Effect and mechanism of surface pretreatment on desulfurization and desilication from low-grade high-sulfur bauxite using flotation

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Abstract: Surface pretreatment using a hot alkaline solution was carried out to improve the effect of desulfurization and desilication on low-grade bauxite with high sulfur content. The results demonstrated that, after surface pretreatment, a maximum grade and recovery of 66.17% and 87.27%, respectively, were achieved, and the sulfur content and ratio of A/S were 0.19% and 7.09, respectively. The surface pretreatment mechanism was further analysed by XRD and SEM analyses. The improved results of desulfurization and desilication were attributed to the selective corrosion of aluminosilicate minerals in coarse particles, reducing the active silicon sites on the surface of coarse particles as well as enhancing the cation exchange between the collector and aluminosilicate minerals.

1.   Introduction

Because of the rapid development of the alumina industry, high-grade bauxite with a low content of sulfur has almost been exhausted; thus, exploiting low-grade bauxite has become increasingly important (Paraskevas et al, 2016). In China, the proportion of diasporic bauxite accounts for 98.46% of bauxite resources (Gao et al, 2008), and the reserves of bauxite with high-content sulfur are approximately 8.1×10^{11} kg. The high-grade bauxite with an A/S ratio larger than 7 represents approximately 57.2%, and this type could be produced through a Bayer process after desulfurization. The middle-low grade bauxite with high-content sulfur occupied approximately 42.8% and, only after desulfurization and desilication, could this part of the mineral be used effectively. Consequently, new methods to reasonably exploit low-grade bauxite with high-sulfur content are urgently needed to increase overall bauxite production.

Currently, flotation has been shown to be an efficient method for the desilication of bauxite (Liu et al., 2007; Massola et al., 2009; Lu et al., 2002), and reverse flotation has shown more advantages for bauxite desilication than direct flotation, such as lower cost, ease of dewatering and less impact on metallurgy (Hu et al., 2001; Wang et al., 2004). For low-grade bauxite with high-content sulfur, some research related to desulfurization and desilication by stepwise flotation is available (Song et al, 2002; Wang et al, 2011). However, until the present study, few studies have been conducted to investigate synchronous desulfurization and desilication from low-grade bauxite with high-content sulfur via flotation.

Surface pretreatment can modify the surface properties of mineral particles and can improve the floatability of minerals (Xia et al., 2013). Surface pretreatment includes grinding pretreatment (Xia and Yang, 2013; Chen et al, 2017), ultrasonic pretreatment (Kursun H, 2014), microwave pretreatment (Su et al, 2010; Fan and Rowson, 2000), magnetic pretreatment (Zheng et al, 2018), electrochemical

pretreatment (Yu et al, 2002), pressure pretreatment (Tominaga H, 2009), heat pretreatment (Ö F Ersoy et al, 2013; M. Çınar, 2009), and other methods. Each method has its own characteristics, and they can all achieve certain effects. There are some applications of alkali liquor pretreatment in mineral processing, such as chlorine removal from high-chlorine rhodochrosite (Zhang et al, 2016) and removal of antimony from refractory antimonial gold and silver ores(Celep et al, 2011) and so on, but the application of alkali liquor pretreatment in bauxite is almost absent. In this study, surface pretreatment using a hot alkaline solution was carried out to improve the results of synchronous desulfurization and desilication of low-grade bauxite with high-sulfur content via flotation, and the mechanism was researched. This study provides good evidence for the cost-effective utilization of low-grade bauxite with high-content sulfur.

2. Materials and methods

This section is also divided by subheadings. We provide sufficient detail to allow the work to be reproduced. Methods already published should be indicated by a reference; only relevant modifications should be described.

2.1. Materials

The bauxite ores used in these tests were supplied from Chongqing China. The ores were crushed and ground until the particles were less than 3 mm and were prepared in 500 grams bags after mixing and splitting.

The composition of the raw ore was analysed by X-ray fluorescence (AXIOS) and is shown in Table 1; the results indicate that the content of alumina was 59.81%. The silicon dioxide content was 13.07%, the A/S ratio was 4.58, and the sulfur content was 1.83%. The results indicate that this mineral was typical low-grade bauxite with high-sulfur content.

Table 1. Chemical analysis results of the actual samples (mass fraction, %).

Composition	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	S	L.O.I	A/S *
wt%	59.81	13.07	9.38	2.51	0.51	0.046	0.87	0.46	1.83	11.51	4.58

* A/S: m (Al_2O_3)/m (SiO_2).

The XRD analysis (Table 2) indicated that the diasporic bauxite and boehmite were the primary aluminium minerals. The composition of silicate minerals was more complex, consisting of chlorite, kaolinite, illite and quartz. Pyrite and siderite were the main iron minerals. Titanium minerals included anatase as well as rutile. Sulfur was also contained in pyrite.

Table 2. Phase composition of the actual samples (mass fraction, %).

Minerals	Diaspore	Boehmite	Kaolinite	Illite	Chlorite	Quartz
wt%	49	5.5	12	5	14.5	2.1
Minerals	Calcite	Dolomite	Anatase	Rutile	Siderite	Pyrite
wt%	1.7	0.9	2.1	0.45	1.9	4.1

The samples, after grinding, were scanned for quantitative image analysis using QEMSCAN with the QS69. Figs. 1-1, 1-2, 1-3, 1-4, 1-5 show the scanning images of different sized fractions of the samples. These images illustrate the dissemination characteristics and dissemination relations among the minerals.

