Minerals Engineering 61 (2014) 16–22

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Fe(III) as an activator for the flotation of spodumene, albite, and quartz minerals

Zhang Jie [a], Wang Weiqing [a,b,*], Liu Jing [a,b], Huang Yang [a], Feng Qiming [a,b], Zhao Hong [a]

[a] *School of Environment and Resource, Southwest University of Science and Technology, Mianyang 621010, PR China*
[b] *Key Laboratory of Solid Waste Treatment and Resource Recycle Ministry of Education, Southwest University of Science and Technology, Mianyang, Sichuan 621010, PR China*

ARTICLE INFO

Article history:
Received 15 October 2013
Accepted 6 March 2014
Available online 27 March 2014

Keywords:
Fe(III)
Spodumene
Flotation
Sodium oleate
Activator

ABSTRACT

The effect of Fe(III) ions on the flotation of spodumene, albite, and quartz minerals using sodium oleate (NaOL) was investigated by micro-flotation tests, zeta-potential measurement space, pyrene fluorescence spectroscopy and X-ray photoelectron spectroscopy (XPS). These minerals were difficult to float in the presence of NaOL alone. However, when Fe(III) ions were used as the activator, the flotation of the minerals improved. Zeta potential testing found the addition of Fe(III) at pH conditions <8 to reduce the negative charge on the spodumene, albite and quartz surfaces, which supports a mechanism where Fe(III) adsorbs onto these mineral surfaces, resulting in an expected increase in NaOL collector adsorption with a concomitant increase in the flotation recoveries. Subsequent pyrene fluorescence spectroscopy of these minerals in the presence of NaOL collector, with and without Fe(III) activator, showed the mineral surfaces to switch from polar to non-polar.

1. Introduction

Spodumene, a type of monoclinic pyroxene with a single-chain structure, mainly occurs in granite pegmatite rock and is the major source of lithium in industry (Moon and Fuerstenau, 2003). Albite, quartz and mica are the gangue minerals commonly associated with spodumene. Mica can be floated easily by the dodecylamine collector (Xu et al., 2013). However, because of the similar surface properties, it is difficult to achieve effective separation of a mixture of spodumene, albite, and quartz minerals (Vidyadhar and Rao, 2007). Currently, flotation is the most common separation method for these minerals. Fatty acid collectors such as sodium oleate (NaOL), naphthenic soap, and oxidized paraffin soap space are widely used in the flotation separation of these minerals (Kulkarni and Somasundaran, 1980; Walker et al., 1997). The component in oxidized paraffin soap is similar to NaOL, and the role of naphthenic soap is to assist the flotation of spodumene using oxidized paraffin soap as the collector. Therefore, NaOL collector was used to study the effect of Fe(III) ions on the flotation of spodumene, albite, and quartz minerals.

In the flotation recovery of spodumene ores (Sichuan, China) using a NaOL collector, a relatively high content of silicon dioxide (SiO_2) in the concentrate was often reported, thus affecting the recovery of lithium. In theory, because of their negatively charged surfaces, quartz and albite cannot be floated using an anionic NaOL collector at alkaline pH. Albite and quartz are considered as dominant SiO_2 minerals because they are generally the majority gangue minerals in the flotation concentrate. Three probable mechanisms have been proposed for the flotation of albite and quartz minerals by the anionic collectors: (i) the entrainment of fine liberated particles from albite and quartz minerals; (ii) the poor liberation of quartz and albite minerals from spodumene; and (iii) the inadvertent activation of albite and quartz minerals by the metal ions dissolved from the minerals present in the ore. In the first mechanism, when the samples are deslimed (-10 μm), the effectiveness of the entrainment is weakened. In the second mechanism, microscopy studies have shown that the naturally non-floating quartz and albite particles in the concentrate are liberated particles, and therefore, they do not, in any way, contribute to the meager quantity of liberated minerals (Orhan and Bayraktar, 2006; Vidyadhar and Rao, 2007).

In the practical mineral separations, the existence of unavoidable metal ions such as Fe(III), Mg(II), and Ca(II), significantly influence the flotation of minerals (Fan and Rowson, 2000; Zhu et al., 2012). These ions can activate the gangue minerals, thereby increasing their flotation by promoting collector adsorption (Ejtemaeia et al., 2012). Wang and Yu (2007) investigated the effects of metal ions on the flotation of spodumene and beryl

---

[*] Corresponding author at: School of Environment and Resource, Southwest University of Science and Technology, Mianyang 621010, PR China.
E-mail address: swustwwq@sohu.com (W. Weiqing).

http://dx.doi.org/10.1016/j.mineng.2014.03.004
0892-6875/© 2014 Elsevier Ltd. All rights reserved.

mineral sand and found that Fe(III) and Ca(II) ions improve their flotation (Wang and Yu, 2007). Fornasiero and Ralston (2005) studied the Cu(II) and Ni(II) activation in the flotation of quartz, lizardite, and chlorite minerals and found that quartz can be activated by these metal ions to float with xanthate at pH 7–10 (Fornasiero and Ralston, 2005). Because the copper and nickel hydroxides are stable species, their adsorbtion/precipitation on the mineral surface improves the flotation of these minerals. All these metal ions, Fe(III), Mg(II), Ca(II), Cu(II), and Ni(II), may have potential as activators in the flotation of albite, spodumene, and quartz minerals.

