Role of dissolved mineral species in quartz flotation and siderite solubility simulation

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Abstract: Quartz is, in most cases, the major gangue mineral found in the iron ores. Although it can be activated by calcium at strong alkaline pH, quartz nevertheless, reports to the concentrate with Fe when the iron ores contain siderite. It causes a poor concentrate grade and separation between quartz and iron minerals. The effect of siderite on reverse anionic flotation of quartz from hematite was studied in our previous investigations. In this work, the effect of siderite dissolution on the quartz recovery in the froth product and the effect of pH, ions and temperature on siderite dissolution were investigated. Microflotation, PHREEQC simulation, solution chemistry calculation and Fourier transform infrared spectroscopy (FTIR) measurements were conducted. It was observed that the dissolved species of siderite exhibited negative impact on quartz flotation. This influence became weak to some extent by either stripping the dissolved species or shortening dissolution time. Siderite was easily dissolved in the presence of calcium ion under strong alkaline conditions and its solubility increased with increasing the calcium ion concentrate and temperature. When the calcium ion was added as an activator of quartz under strong alkaline conditions (pH>9.96), calcium existed mainly in the $CaCO_3$ precipitation form according to the solubility rule in the presence of siderite. This form could adsorb onto quartz surfaces and further the chemical reaction between starch and quartz was monitored by FTIR measurements. This study provides a further supplement for previous study. A potential strategy is suggested that finding a collector used at low temperature or flotation under neutral (or weak alkaline) medium is helpful to the reverse flotation of iron ores containing siderite.

Keywords: quartz, solubility, siderite, calcium ion, temperature, flotation

Introduction

A reverse flotation technology is widely applied to improve the quality of iron concentrates (Mowla et al., 2008; Ma, et al., 2011; Lima et al., 2013). In China,

reverse anionic flotation remains the most popular flotation route used in the iron ore industry. Fatty acids and their salts, calcium ion, and starch are often employed as the collector, activator of quartz and depressant of iron minerals, respectively, based on the iron ore characteristic and technological conditions (Sun, 2005; Chen, 2010; Luo et al., 2012). Quartz is, in most cases, the major gangue mineral found in the iron ores. Although it can be activated by calcium at strong alkaline pH, quartz nevertheless, reports to the concentrate with Fe when the iron ores contain siderite. It causes poor concentrate grade and separation between quartz and iron minerals (Yang et al., 2010; Luo et al., 2016a). We have found that this adverse effect was concerned with siderite dissolution (Luo et al., 2016b).

Dissolution characteristics of salt-type mineral play an important part in determining the nature of interactions taking place in the bulk solution or on the mineral surfaces (Somasundaran and Wang, 2006). The change of pH can cause siderite dissolution and subsequent release of Fe (II), which can be precipitated as iron (oxy) hydroxide minerals at intermediate to alkaline pH range (Silva et al., 2002; Tang et al., 2011). Many studies have undertaken the bulk precipitation and dissolution rate of siderite in different temperatures and pressure environments (Greenberg and Tomson, 1992; Jensen et al., 2002; Silva et al., 2002; Bénézéth et al., 2009; Golubev et al., 2009; Testemale et al., 2009) as well as its formation, dissolution and oxidation (Duckworth et al., 2004; Stel, 2009; Marocchi et al., 2011; Milesi et al., 2015). In addition, siderite dissolution behavior in the presence of the oxidant chromate (chromium ions) has also been studied (Tang and Martin, 2011). Relatively few studies, however, have addressed the dissolution behavior of siderite in the presence of calcium ion at different temperatures. Moreover, the role of dissolved mineral species in quartz flotation under conditions of reverse anionic flotation of iron ores remains unclear.

In this study, the effect of siderite dissolution on quartz flotation in the presence and absence of starch and calcium was examined. The role of pH, ions and temperature in the dissolution behavior of siderite was investigated. Microflotation, PHREEQC simulation, solution chemistry calculation and FTIR measurements were used in the investigation. Results from this study provided a further supplement for previous study and a basis for understanding and quantifying the interactions between quartz and siderite in the presence of starch under conditions of reverse anionic flotation of iron ores.

