The Effect of Regulators on Flotation Desulfurization of High-sulfur Bauxites

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Abstract

Flotation of Chinese high sulfur bauxites for the purposes of desulfurization is more difficult than conventional sulfide flotation in that the finely disseminated sulfide content of these bauxites can lead to significant bubble inclusions and low separation efficiency. Acidification of high sulfur bauxite also makes desulfurizing flotation more difficult. This study systematically investigated different regulators on the flotation desulfurization effect. The results indicate that the regulator can have a great impact on separation efficiency and therefore the desulfurization result. A new regulator (WG) could improve the concentrate recovery rate by 10 % and significantly increase desulfurization efficiency. It was shown to play a promotional role in desulfurization by flotation, and has wide applicability.

Keywords: high-sulfur bauxite, desulfurization, regulator.

1. Introduction

According to the statistics, the high-sulfur bauxite resource exceeds 800 million tons in China [1]. Because the sulfur contained in these bauxites severely disrupt alumina production [2], this resource has not yet been exploited and utilized on a large scale. The research on processing high-sulfur bauxites to date has mainly focused on the main methods of roasting [3, 4, 5] and wet oxidation. The oxidizing agents used in the wet oxidation process are various, including gases such as air [6], oxygen [7] and ozone [8], and solid oxidizing agents such as chlorinated lime, sodium nitrate, etc. Precipitation agents such as lime [9] and barium salts [10] have also been studied. These desulfurization methods can reduce the harmful effects of sulfur in bauxite with a low content, but it cannot eliminate the difficulties and costs for bauxites with high sulfur. Despite all of this work, there are presently no instances of large-scale industrial application of these processing options. Flotation desulfurization [11] can remove the sulfur from the bauxite before entering the alumina refining process and negatively impacting the efficiency and economics of producing alumina from high-sulfur bauxite.

Pyrite is the main sulfide mineral in high-sulfur bauxite [12], which is easily floated by collectors such as xanthate, while aluminum minerals are not easily floated by this collector. Consequently, the separation between pyrite and aluminum minerals should be easily achieved using xanthate or similar collectors. However, the process is not so straightforward, flotation desulfurization of high-sulfur bauxites has its challenges.

High-sulfur bauxite is difficult to handle in flotation. Desulfurization by flotation requires that the crystal surfaces of pyrite are exposed by grinding. Pyrite liberation generally requires fine grinding, particularly where pyrite is present as small grains. Achieving liberation can easily lead to excessive grinding, including of clay of minerals, which may have negative effects on flotation and desulfurization efficiency. Metal sulfide ores on the other hand tend to be brittle, requiring less grinding for liberation.

Average sulfur content of high sulfur bauxites are as low as 1 – 3 %, and the fine grain size of its sulfur minerals results in difficult liberation and separation, while metal sulfide ores generally have higher sulfur content, and its coarse grain size is more easy to liberate and sort.

Acidification of high-sulfur bauxite mainly results from oxidation and acidification of pyrite surfaces. This oxidation-acidification is inevitable in ores with sulfide after exposure to air, and under the influence of temperature, moisture and microbial action. This acidification can disrupt the absorption of the flotation agent on pyrite and decrease the efficiency of mineral floatation. Among the metal sulfide minerals, pyrite is easily oxidized and acidified. Oxidative inhibition of pyrite minerals improves the flotation of the target minerals.

Flotation desulfurization in acid conditions conventionally use copper sulfate or sodium sulfide as activator, xanthate as collector and oil 2 as foaming agent. Production experience shows that this agent regime generally used for sulfide minerals cannot achieve the required desulfurization efficiency for acidified high-sulfur bauxite.

Regulators [13] can change the interaction between collecting agents and ores as well as the floatation properties of pulp, and enhance the selectivity of minerals [14, 15]. In this study, acidified high-sulfur bauxite was used as the research material, where different adjustment agents were tested to eliminate the influence of ions in pulp generated from acidified high-sulfur bauxite. These ions harm flotation, and eliminating their influence improves the separation efficiency.