The objective of this study was to investigate the effect of Fe(III) ions at various concentrations and pH levels in the micro-flotation of spodumene, albite, and quartz minerals using an anionic NaOL collector. The mineral surfaces in the presence of Fe(III) ions and NaOL species, responsible for the floatation of minerals, were analyzed by zeta-potential measurements and pyrene fluorescence spectroscopy.

2. Experimental

2.1. Materials

The pure samples of spodumene, albite, and quartz minerals were hand-picked from the Lijiagou lithium mine of Jinchuan County, Sichuan, China. The chemical compositions of the samples are listed in Table 1. The samples were crushed and ground using in agate mortar. The products were then dry sieved to obtain a particle size of −75 + 38 μm. A portion of the fraction (−38 μm) was further ground using an agate mortar then micro-sieved to obtain a particle size of 5 μm. The coarse fraction (−75 + 38 μm) was used for the micro-flotation tests, and the finer fraction was used for the zeta-potential measurements and pyrene fluorescence spectroscopy. The calcium on the spodumene and albite minerals surfaces were very low, the percentage of calcium were both below 0.2. There has not calcium ion elution after stirring mineral which mean that the calcium had no confound for the experiment.

2.2. Reagents

Sodium oleate ($CH_3(CH_2)_7CH{=}CH(CH_2)_7COONa$) (NaOL) was used as the anionic collector for the micro-flotation tests. Iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) was used as the source of Fe(III) activator. HCl and NaOH were used for the pH adjustment in the experiments. Pyrene was used for pyrene fluorescence spectroscopy. All the chemicals were of analytical grade, and the water used in all the experiments was ultra-pure water (18.25 MΩ cm).

2.3. Micro-flotation tests

The pure mineral particles (2.00 g) were placed in a Plexiglas cell (40 mL), and then filled with 30 mL ultra-pure water. The pulp was continuously stirred for 2 min using a pH regulator, 2 min with the activator, and 3 min with the collector. The pH of the solution was measured before the flotation, and the flotation was conducted for 4 min. The concentrates were weighed after filtering and drying, and the mineral recovery was calculated.

2.4. Measurements of zeta-potential

The zeta-potentials were measured using a Zetasizer Nano Zs90 instrument. The suspensions with 0.01% concentration (mass fraction) of the minerals were dispersed in a beaker for 1 h at room temperature (25 °C) in the presence of different concentration of reagents. The pH sweep direction was 1.5–12. Three measurements of zeta potential were run, and their averages were taken as the final result.

2.5. Pyrene fluorescence probe

An ethanol solution of pyrene was prepared with 0.01 g pyrene and 100 mL ethanol in a beaker. The test suspensions were then prepared by using 0.1 mL ethanol solution of pyrene, 2.0 g minerals (38 μm), the test concentration of the pure collector, and 30 mL water. The suspensions were then oscillated for 24 h using a constant temperature oscillator at room temperature (25 °C).

The pyrene fluorescence spectra of the samples were obtained using a PerkinElmer LS55 fluorescence spectrophotometer. The excitation wave length of pyrene was 334 nm, and the width of excitation and emission slits were 10 and 4 nm, respectively.

2.6. XPS

The minerals were analyzed in freshly powdered form in order to prevent surface oxidation changes. Prior to the analysis the samples were outgassed under vacuum for 72 h. The X-ray photoelectron spectroscopy (XPS) analyses were performed on a Kratos AXIS Ultra with a mono-chromatic Al X-ray source at 150 W. Each analysis started with a survey scan from 0 to 1300 eV with a dwell time of 8 s, pass energy of 150 eV at steps of 1 eV with 1 sweep. For the high resolution analysis the number of sweeps was increased, the pass energy was lowered to 30 eV at steps of 50 meV and the dwell time was changed to 0.5 s.

3. Results and discussion

3.1. Micro-flotation

The objective of this study was to investigate the underlying mechanism of the anionic collectors in the preferential flotation of spodumene mineral from a mixture of albite and quartz minerals. Fig. 1 shows the flotation responses of spodumene, albite, and quartz minerals as a function of pH with the anionic NaOL collector. The results clearly show that the floatability of spodumene, albite, and quartz minerals using the NaOL collector is weak. A maximum recovery of approximately 9.5% of the spodumene mineral was obtained at pH 8.7, and neither albite nor quartz mineral could be floated across the entire pH range. This phenomenon may be attributed to the spodumene was week with the interaction of oleate, resulting in weak floatability.

Subsequent micro-flotation tests found the presence of Fe(III) metal ions to have a positive effect on the flotation separation of spodumene, albite, and quartz minerals. Fig. 2 shows the flotation responses of the spodumene, albite, and quartz minerals as a function of pH with 1.5×10^4 M Fe(III) and 2.0×10^{-4} M anionic NaOL

Table 1
Chemical analysis of pure minerals (%).

Minerals	Li_2O	Na_2O	K_2O	Al_2O_3	SiO_2	CaO	Fe_2O_3	Other	Total
Spodumene	7.82	0.22	0.21	26.71	64.81	0.17	0.04	0.02	100.00
Albite	0.02	11.26	0.32	18.95	69.03	0.18	0.08	0.16	100.00
Quartz	–	–	–	–	99.26	–	0.07	0.67	100.00