International Journal of Minerals, Metallurgy and Materials
Volume 24, Number 7, July 2017, Page 736
DOI: 10.1007/s12613-017-1457-7

Solution chemistry of carbonate minerals and its effects on the flotation of hematite with sodium oleate

*Dong Li*1), *Wan-zhong Yin*1,2), *Ji-wei Xue*1), *Jin Yao*1), *Ya-feng Fu*1), *and Qi Liu*3)

1) School of Resources and Civil Engineering, Northeastern University, Shenyang 110819, China
2) College of Zijin Mining, Fuzhou University, Fuzhou 350116, China
3) Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 1H9, Canada

(Received: 8 December 2016; revised: 4 April 2017; accepted: 5 April 2017)

Abstract: The effects of carbonate minerals (dolomite and siderite) on the flotation of hematite using sodium oleate as a collector were investigated through flotation tests, supplemented by dissolution measurements, solution chemistry calculations, zeta-potential measurements, Fourier transform infrared (FTIR) spectroscopic studies, and X-ray photoelectron spectroscopy (XPS) analyses. The results of flotation tests show that the presence of siderite or dolomite reduced the recovery of hematite and that the inhibiting effects of dolomite were stronger. Dissolution measurements, solution chemistry calculations, and flotation tests confirmed that both the cations (Ca^{2+} and Mg^{2+}) and CO_3^{2-} ions dissolved from dolomite depressed hematite flotation, whereas only the CO_3^{2-} ions dissolved from siderite were responsible for hematite depression. The zeta-potential, FTIR spectroscopic, and XPS analyses indicated that Ca^{2+}, Mg^{2+}, and CO_3^{2-} (HCO_3^-) could adsorb onto the hematite surface, thereby hindering the adsorption of sodium oleate, which was the main reason for the inhibiting effects of carbonate minerals on hematite flotation.

Keywords: hematite; carbonate minerals; solution chemistry; sodium oleate; flotation

1. Introduction

The flotation process, which is based on the differences in surface physicochemical properties of minerals, is regarded as the primary technology for utilizing finely disseminated hematite iron ores. The current collectors used for hematite flotation can be divided into anionic collectors based on organic acids (oleic acid, hydroxamic acid, etc.) and cationic collectors such as amines and their salts [1–3]. Cationic collectors are the most extensively used in the iron ore industry globally. However, in China, anionic collectors are widely used [4–6].

Hematite iron ores containing carbonate minerals (siderite, dolomite, etc.) are a type of refractory iron ores that exist in some regions in China [7–8]. The presence of carbonate minerals adversely affects the separation efficiency of anionic flotation of hematite and decreases the grade and recovery of concentrates [9–11]. The hardness of carbonate minerals is low, leading to slime problems. Carbonate slimes can easily adhere to other minerals and result in similar floatability for gangue and iron oxide minerals, which complicates the separation of hematite from gangue minerals [12–13].

As salt-type minerals, carbonates exhibit relatively high solubility and the dissolved species, which include multivalent metal ions and carbonate ions, can undergo reactions such as hydrolysis, complexation, and adsorption, which can influence the interactions between collectors and minerals [14–18]. Hematite surface properties are sensitive to ionic species in aqueous solutions [19–20]. However, studies about the solubility of carbonate minerals and its potential effects on hematite flotation are scarce.

Therefore, in this work, the dissolution of carbonate minerals (dolomite and siderite) and its influence on the flotation of hematite using sodium oleate (NaOl) as a collector were investigated through flotation tests, supplemented by dissolution and solution chemistry studies, zeta-potential measurements, and Fourier transform infrared (FTIR) spectroscopic and X-ray photoelectron spectroscopy (XPS) analyses.

Corresponding author: Wan-zhong Yin, E-mail: yinwanzhong@mail.neu.edu.cn; Qi Liu, E-mail: qi.liu@ualberta.ca

2. Experimental

2.1. Minerals and reagents

The hematite, siderite, and dolomite samples used in this study were obtained from Anshan, Liaoning Province, China. Hand-picked hematite, siderite, and dolomite were crushed, ground, and wet-sieved to obtain the (−106+45) μm size fractions. The hematite and siderite samples were upgraded using a shaking table to remove light gangue minerals. The results of X-ray diffraction and multi-element chemical analyses confirmed that the purities of the final hematite, siderite, and dolomite samples were 97.4wt%, 90.9wt%, and 99.1wt%, respectively.

NaOl, sodium carbonate (Na_2CO_3), magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), and ferrous chloride ($FeCl_2$) were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) of analytical grade were used as pH regulators. Distilled water was used during all of the experiments.

2.2. Flotation tests

The micro-flotation tests were conducted in a 30-mL cell of an XFG series laboratory flotation machine. A hematite sample or mixtures of hematite with dolomite or siderite (2 g) were placed in the cell, to which 20 mL of distilled water was added. The pulp was stirred for 1 min at a rotating speed of 1750 r/min before the HCl or NaOH solution was added to adjust the pH value. The reagents were added into the cell every 3 min continuously in the order of pH regulator, modifiers, and collector NaOl. The pulp was agitated for 3 min after the desired amounts of all of the reagents had been added, and the flotation was conducted for 3 min. The froth products and tailings were weighed to calculate the recovery after filtering and drying.

2.3. Dissolution tests

To measure the mineral dissolution rate, the suspensions were agitated at 1000 r/min for a fixed period of time after 5.0 g carbonate minerals (dolomite or siderite) were added into 100 mL distilled water. The suspension was then centrifuged at 8000 r/min for 5 min in a model TGL-16 centrifuge, and the concentration of ions in the supernatant was measured by inductively coupled plasma optical emission spectrometry (Optima 4300DV).

In the above dissolution studies, it was observed that the slurry pH value changed when dissolution occurred. To study the dissolution and measure the concentration of ions in mineral-water slurry at a fixed pH value of 9.0, the dolomite or siderite suspensions were preconditioned for 15 min to attain dissolution equilibrium and NaOH or HCl was added to adjust the slurry pH value to 9.0. Afterwards, the mineral slurry was agitated for 10 min at 1000 r/min while the pH value was kept constant. This was followed by centrifugation and metal-ion concentration measurements of the centrifuge supernatant. The average of three individual measurements was calculated and reported.

