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EFFECT OF SPODUMENE LEACHING WITH SODIUM HYDROXIDE ON ITS FLOTATION

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Abstract: Effects of NaOH on flotation of spodumene, quartz and feldspar using oleic acid as a collector were investigated through microflotation and bench scale flotation tests. It was determined that NaOH acted more than a pH regulator in the tests. The X-ray photoelectron spectroscopy revealed that spodumene was preferentially leached by conditioning with high concentration of NaOH in the solution and exposed more Li positive sites on the mineral surface leading to an improved flotation.

Keywords: *spodumene, flotation, preferential leaching, XPS analysis*

Introduction

Spodumene ($LiAl[SiO_3]_2$) is a typical monoclinic pyroxene mineral (Krause, 1968; Moon and Fuerstenau, 2003) with a theoretical Li_2O grade of 8.07%. As the richest lithium bearing minerals in nature, spodumene is one of the main mineral resources of lithium (Rai et al., 2011). The major consumer of spodumene was the aluminum and ceramics industry (Wendt, 1971; Nicholson, 1978). However, a great number of applications of spodumene and lithium compounds were being developed rapidly in the battery and fuel cell industry in recent years (Lu et al., 2013; Thomas, 2009; Whittingham, 2004). Lithium has become a precious commodity, since the application of lithium ion batteries is considered to be the preferred technology for the next generation of electric vehicles.

Spodumene exists generally in granite pegmatite deposits, which contain quartz, feldspar, muscovite as well as some tantalite and niobite. Flotation is the most important process to selective separate spodumene from other aluminosilicates (Jie et al., 2014). Since many investigations on flotation of spodumene have been conducted (Moon, 1985; Menendez et al., 2004; Yi, 2011; Zhong et al., 2012), there is a

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consensus that conditioning in highly alkaline solutions prior to flotation improves spodumene separation effectiveness. However, research on the mechanism of alkali role is insufficient and the effects of alkali on flotation of spodumene have not been clear yet. In the present study, the effects of NaOH on flotation of spodumene, quartz, and feldspar have been investigated, and the mechanisms of NaOH reactions with the minerals were envisaged by X-ray photoelectron spectroscopy (XPS) as well.

Materials and methods

Material of single minerals

Pegmatitic spodumene, quartz and feldspar were obtained from the Koktokay Rare Metal Mine located in Xinjiang Altay district in China. The hand-picked crystals were ground in a porcelain mill with agate balls in it to an appropriate particle size, and then screened by means of stainless steel screens. The samples with the desired size were filtered, vacuum-dried and stored in glass bottles for the use of single mineral flotation tests and measurements. The chemical compositions of the obtained samples are presented in Table 1. It illustrates that the samples were all of high grade, satisfying the requirement for flotation tests.

Table 1. Chemical analysis of three mineral samples (%)

Mineral	Al_2O_3	SiO_2	Li_2O	K_2O	Na_2O	Fe_2O_3	CaO	MnO	Cr_2O_3
Spodumene	28.43	62.09	7.81	0.22	0.32	0.94	0.15	0.16	0.05
Quartz	1.01	98.28	-	0.11	0.14	0.13	0.37	-	0.13
Feldspar	18.86	65.78	-	10.41	2.89	0.13	0.36	-	-

Material of actual ores

Actual spodumene ores from Kangding county in Sichuan, China, were crushed to minus 3 mm by a jaw crusher and a double roll crusher. Based on the X-ray diffraction (XRD) analysis, the mineral constituents of the ores were mainly spodumene (19.97%), quartz (29.50%), feldspar (29.41%), albite (10.81%) and muscovite (6.76%), as shown in Table 2. The chemical compositions of the spodumene ores by chemical assay are given in Table 3.

Table 2. Mineral constituents of spodumene ore (%)

Mineral	Spodumene	Quartz	Feldspar	Albite	Muscovite	Chlorite	Biotite	Others
Constituent	19.97	29.50	29.41	10.81	6.76	0.79	0.25	2.51

Microflotation

Microflotation tests were performed in a laboratory flotation apparatus using -0.105 + 0.038 mm size of single mineral samples as a feed. For each test, 2 g of sample was placed in a plexiglass cell (40 cm^3), which was then filled with ultra-pure water. The sample was conditioned for 3 min after each reagent addition, and the flotation time was 5 min. All flotation tests were carried out at a room temperature of about 25 °C. The concentrates and tailings were filtered, dried, and weighed to calculate the flotation recovery under various flotation conditions.

