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Effect of carbonate minerals on quartz flotation behavior under conditions of reverse anionic flotation of iron ores

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ABSTRACT

Reverse anionic flotation of carbonate-containing iron ores is quite a challenging process. Studies on this ores conducted in many laboratories or beneficiation plants have obtained poor concentrate grades and separation between quartz and iron minerals, even when valuable minerals are adequately liberated. The presence of carbonate minerals, such as siderite, causes a detrimental effect on quartz flotation recovery (froth product) and separation selectivity between quartz and iron minerals. In this work, the effect of carbonate minerals on quartz flotation from iron mineral was investigated using sodium oleate as collector, starch and calcium as regulators. Microflotation, adsorption, PHREEQC calculation, and Fourier transform infrared spectroscopy (FTIR) measurements were conducted in the investigation. Carbonate minerals (i.e., siderite and dolomite) adversely affected the floatability of quartz and separation between quartz and hematite. Starch dosage experiment results clearly showed that the reduction of quartz recovery in the presence of carbonate minerals was mainly related to starch. In addition, mineral dissolution and sodium carbonate dosage experiments evidently exhibited that CO_3^{2-} dissolved species of carbonate minerals passively affected quartz flotation recovery. By contrast, both starch and CO_3^{2-} dissolved species of carbonate minerals adversely affected the flotation recovery. FTIR showed that the strong drop-off in quartz recovery in the presence of carbonate minerals was due to the adsorption of $CaCO_3$ precipitations on quartz surfaces and further their interaction with starch molecules. The appearance of $CaCO_3$ precipitations was caused by reaction of Ca^{2+} from the hydrolysis of $CaCl_2$ and CO_3^{2-} dissolved species of carbonate minerals. To decrease the passive effect, a potential strategy to improve the flotation performance of iron ores that contain carbonate minerals at strong alkaline pH is suggested to remove carbonate minerals before separation between hematite and quartz.

1. Introduction

Cationic/anionic reverse flotation is a widely applied technology to improve the quality and reduce impurity of iron concentrates (Neymayer et al., 2013; Ma et al., 2011; Mowla et al., 2008). During flotation, quartz particles attach to air bubbles and float upward into the froth layer leaving iron minerals as sink fraction. Different starches are generally used as depressants for iron ore flotation (Kar et al., 2013; Turrer and Peres, 2010; Nanthakumar et al., 2009; Pavlovic and Brandão, 2003; Mattedi and Oliveira, 2001). Reverse cationic flotation remains the most popular flotation route used in the iron ore industry (Filippov et al., 2014; Lima et al., 2013). In China, reverse anionic flotation of iron ores is successfully used. Fatty acid, calcium ion, and starch are often employed as collector, activator of quartz, and depressant of iron minerals, respectively, based on iron ore characteristic and technological conditions (Luo et al., 2012; Chen, 2010; Sun, 2005).

Use of the aforementioned reagents under strong alkaline pH is difficult in reverse anionic flotation of carbonate-containing iron ores. Studies on these ores conducted in many laboratories or beneficiation plants have obtained poor concentrate grades and separation between quartz and iron minerals, even when valuable minerals are adequately liberated (Yang, 2010a; Zhang et al., 2007). The Fe grade in sink product decreases with the increase of carbonate mineral content in iron ores. The exact reasons for the observed poor separation remain unclear.

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Carbonates are salt-type minerals. Their dissolution characteristics play a major role in determining the nature of the interactions that occur in bulk solution or on mineral surfaces (Chen and Tao, 2004; Van Cappellen et al., 1993). Dissolved mineral species can undergo reactions, such as hydrolysis, complexation, adsorption, and surface and bulk precipitations, which can inhibit the selective interaction between reagents and minerals (Nunes et al., 2011; Vučinić et al., 2010; Hu, 1989). Investigating solution chemistry is particularly important for salt-type mineral flotation (Hu et al., 2003).

In this study, flotation tests, solution chemistry calculations, adsorption measurements, and Fourier transform infrared spectroscopy (FTIR) measurements were conducted to determine how carbonate minerals affect the floatability of quartz and to find ways to decrease their unwanted effects.

2. Experimental

2.1. Materials

Pure siderite sample was obtained from Anshan City, Liaoning Province, China. Pure quartz and dolomite samples were purchased from Yingkou City, Liaoning Province, China. The siderite and hematite samples were carefully ground in an iron ball mill and processed by gravity concentration. The dolomite and quartz samples were 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 and −45 μm, which were employed for pure mineral flotation experiment and adsorption and FTIR measurements, respectively. X-ray diffraction and chemical analyses showed that siderite, dolomite, and quartz samples were of high purity. The siderite and hematite samples contained about 44.65% Fe and 67.45% Fe, respectively, and the dolomite sample had about 30.13% CaO and 21.33% MgO. The quartz sample had a purity of 99.77% SiO_2. Chemical element analyses of samples are shown in Table 1.