Experimental

Materials

The siderite sample obtained from Anshan City, Liaoning Province, China was carefully ground in an iron ball mill and processed by gravity concentration. The quartz sample purchased from Yingkou City, Liaoning Province, China was carefully ground in a porcelain ball mill with porcelain grinding balls. All products were wet

sieved to obtain particle size fractions in the range of −106+45 μm employed for a pure mineral flotation experiment. X-ray diffraction and chemical analyses showed that siderite, hematite and quartz samples were of high purity. The siderite sample had a purity of 44.65% Fe, and the quartz sample contained about 99.77% SiO_2.

Reagents

Sodium oleate with 98% purity was used as an anionic collector. Calcium chloride with 99% purity was used as an activator for quartz. Corn starch was employed as a depressant of iron minerals, which was dissolved in distilled water by adding 20% NaOH by weight at 50 °C on a hot plate. Analytical grade NaOH was used for pH adjustment.

Methods

Microflotation

Direct flotation and flotation after stripping dissolved species of siderite experiments were conducted to determine the effect of siderite dissolution on the quartz flotation recovery. The experiment, where dissolved species of siderite were not stripped, was called direct flotation, otherwise, it was called flotation after stripping dissolved species.

Direct flotation experiments were carried out in a 30 cm^3 flotation cell at 1500 rpm impeller speed. A −106+45 μm sample was composed of quartz and siderite in different proportions by weight according to test design. It was mixed with 25 cm^3 of distilled water in the flotation cell for 1 min. NaOH was added to maintain pH in the range of 7 to 13, and the pulp was conditioned for 2 min. Afterwards, calcium chloride, corn starch and sodium oleate were then separately added, and the pulp was conditioned for 2 min with each reagent. Finally, flotation was performed for 3 min at room temperature. The froth and sink products were collected, filtered, dried, weighed and analyzed.
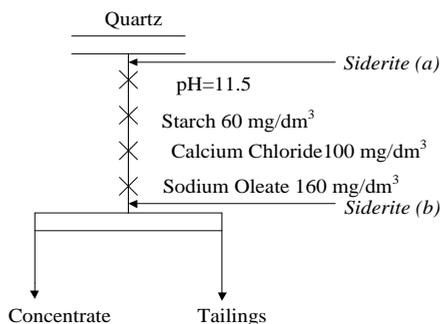
Fig. 1. Flowsheet and corresponding flotation conditions of test

The flotation method after stripping dissolved species was as follows. First, a siderite sample was dissolved in distilled water for 30 min. Then, the siderite sample

was extracted from dissolved species, cleaned thrice with distilled water. Next, the obtained sample was mixed with quartz as the test sample. Second, the test sample was mixed in the flotation cell for 1 min. The rest of the steps were the same as the direct flotation experiments.

The flotation flowsheet to determine the effect of siderite (7.5%) addition order on quartz recovery in froth product is shown in Fig.1.

Siderite solubility simulation by using PHREEQC

PHREEQC is a geochemical model to study aqueous ion reaction equilibrium in water systems (Parkhurst and Appelo, 1999; Kim et al., 2008). In this paper, PHREEQC provided by United States Geological Survey (USGS) was applied to simulate the siderite solubility in the absence and presence of calcium and chloride ions over the whole pH range at different temperatures, pressure 1 atm and other factors (dissolution equilibrium, carbonic acid equilibrium, ion activity, salt effect, common-ion effect, etc.) taken into consideration. The composition and condition of a solution and thermodynamic data (such as the reaction equilibrium constant, reaction enthalpy, free energy, etc.) were obtained from the PHREEQC database. They were inputted into the PHREEQC code in order to calculate the solubility of siderite. When the saturation index was zero, the concentration was accepted as a solubility value of siderite.

FTIR measurements

A Perkin Elmer Spectrum One FTIR spectrometer was used to determine the reagent adsorption on quartz with the type of Nicolet 380 FTIR. Prior to the test, quartz was ground to −2 μm in an agate mortar, and then conditioned with reagents in the solution at pH about 11.5. The concentration of the reagents used in the FTIR study was twenty times as much as that used in microflotation experiments. It was twice as that used in previous study (Luo et al., 2016b). The fully interacted sample was filtered and washed thrice with the corresponding pH solution. The obtained solid was dried overnight at room temperature. In a typical measurement, 2 mg of the powdered solid sample was weighed and mixed with 50 mg of KBr in an alumina mortar. The spectra were obtained in the range of 4000–400 cm^{-1} with 4 cm^{-1} resolution. A total of 256 scans were collected for each specimen, which was also twice as that used in previous study (Luo et al., 2016b).