The "Al.Si complex" in these images is a combination of aluminium and silicon, consisting of 40% diaspore and boehmite, 40% kaolinite and 20% iron-containing kaolinite. Each of these mineral particles was finer than 1μm and associated with each other closely. These minerals accounted for approximately 3% of the total minerals and were difficult to separate by milling. If these minerals were involved in the concentrate, it would lower the concentrate grade. Additionally, the A/S ratio would be increased if it were involved in tailings.
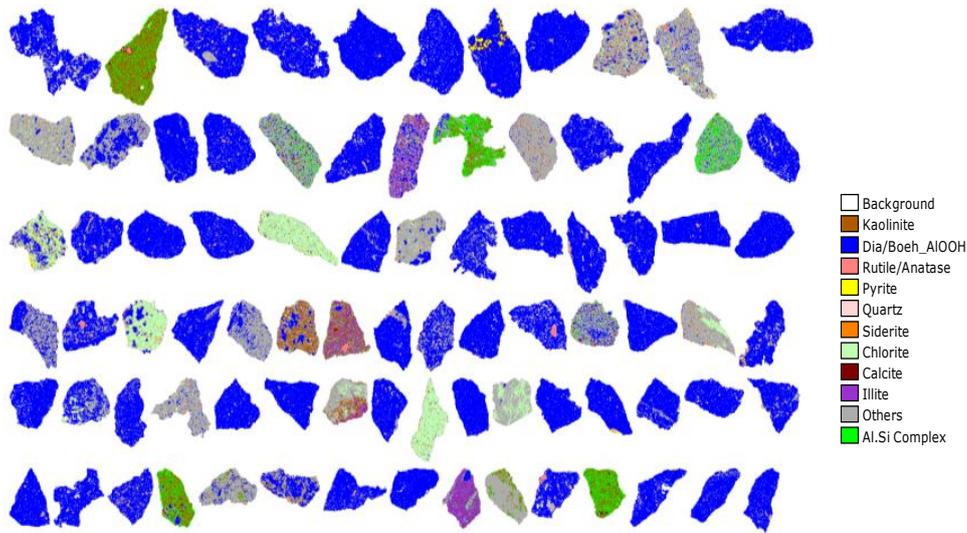
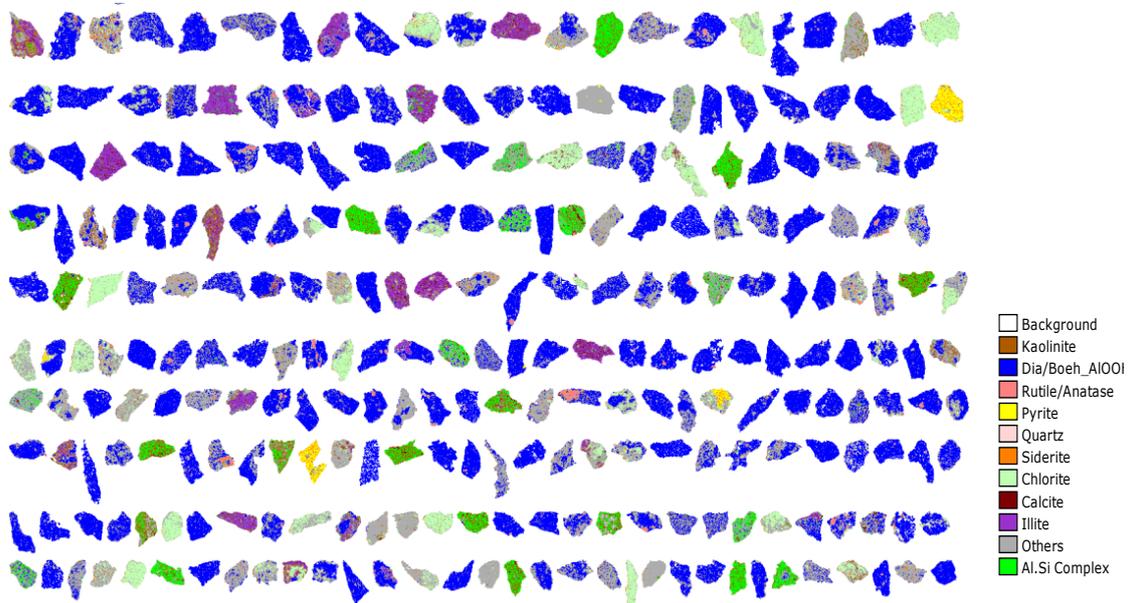Fig. 1-1. +100 mesh mineral size scanning