2.4. Zeta-potential measurements

Zeta-potential measurements were conducted on a Nano-ZS90 zeta-potential analyzer of Malvern Instruments. A mineral suspension containing 0.01wt% −5-μm hematite in 1×10^{-3} mol/L KNO_3 background electrolyte solution was conditioned in a beaker for 15 min at a given pH value and reagent concentration. The zeta potentials of hematite were measured under each condition, and the average of at least ten individual measurements was calculated and reported.

2.5. FTIR spectral analyses

The hematite samples were ground to −2 μm in an agate mortar. Then, 1 g of the sample was added into 50 mL aqueous solution with or without 4×10^{-4} mol/L $CaCl_2$, 4×10^{-4} mol/L $MgCl_2$, and 2×10^{-4} mol/L Na_2CO_3, respectively at pH 9.0 and preconditioned for 5 min. Afterwards, NaOl was added to the mineral suspension to a concentration of 160 mg/L and the slurry was conditioned for 30 min. Finally, the treated samples were filtered, washed three times with distilled water, and dried in a vacuum oven at 40°C for 24 h. The Fourier transform infrared (FTIR) spectra of the NaOl reagent and the untreated and treated minerals were recorded through the attenuated total reflection (ATR) mode by a Bruker Alpha FTIR spectrophotometer.

2.6. XPS analyses

Hematite samples untreated or treated with $CaCl_2$, $MgCl_2$, or Na_2CO_3 at pH 9.0 were prepared. The samples were then compacted using a tablet machine into a pressed pellet for XPS analysis. XPS spectra were recorded with a Kratos AXIS 165 spectrometer using monochromatic (Al) K_α X-rays as the sputtering source. A value of 284.8 eV was adopted as the standard C (1s) binding energy for calibrating the results.

3. Results and discussion

3.1. Effects of carbonate minerals on hematite flotation

The recoveries of hematite, siderite, and dolomite single minerals in flotation in a range of NaOl concentrations (40–240 mg/L) are presented in Fig. 1. As shown in Fig. 1, the recoveries of the three single minerals increased rapidly with increasing NaOl concentration up to 160 mg/L. At higher NaOl concentrations, the increase in recovery was much slower. Therefore, the subsequent experiments were conducted by fixing the sodium oleate concentration at 160 mg/L.

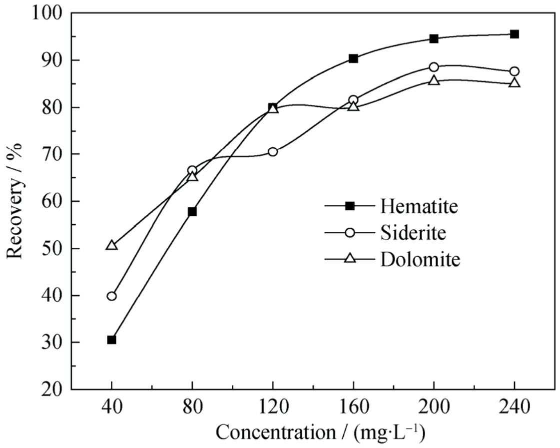

Fig. 1. Influence of sodium oleate concentration on the flotation of single minerals at pH 9.0.

To explore the effects of carbonates on hematite flotation, the theoretical recovery (ε_T) of mixtures (hematite mixed with siderite or dolomite) is defined as follows:

$$\varepsilon_T = \gamma_1\varepsilon_1 + \gamma_2\varepsilon_2 \quad (1)$$

where ε_1 and ε_2 are the recovery of hematite and carbonate mineral (siderite or dolomite) in single mineral flotation, respectively, γ_1 is the mass fraction of hematite in the mixtures, and γ_2 is the mass fraction of siderite or dolomite in the mixtures. If the flotation recovery of mixtures approximately equals the theoretical recovery, it can be assumed that hematite and carbonate minerals did not affect the flotation of each other; otherwise, it indicates that carbonate minerals might interact with hematite and influence its floatability.

The effects of siderite and dolomite on hematite flotation are shown in Fig. 2, and theoretical recoveries of mixtures, namely $\varepsilon_{T(HS)}$ for hematite–siderite mixtures, and $\varepsilon_{T(HD)}$ for hematite–dolomite mixtures, were calculated on the basis of Eq. (1). It can be seen from Fig. 2 that the recovery of hematite–siderite mixture decreased from approximately 90% to 66% when the siderite mass fraction was increased from 0 to 20%; the recovery of hematite–dolomite mixture decreased more significantly and was only at approximately 40% when the mass fraction of dolomite was 20%. Therefore, both siderite and dolomite inhibited hematite flotation, and the inhibiting effects of dolomite were stronger. Although the addition of carbonate minerals to hematite might slightly increase reagent consumption and potentially influence the flotation results, the degree of recovery reduction was much more than that could be accounted for reagent consumption.

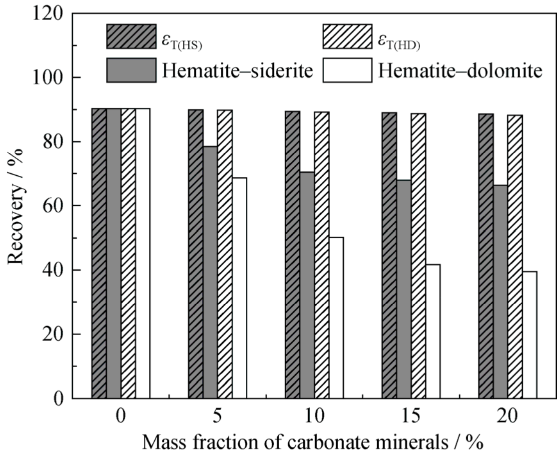

Fig. 2. Influence of carbonate minerals on the flotation of hematite (pH 9.0; sodium oleate concentration: 160 mg/L).