2. Experimental

2.1. Test sample ores

The acidified high-sulfur bauxite used in this test came from bauxite mines in Henan province (1#), Zunyi province (2#), Gongyi Henan province (3#) and Changtong Henan province (4#). The main chemical compositions of these bauxite ores are shown in Table 1, while their mineral phase analysis is shown in Table 2.

The bauxite was ground to 78 % ± 2 % < 0.075 mm, with a 30 % pulp density. Measured with a pH meter, the pH value of the untreated slurries are listed in Table 3.

Table 1. Chemical composition of Experimental Bauxites (%)*.

Chemical composition	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	S
Ore 1#	64.48	8.30	6.06	2.79	1.21	0.018	0.56	0.34	2.32
Ore 2#	65.61	7.97	6.19	2.88	1.22	0.04	0.13	0.14	0.86
Ore 3#	59.61	19.22	2.54	2.51	0.39	0.01	0.27	0.21	1.18
Ore 4#	47.58	11.56	11.39	2.30	2.18	0.023	2.57	0.79	6.83

*X-fluorescence analysis.

Table 2. Mineral phase analysis of experimental Bauxites (%)*.

Ore	Diaspore	Pyrophyllite	Kaolinite	Chlorite	Illite	Quartz	Pyrite
1#	68.5	/	4.5	/	11.5	1.0	3.9
2#	69.0	/	4.5	3.0	11.5	/	3.0
3#	59.0	19.0	9.0	1.6	4.0	1.0	2.0

4#	49.0	/	/	/	23.0	/	12.5
	Goethite	**Gypsum**	**Dolomite**	**Calcite**	**Anatase**	**Rutile**	
1#	4.0	/	1.5	/	2.0	0.7	
2#	3.0	/	/	/	1.8	1.0	
3#	/	1.0	/	1.0	1.8	0.6	
4#	/	2.0	3.5	1.5	1.0	1.3	

* X-ray diffraction analysis.

The bauxite samples' sulfur content were analyzed at between 0.86 % and 6.83 %. The main sulfide minerals are pyrite, while the main aluminum containing mineral is diaspore, and the main silicon minerals are kaolinite, illite and quartz. The calcium mineral contents were higher in Ore 3# and Ore 4#.

2.2. Experimental Agents

Activator: Pentahydrate copper sulfate;
Collector: Butyl;
Foaming agent: No 2 oil;
Regulators: sodium hexametaphosphate; modified starch; WG.

2.3. Flotation Desulfurization Tests

The flotation desulfurization test-work used a single flotation cell of 1.5 L. Each test run of bauxite used 500 g, which was ground to 75 % – 80 % < 0.075 mm and loaded into the flotation tank. The pulp pH was adjusted to the target test pH value, and in turn, the adjusting agent, activator, collecting and foaming agents were added. The air flotation desulfurization process was begun after stirring for 2 minutes, with the pulp temperature maintained at 30 °C. The test process flowchart is shown in Figure 1.

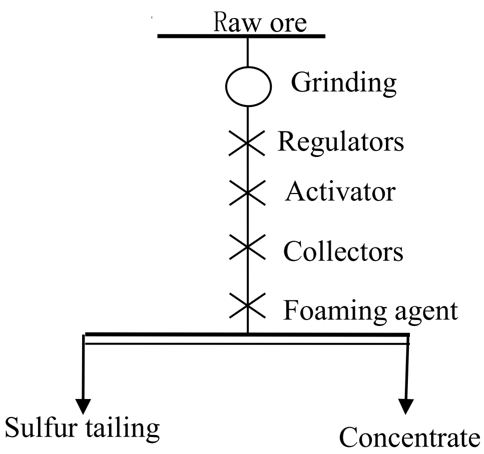

Figure 1. The flowchart of laboratory desulfurization flotation test.

2.4. Degree of Acidification Measurements

The pulp's natural pH value was measured after the test sample ore was ground to 78 %±2 % < 0.074 mm, and pulp density was controlled to 30 %. The SO_4^{2-} ion concentrations were also measured by ion chromatograph. The results are shown in Table 3.

Table 3. The natural pH of experimental bauxites*.