Table 3. Multi-elements analysis of spodumene ore

Element	Percentage (%)	Element	Percentage (%)
Li_2O	1.48	CaO	0.21
Al_2O_3	14.43	MgO	0.13
SiO_2	73.29	S	0.096
K_2O	4.41	BeO	0.01
Na_2O	1.72	Nb_2O_5	0.011
Fe_2O_3	2.01	Ta_2O_5	0.009
C	0.35	Loss on ignition	0.43

Bench scale flotation

A 500 g sample of spodumene ores was ground to 70% passing 0.074 mm in a Φ200×400mm XMB-type steel mill at a pulp density of 60% (by weight). The pulp was transferred to a 1.5 L XFD-type flotation cell and diluted to a density of about 30%. Following the given flowsheet, various reagents were added successively, and the pulp was conditioned for a settled time. The froth product was gathered for 5 min. The concentrates and tailings were separately dried, weighed and assayed to calculate the yield and recovery of Li_2O.

Reagents

Oleic acid was used as the collector for the flotation tests. HCl and NaOH were used for the pH adjustment in the experiments. Na_2CO_3 and $CaCl_2$ were used as a modifier in the flotation of spodumene actual ores. All the reagents were of analytical grade, water used in micro flotation was ultra-pure water (18.25 MΩ·cm), and water used in actual ores was tap-water of the Changsha city.

XPS analysis

Dry powder samples of three minerals at a particle size of minus 2 μm were used for the XPS analysis, which was performed using an X-ray photoelectron spectrometer (Thermo Fisher, ESCALAB 250Xi, England) with a mono-chromatic Al X-ray source at 150 W to study the distribution density and binding energy of the elements on the mineral surface. The vacuum pressure was approximately 10^{-9} mbar. Each analysis started with a survey scan from 0 to 1200 eV with pass energy of 200 eV at steps of 1 eV with 1 sweep. For each element appearing on the full spectrum scan, fine spectrum scans (resolution of 0.1 eV) were carried out with pass energy of 30 eV at steps of 0.1 eV. Relative proportions of all the elements on mineral surfaces were calculated by the ratios of the normalized peak areas on the intensity vs binding energy curve.

Results and discussion

Microflotation tests

Microflotation of spodumene, quartz and feldspar as a function of pH using oleic acid as the collector has been conducted and the results shown in Figure 1. It can be seen that flotation of spodumene is much better than that of quartz and feldspar, especially in the weak alkaline pH range. The maximum recovery of spodumene reaches approximately 80% at pH 8.7, while in the entire pH range, feldspar and quartz minerals float poorly with maximum recoveries of about 20%. It can be noticed that the recovery of spodumene turns good again at highly alkaline pH of 12.5. The tendency of spodumene recovery at still higher pH is of great interest to be investigated.

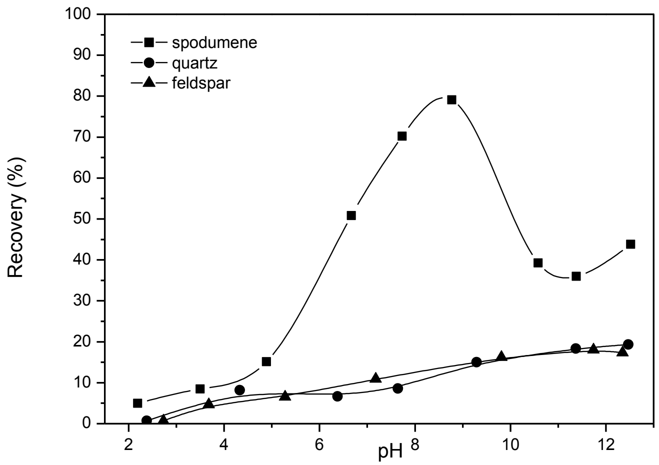

Fig. 1. Flotation recoveries of single minerals as a function of pH using 6.0×10^{-4} M oleic acid

Figure 2 illustrates that the flotation recovery of three minerals vs. NaOH dosage, with the oleic acid concentration of 6.0×10^{-4} M. Since it is hard to measure precisely the pH values in extremely alkaline solutions, the horizontal ordinate in Figure 2 reflects NaOH dosages instead of pH values. The solution with the dosage of NaOH 250 $mg\cdot dm^{-3}$ agrees with the measured pH value of about 11.8. Figure 2 indicates that the flotation recovery of spodumene increases as the dosage of NaOH in solution increases, while the quartz recovery remains nearly stable and the feldspar recovery decreases gradually. It can be concluded that NaOH has a considerable effect on the flotation of spodumene.