Results and discussion

Microflotation experiments

Table 1 presents the mineral recovery in froth product using sodium oleate as the collector, starch as the depressant and calcium chloride as the activator at pH 11.5. Almost all amount of hematite and siderite minerals went into a sink product, while quartz went into a froth product. Therefore, hematite and quartz were easily separated in the presence of sodium oleate, starch and calcium chloride at pH 11.5. However,

results from our study (Luo et al., 2016b), which were consistent with observations reported by Zhang et al. (2007) and Yang (2010), who indicated that siderite had a strong negative impact on reverse flotation of hematite in the presence of sodium oleate, calcium ion and starch. The quartz recovery in the froth product decreased with increase in the siderite percentage, thereby decreasing Fe grade of concentrate in the sink product.

Table 1. Mineral recovery in froth product at pH 11.5

Reagent (mg/dm^3)	Mineral	Recovery (%)
Sodium oleate 160 Calcium chloride 100 Corn starch 60	Hematite	0.02
	Siderite	0.51
	Quartz	90.05
	Quartz+siderite (5%)	44.88 (quartz recovery)

Figure 2 presents the quartz recovery in the froth product using sodium oleate as the collector as a function of pH in the presence and absence of calcium chloride and starch. As presented in Fig. 2, the low recovery of quartz was observed without calcium chloride. It was below 5% in the pH range of 7 to 13. It increased, however, in the presence of sodium oleate and calcium chloride, when pH was above 10, i.e. when Ca^{2+} and $CaOH^+$ were formed in solution (Hu, 1989). Significant change was not observed in the recovery of calcium-activated quartz in the absence and presence of starch. This result indicated that starch had little or no impact on calcium-activated quartz flotation in the absence of siderite. However, starch had the strong impact on quartz flotation in the presence of siderite (shown in Table 1). These results are consistent with observations reported by Ma (2006).
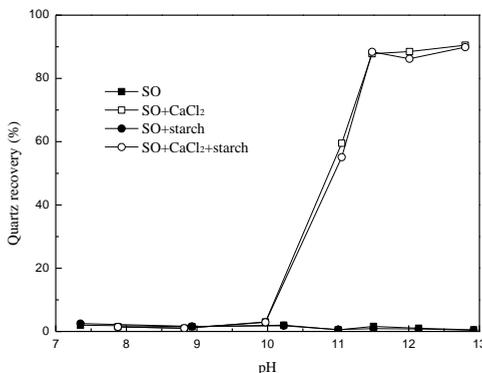
Fig. 2. Quartz recovery in froth product as a function of pH
(sodium oleate (SO) 160 mg/dm^3, calcium chloride 100 mg/dm^3, starch 60 mg/dm^3)

Figure 3 shows the effect of siderite dissolution on the quartz recovery in the froth product in the presence of sodium oleate, calcium chloride and corn starch. The quartz recovery greatly decreased with increasing siderite percentage by direct flotation.

However, siderite moderately affected the quartz recovery by flotation after stripping the dissolved species. After stripping the dissolved species, the quartz recovery in the froth product in the presence of siderite (7.5%) increased from 19.5 to 77.4% (increase by 57.9%). The results indicated that the dissolved species exhibited the negative effect on quartz flotation in the presence of calcium and starch.
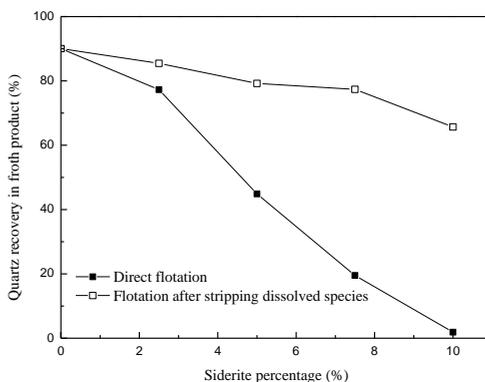
Fig. 3. Effect of siderite dissolution on quartz recovery in froth product
(sodium oleate 160 mg/dm^3, starch 60 mg/dm^3, calcium chloride 100 mg/dm^3, pH 11.5)
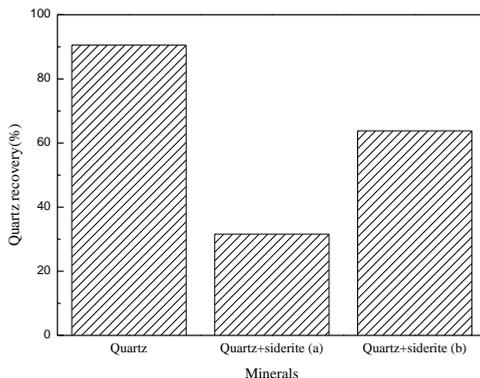
Fig. 4. Effect of siderite addition order on quartz recovery in froth product
(sodium oleate 160 mg/dm^3, starch 60 mg/dm^3, calcium chloride 100 mg/dm^3, pH 11.5)