Test sample ore	Natural slurry pH value	SO_4^{2-} (g/L)
Sample ore 1#	4.2	1.21
Sample ore 2#	2.5	4.69
Sample ore 3#	6.0	0.78
Sample ore 4#	5.5	0.96

*Grind: 78 % ± 2 %, < 0.075mm, pulp density 30 %.

The result of these oxidation and acidification measurements for the four kinds of ores showed that sample ore 1# was partly acidified. The ground pulp's pH was 4.20 at a pulp density of 30 %, and the SO_4^{2-} concentration in pulp was 1.21 g/L. Acidification of sample ore 2# was more significant, the ground pulp's pH was 2.50 (at a pulp density of 30 %), and the pulp's SO_4^{2-} concentration was 4.69 g/L. Oxidation and acidification of the two ores were due to oxidation of iron pyrite. The degree of acidification of bauxite sample 3# and 4# were weaker.

3. Result and Analysis

3.1. Sodium Hexametaphosphate

Ore 1# was taken as the subject of a study on the effect of the dose of hexametaphosphate. The sample was ground to 75 % < 0.075 mm, pulp density was 30 %, and the pulp pH adjusted to 8.0. Sodium hexametaphosphate, activator, collectors and foaming agent were added in turn for flotation desulfurization. The effect of sodium hexametaphosphate dosage on flotation desulfurization was studied by comparing the yield and sulfur content of aluminum concentrates. Test results are shown in Figure 2.

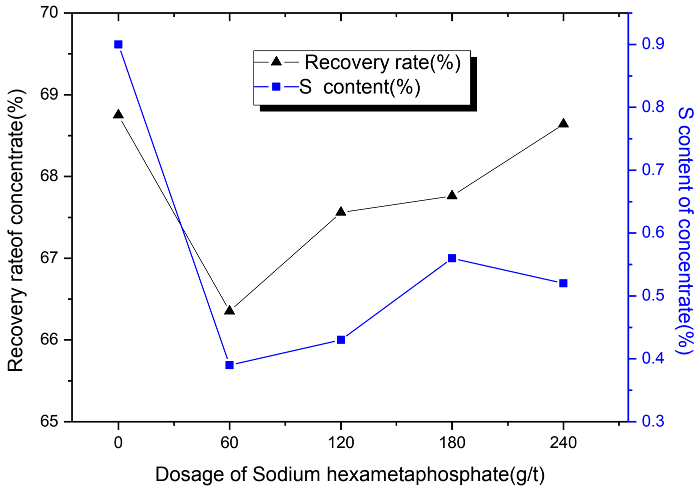

Figure 2. The effect of sodium hexametaphosphate on the recovery and sulfur content of flotation concentrate.

Figure 2 shows that the addition of sodium hexametaphosphate caused a decrease in aluminum concentrate yield during the process of flotation desulfurization. At a dose of 60 g/t there was an obvious decrease in concentrate yield, and as the dose was increased from 60 g/t to 240 g/t, the concentrate yield gradually increased with increasing sodium hexametaphosphate dose.

Hexametaphosphate is an effective dispersing agent and inhibitor of aluminosilicate ore flotation. At low dose, the ore had good initial dispersibility during the process of flotation, resulting in fine particles' entrainment in flotation froth, and caused a decrease in aluminum concentrates yield. With increasing hexametaphosphate dose, its inhibitory effect on aluminosilicate ore was more obvious, reducing the flotation of aluminosilicate ore, and increasing aluminum concentrate yield.

The addition of sodium hexametaphosphate at 60 g/t clearly causes a decrease in sulfur content of aluminum concentrates. As the dose was increased from 60 – 240 g/t, like aluminum concentrate yield, the sulfur content of concentrate also increased. The test results showed that the lowest sulfur content of aluminum concentrate was at the 60 g/t dose, but did not fall below 0.3 %.

