

BX03 - The Research of Technology for Combined Desulfurization of Refractory Ultra-High Sulfur Bauxite by Gravity Flotation

Jianqiang Zhang¹, Du Wuxing² and Ma Junwei³

1. Assistant Director

2. Engineer

3. Senior engineer

Institute of Comprehensive Utilization of Resources,
Zhengzhou Non-ferrous Metal Research Institute co. LTD of CHALCO, Zhengzhou, China
Corresponding author: zyy_dw@rilm.com.cn

Abstract

China is rich in high sulfur bauxite resources, and some ultra-high sulfur bauxites with sulfur content of more than 4 % have poor washability. It is difficult to obtain qualified aluminium oxide concentrate only by a single flotation process. In view of the difficult problems in the development and utilization of refractory ultra-high sulfur bauxite in Zunyi area, this paper introduces the gravity separation method into the bauxite beneficiation process and developed the process technology of "raw ore classification / desliming - primary slime acid flotation / desulfurization - coarse particle gravity flotation and combined desulfurization". This technology is used to treat refractory ultra-high sulfur bauxite with sulfur content of 7.12 %. Finally, an aluminium oxide concentrate with yield of 80.60 % and sulfur content of 0.40 % and a sulfur concentrate with yield of 19.40 % and sulfur content of 35.94 % were obtained. The successful development of this technology provides a practical technical prototype for the development and utilization of refractory ultra-high sulfur bauxite resources in China.

Keywords: Ultra high sulfur bauxite, Gravity floating combination, Primary slime, Secondary slime, Butyl xanthate.

1. Introduction

As a supplementary resource for alumina production, high sulfur Bauxite has been used in alumina production. Some high sulfur Bauxite with sulfur content less than 1 % enters alumina production in the form of ore blending. Some enterprises in Henan, Guizhou, Chongqing, and other regions use flotation method for desulfurization and then use it for alumina production. The research on the application of high sulfur Bauxite to produce alumina has made some progress, among which flotation desulfurization is an effective and industrialized method for the comprehensive utilization of high sulfur Bauxite [1-3]. Relevant investigations found that the ultra-high sulfur Bauxite resources in Zunyi and surrounding areas with sulfur content more than 4% exceeded 8 million tons, and the mined ores were seriously oxidized and acidified due to stacking conditions. Through a series of flotation desulfurization tests on it, it was found that the ore sample undergoes flotation desulfurization under acidic conditions, which severely corrodes the equipment; flotation desulfurization under alkaline conditions can only be conducted when the amount of sodium carbonate is more than 30kg/t - raw ore to adjust the pulp pH value to 8.0~9.0. Not only is the cost of flotation reagent high, but also when the amount of pH regulator is too large, the flotation foam will become sticky and have serious inclusions, and the flotation desulfurization separation index will become worse [4-6]. To develop and utilize refractory and ultra-high sulfur Bauxite resources and solve the environmental problems caused by ore acidification, it is necessary to accelerate the development and improve the comprehensive utilization technology of refractory and ultra-high sulfur Bauxite.

2. Research on the Properties of Ore

2.1 Analysis of Mineral Sample Properties

The test sample was taken from a high-sulfur bauxite mine in Zunyi. In order to determine the type, content and mineral composition of elements in the raw ore, multi-element analysis and phase analysis were carried out. The analysis results are shown in Table 1 and Table 2.

Table 1. Multi-element analysis results of raw ore (%).

Element	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	CaO	MgO	S	LOI
Content	52.86	11.91	12.17	2.24	2.32	0.058	0.20	0.26	7.29	16.80

Table 2. The original mineral phase analysis results (%).

Mineral	Diaspore	Illite	Chlorite	Pyrite	Anatase	Rutile
Content	50.00	23.50	6.00	14.00	1.80	0.40

As can be seen from Table 1, the Al₂O₃ content in the raw ore sample is 52.86 %, the SiO₂ content is 11.91 %, and the sulfur content in the ore is 7.29 %, which belongs to a typical ultra-high sulfur bauxite. It can be seen from Table 2 that the useful, for alumina extraction, mineral in the ore is mainly diaspore, the gangue minerals are mainly silicate minerals such as illite and chlorite, and the sulfur minerals are mainly in the form of pyrite.

2.2 Ore Sample Size

In order to understand the particle size characteristics and distribution of sulfur content of raw ore and provide a basis for the control of grinding particle size in the subsequent grinding process, the particle size screening analysis of ultra-high sulfur bauxite raw ore was carried out. The analysis results are shown in Table 3.

Table 3. Particle size screening analysis results of raw ore (%).