Figure 4 shows the effect of siderite addition order on the quartz recovery in the froth product. The flotation method of adding siderite at "*a*" (shown in Fig. 1) was the same as the direct flotation experiments and siderite was added before all reagents. However, adding siderite at "*b*" means that siderite was added after all reagent and flotation was performed after the pulp was conditioned for 2 min. As shown in Fig. 4, no matter where siderite was added, the quartz recovery in the froth product decreased in the presence of siderite compared with that in the absence of siderite. However, the quartz recovery in the case of "*b*" (63.8%) was higher than that determined for "*a*"

(31.6%, with difference equal to 32.2%). These results also indicated that siderite dissolution had the detrimental effect on the quartz flotation recovery. In comparison with the "b" case, more dissolution ions were generated during the "*a*" case, because the dissolution time was longer.

PHREEQC simulation

Effect of calcium chloride on siderite solubility

Figure 5 shows siderite solubility as a function of pH in the absence and presence of calcium chloride calculated by using PHREEQC (Merkel et al., 2002). Siderite solubility was high under strong acid and strong alkaline conditions, and it increased in the presence of calcium chloride. Solubility of siderite in $CaCl_2$ solution (100 mg/dm^3) at pH 11.5 was about twice as much as that in water. The results indicated that siderite was more easily dissolved in the $CaCl_2$ solution than in water.
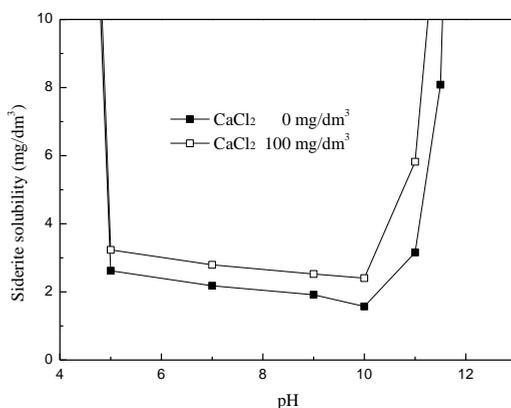
Fig. 5. Siderite solubility as a function of pH in the absence
and presence of calcium chloride ($T = 25$ °C, $P = 1$ atm)
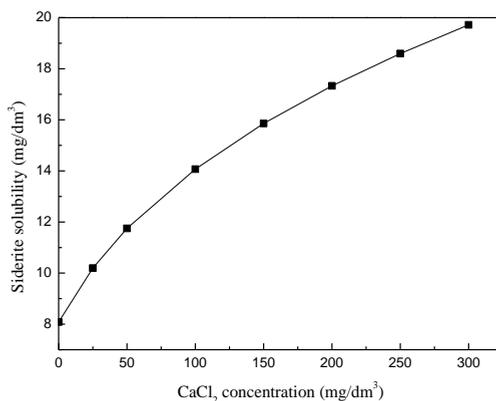
Fig. 6. Siderite solubility as a function of calcium chloride concentration
at pH 11.5 ($T = 25$ °C, $P = 1$ atm)

Figure 6 shows siderite solubility as a function of calcium chloride concentration at pH 11.5. The siderite solubility increased with increasing calcium chloride concentration. The siderite solubility increased from 8.1 to 19.7 mg/dm^3 (i.e. by 11.6 mg/dm^3), when the calcium chloride concentration increased from 0 to 300 mg/dm^3. The presence of calcium chloride benefited siderite dissolution.

Effect of calcium or chloride ions on siderite solubility

Figure 7 presents the effect of calcium and chloride ions on siderite solubility over the whole pH range. The presence of calcium ions benefited siderite dissolution but the dissolution was also slightly affected by the presence of chloride ions. Nevertheless, easier dissolution of siderite in $CaCl_2$ was mainly related to the calcium ions presence.