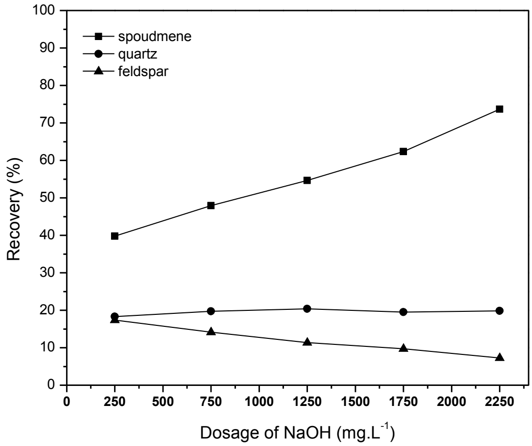

Fig. 2. Effect of NaOH dosage on the recovery of investigated minerals at oleic acid concentration of $6.0 \cdot 10^{-4}$ M

The effects of NaOH solution leaching of the minerals prior to their flotation were investigated in the next tests. The mineral pulps were conditioned for 10 min in alkaline solution with various NaOH dosages, then filtered and water-washed to neutral pH. The flotation recoveries of the prepared minerals at pH 8.70 ± 0.20, using oleic acid at a concentration of $6.0 \cdot 10^{-4}$ M are demonstrated in Figure 3. It is shown there, that the flotation recovery of spodumene increases after leaching treatment in NaOH solution. It can be seen that the bigger of the NaOH dosage, the higher recovery is achieved. The maximum recovery of spodumene is up to 94% as the NaOH dosage is at 2250 mg·dm^{-3}. The flotation recovery of quartz remains approximately constant while feldspar recovery declines slowly with the increase of NaOH dosage.

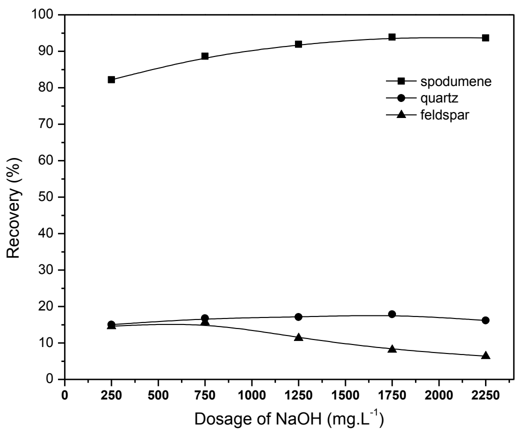

Fig. 3. Effects of NaOH leaching on flotation recovery of three investigated minerals

Bench scale tests

Bench scale tests were carried out for the actual ore to investigate the effects of NaOH on the flotation of spodumene ore. Figure 4 shows the flowsheet of tests for exploring the effects of NaOH dosage on spodumene flotation, and Figure 5 presents the grade and recovery of spodumene concentrates as a function of NaOH dosage. It can be seen from Figure 5 that the grades of the concentrates decrease and the recoveries increase as the dosage of NaOH increases. This could be attributed to the fact that highly alkaline pH improves not only the flotation of spodumene, but also the gangue minerals, using $CaCl_2$ as activating agent (Fuerstenau and Pradip, 2005; Yu et al., 2014). NaOH acts as pH regulator only in this set of tests.

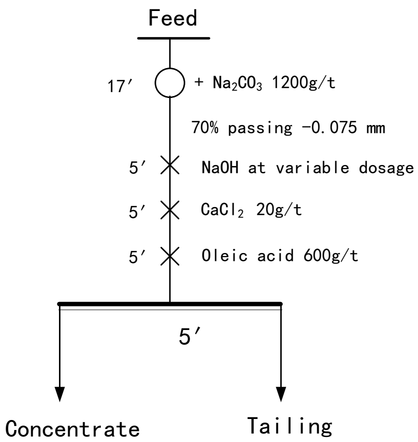

Fig. 4. Flowsheet of tests to explore the effects of NaOH dosage on spodumene flotation

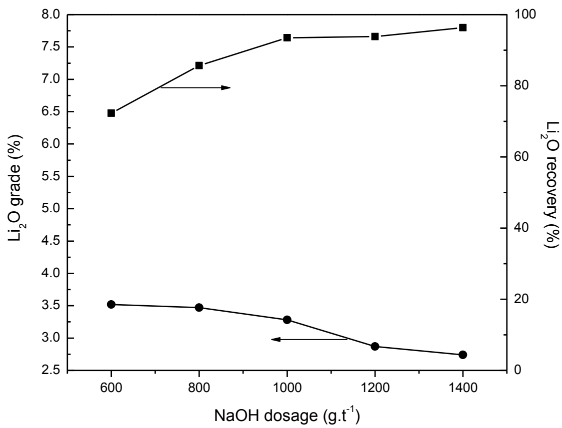

Fig. 5. Effects of NaOH dosage on the grade and recovery of spodumene concentrates