Particle size	Yield	S grade	S distribution rate
+5mm	24.01	9.86	31.12
-5~+3mm	8.70	8.89	10.16
-3~+1mm	13.26	10.28	17.90
-1~+0.15mm	19.34	9.82	24.95
-0.15~+0.074mm	10.91	6.50	9.32
-0.074~+0.037mm	2.65	5.88	2.04
-0.037~+0.023mm	1.06	4.83	0.67
-0.023mm	20.07	1.43	3.77
Total	100.00	7.61	100.00

[where: Yield expresses the % mass of each particle size, S grade the % of S in each particle size and S distribution rate the distribution of S over each particle size]

It can be seen from Table 3 that the +5 mm and -0.023 mm grain sizes account for the largest proportion in the raw ore, while the sulfur content generally shows a decreasing trend with the

finer grain sizes. Among them, the primary slime with a content of 20.07 % -0.023 mm increases the difficulty of obtaining a target quality aluminum oxide concentrate (herein under – aluminium concentrate) by flotation desulfurization. However, the coarser grain size of +0.074 mm has more connected bodies, which requires grinding treatment to achieve monomer dissociation of useful minerals and gangue minerals. When the pulp concentration is 30 %, the pH value of the raw ore is about 3.5, and the ore acidification is more serious.

3. Results and Discussion

According to the basic properties of ultra-high sulfur bauxite ore, there is a large difference in the specific gravity between pyrite and diaspore. According to the calculation of formula 1, the selectivity coefficient of heavy separation desulfurization of refractory ultra-high sulfur bauxite is about 2, and the feasibility of heavy separation desulfurization is strong [7]. This paper adopts the combined method of gravity separation and flotation to conduct desulphurization experiment on refractory ultra-high sulfur bauxite. Some pyrite in the refractory ultra-high sulfur bauxite has coarse distribution particle size, which can be better dissociated by fine crushing or coarse grinding. The refractory ultra-high sulfur bauxite can be treated by gravity separation method to achieve effective separation of some pyrite and aluminum minerals. After gravity separation, flotation desulfurization is carried out, which can effectively eliminate the influence of sulfate ions on flotation desulfurization. Therefore, the raw ore is screened and crushed according to the process shown in Figure 1 to obtain the primary slime and the sifted ore.

$$E = (\delta_2 - \rho) / (\delta_1 - \rho) \quad (1)$$

where:

- E Reselection optionality coefficient
- δ_2 Specific gravity of heavy mineral
- δ_1 Specific gravity of light mineral
- ρ Separating medium density

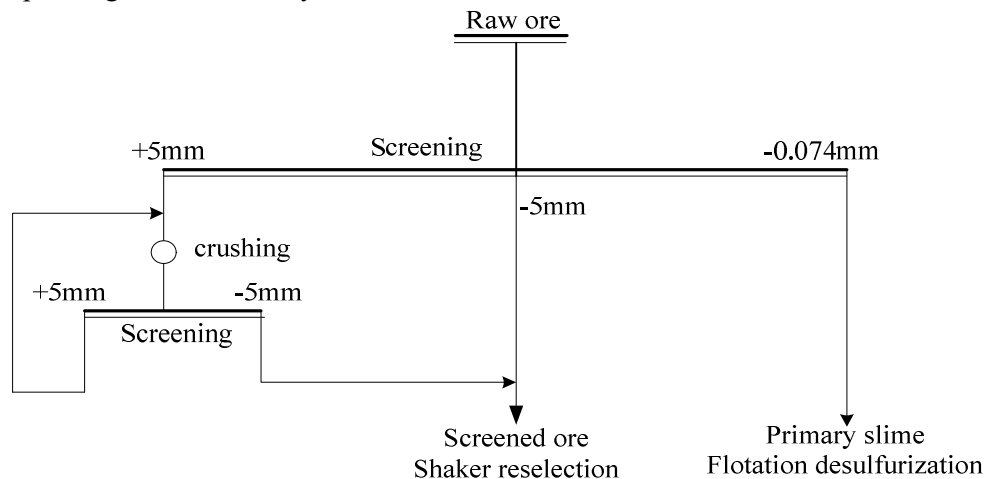


Figure 1. Screening and crushing process diagram of raw ore.

3.1 Shaker Gravity Desulfurization Test

3.1.1 Grinding Method Test

Shaker is the most widely used gravity beneficiation equipment for the separation of fine-grained materials. It has the advantages of high separation accuracy, large enrichment ratio, and can separate high-grade concentrate, middle ore and tailings products in one go [8]. According to the

conditional test, it is more favorable to adopt a two-stage shaker to improve the removal rate of sulfur minerals. The shaker gravity separation is to remove sulfur minerals in bauxite as far as possible without producing a large amount of secondary slime. Therefore, when the ore grinding size is -0.074 mm and the content is 50.00 %, two grinding methods of ball milling and rod grinding are tested according to the process shown in Figure 2. The test results are shown in Table 4.

Table 4. Test results of the same grinding method (%).