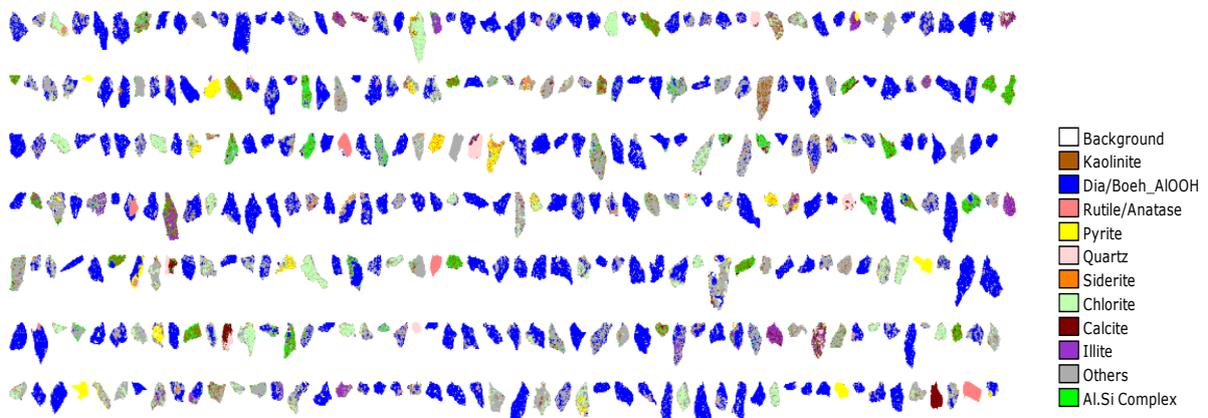Fig. 1-2. +200 mesh mineral size scanning

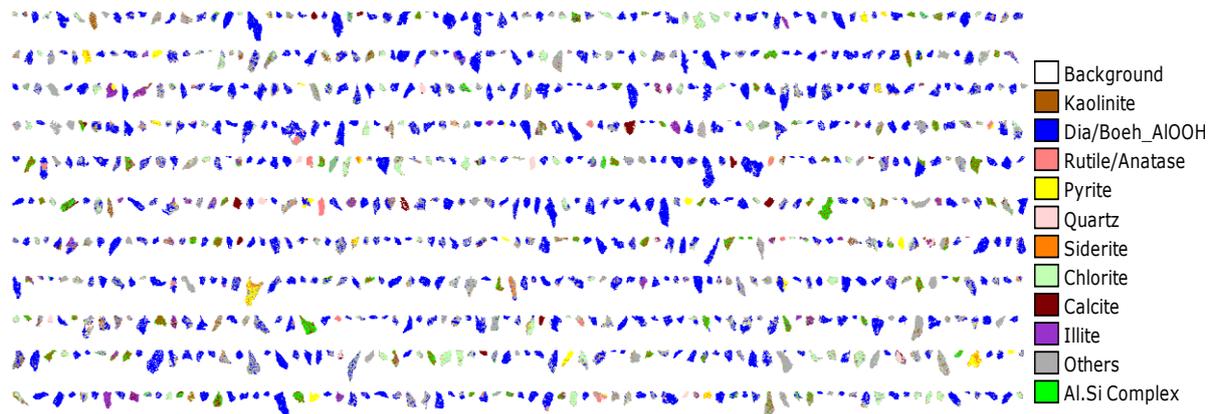Fig. 1-3. +400 mesh mineral size scanning
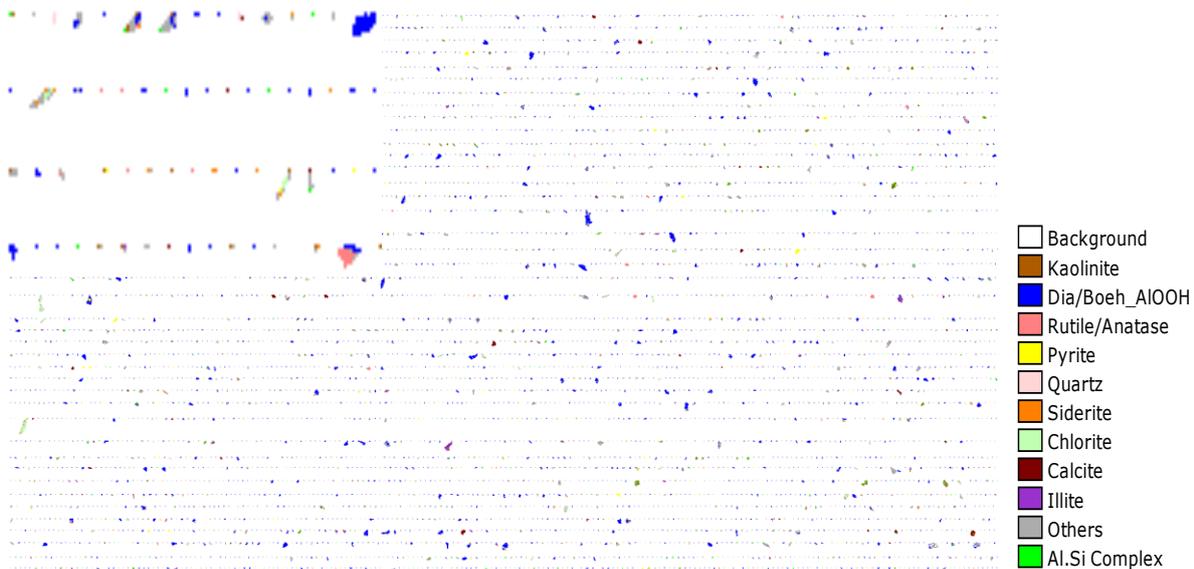
Fig. 1-4. +600 mesh mineral size scanning

Fig. 1-5. -600 mesh mineral size scanning

It can be seen from Figs. 1-1, 1-2, 1-3, 1-4, 1-5 that the pyrite with a particle size <0.075 mm has a great degree of liberation. Some of the diasporic bauxite also had a good degree of liberation. However, kaolinite is often associated with illite and chlorite, and these minerals have very fine particles. In addition, these minerals were sprinkled in the diasporic bauxite in the granular group. The chlorite grains appeared to be spherical, irregular, granular and flaky. Chlorite with these three conditions had a complicated dissemination relationship with diasporic bauxite. The diasporic bauxite, pyrite, rutile and anatase were often found in combination with illite, kaolinite and chlorite. Because of the complex mineral structure, fine dissemination size, high-content kaolinite in the gangue and a large amount of combined aluminium and silicon, desilication by flotation is not practical.