3.2. Dissolution of carbonate minerals

The mineral dissolution rate is defined as the quantity of lattice ions released to solution as a function of time, and the complexation reactions of dissolved lattice ions can lead to a pH change, so the dissolution rate can also be measured by the change of solution pH value [21–22]. Fig. 3 shows the solution pH value and cation concentrations as a function of stirring time (the partial pressure of CO_2 was calculated on the basis of the volume fraction of CO_2 in the atmosphere under standard conditions). As shown in Fig. 3, the degree of dolomite dissolution is greater than siderite, and more cations dissolved from dolomite. The dolomite slurry pH value increased steadily and reached dissolution equilibrium at pH 9.1.

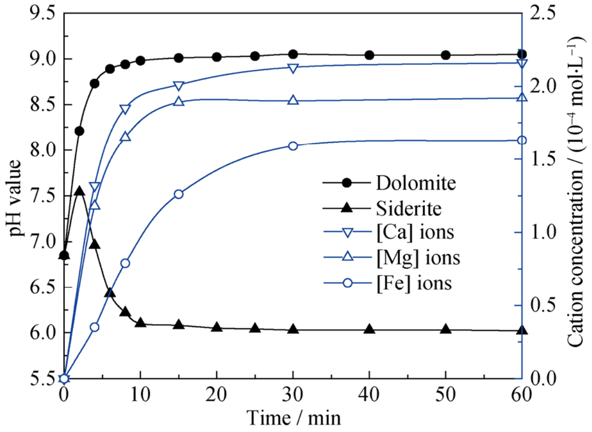

Fig. 3. Slurry pH value and cation concentrations of the mineral–H_2O–CO_2(g) (P_{CO_2} = 32 Pa) system as a function of stirring time.

The slurry pH value reached approximately 7.5 sharply after siderite was immersed in aqueous media. However, the pH value then decreased and eventually reached approximately 6.0 with increasing stirring time. This phenomenon might be due to the difference in hydrolysis rate and the strength of ferrous ions and carbonate ions. The protonation of hydrated CO_3^{2-} is faster, and this process dominates at the beginning of dissolution, leading to increasing solution pH value; however, the deprotonation of hydrated Fe^{2+} is stronger and becomes dominant with increasing stirring time, resulting in the eventual decrease of slurry pH value [23–24].

The concentrations of Ca^{2+}, Mg^{2+}, and Fe^{2+} dissolved from dolomite and siderite in distilled water were also determined by fixing the solution pH value at 9.0. The results are shown in Fig. 4 and indicate that the concentration of cations dissolved from dolomite is greater than that of cations from siderite, which agrees with the dissolution rate tests. The results of dissolution study suggested that the dissolution of carbonate minerals might influence hematite flotation. Therefore, solution chemistry calculations were conducted to investigate the solution species of siderite and dolomite and to identify the species responsible for the flotation depression.

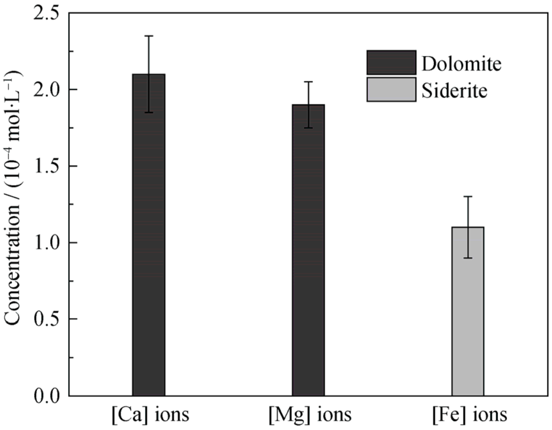

Fig. 4. Concentrations of cations dissolved from carbonates in distilled water (pH 8.95–9.05; P_{CO_2} = 32 Pa).

3.3. Solution chemistry calculations

In the flotation process, the residence time is usually too short for equilibration to be established between dissolved CO_2 and the carbonate species, especially in the slight alkaline region, where the dissolution of CO_2 becomes more difficult [22–23]. Therefore, in this work, solution chemistry calculations of carbonate minerals in a closed system were carried out. The corresponding reactions and constants used in the calculations are listed in Table 1.

Table 1. Chemical reactions and equilibrium constants for solution chemistry calculations [25]

Reaction	Equilibrium constant
$H_2O \rightleftarrows H^+ + OH^-$	$K_w = 10^{-14}$
$FeCO_{3(s)} \rightleftarrows Fe^{2+} + CO_3^{2-}$	$K_{sp1} = 10^{-10.68}$
$CaMg(CO_3)_{2(s)} \rightleftarrows Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	$K_{sp2} = 10^{-16.56}$
$Fe^{2+} + OH^- \rightleftarrows FeOH^+$	$\beta_1 = 10^{4.5}$
$Fe^{2+} + 2OH^- \rightleftarrows Fe(OH)_2$	$\beta_2 = 10^{7.4}$
$Fe^{2+} + 3OH^- \rightleftarrows Fe(OH)_3^-$	$\beta_3 = 10^{10.0}$
$Fe^{2+} + 4OH^- \rightleftarrows Fe(OH)_4^{2-}$	$\beta_4 = 10^{9.6}$
$Ca^{2+} + OH^- \rightleftarrows CaOH^+$	$\beta_5 = 10^{1.4}$
$Ca^{2+} + 2OH^- \rightleftarrows Ca(OH)_2$	$\beta_6 = 10^{2.77}$
$Mg^{2+} + OH^- \rightleftarrows MgOH^+$	$\beta_7 = 10^{2.58}$
$Mg^{2+} + 2OH^- \rightleftarrows Mg(OH)_2$	$\beta_8 = 10^{1.0}$
$CO_3^{2-} + H^+ \rightleftarrows HCO_3^-$	$K_1 = 10^{10.33}$
$HCO_3^- + H^+ \rightleftarrows H_2CO_3$	$K_2 = 10^{6.35}$