Grinding method	Product name	Yield	S grade	Sulfur removal rate	Accumulated sulfur removal rate
Ball mill	Sulfur concentrate1	8.48	43.78	39.38	39.38
	Sulfur concentrate2	1.06	40.62	4.57	43.95
	Gravity separation of aluminum concentrate	48.02	5.26	26.79	70.74
	Secondary slime	42.44	6.50	29.26	100.00
	Total	100.00	9.43	100.00	
Buffing	Sulfur concentrate1	10.28	47.45	52.87	52.87
	Sulfur concentrate2	2.07	36.87	8.27	61.15
	Gravity separation of aluminum concentrate	50.29	3.16	17.23	78.37
	Secondary slime	39.43	5.06	21.63	100.00
	Total	100.00	9.23	100.00	

According to the test results in Table 4, it can be seen that when the fineness of ore grinding is -0.074 mm and 50.00%, high-quality sulfur concentrate can be obtained from the slurry after ball milling and rod milling after shaking table gravity separation. However, the sulfur content of the gravity aluminum concentrate after rod milling is relatively low, and the cumulative removal rate of sulfur reaches 57.79 %, which is higher than 43.95 % of ball milling. At the same time, rod milling produces fewer secondary slimes. Considering that the linear contact of rod grinding media has advantages over point contact ball milling in terms of product particle size uniformity and grinding energy consumption [9]. After comprehensive consideration, it is determined to use rod grinding as the grinding method for shaking table gravity separation.

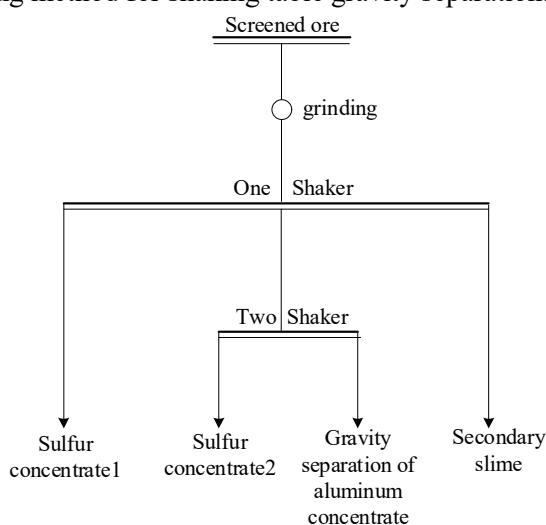


Figure 2. Flow chart of shaker reselection conditional test.

3.1.2 Grinding fineness test

Reasonable grinding fineness not only has an important impact on the process indicators of shaking table gravity separation, but also affects the subsequent flotation desulfurization of ore and the settling performance of concentrate products. To obtain better indicators for the re-selection of the shaking table, the grinding fineness test was conducted according to the process shown in Figure 2 when the first stage stroke was 9 mm, the second stage stroke was 7 mm, the bed surface slope of the first stage shaking table was 5° , and the bed surface slope of the second stage shaking table was 4° . The test results are shown in Figure 3.

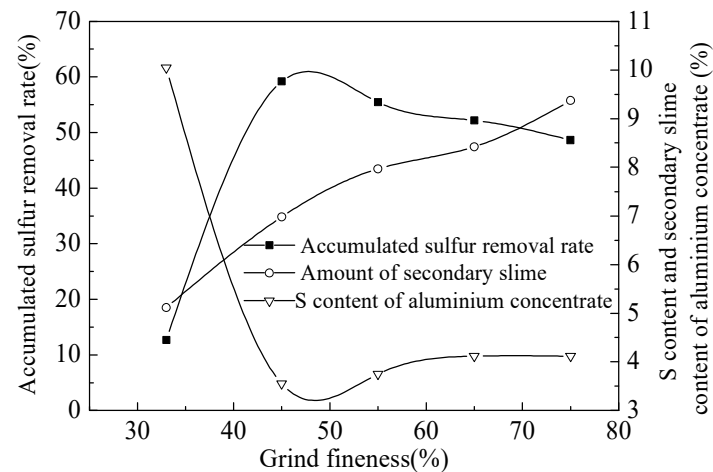


Figure 3. Test results of shaker reselection grinding fineness.

According to the experimental results in Figure 3, as the grinding fineness of the rod mill continues to increase, the sulfur removal rate of the sulfur concentrate first increases and then decreases, while the production of secondary slime continues to increase. When the grinding fineness of the rod mill is -0.074 mm and the content is 45.00 %, the separation index of the two-stage shaking table gravity desulfurization is good. At this time, the sulfur removal rate of the two-stage shaking table is 63.79 %, and the sulfur content of the aluminum concentrate is 3.16 %. Therefore, the grinding fineness of -0.074 mm is determined to be 45.00 %.

3.1.3 Shaker Slope Test

In order to achieve better desulfurization effect by shaking table gravity separation, experimental research on the optimal parameters of the first stage and second stage shaking tables was carried out. The main purpose of this study is to investigate the effect of the slope of the shaking table on the desulfurization index of the shaking table gravity separation. Under the conditions of a grinding fineness of -0.074 mm with a content of 45.00 %, a first stage stroke of 9 mm, and a second stage stroke of 7 mm, the effect of the slope of the bed surface on the separation index of the shaking table was investigated according to the process shown in Figure 2. The experimental results are shown in Figure 4.