2.2. Methods

2.2.1 Surface Pretreatment

Surface pretreatment was carried out using a hot alkaline solution. For each test, 500 g bauxite samples was put into a 6.25 dm^3 240×90 conical ball mill, and then a hot alkali solution with a specified temperature and density was added into the mill before grinding. The grinding density was set at 50%. The qualified grinding pulp was placed into a 5 dm^3 beaker until more than 77.32% of the bauxite particles passed through a 0.074 mm sieve. Next, 5 dm^3 distilled water was carefully added to the beaker and agitated. The pulp was then allowed to settle for 5 min before the upper part was

siphoned off for dealkalization. The process was repeated many times until obtaining a pulp pH value close to 7. And the bauxite ores obtained from grading with hot aqueous alkali and with distilled water were screened using a 0.045 mm mesh sieve, and particles larger than 0.045 mm were analysed by X-ray diffraction.

2.2.2 Flotation test

All flotation tests were conducted in a 1.5 dm³ XFD flotation cell at 25 °C. The air flow rate was 100 dm³/h and the agitation speed was 2200 rpm. The pulp obtained from the surface pretreatment processes was added into the cell of the flotation machine with distilled water and stirred for 1 min. After adding the pH regulator, the pulp was stirred for an additional 2 min, and the pH value was measured. Next, the activators and depressant were added to the slurry and conditioned for 3 min and 1 min, respectively. Then, the collectors for desulfurization and frothers were added and agitated for 2 min. Before aeration, the collectors for desilication were added, with another 3 min of stirring. After 4 mins of flotation, the flotation concentrate and tailings were filtered, dried at 60 °C for 6 h, and weighed. The flotation tests were conducted in accordance with the flow sheet shown in Fig. 2.

The Yield and Recovery was calculated using equation 1 and equation 2, respestively.

$$Yield(\gamma)=(q/Q) \times 100\% \tag{1}$$

$$Recovery=(\beta r/\alpha) \times 100\% \tag{2}$$

where q is the quality of concentrates and Q is the quality of raw ore, γ is the Yield, β is the grade of concentrate and α is the grade is the grade of raw ore.
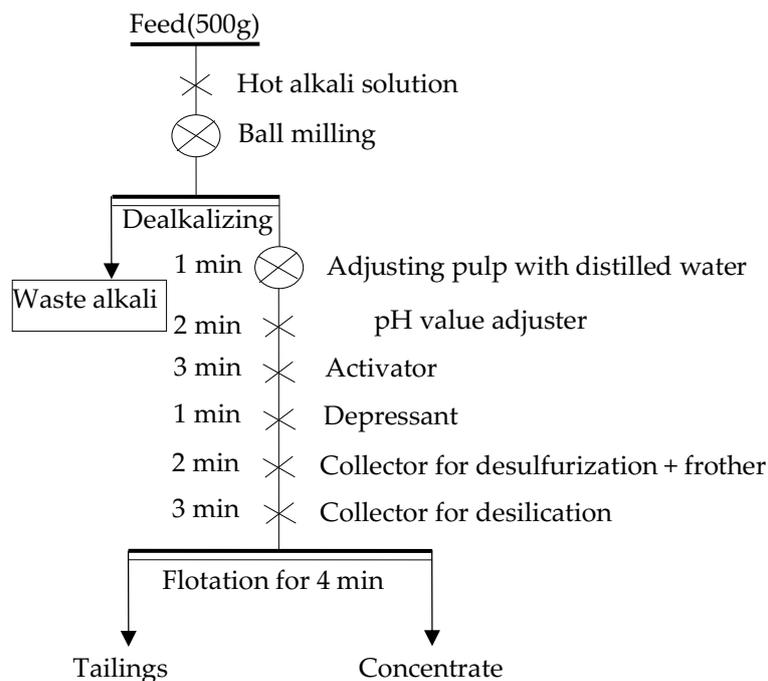

Fig. 2. Flotation flowsheet of the test samples

2.3. Reagents and equipment

The reagents used in the flotation test included sodium hydroxide (alkali), cupric sulphate (activators), sodium n-butyl xanthate (collectors for desulphurization), pine camphor oil (frothers for desulphurization), and hydrochloric acid and sodium carbonate (pH value regulators). Modified inorganic polymeric silicate and polyamines combined collectors (both synthetized in the laboratory) were used as depressants and collectors for desilication, respectively. One-off distilled water(The resistivity of one-off distilled water is 18.3 MΩ•cm at 25℃) was used in all the tests.

An X-ray fluorescence analysis (XRF) was conducted using an AXIOS system (PANalytical. B.V, Co., Ltd., Ea Almelo, the Netherlands), and an X-ray diffraction (XRD) analysis was performed with

an RU-200B (Rigaku Co., Ltd., Tokyo, Japan). The pH metre used for this study was an HM-40V (TOA Denpa Togyo, Co., Ltd., Tokyo, Japan), and energy dispersive spectroscopy (EDS) analysis was carried out using a "Zeiss Ultra Plus" (Carl Zeiss AG, Germany).