Fig. 7. Siderite solubility as a function of pH in the absence and presence
of calcium ion or chloride ion ($T = 25$ °C, $P = 1$ atm)

Siderite is easily dissolved under conditions of reverse anionic flotation of iron ores where the calcium ion is added under strong alkaline condition. This phenomenon is evident in Figs. 6 and 7. The equilibrium equation of siderite is as follows. When calcium is added to activate quartz in reverse anionic flotation of iron ores, the presence of calcium ion shifts equilibrium (1) to the right. This phenomenon favored siderite dissolution as was explained by the salt effect (Quast, 2006).

$$FeCO_3 \rightleftharpoons Fe^{2+} + CO_3^{2-}$$
$$+$$
$$Ca^{2+}$$
$$\rightleftharpoons$$
$$Ca(CO_3)_{(S)} \tag{1}$$

Effect of temperature on siderite solubility

Fatty acids and their salts are mostly used as collectors in reverse anionic flotation of iron ores (Quast, 2006). Higher pulp temperature (about 40 °C) is required to maintain

activity and solubility of fatty acid (Clifford et al.,1998; Sis and Chander, 2003). The relationship between siderite solubility and temperature at pH 11.5 in the absence and presence of calcium chloride is given in Fig. 8. The increment of temperature had an effect of greatly increasing siderite solubility. Hence, siderite is more easily dissolved in the flotation environment of iron ores, where fatty acids are used at high temperature. Therefore, finding a collector used at low temperature would be helpful in facilitation of reverse flotation of iron ores containing siderite.
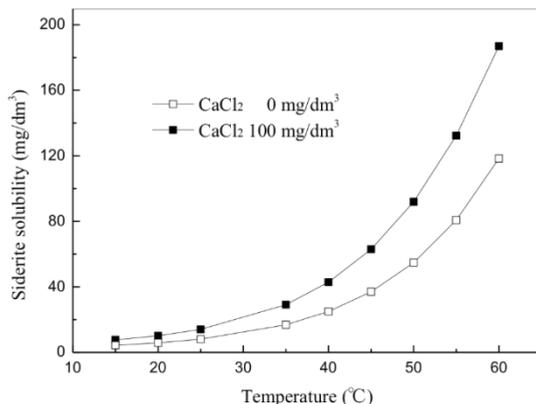
Fig. 8. Siderite solubility as a function of temperature at pH 11.5 ($P = 1$ atm)

Solution chemistry calculation

Calcium is often added to activate quartz in reverse anionic flotation of iron ores. The results above indicated that the presence of calcium ion favors siderite dissolution:

$$Ca(CO_3)_{(s)} = Ca^{2+} + CO_3^{2-} \qquad K_{sp,CaCO_3} = 10^{-8.35}$$
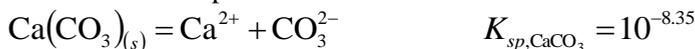
$$Q = [Ca^{2+}] \times [CO_3^{2-}]$$

where Q is the ionic product constant, $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the actual activities of Ca^{2+} and CO_3^{2-} in the solution, respectively.

The nature of the complex equilibrium involving a mass of reactions determines the interfacial properties of the particles and, thus, their flotation behavior (Somasundaran and Wang, 2006). The actual activities of Ca^{2+} and CO_3^{2-} in the solution could be expressed as follows

$$[Ca^{2+}] = \frac{0.9 \times 10^{-3}}{1 + 10^{pH-12.6} + 10^{2pH-25.23}} \quad [Ca^{2+}] = \frac{0.9 \times 10^{-3}}{1 + 10^{pH-12.6} + 10^{2pH-25.23}}$$

$$[CO_3^{2-}] = \sqrt{\frac{10^{-10.68} \times (1 + 10^{pH-9.5} + 10^{2pH-20.6} + 10^{3pH-32} + 10^{4pH-46.4})}{1 + 10^{10.33-pH} + 10^{16.68-2pH}}}.$$

according to reaction formulas in Table 2 and balance equations in Table 3. When the $CaCl_2$ concentration was 100 mg/dm^3, the concentration of chloride ion ([Cl$^-$]) and total calcium ion ([Ca^{2+}]$_T$) were 1.8×10^{-3} mol/dm^3 and 0.9×10^{-3} mol/dm^3, separately.