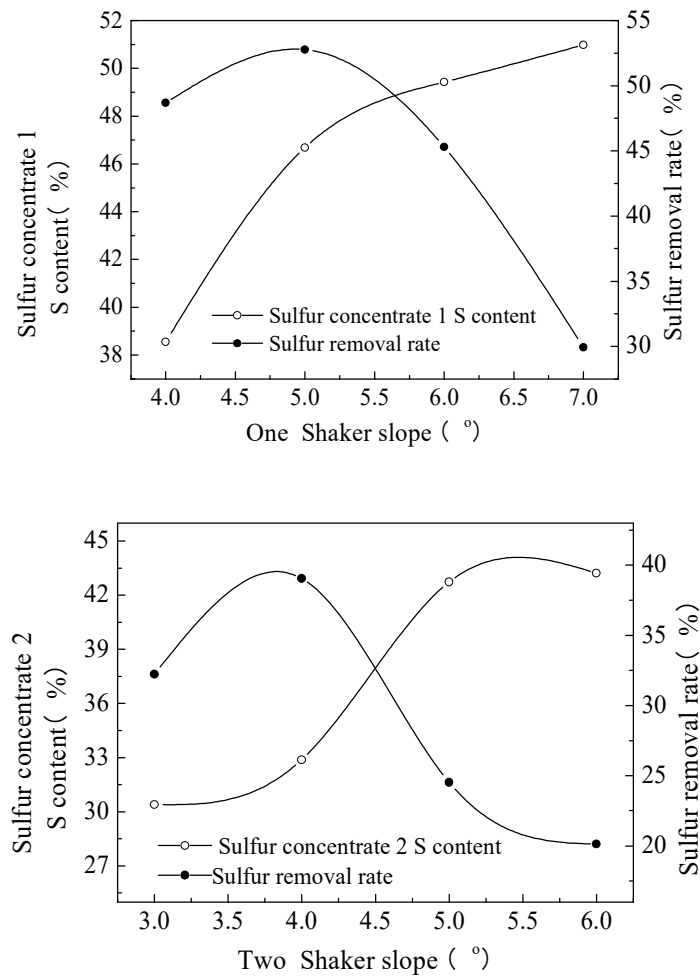


Figure 4. Result of shaking table re selection shaking table slope test.

From the experimental results in Figure 4, it can be seen that the sulfur removal rates of the first and second stage shaking tables both increase first and then decrease with the increase of bed slope. When the bed slope of the first stage shaking table is 5° and the bed slope of the second stage shaking table is 4°, the shaking table has the best desulfurization index. Therefore, it is determined that the bed slope of the first section of the shaking table is 5°, and the bed slope of the second section of the shaking table is 4°.

3.2 Primary Slime Flotation Desulfurization Test

3.2.1 Activator Dosage Test

Due to the serious acidification of raw ore, the pH value of screened primary slime is about 3.5. If the pH value is adjusted to alkaline condition, more sodium carbonate will be consumed, which will increase the cost of beneficiation, and at the same time, lead to problems such as sticky flotation foam and worsening flotation desulfurization indicators. According to relevant literature, the Surface states of Pyrite is related to the pH value of pulp. In acidic medium, the reaction of $FeS_2 \rightarrow FeS + S$ may occur on its surface, improving its own oxidation potential and thus improving its own floatability [10]. This test directly carries out flotation desulfurization under natural pH conditions, and the activator Copper (II) sulfate in the flotation system improves the oxidation potential of Pyrite surface itself and dissolves hydrophilic substances adsorbed on the

Pyrite surface, increasing the surface hydrophobicity of Pyrite to improve its floatability [11]. To obtain the best desulfurization effect of primary slime, the effect of the amount of activator Copper (II) sulfate on flotation desulfurization of primary slime was investigated according to the flow chart shown in Figure 5. The test results are shown in Figure 6.

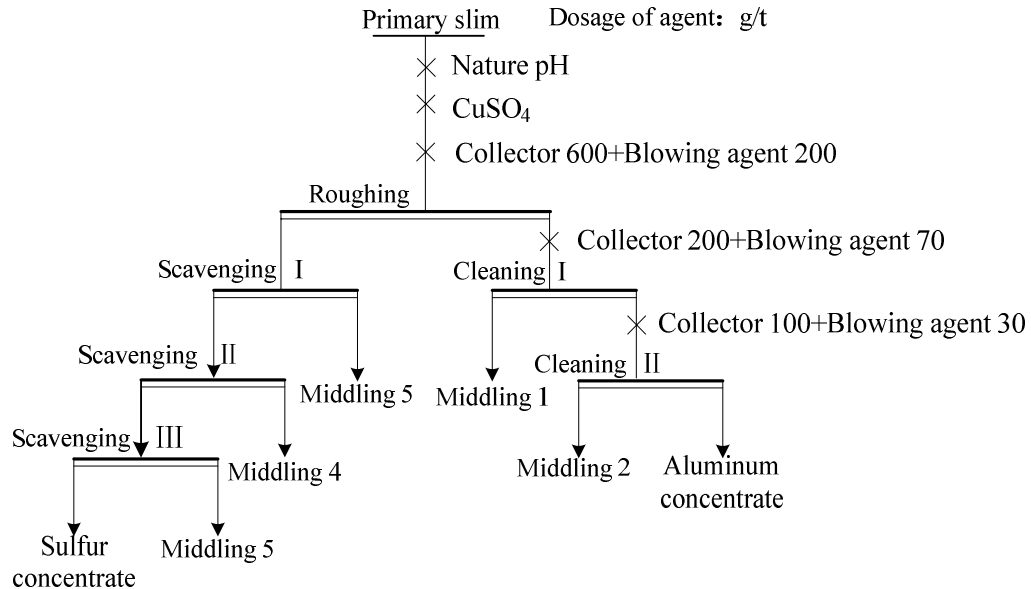


Figure 5. Flow chart of primary mud test.

