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Technical note

A novel method to improve depressants actions on calcite flotation

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ABSTRACT

In this study, the flotation behavior, contact angle and surface adsorption of calcite were investigated in aqueous solution containing excess lattice ions (Ca^{2+} and CO_3^{2-}). Flotation results show that adding lattice ions makes three kinds of depressants more effective. The contact angle test suggests that the use of both Ca^{2+} and CO_3^{2-} results in a remarkable decrease in calcite surface hydrophobicity with sodium oleate and depressants, while it has little influence on calcite surface hydrophobicity without sodium oleate. Adsorption data indicates calcium carbonate coating on calcite surfaces may change the adsorption mechanism of depressants. The study presented that added lattice ions change reactivity of the calcite surface and improve depressants actions on calcite flotation.

1. Introduction

Calcite is a common and important component of sediments and sedimentary rocks (Morse, 1990). However, when it is found intergrown with other valuable minerals, calcite is often the least valuable component and must be separated from the ore (Hernáinz Bermúdez de Castro and Gálvez Borrego, 1996).

Calcite is one of the most extensive carbonate gangue minerals in flotation of smithsonite, fluorite, scheelite, apatite and celestite (Antti and Forssberg, 1989; Hiçyìlmaz et al., 1993; Irannajad et al., 2009; Martínez-L et al., 2003; Shi et al., 2013a; Song et al., 2006). Separation of calcite and valuable minerals is extremely complex due to the similar chemical composition and the impact of the dissolved ions. Meanwhile, sodium oleate is the major collector in the separation of these minerals, but the selectivity in separation of these minerals from calcite is often inadequate (Hernáinz Bermúdez de Castro and Calero de Hoces, 1993; Sadowski, 1993).

More recently, it has been found that both lattice ions (Ca^{2+} and CO_3^{2-}) adsorb onto the mineral surface and thus alter the mineral surface potential (Eriksson et al., 2008). Also the lattice ions entering the pulp can generate complex ions and compounds. These species inhibit the interaction between the reagents and calcite through the formation of surface precipitates on the calcite surface (Shi et al., 2013b). However, there are a limited number of studies focused on the effect of lattice ions on calcite flotation. In this work, calcite flotation and surface adsorption in the presence of excess lattice ions were investigated.

2. Experimental section

2.1. Materials

High purity minerals of calcite were collected from Hunan province, China. The sample was gently ground manually in an agate mortar and then screened to obtain the −104 μm fraction. Hydrochloric acid (HCl) and sodium carbonate (Na_2CO_3) were used as pH regulators. Sodium hexametaphosphate (SH), sodium silicate and starch were used as representatives of inorganic and organic depressants. Sodium oleate (NaOL) was used as the collector. All reagents are of analytical grade. Deionized water was used in all experiments.

2.2. Flotation procedure

All of the flotation tests were carried out in a mechanically agitated flotation machine at a constant rate. The calcite suspension was prepared by adding 2.0 g minerals to 40 ml of solutions under agitation. $CaCl_2$ solution (17 mmol/L) was first added into the slurry for 3 min if necessary. The pH of the suspension was adjusted to a desired value pH = 10 by adding Na_2CO_3 stock solution. The prepared depressant (sodium hexametaphosphate, silicate or starch) stock solution was added to a desired concentration. Then a constant amount of collector stock solution was added and the slurry was conditioned for another 3 min. Total flotation time was 4 min. The floated and unfloated particles were collected, filtered and dried. The flotation recovery was calculated based on solid weight distributions between these two products.

2.3. Contact angle calculation

In this study the contact angle of calcite was tested by the Mini-Lab ILMS (GBX, France). Before every single test, the calcite block

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had been grounded by metallographic sandpaper and then washed by deionized water. The prepared calcite block was conditioned with the same conditioning regime as the flotation tests. Then let it air dried and tested in the machine.

2.4. Adsorption experiment

The sample was prepared with the same conditions as the flotation tests. The suspensions were separated at 9000 rpm for 10 min by means of a centrifuge. Reagents adsorption onto the calcite minerals was determined indirectly by measuring the amount of reagent in solution which has not adsorbed onto the mineral. The concentration of P, Ca and Si in the supernatant liquid was measured by ICP optical emission spectrometry. The method of phenol–sulfuric acid was used to detect the starch by ultraviolet spectrophotometer.

3. Results and discussions

3.1. Flotation studies

Fig. 1 shows the behavior of calcite recovery as a function of depressants concentration in the absence and presence of added lattice ions. It can be seen from Fig. 1 that the floatability of calcite with 2.5×10^{-4} mol/L oleate collectors is higher than 90%. The high recovery is attributed to chemisorption of oleate on calcite surface (Young and Miller, 2000). In the absence of excess lattice ions, the floatability of calcite decreases with increasing sodium hexametaphosphate (SH) concentration. Minimum recovery (21%) is achieved by increasing SH concentration to 20 mg/L. Also the calcite recovery decreases with increasing sodium silicate and starch concentration. The results suggest that calcite is depressed by SH, sodium silicate and starch.

In the presence of excess lattice ions, the recovery of calcite decrease from 50.4% to 5.9% at 2 mg/L SH, and minimum recovery (2%) is achieved by increasing SH concentration to 5 mg/L. Meanwhile, the recovery of calcite also decreases from 87.8% to 47.3% at 40 mg/L sodium silicate and decreases from 85.8% to 5.3% at 20 mg/L starch with added lattice ions, respectively. The similar phenomena are observed, which indicates the adsorption or precipitation of excess lattice ions on calcite surface make depression more effective.