2.2. Reagents

Sodium oleate, calcium chloride, corn starch and sodium hydroxide with more than 98% purity were obtained from different chemical companies in China. Sodium oleate was used as anionic collector, and calcium chloride was used as quartz activator. Unmodified corn starch (the ratio of amylopectin to amylose is 2.85) that was employed as the depressant of iron minerals, was dissolved in distilled water by adding 20 wt.% NaOH at 50 °C on a hot plate. Analytical grade NaOH was used to maintain the pH at about 11.4. Distilled water was employed in all experiments.

2.3. Methods

2.3.1. Microflotation

Microflotation experiments were carried out in a 30 mL flotation cell at 1500 rpm impeller speed. A −106 + 45 μm sample composed of quartz, hematite, siderite, and dolomite in different proportions by weight according to test design was mixed with 25 mL of distilled water in flotation cell for 1 min. NaOH was added to maintain the pH at about 11.4, and the pulp was conditioned for 2 min. Calcium chloride, starch, and sodium oleate were then separately added, and the pulp was conditioned for 2 min with each reagent. The flotation time was fixed for 3 min at room temperature (25 °C). The froth and sink products were collected, filtered, dried, weighed, and analyzed.

Table 1
Chemical element analysis of minerals.

Element / Minerals	TFe (%)	FeO (%)	SiO_2 (%)	Al_2O_3 (%)	MgO (%)	CaO (%)	P (%)	S (%)
Hematite	67.45	≤0.15	1.25	0.29	0.03	<0.05	0.03	0.08
Siderite	44.65	50.96	1.52	0.16	1.16	0.32	0.005	1.12
Dolomite	—	—	0.58	—	21.33	30.13	—	—
Quartz	0.04	—	99.77	0.12	<0.02	<0.02	<0.01	0.007

2.3.2. Comparison flotation experiments to evaluate the effect of carbonate mineral dissolution on quartz flotation recovery

Comparison flotation experiments were conducted to determine the effect of carbonate mineral dissolution on quartz flotation recovery. The experiment where dissolved species of carbonate minerals are not stripped is called "direct flotation"; otherwise, it is called "flotation after stripping dissolved species of carbonate minerals."

The direct flotation method is as follows. A 2.0 g of sample (quartz (2.0-X) g and carbonate mineral X g) was mixed in flotation cell for 1 min. NaOH was then added to maintain the pH at 11.4, and the pulp was conditioned for 2 min. Afterward, calcium chloride, starch, sodium oleate were added and conditioned for 2 min with each reagent. Finally, flotation was performed for 3 min.

The flotation method after stripping dissolved species of carbonate minerals is as follows. First, a carbonate mineral sample (X g) was dissolved in distilled water for 30 min, and then the carbonate mineral sample was extracted from dissolved species, cleaned thrice with distilled water, and mixed with quartz (2.0-X g) as the test sample. Second, the test sample was mixed in flotation cell for 1 min. The rest of the steps were the same as the direct flotation method.

2.3.3. Adsorption measurements

Ultraviolet spectrophotometry was performed to measure the amount of sodium oleate adsorption on the mineral surface before and after adding starch in the absence and presence of carbonate minerals. This method aims to show the effect of starch on the adsorption of sodium oleate on quartz. A 2.0 g of sample (quartz and carbonate mineral in different proportions by weight) was mixed with 25 ml of distilled water in a 50 ml volumetric flask for 1 min. NaOH was added to maintain the pH at about 11.4. Afterward, the reagents were separately added and the pulp was conditioned for 5 min with each reagent. The solids were allowed to stand for 3 min and then filtered. Only the supernatant was collected for UV spectrometry analysis. The absorbance of sodium oleate was obtained by using a Spectro Flex 6600 spectrophotometer with a wave length of 204 nm. The residual concentration of sodium oleate was calculated based on the absorbance. Based on the residual concentration of sodium oleate remaining in the solution, the adsorption amount of sodium oleate on the mineral surface can be calculated as follows:

$$\Gamma = \frac{(C_0 - C) \times V}{w}$$

where Γ is the adsorption amount, mg/g; C_0 is the initial concentration of sodium oleate in the solution, mg/L; C is the residual concentration of sodium oleate in the supernatant, g/L; V is the solution volume, L; and w is the mineral weight, g.

2.3.4. FTIR measurements

Perkin Elmer Spectrum One FTIR spectrometer was used to determine the reagent–mineral interaction with the type of Nicolet 380 FTIR. Prior to the test, pure minerals were 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. The fully interacted sample was filtered and washed thrice with the corresponding pH solution. The obtained solid was