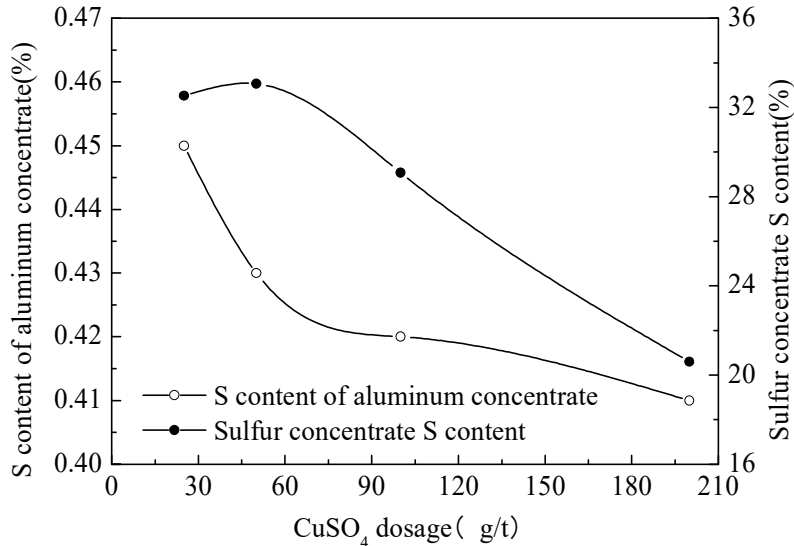


Figure 6. Experimental results of the dosage of primary ore mud activator.

As can be seen from the test results in Figure 6, the sulfur content of aluminum concentrate gradually decreases with the increasing of the amount of copper sulfate, while the sulfur content of sulfur concentrate first increases and then decreases. When the amount of copper sulfate is 50 g/t, the sulfur content of sulfur concentrate is the highest, and the sulfur content of aluminum concentrate is 0.43 %. With the continuous increase of the amount of copper sulfate, the sulfur content of aluminum concentrate decreases less. Considering the sulfur content of aluminum concentrate, sulfur concentrate and flotation cost, the dosage of primary slime activator is 50 g/t.

3.2.2 Collector Type Test

In the flotation system, the collector will adsorb the exposed Chemical bond on the surface of Pyrite chemically, to improve the floatability of Pyrite and achieve the purpose of flotation separation from aluminum minerals. The selection of collector type is crucial to the flotation desulfurization index [12]. Under the condition of natural pH value and an activator CuSO_4 dosage of 50 g/t, the experimental study on the types of primary ore mud desulfurization collectors was conducted according to the process shown in Figure 5. The experimental results are shown in Figure 7.

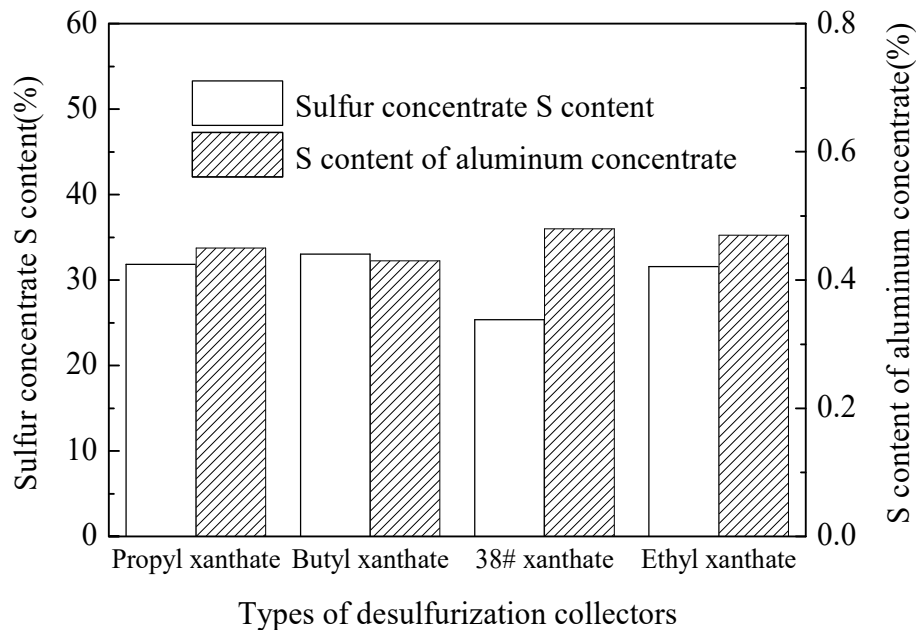


Figure 7. Test results of the types of primary ore mud collectors.

From the experimental results in Figure 7, it can be seen that in the case where the sulfur content of the sulfur concentrate is not significantly different, by comparing the sulfur content of the aluminum concentrate, it was found that butyl xanthate has better desulfurization effects than propyl xanthate, and ethyl xanthate. Therefore, butyl xanthate was used as a collector for primary ore mud desulfurization.