Table 2. Chemical reaction equations and equilibrium constant for solution chemical calculations in $CaCl_2$–NaOH–siderite open to the atmosphere at 25 °C (Wang and Hu, 1987)

Reaction	Equilibrium constant	Reaction	Equilibrium constant
$FeCO_{3(S)} \rightarrow Fe^{2+} + CO_3^{2-}$	$K_{sp,FeCO_3} = 10^{-10.68}$	$Ca^{2+} + OH^- \rightarrow CaOH^+$	$\beta_5 = 10^{1.4}$
$Fe^{2+} + OH^- \rightarrow FeOH^+$	$\beta_1 = 10^{4.5}$	$Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2$	$\beta_6 = 10^{2.77}$
$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$	$\beta_2 = 10^{7.4}$	$Ca(OH)_{2(S)} \rightarrow Ca^{2+} + 2OH^-$	$K_{sp,Ca(OH)_2} = 10^{-5.22}$
$Fe^{2+} + 3OH^- \rightarrow Fe(OH)_3^-$	$\beta_3 = 10^{10}$	$H^+ + CO_3^{2-} \rightarrow HCO_3^-$	$K_1^H = 10^{10.33}$
$Fe^{2+} + 4OH^- \rightarrow Fe(OH)_4^{2-}$	$\beta_4 = 10^{9.6}$	$H^+ + HCO_3^- \rightarrow H_2CO_3$	$K_2^H = 10^{6.35}$
$Ca(CO_3)_{(S)} \rightarrow Ca^{2+} + CO_3^{2-}$	$K_{sp,CaCO_3} = 10^{-8.35}$		

Table 3 Balance equations in $CaCl_2$–NaOH–siderite open to the atmosphere at 25°C (Wang and Hu, 1987)

Charge balance equation (CBE)	$[H^+] + 2[Ca^{2+}] + [CaOH^+] + 2[Fe^{2+}] + [FeOH^+] + [Na^+] = [OH^-] + 2[CO_3^{2-}]$ $+ [HCO_3^-] + [Fe(OH)_3^-] + 2[Fe(OH)_4^{2-}] + [Cl^-]$
Mass balance equation (MBE)	$[Fe^{2+}] + [FeOH^+] + [Fe(OH)_3^-] + [Fe(OH)_4^{2-}] = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3]$ $[Cl^-] = 2\{[Ca^{2+}] + [CaOH^+] + [Ca(OH)_2]\}$ $[Ca^{2+}]_T = [Ca^{2+}] + [CaOH^+] + [Ca(OH)_2]$
Solubility product constant	$K_{sp,FeCO_3} = [CO_3^{2-}][Fe^{2+}]$
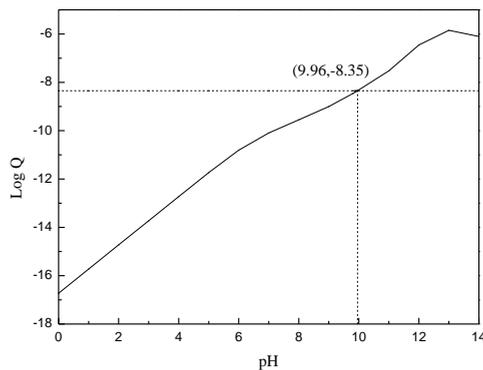
Fig. 9. Log Q as a function of pH in $CaCl_2$-NaOH-siderite system ($C_{(CaCl2)}$ = 100 mg/dm^3, log $K_{sp,CaCO3}$ = -8.35)

Figure 9 shows the $\log(Q)$ as a function of pH in the $CaCl_2$-NaOH-siderite system. When pH is above 9.96, $CaCO_3$ precipitates according to the rule of solubility product. Therefore, when calcium ion is added as the activator for quartz in the presence of siderite at pH 11.5, calcium exists mainly in the $CaCO_3$ precipitation form.

FTIR measurements

Figure 10 shows the FTIR spectra of quartz before and after reaction with sodium carbonate, calcium chloride and starch. The concentration of the reagents used in the FTIR study was twice as that used in previous study (Luo et al., 2016b). Therefore, besides a new peak at 1404.53 cm^{-1}, extra three new peaks at 1055.48, 914.14 and 879.19 cm^{-1} appeared on the spectrum of quartz after treatment with above-mentioned reagent. It could provide a more convinced evidence for adsorption of starch onto the quartz surface via $CaCO_3$ precipitations.