Hu Yue-hua [15] et al researched the phosphate effection on the reverse flotation system. They drew the conclusion that if the dosage of sodium hexametaphosphate in the diaspore reverse flotation system was low, the inhibition effect of sodium hexametaphosphate on diaspore was weak. When the dose was high, the inhibition effect on diaspore was strong. The inhibition effect of sodium hexametaphosphate on diaspore can be explained as follows; when the dose is high, adsorption density of sodium hexametaphosphate on the surface of diaspore is high, and its surface may be fully covered by sodium hexametaphosphate. $Na_4P_6O_{18}^{2-}$ ionized by sodium hexametaphosphate reacts with aluminum ions yielding insoluble salts, then transfers to stable soluble complexes, resulting in diaspore inhibition [16].

3.2. Modified Starch

Ore 1# was taken as the subject of a study examining the effect of different doses of modified starch on flotation desulfurization. The results are presented in Figure 3. The results show that when the dose of modified starch is low, it can improve aluminum concentrate yield, and reduce sulfur content of aluminum concentrates to a certain extent. When the dose of modified starch increases, aluminum concentrate yield obviously reduces, and sulfur content of aluminum concentrate increases continuously.

The main chain of modified starch is composed of glucose monomer rings, linked by glucosidic bonds. Its cyclic structure gives improved rigidity. The absorbed forms of modified starch on the surface of ores are mainly ring type adsorption. When reacted with ores, modified starch reacts with aluminum ions on the surface of diaspore, and yields the chemical bond Al-O. This means that chelation between them occurs, so electrostatic charge of bonding atoms in agent molecules increases, and electron cloud transfers to the aluminium ion. The study of Li Changkai et al [17] showed that during the process of flotation desulfurization, modified starch inhibited diaspore to a certain extent, and reduced the loss of Al_2O_3 into high-sulfur tailings. When the dose of modified starch increased, its special structure covered micromolecular collectors, and consequently reduced the separation performance of agents, so affecting flotation desulfurization.

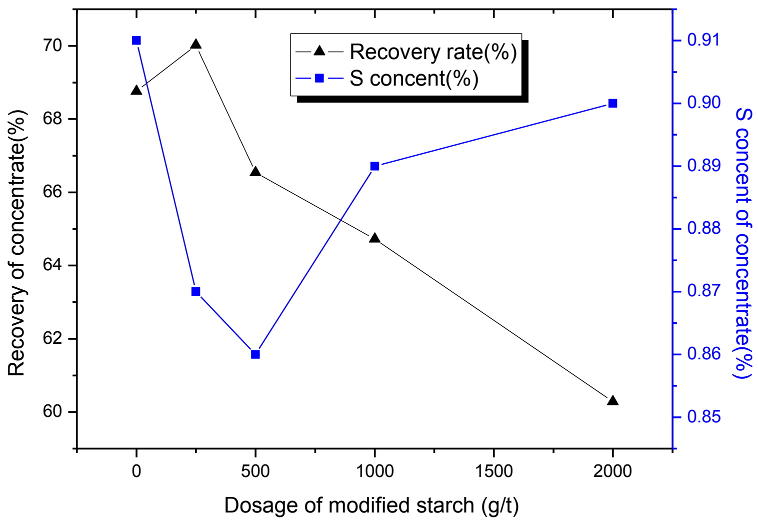

Figure 3. The effect of modified starch to the recovery rate and sulfur content of flotation concentrate.

3.3. WG

Ore 1# was taken as the subject of a study on the effect of different doses of WG on flotation desulfurization. WG is a regulator developed for acidified high-sulfur bauxites, and it can activate sulfur minerals while inhibiting aluminosilicate minerals. From the results shown in Figure 4, the addition of WG can improve aluminum concentrate yield and reduce sulfur content of the concentrate during flotation desulfurization. Under uniform dosing of agents and flotation conditions, a roughing desulfurization can reduce sulfur content of aluminum concentrates from 0.90 % to 0.29 %. When the dose of WG is 1000 – 3000 g/t of raw ore, sulfur content of the aluminum concentrate is low and stable. So for significantly acidified high-sulfur bauxite ore 1#, WG can obviously improve separation, as reflected in a decrease in sulfur in aluminum concentrate, and increased aluminum concentrate yield.