On the bases of solubility equilibrium, charge conservation, and constant ionic product of water in the solution, the ionic species distribution of siderite and dolomite as a function of pH in the closed system was calculated; the results for siderite and dolomite are shown in Figs. 5(a) and 5(b), respectively. Some species are not shown in the figure because of their low concentrations. As evident in Fig. 5(a), Fe^{2+} and HCO_3^- are the main species in the siderite–water system when the solution pH is approximately 9.0. Fig. 5(b) shows that the concentrations of Ca^{2+} and Mg^{2+} are almost the same in the dolomite–water system, independent of solution pH. When the pH value of the solution is approximately 9.0, the species Ca^{2+}, Mg^{2+}, and HCO_3^- are dominant in the solution. The results of solution chemistry calculations and dissolution tests indicate that multivalent metal ions and CO_3^{2-} (HCO_3^-) ions dissolved from minerals might be the main species inhibiting the flotation of hematite.

3.4. Effects of cations and carbonate ions on hematite flotation

The recovery of hematite as a function of cation concentration is presented in Fig. 6(a), which shows the effects of cations dissolved from carbonate minerals, namely Ca^{2+}, Mg^{2+}, and Fe^{2+} ions, on the flotation of hematite. As shown in Fig. 6(a), hematite recovery decreased with increasing concentration of Ca^{2+} and Mg^{2+}. This result indicates that both Ca^{2+} and Mg^{2+} inhibit hematite flotation. However, the flotation results shown in Fig. 6(a) demonstrate that Fe^{2+} did not affect the flotation of hematite. To further investigate the

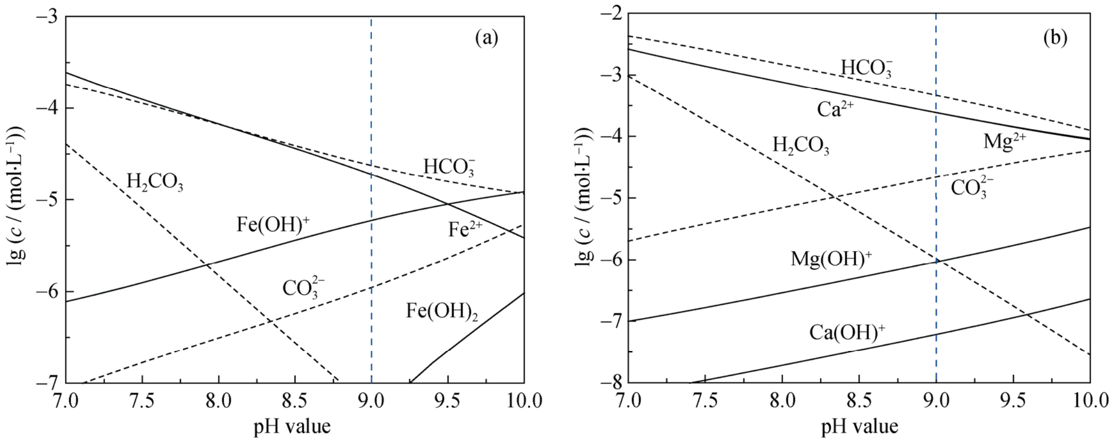

Fig. 5. Speciation diagrams in the closed aqueous system: (a) siderite; (b) dolomite.

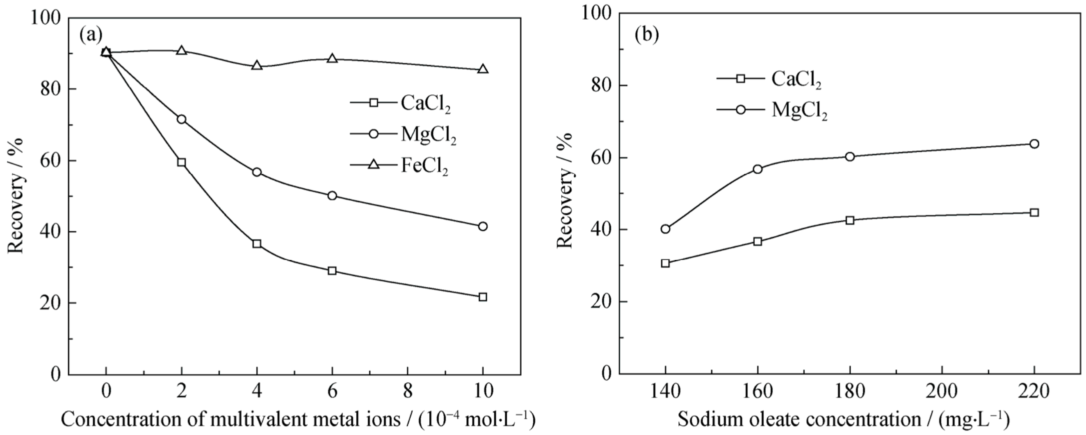

Fig. 6. Effect of cations on hematite flotation (pH 9.0; sodium oleate concentration: 160 mg/L) (a) and effect of sodium oleate concentration on hematite flotation in the presence of cations (pH 9.0; $CaCl_2$, 4×10^{-4} mol/L; $MgCl_2$, 4×10^{-4} mol/L) (b).

inhibiting effects of Ca^{2+} and Mg^{2+}, experiments were conducted in which the NaOl concentration was varied; the results are shown in Fig. 6(b). The recoveries of hematite increased slightly with increasing concentration of NaOl, and the inhibition of Ca^{2+} and Mg^{2+} could not be effectively dispelled by increasing collector concentration. These results indicate that the NaOl consumption by Ca^{2+} and Mg^{2+} is not the main reason that Ca^{2+} and Mg^{2+} depressed hematite flotation, and the inhibition mechanism therefore required further investigation.

Na_2CO_3 is a strong base–weak acid salt that can be used to regulate the solution pH value. Because carbonate ions are suspected to affect hematite flotation, flotation tests were carried out in which the pulp pH value was adjusted with either NaOH or Na_2CO_3, and the results are shown in Fig. 7. As evident in Fig. 7, compared with NaOH, the recovery of hematite was lower when Na_2CO_3 was used as a pH regulator. These results indicate that carbonate ions adversely affected hematite flotation.