3. Results and discussion

3.1. Effect of hot alkaline solution mass concentration on the flotation results

The effect of hot aqueous alkali mass concentration on the flotation index was studied at a temperature of 50 °C. The results are shown in Fig. 3.
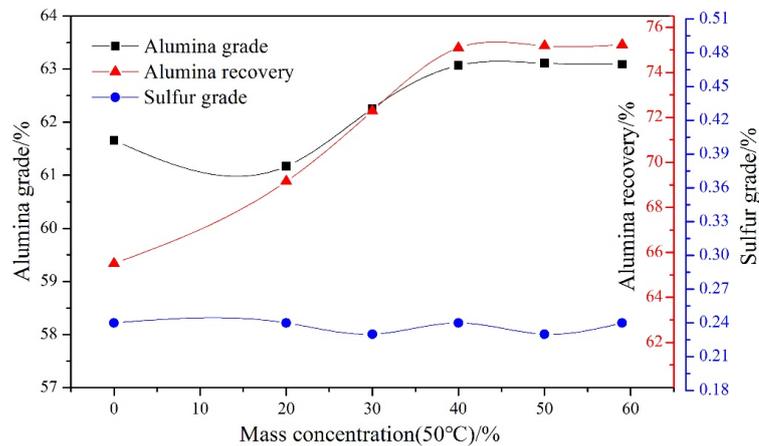

Fig. 3. Effect of mass concentration (50°C) on desulfurization and desilication towards concentrate indexes through synchronous flotation

As seen in Fig. 3, with the mass concentration of hot aqueous solution increased from 0% to 40%, the recovery was increase from 65.51% to 75.09% while grade from 61.66% to 63.07%.It was observed that the increase in the mass concentration significantly increased the recovery of alumina. A further increase in the mass concentration did not show any improvement in the grade or recovery of alumina. The grade of sulfur in the concentrate varied between 0.23% and 0.24% with different mass concentrations, indicating that different mass concentrations have almost no impact on the desulfurization index. Therefore, all further experiments were carried out using 40% mass concentration of hot aqueous alkali.

3.2 Effect of hot alkaline solution temperature on the flotation results

The effect of the temperature of hot aqueous alkali on the flotation index was studied using a 40% mass concentration. The results are shown in Fig. 4.
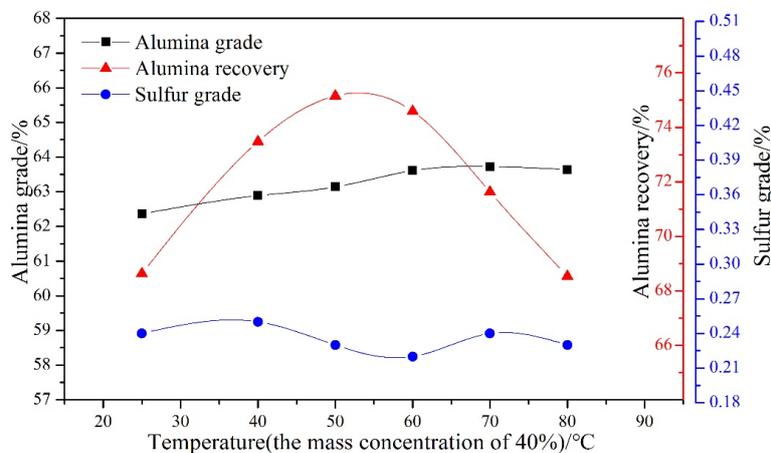

Fig. 4. Effect of hot alkali solution temperature (40% mass concentration) on desulfurization and desilication towards concentrate indexes through synchronous flotation

The results (Fig. 4) indicate that the recovery of alumina increased from 68.63% to 75.15% with increasing temperatures from 25 °C to 50 °C, and a continued increase in temperature led to a significant decrease in the recovery of alumina. The grade of alumina increased with the increase in temperature in the test range, and the grade of sulfur in the concentrate changed from 0.22% to 0.25% at different temperatures. This finding demonstrates that the pretreatment of hot aqueous alkali has no obvious influence on the desulfurization index. Therefore, 50°C can be chosen as the further experiment's temperature , and the grade and recovery of alumina as well as the grade of sulfur in the concentrate were 63.14%, 75.15% and 0.23%, respectively.

3.2. Laboratory Closed-circuit Experiment

The laboratory closed-circuit experiment was carried out according to the flowsheet shown in Fig. 5. Additional parameters of the flotation tests are also given in Fig. 5.