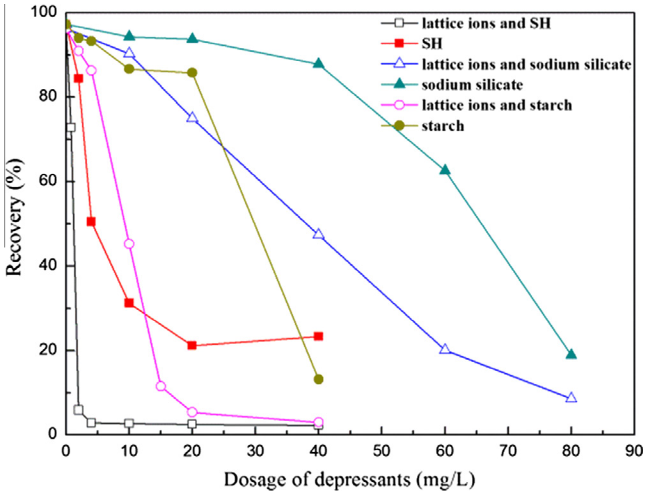

Fig. 1. Flotation recovery of calcite as a function of depressants dosage using 2.5×10^{-4} mol/L NaOL at pH 10.

3.2. Contact angle studies

Contact angle of calcite was tested to further confirm the influence of lattice ions on calcite flotation. The test results are shown in Table 1. Without any depressants and collectors, the contact angle of calcite changes little after the addition of calcium and carbonate ions. With 2.5×10^{-4} mol/L collector, the contact angle of calcite increases from 29° to 75° indicating a strong hydrophobic surface character even in the presence of SH which could make calcite surface hydrophilic. However, surface hydrophobicity achieves a significant reduction when calcium chloride and sodium carbonate are added before the depressants. The contact angle decreases from 75° to 9.0°, which indicates the calcite surface develops a strong hydrophilic tendency. Although to a lesser degree, similar results were observed using sodium silicate and starch as depressants. The data illustrates that the lattice ions play a significant role in changing the interaction between calcite surface and reagents, rather than altering the intrinsic hydrophobicity of calcite.

3.3. Adsorption mechanism studies

Fig. 2 shows the total concentration of Ca^{2+} in the bulk solution as a function of depressants dosage at pH 10. As the SH concentration increases, the total concentration of Ca^{2+} increases in the absence of excess lattice ions, while it changes little with the addition of Ca^{2+} and CO_3^{2-}. Similarly, the concentration of Ca^{2+} increases with increasing starch concentration in the absence of excess lattice ions, while it decreases with increasing starch concentration in the presence of excess lattice ions. SH could remove calcium ions from the calcite surface through a chelating effect, thereby producing a depression mechanism for SH through the selective complexing of calcium ions from the calcite surface was proposed (Changgen and Yongxin, 1983; Komlev and Potapenko, 1972). Therefore, this difference in calcium solubility illustrates that the reactivity of calcite surface with the addition of Ca^{2+} and CO_3^{2-} may be different from that without excess lattice ions.

According to Fig. 2, the total concentration of Ca^{2+} in the bulk solution is 0.24 mmol/L with the addition of Ca^{2+} and CO_3^{2-}, which is lower than the initial value (17 mmol/L). The change of concentration of Ca^{2+} indicates that precipitation of calcium species can occur under these conditions. Fig. 3 shows the saturation index of Ca-precipitates as a function of pH with the addition of 17 mmol/L Ca^{2+} and CO_3^{2-}. Saturation index (SI), defined as: $SI = log(IAP/K_{sp})$, is used to present the degree of saturation. PHREEQC was used for calculating the saturation index of calcium species based on the natural dissolved equilibrium of calcite (Parkhurst and Appelo, 1999). It is clear from Fig. 3 that the solution is supersaturated with respect to calcite and aragonite at $7.0 < pH < 12.0$ with the addition of 17 mmol/L Ca^{2+} and CO_3^{2-}. Therefore, it is possible that Ca ions precipitate as $CaCO_{3(s)}$ on the calcite surface.

Both theoretical and experimental studies provide evidence for distinct properties of the calcite with freshly adsorbed or precipitated $CaCO_{3(s)}$ at the calcite-water interface (Heberling et al., 2011; Wolthers et al., 2008). It is reported freshly precipitated $CaCO_{3(s)}$ have an important influence on electrokinetic properties of calcite, and there is time dependent changes for zeta potential of freshly precipitated $CaCO_{3(s)}$ (Chibowski et al., 2003; Lin and Singer, 2005). Also a fundamental understanding of $CaCO_{3(s)}$ precipitation reactions based on information about the structural evolution is reported. The formation of $CaCO_{3(s)}$ precursors is observed after several minutes at the beginning of the precipitation, and $CaCO_{3(s)}$ precursors will be recrystallized to form calcite crystal after about half-hour (Rieger et al., 2000). Therefore, the structure and reactivity of freshly $CaCO_{3(s)}$ is different from that of calcite, and freshly $CaCO_{3(s)}$ adsorbed or precipitated on calcite surface may play a vital role in the reactivity of calcite with reagents.