Therefore, it can be concluded that the main reasons for the depressed hematite flotation recovery in the presence of dolomite were the inhibiting effects of Ca^{2+}, Mg^{2+}, and CO_3^{2-} dissolved from dolomite. However, only the CO_3^{2-} ions dissolved from siderite depress the flotation of hematite, which might explain why the inhibition effect of siderite is weaker than that of dolomite.

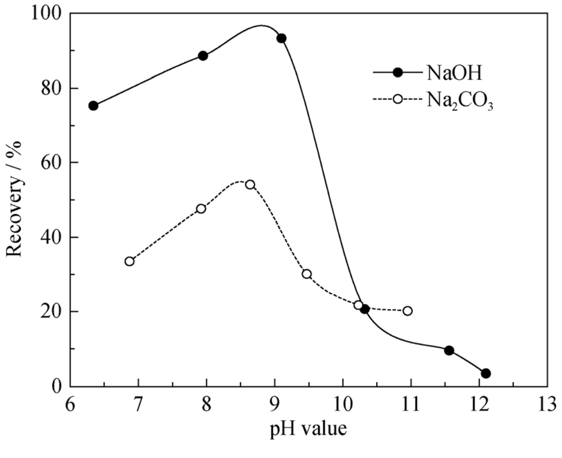

Fig. 7. Effect of pH regulators on the flotation of hematite (sodium oleate concentration: 160 mg/L).

3.5. Zeta-potential analyses

Zeta potentials of hematite as a function of pH value in the absence and presence of Ca^{2+}, Mg^{2+}, and CO_3^{2-} were measured and the results are shown in Fig. 8. The isoelectric point (IEP) of hematite was determined to be approximately 6.0, in agreement with previously reported values [26–27]. In the presence of Ca^{2+} and Mg^{2+} ions, the zeta potentials of hematite shifted to more positive values in the pH range from 6.5 to 11.5. However, the zeta potentials were unchanged in the pH range from 2.0 to 6.0. These results indicate that Ca^{2+} and Mg^{2+} adsorb onto the hematite surface more readily in a basic pH environment, which coincides with the pH range where the hydrolysis of Ca^{2+} and Mg^{2+} ions occurs.

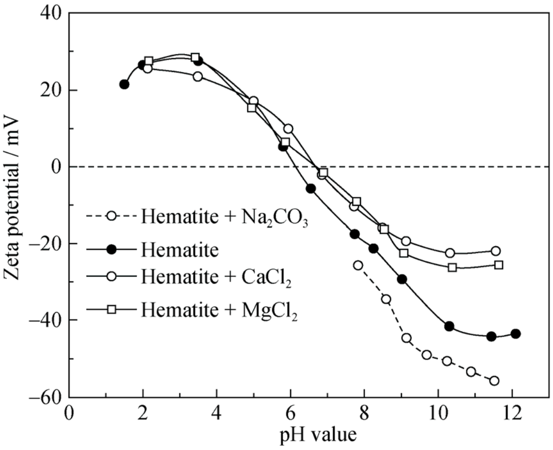

Fig. 8. Zeta potentials of hematite as a function of pH value ($CaCl_2$, 4 × 10^{-4} mol/L; $MgCl_2$, 4 × 10^{-4} mol/L; Na_2CO_3, 2 × 10^{-4} mol/L when used).

The Ca^{2+} and Mg^{2+} ions may adsorb onto hematite surfaces through the first-order hydroxyl species $CaOH^+$ and $MgOH^+$ because of their higher surface activities despite their low concentrations in the bulk (Fig. 5). The zeta potentials of hematite shifted to more negative values in the presence of Na_2CO_3 in the pH range of 8.0–11.0, where HCO_3^- and CO_3^{2-} are the main species. The results imply that HCO_3^- and CO_3^{2-} could overcome electrostatic repulsion and adsorb onto negatively charged hematite surfaces. This adsorption affinity might be attributable to chemical interactions and hydrogen bonding [28–29]. The results of the zeta-potential measurements show that the cations and CO_3^{2-} (HCO_3^-) ions could absorb onto hematite, influencing its interactions with NaOl.

3.6. FTIR spectral analysis

The FTIR spectra of hematite, NaOl, and hematite conditioned with 160 mg/L NaOl at pH 9.0 in the spectral range from 1300 to 3100 cm^{-1} are shown in Fig. 9. The infrared spectrum of NaOl in curve (3) of Fig. 9 shows peaks at 2920 and 2851 cm^{-1}, which are assigned to the asymmetric stretching vibration and the symmetric stretching vibration of $-CH_2$, respectively. The asymmetric vibration frequencies of $-COO^-$ groups are observed at 1560 cm^{-1}, and the symmetric vibration frequencies of $-COO^-$ groups are observed at 1445 and 1422 cm^{-1} [30–32]. Compared with the infrared spectrum of hematite in curve (1) of Fig. 9, new strong peaks of $-COO^-$ (1568, 1461, and 1413 cm^{-1}) and $-CH_2$ (2914 and 2845 cm^{-1}) stretching vibrations are observed in the spectrum of hematite treated with NaOl in curve (2) of Fig. 9. These new peaks indicate that NaOl interacted with hematite and absorbed onto the surface of hematite, consistent with previously published results [33–34].

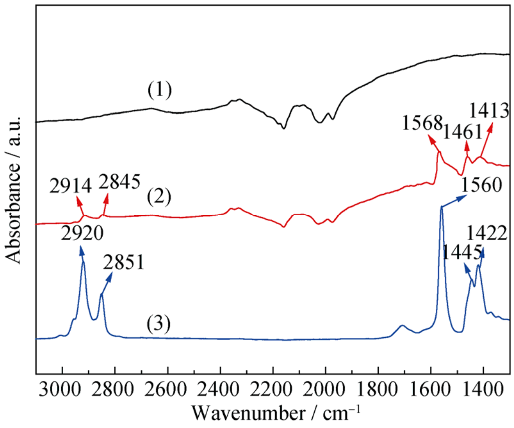

Fig. 9. FTIR spectra of (1) hematite, (2) hematite treated with 160 mg/L sodium oleate at pH 9.0, and (3) sodium oleate.