In the spectrum of starch (Fig. 10a), the peaks at 3416.60 and 2930.13 cm^{-1} were assigned to stretching vibration of $-OH$ and $-CH_2-$, respectively. The peaks located in the positions of 1645.79, 1459.45 and 1374.95 cm^{-1} belonged to bending vibration of $H-O-H$, $-CH_2-$ and $-CH-$, separately. While the peak at 1157.72 cm^{-1} characterized the stretching vibration of $C-O-C$. The peaks at 1082.80 and 1017 cm^{-1} were due to bending vibration of $C-O-H$ and coupled vibration of $C-C$, respectively. The peak at 929.04 cm^{-1} belonged to skeleton vibration of $\alpha-1,4$ glycosidic linkage, and 859.44 cm^{-1} was the characteristic absorption peak of glycosidic bond. The peaks at 859.44 and 764.66 cm^{-1} were due to the vibration of pyranose ring (Abdel-Aal et al., 2006; Wei, 2010) .

In the spectrum of quartz (Fig. 10b), the peaks at 3423.98, 1879.83 and 1620.41 cm^{-1} were attributed to the stretching vibration of $-OH$ from $Si-OH$ silanol group in defect sites and moisture absorbed by the atmosphere (Mohammadnejad et al., 2013). The peak at 1080.56 cm^{-1} was assigned to $Si-O-Si$ asymmetric stretching vibration, which was the first characteristic absorption peak of quartz. While peaks at 469.41 and 779.43 cm^{-1} were due to symmetric stretching vibrations of $Si-O$. The peak at 692.38 cm^{-1} was attributed to symmetric bending vibration (Chaikina et al., 2004; Saikia et al., 2008).

The spectrum of quartz after treatment with sodium carbonate, calcium chloride, and starch is shown in Fig. 10c. Besides a new peak at 1404.53 cm^{-1}, extra three new peaks at 1055.48, 914.14 and 879.19 cm^{-1} appeared on the spectrum of quartz after treatment with sodium carbonate, calcium chloride and starch. The peak at 914.14 cm^{-1} was due to asymmetric stretching skeleton vibration of starch. The peak located in the position of 1055.48 cm^{-1} was assigned to stretching vibration of $C-O-C$, while the peak at 879.19 cm^{-1} belonged to $C-O$ bending vibration of calcium carbonate. The peak at 1404.53 cm^{-1} was ascribed to $C-O$ stretching vibration of CO_3^{2-} group. Moreover, the peaks shifted from 469.41 and 3423.98 to 455.92 and 3445.48 cm^{-1}, respectively. These new peaks and the peak-shifts suggested that calcium carbonate precipitates on the quartz surface, favoring adsorption of starch onto quartz.
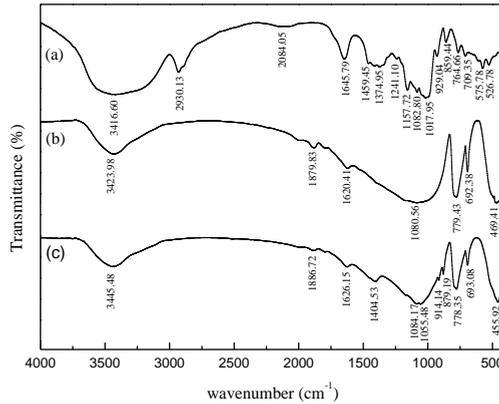
Fig. 10. Infrared spectra of (a) starch, (b) quartz and (c) quartz treated
with sodium carbonate, calcium chloride and starch

Conclusions

The dissolved species of siderite exhibited the passive impact on quartz flotation in the presence of calcium and starch at pH 11.5. The quartz recovery in the presence of siderite increased, when flotation after stripping the dissolved species was performed, compared with that by direct flotation. The quartz recovery, by adding siderite after all reagents, increased compared with that by adding siderite before all reagent.

High pulp temperature and calcium ions were required to maintain activity and solubility of fatty acid and activate quartz, respectively, in reverse anionic flotation of iron ores. The increase of both calcium ions and temperature can benefit siderite dissolution, thereby obtaining more CO_3^{2-} dissolved species, resulting in forming more $CaCO_3$ precipitates in the presence of calcium ion under strong alkaline condition. Calcium carbonate precipitated on the quartz surface, favoring adsorption of starch onto quartz.

A potential strategy was suggested that finding a collector used at low temperature or flotation under neutral (or weak alkaline) medium would be advantageous in reverse flotation of iron ores containing siderite.

Acknowledgements

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