3.2.3 Primary Slime Closed Circuit Test

On the basis of the original ore slurry condition test, in order to investigate the reliability and feasibility of the closed-circuit process, a desulfurization closed circuit test of "one coarse, two fine, and three sweeps" of the original ore slurry was carried out according to the process shown in Figure 8. The test results are shown in Table 5.

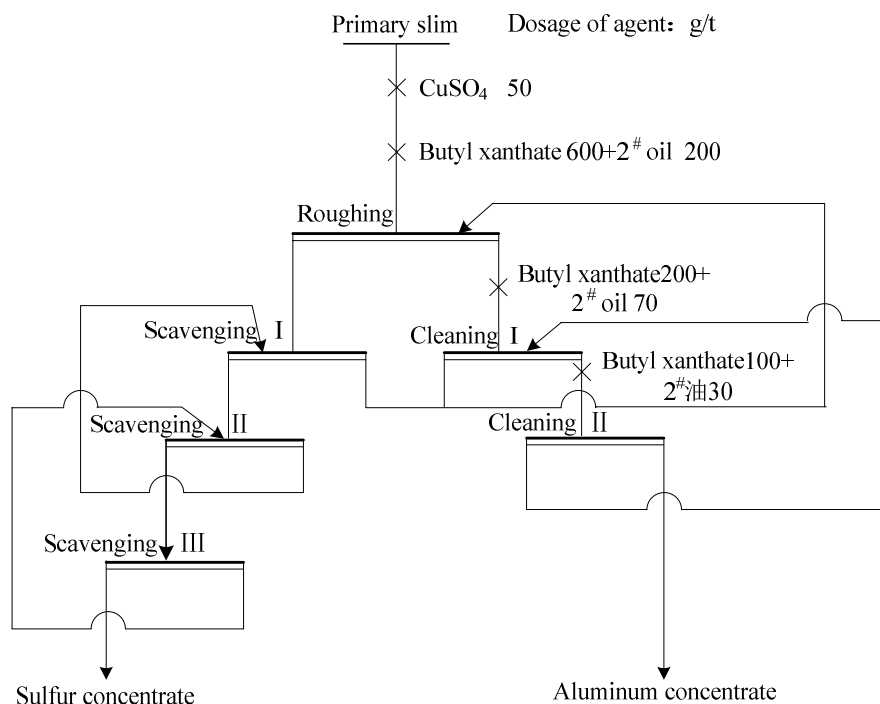


Figure 8. Flow chart of closed circuit test for primary mud.

Table 5. Closed circuit test results of primary mineral mud (%).

Product name	Yield	S grade	Sulfur removal rate
Aluminum concentrate	93.35	0.61	27.92
Sulfur concentrate	6.65	22.22	72.08
Total	100.00	2.05	100.00

According to the results of the closed-circuit flotation test of the primary ore slurry in Table 5, it can be seen that after the "one coarse, two fines, and three sweep" closed circuit flotation test, the aluminum concentrate with a yield of 93.35 % and a sulfur content of 0.61 %, as well as the sulfur concentrate with a sulfur content of 22.22 %, can be obtained.

3.3 Flotation Desulfurization Test of Gravity Separation Aluminium Concentrate

After being processed, the ore is separated by a shaking table to obtain not only sulfur concentrate, but also secondary slime with sulfur content of 5.06 % and 3.16 %, as well as gravity selected aluminum concentrate. The sulfur content of both is greater than 3 %. To obtain qualified aluminum concentrate, flotation desulfurization treatment must be carried out. The "one coarse, two fine, and three sweep" closed circuit test of gravity selected aluminum concentrate with sulfur content of 3.16 % is carried out according to the process shown in Figure 9. The test results are shown in Table 6.