In the case of the hematite treated with $CaCl_2$ and NaOl (curve (3) in Fig. 10), new peaks for $-CH_2$ asymmetric and symmetric stretching vibrations appeared at 2916 and 2846 cm^{-1}, respectively. In the case of the hematite treated with

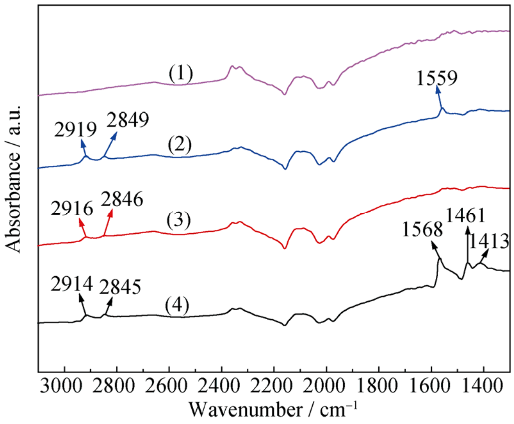

Fig. 10. FTIR spectra of hematite treated with (1) 2 × 10^{-4} mol/L Na_2CO_3 and 160 mg/L sodium oleate, (2) 4 × 10^{-4} mol/L $MgCl_2$ and 160 mg/L sodium oleate, (3) 4 × 10^{-4} mol/L $CaCl_2$ and 160 mg/L sodium oleate, and (4) 160 mg/L sodium oleate.

$MgCl_2$ and NaOl (curve (2) in Fig. 10), new peaks of $–COO^-$ (1559 cm^{-1}) and $–CH_2$ (2919 and 2849 cm^{-1}) stretching vibrations are observed. No new absorption peaks are observed in the spectrum of hematite treated with Na_2CO_3 and NaOl (curve (1) of Fig. 10). Compared with the absorption peaks of $–COO^-$ and $–CH_2$ in the spectrum of hematite treated with NaOl (curve (4) of Fig. 10), those in the spectra shown in curves (1), (2), and (3) are weaker. It can be concluded that cations (Ca^{2+} and Mg^{2+}) and CO_3^{2-} ions lowered the adsorption of NaOl onto hematite.

3.7. XPS analyses

To further investigate the mechanism of cations (Ca^{2+} and Mg^{2+}) and CO_3^{2-} ions lowering the amount of NaOl adsorbed onto hematite, XPS analyses were carried out and the results are presented in Fig. 11 and Table 2. The C (1s) peak in the XPS spectrum of hematite (Fig. 11) was due to the sample surface contaminants caused by air exposure [35]. The peaks at approximately 710.84 and 530.21 eV correspond to the presence of iron and oxygen, respectively.

The results in Table 2 reveal that Ca and Mg appeared on the surface of hematite when treated with $CaCl_2$ and $MgCl_2$, respectively. Changes in the binding energy of O and Fe elements before and after treatment with Ca^{2+} and Mg^{2+} were less than the measurement error and can be neglected. These results indicate that Ca^{2+} and Mg^{2+} might adsorb onto the hematite surface through physical adsorption, such as hydrogen bonding or other mechanisms, consistent with the results of the zeta-potential analyses. Hence, the depressive effect of Ca^{2+} and Mg^{2+} on hematite flotation by NaOl can be attributed to two main reasons. First, as shown in Eq. (2), the first-order hydroxyl species $CaOH^+$ and $MgOH^+$ might occur on the protonated ferric sites via hydrogen bonding:

$$\equiv FeOH + MeOH^+ \rightleftharpoons \equiv FeOH \cdots OHMe^+ \quad (2)$$

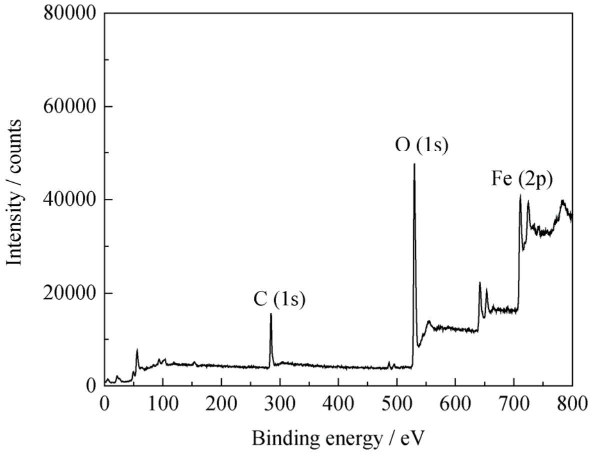

Fig. 11. XPS spectrum of hematite mineral.

The solubility products of calcium oleate (15.4) and magnesium oleate (13.8) are lower than that of ferric oleate (34.2); thus, the $CaOH^+$- and $MgOH^+$-covered hematite surface is less likely to retain adsorbed oleate species than the uncovered hematite surface [19,25,36–37]. Second, $CaOH^+$ and $MgOH^+$ species may bridge the deprotonated ferric sites (oxygen sites), as shown in Eq. (3), forming a hydration sheath on the surface of hematite and increasing the surface hydrophilicity [18,20].

$$\equiv FeO^- + MeOH^+ \rightleftharpoons \equiv FeOMeOH \quad (3)$$

Meanwhile, free metal cations in the solution could consume a certain amount of NaOl.