The NaOH dosage of 1 kg/Mg was adopted in the next tests to inspect the effects of conditioning time of NaOH solution on spodumene flotation. Figure 6 illustrates the tests flowsheet and Figure 7 shows the tests results. The results demonstrate that the conditioning time of NaOH solution has an obvious impact on the flotation of spodumene ore. The grades of the concentrates increase and the recoveries decrease as the conditioning time goes up. It could be deduced that the effects of NaOH on the flotation of spodumene are greater than expected from NaOH acting as the pH regulator.

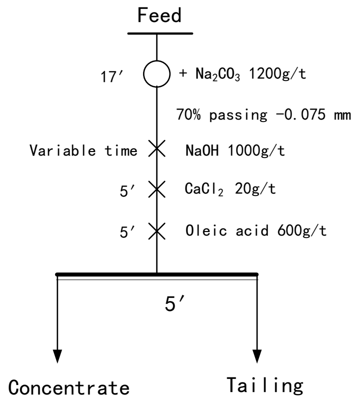

Fig. 6. Flowsheet of tests to explore effects of conditioning time of NaOH on spodumene flotation

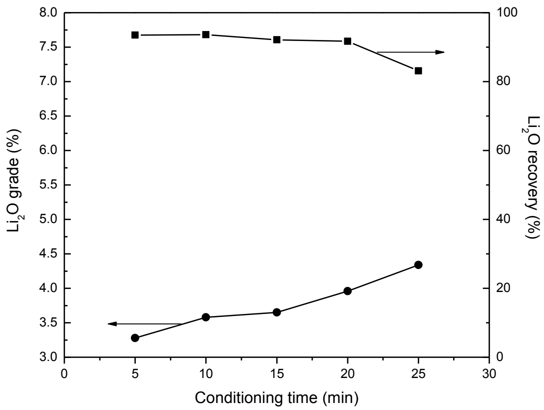

Fig. 7. Effects of conditioning time of NaOH solution on grade and recovery of spodumene concentrates

XPS analysis results

Based on the results of micro-flotation and bench scale flotation tests, it can be concluded that NaOH could change the flotation behavior of spodumene significantly. Since flotation behavior is determined by the mineral surface characteristics, the X-ray photoelectron spectroscopy (XPS) technique was applied to get information on elements of the sample surface layers. For the purpose of comparing the state of the surface before and after NaOH leaching, both samples, untreated and treated in NaOH solution, were investigated. Samples of the latter were stirred in NaOH solution at a concentration of 2250 mg·dm^{-3} for 10 min, which were then filtered and water-washed to a neutral pH. The vacuum-dried samples were sent for the XPS measurements.

The XPS spectra of spodumene, quartz and feldspar before and after NaOH leaching are shown in Fig. 8. The XPS spectral results are summarized in Table 4. It should be noted that the C (1s) detected in the samples is impurity, which was adsorbed at the surface inevitably during the sample preparation and XPS testing process (Liu et al., 1988). Table 4 demonstrates that no significant chemical shifts in the binding energy of the elements in three mineral samples are observed after NaOH leaching treatment. For the relative percentages of elements on mineral surfaces, the most obvious change occurs on Li (1s) element on spodumene surface, which increases from 6.63% to 7.35% after leaching in NaOH solution. The 0.72% percentage change of Li (1s) is big enough to eliminate the errors caused by the irreproducibility of XPS measurements.

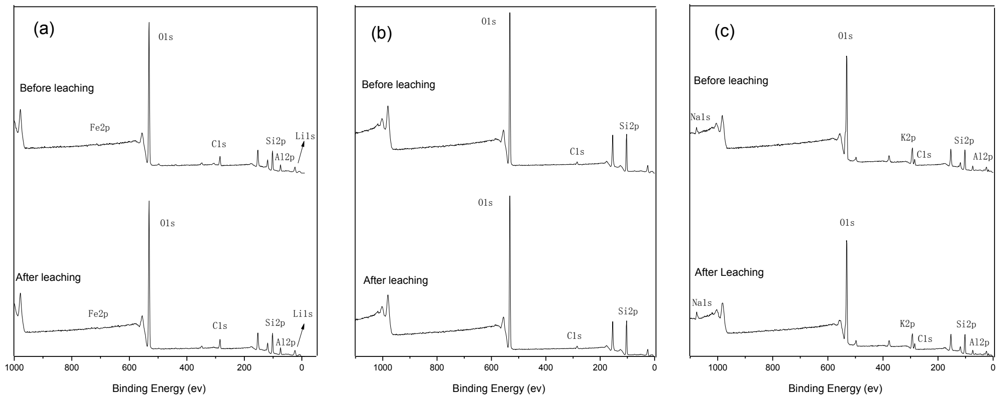

Fig. 8. XPS spectra of minerals before and after leaching in NaOH solution,
(a) spodumene; (b) quartz; (c) feldspar

