Si	Ca
Magnesite	284.8	531.70	50.54		
Magnesite + mixed collector	284.8	532.20	51.18		
Offset, eV	0.00	0.50	-0.64		
Hornblende	284.8	532.10	52.55	103.10	349.30
Hornblende + mixed collector	285.00	531.50	53.21	103.30	349.40
Offset, eV	0.02	-0.60	-0.57	-0.2	-0.1

These peaks centered at 49.54 eV and 55.56 eV were correlated with Mg2p origined from untreated hornblende, and altered to 50.10 eV and 56.14 eV in treated hornblende, as shown in Fig.14, suggesting such adsorption of the mixed collector on Mg sites on the surface of hornblende was weaker than that on the surface of magnesite.

Based on the above results, the magnesium is the main adsorption site for both cases, and the binding bond between the mixed collector and hornblende was weaker than that between the mixed collector and hornblende magnesite. Combining with Table 3 results, this discrepancy of mixed collector adsorption on magnesite and hornblende surfaces is due to the discrepancy of atomic concentration (at.%) of Mg adsorption site.

3.6. Discussion

The results indicate that the Ca, Fe, Al contents on the hornblende surface were more than twice the Mg content. Additionally, the adsorption sites of the mixed collector on the magnesite surface were stronger than those on the hornblende surface, and the bond strength at the Mg sites was greater than that at the Ca, Fe, Al sites. Therefore, the adsorption of the mixed collector on the magnesite was stronger than that on the hornblende. Yao et al. found that the adsorption of mixed collector on magnesium is stronger than that on calcium (Yao et al., 2020). The binding strength of magnesium sites is greater than
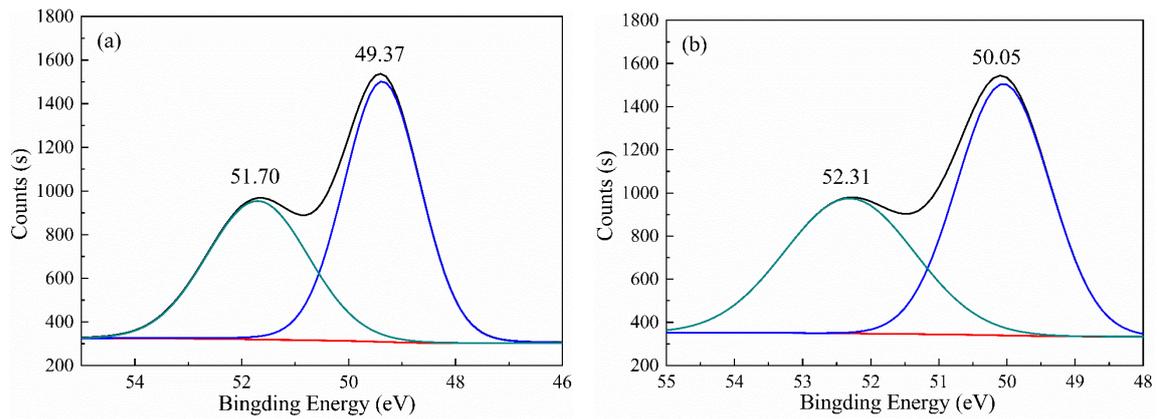
Fig. 13. Binding energy of Mg on magnesite:(a) magnesite, (b) magnesite + mixed collector
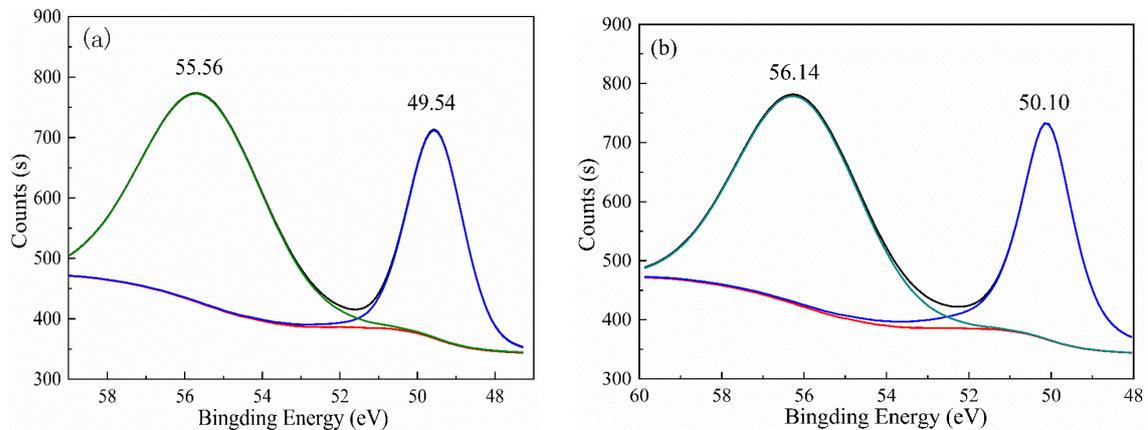

Fig. 14. Binding energy of Mg on hornblende:(a) hornblende, (b) Hornblende + mixed collector

that of calcium sites, and thus the collector mixture adsorption on magnesite was more efficient than that on hornblende.