Table 2. XPS characterization of reference compounds

Sample	Content / at% (Binding energy / eV)				
	Fe (2p)	O (1s)	C (1s)	Ca (2p)	Mg (2s)
Hematite	13.94 (710.84)	51.69 (530.21)	34.37 (284.8)	—	—
Hematite with Ca^{2+}	13.56 (710.82)	53.09 (530.24)	32.66 (284.8)	0.69 (347.14)	—
Hematite with Mg^{2+}	13.07 (710.74)	52.36 (530.20)	33.72 (284.8)	—	0.85 (90.21)
Hematite with CO_3^{2-}	13.95 (711.52)	53.50 (530.27)	32.55 (284.8)	—	—

As shown in Table 2, the change in binding energy of Fe species after treatment with Na_2CO_3 was 0.68 eV, which is greater than the experimental error and indicates that adsorption between CO_3^{2-} and hematite is complex. The depressive effects of CO_3^{2-} or HCO_3^- ions are possibly due to competitive adsorption between CO_3^{2-} (HCO_3^-) ions and oleate ions. Based on the studies, CO_3^{2-} ions could interact with the Fe sites on the hematite surface mainly through the conceptual models shown in Fig. 12, resulting in a decrease in the amount of NaOl adsorbed onto the hematite surface [28–29,38].

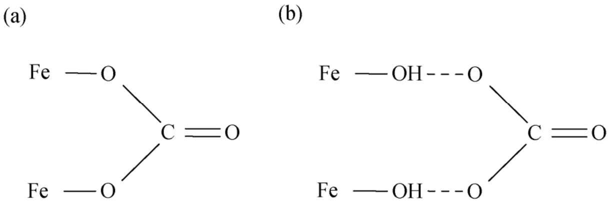

Fig. 12. Conceptual models of CO_3^{2-} / HCO_3^- bonding to hematite surfaces: (a) monodentate binuclear surface complex; (b) hydrogen-bonded surface complex. Dashed lines represent hydrogen bonding interactions [38].

4. Conclusions

The effects of carbonate minerals (dolomite and siderite) on hematite flotation using NaOl as a collector were investigated, and the underlying interaction mechanisms were studied. The main observations and conclusions are as follows.

(1) Micro flotation results showed that both siderite and dolomite reduced the recovery of hematite and that the inhibiting effects of dolomite were stronger. Dissolution measurements confirmed that the dissolution of dolomite was stronger than siderite at pH 9.0.

(2) Solution chemistry calculations and the corresponding flotation tests indicated that the cations (Ca^{2+} and Mg^{2+}) and CO_3^{2-} ions at pH 9.0 dissolved from dolomite were the main species inhibiting the flotation of hematite, whereas only the CO_3^{2-} ions dissolved from siderite were responsible for hematite depression. This probably explains why the depressive effect of siderite was weaker than that of dolomite.

(3) Zeta potential, FTIR spectroscopic, and XPS analyses indicated that Ca^{2+}, Mg^{2+}, and CO_3^{2-} (HCO_3^-) could adsorb onto the hematite surface, hindering the adsorption of NaOl, which was the main reason for the inhibiting effects of carbonate minerals on hematite flotation.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Nos. 51374079 and 51504053), the Hundred, Thousand and Ten Thousand Talent Project of Liaoning Province, China (No. 2014921014), and the Postdoctoral Science Foundation of China (No. 2015M571324). Dong Li also appreciates China Scholarship Council for the financial support for his visiting study to the University of Alberta, Canada.

References

[1] A.C. Araujo, P.R.M. Viana, and A.E.C. Peres, Reagents in iron ores flotation, *Miner. Eng.*, 18(2005), No. 2, p. 219.

[2] H.D.G. Turrer and A.E.C. Peres, Investigation on alternative depressants for iron ore flotation, *Miner. Eng.*, 23(2010), No. 11-13, p. 1066.

[3] Z. Cao, Y.H. Zhang, and Y.D. Cao, Reverse flotation of quartz from magnetite ore with modified sodium oleate, *Miner. Process. Extr. Metall. Rev.*, 34(2013), No. 5, p. 320.

[4] X. Ma, M. Marques, and C. Gontijo, Comparative studies of reverse cationic/anionic flotation of Vale iron ore, *Int. J. Miner. Process.*, 100(2011), No. 3-4, p. 179.

[5] A. Vidyadhar, N. Kumari, and R.P. Bhagat, Adsorption mechanism of mixed collector systems on hematite flotation, *Miner. Eng.*, 26(2012), p. 102.

[6] W.G. Liu, W.B. Liu, X.Y. Wang, D.Z. Wei, and B.Y. Wang, Utilization of novel surfactant N-dodecyl-isopropanolamine as collector for efficient separation of quartz from hematite, *Sep. Purif. Technol.*, 162(2016), p. 188.

[7] W.Z. Yin, Y.X. Han, and F. Xie, Two-step flotation recovery of iron concentrate from Donganshan carbonaceous iron ore, *J. Cent. South Univ. Technol.*, 17(2010), No. 4, p. 750.

[8] L.X. Li, W.Z. Yin, Y.B. Wang, and S.J. Tao, Effect of siderite on flotation separation of martite and quartz, *J. Northeast. Univ. Nat. Sci.*, 33(2012), No. 3, p. 431.

[9] X.M. Luo, W.Z. Yin, J. Yao, C.Y. Sun, Y. Cao, Y.Q. Ma, and Y. Hou, Flotation separation of magnetic separation concentrate of refractory hematite containing carbonate with enhanced dispersion, *Chin. J. Nonferrous Met.*, 23(2013), No. 1, p. 238.

[10] A.L. Shao, Flotation separation of Donganshan carbonates-containing hematite ore, *J. Cent. South Univ. Sci. Technol.*, 44(2013), No. 2, p. 465.

[11] X.M. Luo, Y.F. Wang, S.M. Wen, M.Z. Ma, C.Y. Sun, W.Z. Yin, and Y.Q. Ma, Effect of carbonate minerals on quartz flotation behavior under conditions of reverse anionic flotation of iron ores, *Int. J. Miner. Process.*, 152(2016), p. 1.

[12] J.J. Zhu, W.Z. Yin, Y. Hou, N.L. Wang, J. Yao, and Y.L. Wang, Experimental study on dispersion flotation of Dong'anshan middling containing carbonate, *China Min. Mag.*, 24(2015), No. 7, p. 72.