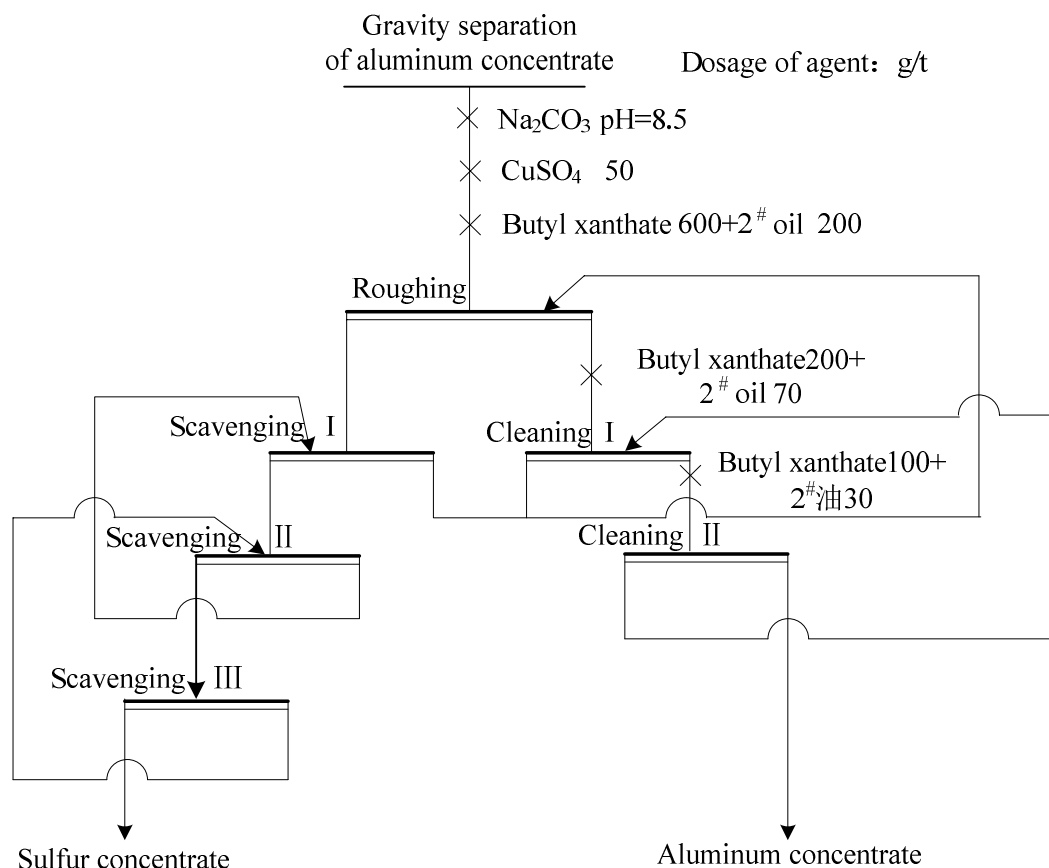


Figure 9. Flow chart of closed-circuit flotation test for aluminium concentrate.

Table 6. Closed-circuit flotation test results of aluminium concentrate (%).

Product name	Yield	S grade	Sulfur removal rate
Sulfur concentrate	9.15	32.71	94.71
Aluminum concentrate	90.85	0.18	5.29
Total	100.00	3.16	100.00

According to the closed-circuit test results in Table 6, after the closed-circuit process of "one crude, two refined and three swept", the re-sorting aluminum concentrate can obtain a sulfur concentrate with a yield of 9.15 % and a sulfur content of 32.71 % and an aluminum concentrate with a yield of 90.85 % and a sulfur content of 0.18%. The sulfur content of the aluminum concentrate is low, which can meet the raw material requirements for alumina production.

3.4 Secondary Slime Flotation Desulfurization Test

In order to obtain qualified aluminum concentrate, the desulfurization closed-circuit test of "one crude, two refined and three swept" was carried out on the secondary slime with sulfur content of 5.06 % according to the process shown in Figure 10. The test results are shown in Table 7.

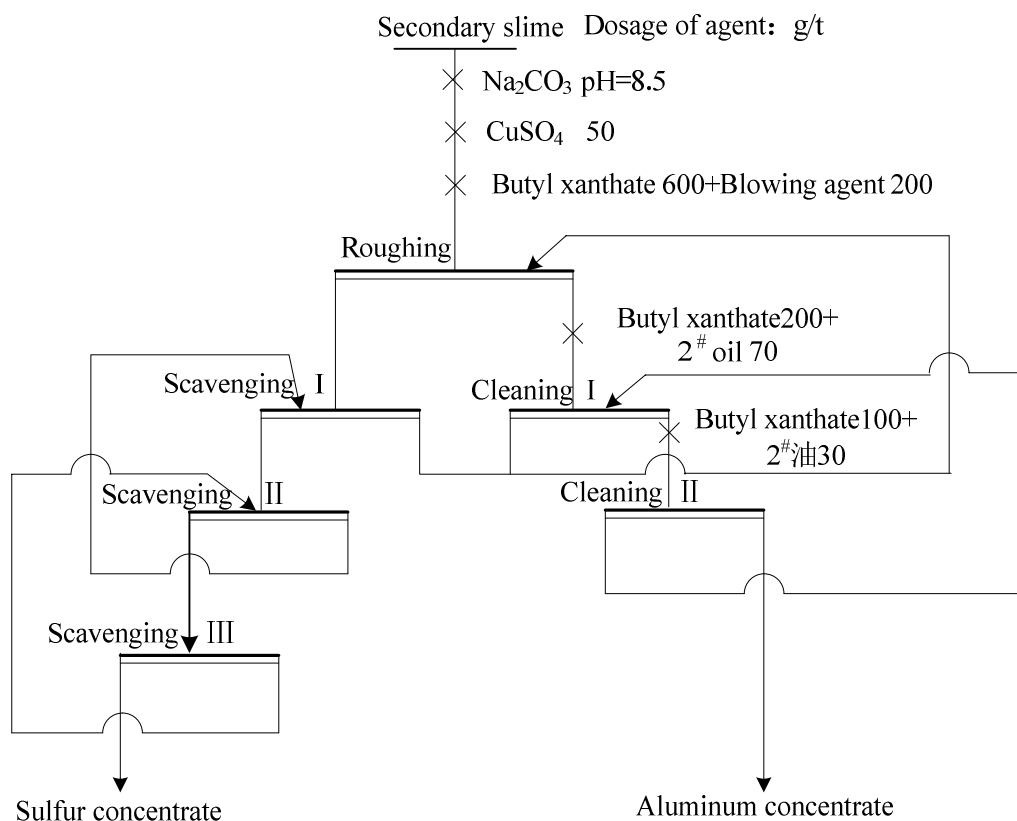


Figure 10. Flow chart of secondary mud closed-circuit test.