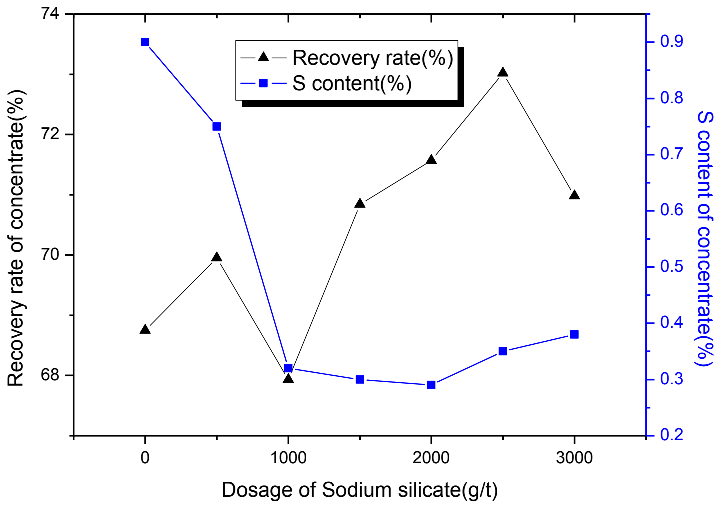

Figure 4. The effect of WG on the recovery rate and sulfur content of flotation concentrate.

WG was taken as a flotation desulfurization regulator for the other sulfur bauxites; Ore 2#, Ore 3# and Ore 4#. The flotation desulfurization tests were performed according to the flotation test flowsheet as shown in Figure 1. According to the different degree of ore acidification, WG dosage was different. For highly acidified ores, the regulator dose was increased. Doses of regulator for Ore 2#, Ore 3# and Ore 4# were 2500 g/t, 1000 g/t, 1500 g/t respectively. Control tests were performed without addition of regulator. The test results are shown in Table 4.

Table 4. Flotation desulfurization results of test bauxites using WG adjustment agent.

Test sample	WG Dose (g/t)	Products	Yield %	Grade of S %	S Recovery rate %
Ore 2#	0	Concentrate	66.07	0.15	11.66
		Sulfur tailings	33.93	2.22	88.62
		Total	100	0.85	100.00
	2500	Concentrate	86.95	0.19	21.26
		Sulfur tailings	13.05	4.69	78.74
		Total	100	0.78	100.00
Ore 3#	0	Concentrate	69.91	0.26	15.96
		Sulfur tailings	30.09	3.18	84.04
		Total	100	1.14	100.00
	1000	Concentrate	79.75	0.24	15.56
		Sulfur tailings	20.25	5.13	84.44

		Total	100	1.23	100.00
Ore 4#	0	Concentrate	68.47	0.94	9.70
		Sulfur tailings	31.53	19.01	90.30
		Total	100	6.64	100
	1500	Concentrate	71.37	0.62	6.47
		Sulfur tailings	28.63	22.35	93.53
		Total	100	6.84	100

Test results in Table 4 show that for bauxites with different sulfur content and different degrees of acidification, WG can obviously improve the separation efficiency of flotation desulfurization. Consequently, future studies should focus in detail on the optimization of flotation indices and improving the mechanism of WG on the separation. The flotation test results obviously show that WG is an effective regulator for flotation desulfurization and can not only improve inhibition of pyrite caused by acidification of ores, but also solves adverse effects on flotation, such as ore sliming, a common characteristic of oxidized ores. WG appears to have wide applicability for high-sulfur bauxite based on its impact on all of the bauxites tested.

4. Conclusion

Flotation desulfurization of high-sulfur bauxites could be the most economical and effective method for the treatment these bauxites. The special properties of high-sulfur bauxites make flotation experience from other sulfide ores difficult to apply to industrial flotation desulfurization of these materials. The application of a suitable regulator is essential to achieve efficient flotation separation. Research shows that the novel regulator WG can not only improve inhibition of pyrite caused by acidification of ores, but also solve adverse effects on flotation, such as ore sliming. Sulfur content of aluminum concentrates can be reduced significantly, and meeting the requirement for sulfur content of ores for the production of aluminium oxide. It can increase aluminum concentrate yield by 10 %, and moreover, WG has wide applicability to different kinds of high-sulfur bauxites.

5. References

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