[13] W.Z. Yin, D. Li, X.M. Luo, J. Yao, and Q.Y. Sun, Effect and mechanism of siderite on reverse flotation of hematite, *Int. J. Miner. Metall. Mater.*, 23(2016), No. 4, p. 373.

[14] Y.H. Hu, R. Chi, and Z.H. Xu, Solution chemistry study of salt-type mineral flotation systems: role of inorganic dispersants, *Ind. Eng. Chem. Res.*, 42(2003), No. 8, p. 1641.

[15] G.L. Chen and D. Tao, Effect of solution chemistry on flotability of magnesite and dolomite, *Int. J. Miner. Process.*, 74(2004), No.1-4, p. 343.

[16] R. Rahnemaie, T. Hiemstra, and Willem H. van Riemsdijk, Carbonate adsorption on goethite in competition with phosphate, *J. Colloid Interface Sci.*, 315(2007), No. 2, p. 415.

[17] B. Feng and X.P. Luo, The solution chemistry of carbonate and implications for pyrite flotation, *Miner. Eng.*, 53(2013), p. 181.

[18] W. Zhang, R.Q. Honaker, and J.G. Groppo, Flotation of monazite in the presence of calcite part Ⅰ: Calcium ion effects on the adsorption of hydroxamic acid, *Miner. Eng.*, 100(2016), p. 40.

[19] P. Trivedi, L. Axe, and J. Dyer, Adsorption of meal ions onto goethite: single-adsorbate and competitive systems, *Colloids Surf. A*, 191(2001), No. 1-2, p. 107.

[20] G. Lefèvre, *In situ* Fourier-transform infrared spectroscopy studies of inorganic ions adsorption on metal oxides and hydroxides, *Adv. Colloid Interface Sci.*, 107(2004), No. 2-3, p. 109.

[21] O.S. Pokrovsky and J. Schott, Surface chemistry and dissolu-

tion kinetics of divalent metal carbonates, *Environ. Sci. Technol.*, 36(2002), No. 3, p. 426.

[22] Q. Shi, G.F. Zhang, Q.M. Feng, and H. Deng, Effect of solution chemistry on the flotation system of smithsonite and calcite, *Int. J. Miner. Process.*, 119(2013), p. 34.

[23] J.O. Amankonah, P. Somasundaran, and K.P. Ananthapadmabhan, Effects of dissolved mineral species on the dissolution/precipitation characteristics of calcite and apatite, *Colloids Surf.*, 15(1985), p. 295.

[24] C.A.R. Silva, X.W. Liu, and F.J. Millero, Solubility of siderite ($FeCO_3$) in NaCl solutions, *J. Solution Chem.*, 31(2001), No. 2, p. 97.

[25] D.Z. Wang and Y.H. Hu, *Solution Chemistry of Flotation*, Hunan Science and Technology Press, Changsha, 1988.

[26] M. Pattanaik, S.K. Biswal, and S.K. Bhaumik, A comparative physicochemical study of hematite with hydroxamic acid and sodium oleate, *Sep. Sci. Technol.*, 35(2000), No. 6, p. 919.

[27] K. Quast, The use of zeta potential to investigate the interaction of oleate on hematite, *Miner. Eng.*, 85(2016), p. 130.

[28] J.J. Carlson and S.K. Kawatra, Effects of CO_2 on the zeta potential of hematite, *Int. J. Miner. Process.*, 98(2011), No.1-2, p. 8.

[29] H.J. Haselhuhn, K.P. Swanson, and S.K. Kawatra, The effect of CO_2 sparging on the flocculation and filtration rate of concentrated hematite slurries, *Int. J. Miner. Process.*, 112-113(2013), p. 107.

[30] L. Wang, W. Sun, Y.H. Hu, and L.H. Xu, Adsorption mechanism of mixed anionic/cationic collectors in muscovite-quartz flotation system, *Miner. Eng.*, 64(2014), p. 44.

[31] L.H. Xu, Y.H. Hu, F.Q. Dong, Z.Y. Gao, H.Q. Wu, and Z. Wang, Anisotropic adsorption of oleate on diaspore and kaolinite crystals: Implications for their flotation separation, *Appl. Surf. Sci.*, 321(2014), p. 331.

[32] Y.H. Yang, L.H. Xu, Y.C. Liu, and Y.X. Han, Flotation separation of ilmenite from titanaugite using mixed collectors, *Sep. Sci. Technol.*, 51(2016), No. 11, p. 1840.

[33] R.D. Kulkarni and P. Somasundaran, Flotation chemistry of hematite/oleate system, *Colloids Surf.*, 1(1980), No. 3-4, p. 387.

[34] S.S. Rath, N. Sinha, H. Sahoo, B. Das, and B.K. Mishra, Molecular modeling studies of oleate adsorption on iron oxides, *Appl. Surf. Sci.*, 295(2014), p. 115.

[35] T. Parker, F.N. Shi, C. Evans, and M. Powell, The effects of electrical comminution on the mineral liberation and surface chemistry of a porphyry copper ore, *Miner. Eng.*, 82(2015), p. 101.

[36] X.Z. Xie, Y.H. Wang, Y.Q. Jiang, P. Huang, and Y. Zhang, Flotation separation of limonite and calcite by using NaOL as collector and action mechanisms, *J. Cent. South Univ. Sci. Technol.*, 42(2011), No. 12, p. 3605.

[37] X.M. Luo, W.Z. Yin, Y.F. Wang, C.Y. Sun, Y.Q. Ma, and J. Liu, Effect and mechanism of dolomite with different size fractions on hematite flotation using sodium oleate as collector, *J. Cent. South Univ.*, 23(2016), No. 3, p. 529.

[38] J.R. Bargar, J.D. Kubicki, R. Reitmeyer, and J.A. Davis, ATR-FTIR spectroscopic characterization of coexisting carbonate surface complexes on hematite, *Geochim. Cosmochim. Acta*, 69(2005), No. 6, p. 1527.