The flotation experiment without surface pretreatment was carried out using the same technical parameters, flowsheet, and reagent system as those in the flotation process after surface pretreatment. The comparisons of the flotation indexes are shown in Table 3.
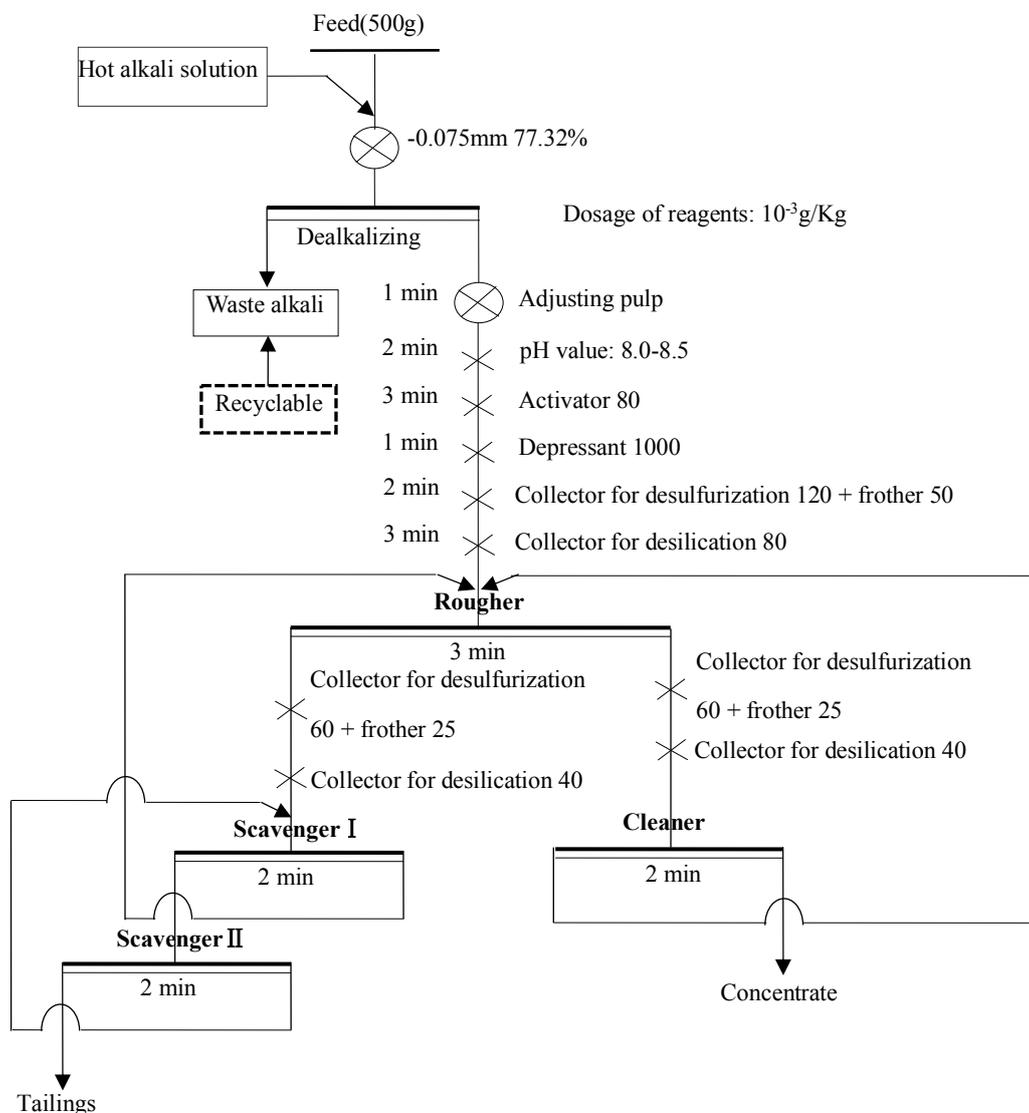

Fig. 5. Closed-circuit flotation flowsheet on desulfurization and desilication with a new process of surface pretreatment

Table 3. Comparison of the experimental results in the normal process and new process

Conditions	Products	Yield/wt %	Al_2O_3/%	SiO_2/%	A/S	Recovery/%	S/%
	Concentrate	76.37	65.35	9.85	6.63	83.47	0.19
Without surface pretreatment	Tailings	23.63	41.83	23.00	1.82	16.53	7.07
	Feed	100.00	59.79	13.06	4.58	100.00	1.82
	Concentrate	78.91	66.17	9.33	7.09	87.27	0.19
With surface pretreatment	Tailings	21.09	36.11	26.03	1.39	12.73	7.88
	Feed	100.00	59.83	13.06	4.58	100.00	1.81

As seen in Table 3, the grade of alumina and sulfur in the concentrate obtained with surface pretreatment was 59.83% and 1.81%, respectively, and the A/S ratio was 4.58. After the laboratory closed-circuit experiment with surface pretreatment, the grade of alumina was increased to 66.17%, with a recovery of 87.27%; furthermore, the grade of sulfur was decreased to 0.19%, and the A/S ratio was 7.09. The grade of alumina in tailings was only 36.11%, and the A/S ratio was decreased to 1.39. The sulfur in the concentrate declined to the requirement of under 0.5%. Compared to the values of the process without surface pretreatment, the grade and recovery of alumina and the A/S ratio were increased by 0.82%, 3.80% and 0.46, respectively. This finding indicates clearly that surface pretreatment with hot aqueous alkali can improve the desilication results. However, this process has no major impact on the desulfurization index.