In the case of the weak alkaline, dodecyl phosphate and sodium oleate are in the form of $C_{12}H_{25}OPO_3^{2-}$ (Yao et al., 2020) and oleate ions, respectively, and the ion-molecule association can consequently occur when they coexist. Based on FTIR results concerning the magnesite surface, such phenomenon that all of the mixed collector adsorbed on the mineral surface was observed, as presented in Fig. 11. Otherwise, Fig. 11 elucidates the two characteristic peaks located at 2974.04 cm^{-1} and 2923.90 cm^{-1}, are associated with the symmetric and asymmetric tensile vibration of -CH_3 and -CH_2, respectively. On the other hand, one new peak emerging at 1051.14 cm-1 is correlated with the tensile vibration absorption peak of the trans-P-O bond, and produces an anchoring effect, manifesting the chemical adsorption occurs originated from a mixed collector on magnesite surface (Yao et al., 2020; Yang et al., 2020). Yao et al. studied and found that the FTIR peak positions of magnesite before and after adsorption with collector were at 2883.18 cm^{-1}, 2949.22 cm^{-1}, and 2853.85cm^{-1}, 2922.86 cm^{-1}, respectively, which fits well with our results. The results of XPS shown in Table 3 indicated that the binding energy shifts of Mg2p in hornblende and magnesite are 0.57 eV and 0.64 eV, respectively. In contrast, the binding energy shift for Ca2p in hornblende was not obvious, which represents this mixed collector was mainly adsorbed on these sites of magnesium on the sample surface. Yao et al. also observed that the binding energy shift of Mg1s in magnesite was 0.91 eV (Yao et al., 2020), which is consistent with the results of this work as well. XPS analyses illustrated that chemisorption of dodecyl phosphate possibly occurs via releasing H^+ derived from –OH and generating Mg–O bond (Li et al., 2020; Tan et al., 2020).

There are two main reasons for the influence of mixed collector on the selectivity of flotation tests. On the one hand, the distribution of magnesium on the magnesite surface is different from that on the hornblende surface, whose amount on the surface of magnesite is appropriately three times than that on the surface of the hornblende. On the other hand, the ability of this mixed collector to combine

magnesium ions is stronger than that to combine calcium ions. The reason why the magnesite recovery increases may be that the mixed collector with negative charge adsorbs on the surface of magnesite with plenty of stable magnesium adsorption sites, as shown in Fig. 15. Since the solubility of calcium citrate is smaller than that of magnesium citrate, citric acid is more easily adsorbed on the calcium ions on the surface of the hornblende. Thus hornblende is more hydrophilic. The electronegativity of the surface of magnesite at pH 10 is lower than that of hornblende, so calcium ions are more easily adsorbed on the surface of magnesite. In contrast, the worse floatability of hornblende is due to the less adsorption on the calcium sites.
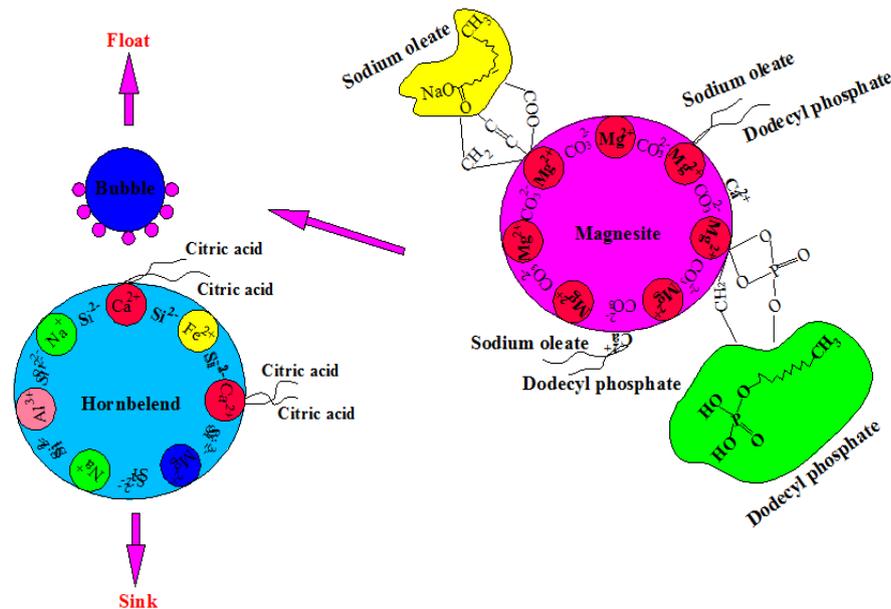

Fig. 15. Schematic of the reaction of the mixed collector on magnesite and hornblende

4. Conclusions

In this study, a mixture of sodium oleate and dodecyl phosphate was first introduced as a collector to improve the separation of magnesite and hornblende. We found that a novel reagent scheme can achieve the selective flotation of magnesite and hornblende. Combined with a series of analysis methods, including zeta-potential studies, FTIR measurements, and XPS analyses, the selective absorption mechanism of the mixed collector in the magnesite-hornblende flotation system was revealed. These conclusions were obtained as follows:

(1) In single mineral flotation, as sodium oleate to dodecyl phosphate of 5:1 (mol.%) was employed, the amount for the mixed collector and depressant dosages as well as activators were 6.70×10^{-4} mol/L, 5.21×10^{-4} mol/L and 2.25×10^{-4} mol/L, respectively. The separation in terms of magnesite and hornblende can be realized, and the flotation recovery for magnesite and hornblende was 89.47% and 60.01%, respectively. The difference of recovery rate was maximum value.

(2) In artificially mixed mineral flotation, as sodium oleate to dodecyl phosphate of 5:1 (mol.%) was employed, the amount for the mixed collector and depressant dosages as well as activators were 6.70×10^{-4} mol/L, 5.21×10^{-4} mol/L and 2.25×10^{-4} mol/L, respectively, artificially mixed mineral (concentrates grade: 47.10% (MgO content), concentrate recovery: 84.45%) was obtained by micro flotation test.

(3) The influence of the mixed collector on the surfaces of both magnesite and hornblende depends on the distribution of magnesium on the adsorption sites. Moreover, the binding strength for the mixed collector at calcium sites is weaker than that at magnesium sites.

Acknowledgments

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