Table 4. XPS analysis of three minerals before and after leaching in NaOH solution

Mineral	Element	Valence	Binding energy (eV)		Relative percentage (%)	
			Before leaching	After leaching	Before leaching	After leaching
Spodumene $LiAl[Si_2O_6]$	Li 1s	1	56.05	56.07	6.63	7.35
	Al 2p	3	74.58	74.61	9.65	9.74
	Si 2p	4	102.45	102.49	19.79	19.76
	O 1s	-2	531.72	531.72	53.73	53.24
	Fe 2p	3	712.17	712.26	0.37	0.27
	C 1s	4	284.80	284.84	9.83	9.64
Quartz SiO_2	Si 2p	4	103.26	103.31	34.90	34.94
	O 1s	-2	532.43	532.49	61.74	61.88
	C 1s	4	284.79	284.80	3.35	3.18
Feldspar $KAl[Si_3O_8]$	Al 2p	3	74.51	74.41	7.17	7.33
	Si 2p	4	102.91	102.80	24.06	23.87
	O 1s	-2	532.00	531.95	54.94	54.83
	K 2p	1	293.27	293.21	5.90	5.70
	Na 1s	1	1075.97	1076.01	1.58	2.36
	C 1s	4	284.84	284.77	6.35	5.91

The surface of spodumene exposes more Li positive sites after NaOH solution leaching. This increases adsorption of the anionic collector. Accordingly, the flotation of spodumene improves after leaching in the NaOH solution. This conclusion coincides well with the previous microflotation tests results and bench scale tests. It is also worth to note that flotation of quartz stays the same and flotation of feldspar declines slightly after NaOH leaching. The percentages of Si (2p) and O (1s) on quartz surface changes rarely after NaOH leaching, which leads to a stabilized flotation of quartz. For feldspar mineral, the generation of Na_2SiO_3 may be the reason for the decline of feldspar recovery. Since the Si (2p) percentage on feldspar surface decreases from 24.06% to 23.87% after leaching, the dissolved Si transfers to Na_2SiO_3 in NaOH solution by chemical reaction. Na_2SiO_3 is a depressant which can depress the flotation of gangue minerals significantly (Chulhyun and Hoseok, 2010; Rao, 2010). In the bench scale flotation tests, the grade of concentrate increases and the recovery decreases as the conditioning time of NaOH solution goes up. The possible explanations for this phenomenon may also contribute to the spontaneous sodium silicate generated in the alkaline pulp after conditioning for adequate time, which depresses the flotation of the minerals selectively.

Conclusions

The microflotation tests revealed that the flotation recovery of spodumene increases at extremely alkaline pH while for quartz it remains nearly constant and decreases slightly for feldspar, as the dosage of NaOH increases. The flotation of spodumene is enhanced by leaching at high concentrations of NaOH solution before flotation. For quartz and feldspar NaOH leaching does not promote their flotation and the recovery of feldspar even declines. The grades of the concentrates decrease and the recoveries increase with the increase of the NaOH dosage in bench scale tests. Moreover, conditioning time of NaOH solution has a significant impact on the flotation of the spodumene ore. The grades of the concentrates increase and the recoveries decrease as the conditioning time goes up. It is concluded that NaOH acts more than a pH regulator in these tests.

The XPS analysis revealed that spodumene was preferentially leached by conditioning at high concentrations of NaOH and exposed more Li positive sites on the mineral surface. The percentages of Si and O on quartz surface do not change after NaOH leaching. The generation of Na_2SiO_3 may be the reason for the decline of the feldspar recovery. Because the Si percentage on feldspar surface decreases after NaOH leaching treatment and the dissolved Si in NaOH solution can be transferred to Na_2SiO_3 it leads to depression of aluminosilicate minerals flotation. The spontaneously generated sodium silicate in the alkaline pulp after conditioning for adequate time is the possible explanation for the fact that the grades of concentrates increase and the recoveries decrease as the conditioning time of NaOH solution rises.

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