4.   Mechanism of Surface Pretreatment Process

4.1. Selective Corrosion of aluminosilicate minerals in coarse particles

Fig. 6-1 shows the XRD pattern of the coarse particles ground with the distilled water treatment. Fig. 6-2 shows the XRD pattern of the coarse particle with the hot aqueous alkali pretreatment(also referred to as surface pretreatment).
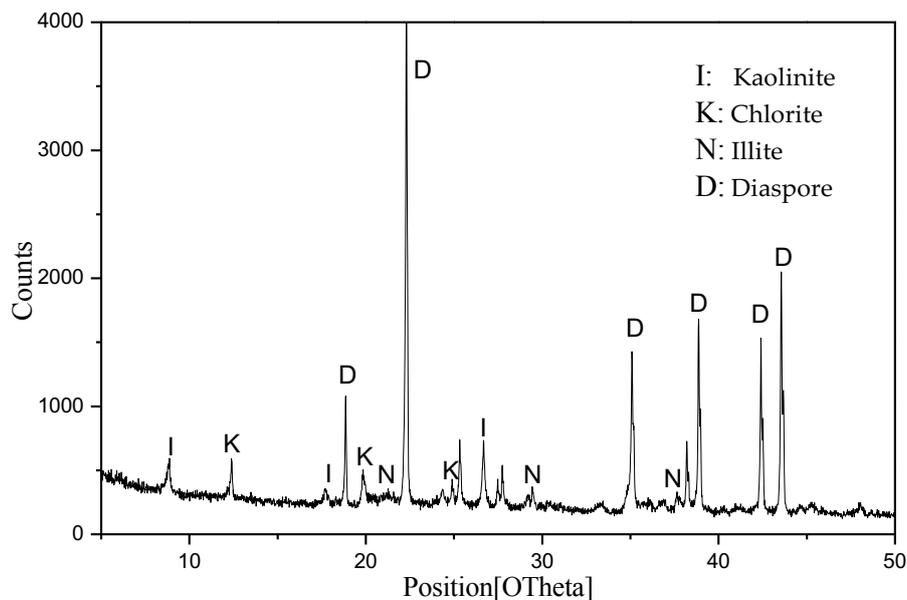

Fig. 6-1. XRD analysis of coarse particles with the distilled water pretreatment

As Figs. 6-1 and 6-2 illustrate, in the XRD pattern of the >0.045 mm coarse particles with surface pretreatment, the diffraction peak intensities of kaolinite, chlorite, and illite decreased. The diffraction

peak intensities of diasporic bauxite showed no change. This result indicates that, after pretreatment, selective corrosion occurs to the aluminosilicate minerals, and there is no reaction between diasporic bauxite and hot aqueous alkali. Using this mechanism, the recovery of the coarse particles by entrainment in reverse flotation for desulfurization can be reduced.
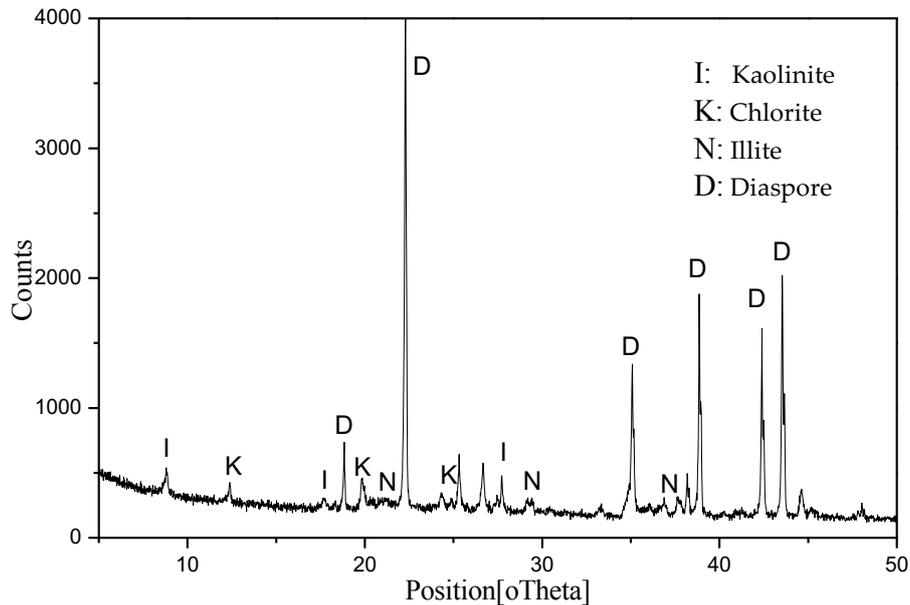

Fig. 6-2. XRD analysis of coarse particles with surface pretreatment

4.2. Reducing the Active Sites of Silicon on the Surface of Coarse Particles

Coarse particles with surface pretreatment and without pretreatment were both analysed by EDS analysis. Fig. 7-1 shows the spectra of coarse particles with the distilled water pretreatment. Fig. 7-2 shows the spectra of coarse particles with surface pretreatment. In the figure, the red colour indicates active silicon sites, and green indicates the active aluminium sites.

As Figs. 7-1, 7-2 show, after pretreatment, the active silicon sites >0.045 mm coarse particles were reduced by 21.88 percent. The difference between the active sites of silicon and aluminium on the mineral surface was enhanced, which can strengthen the selectivity of polyamines combined with the collector for desilication and can improve the results of desilication in reverse flotation.

4.3. Enhancing the Cation Exchange Between the Collector and Aluminosilicate Minerals

The main gangue minerals in bauxite had layered crystal structures. The Si^{4+} can be substituted by Al^{3+} in the silicon-oxygen tetrahedron, leading to a charge imbalance in the crystal structure. An alkali metal with small volume can substitute into the lattice structure and balance the charge. In the crystal structure, the layers are held together by Van der Waals forces. In aqueous solution, the silicate minerals can expand, which enlarges the layer spacing. Therefore, there is the possibility that small volume inorganic metal cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+} in the crystal layer structure can spread into solution. Since these metal cations spread from the lattice to the outside, this leads to a positive charge vacancy inside the lattice. When the polyamine collector is added, the amine polar groups are concentrated at the interface due to the existence of hydrophobic carbon chains in amine ions and the surface activity of ions. Because of the positive charge vacancy inside the mineral particles, the particles show negative charges. This result enables the amine cation to absorb between the interface of the mineral and water via electrostatic forces. Furthermore, these results also play roles in neutralizing the positive charge vacancy in the lattice. When the hot aqueous alkali is added, the complex of OH^- with Ca^{2+} and Mg^{2+} enables the alkali metal in the crystal structure of aluminosilicate to spread outside the lattice. After the polyamine collector is added, the cation exchange within aluminosilicate is greater and results in improved efficiency of the collectors.
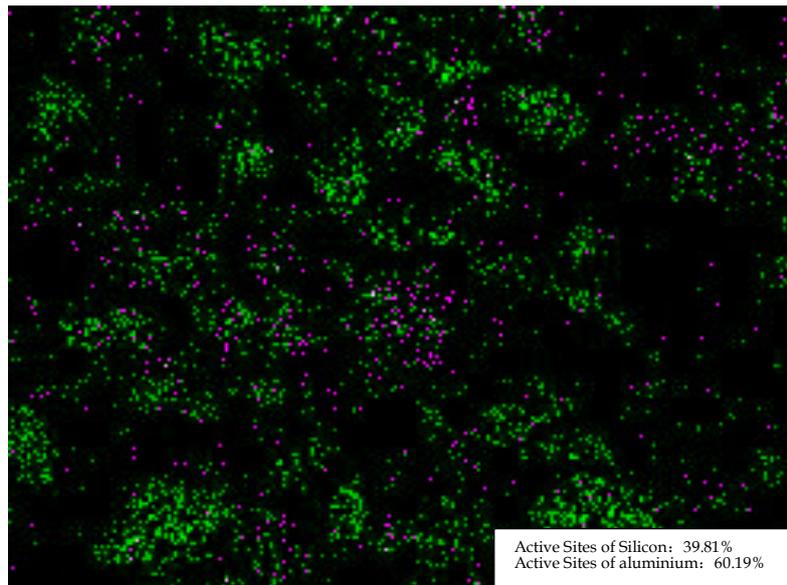
Fig. 7-1. Spectrum picture of coarse particles with the distilled water pretreatment
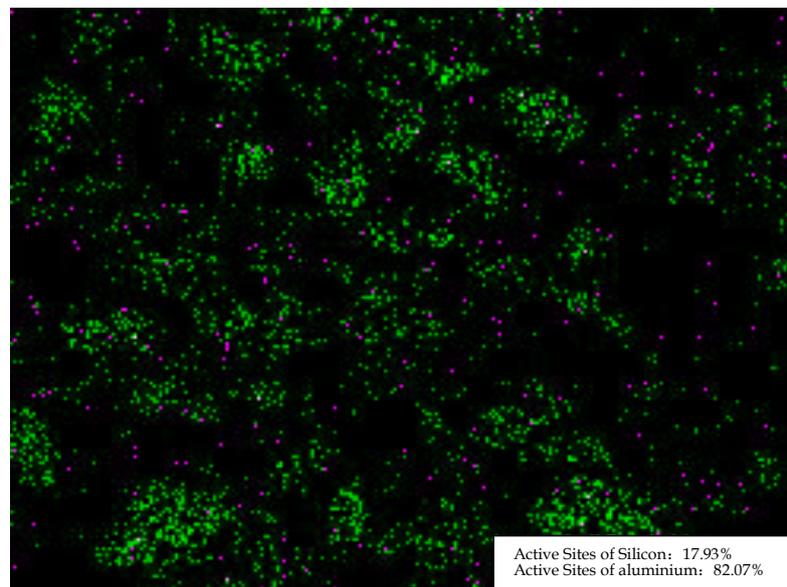

Fig. 7-2. Spectrum picture of coarse particles with surface pretreatment

5. Conclusions

Diasporic bauxite was the primary aluminium mineral in this low-grade, high-sulfur bauxite. The sulfur mineral was pyrite. Silicate minerals consisted of kaolinite, chlorite, illite and quartz. In the conditions of that: 40% mass concentration hot aqueous alkali, 50°C, 77.32% -0.075 Mm size fraction, 0.08 g/kg activator, 1 g/kg depressant, 0.24 g/kg collector for desulfurization and 0.1 g/kg frother, 0.16 g/kg collector for desilication and a pH value from 8.0-8.5, the flotation results were best. The raw mineral contained 59.79% alumina, 1.82% sulfur and an A/S ratio of 4.58. After the one-roughing, one-cleaning, two-scavenging closed-circuit flotation process, the concentrate contained 66.17% alumina, 0.19% sulfur with 87.27% alumina recovery and 7.09 A/S ratio. The content of alumina in tailings decreased to 36.11%, and the A/S ratio decreased to 1.39.

Compared to the contents in the normal process, the content of alumina, the A/S ratio, and the recovery increased by 0.82%, 0.46 and 3.80%, respectively, using the surface pretreatment process.

Research about the mechanism of surface pretreatment indicated that it selectively corroded the aluminosilicate minerals in coarse particles, reduced about 21.88 percent the active sites of silicon on

the coarse particle surface, and enhanced the cation exchange between the collector and aluminosilicate minerals.

Acknowledgements

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