Table 7. Closed-Circuit Test Results of Secondary Mud (%).

Product name	Yield	S grade	Sulfur removal rate
Aluminum concentrate	83.11	0.53	8.67
Sulfur concentrate	16.89	27.36	91.33
Total	100.00	5.06	100.00

According to the results of the closed-circuit flotation test for secondary ore mud in Table 7, it can be seen that after the "one coarse, two fines, and three sweep" closed circuit flotation test, the secondary ore mud can obtain an aluminum concentrate with a yield of 83.11 %, a sulfur content of 0.53 %, and a sulfur concentrate with a sulfur content of 27.36 %.

3.5 Full process testing

Based on shaking table gravity separation, aluminum concentrate flotation, and primary ore slurry flotation condition tests, a full process closed circuit test was conducted according to Figure 11. The test results are shown in Table 8.

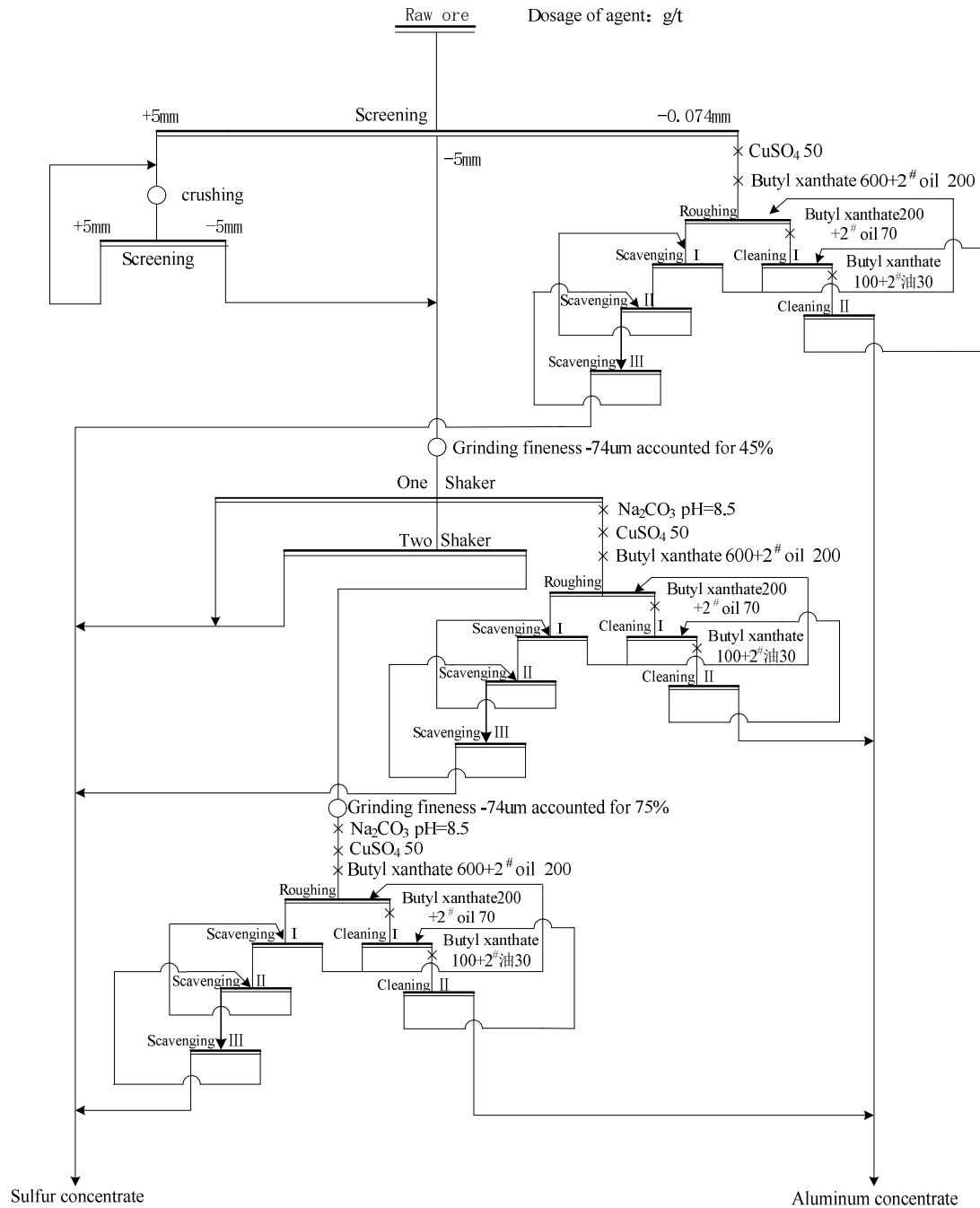


Figure 11. Full process test diagram of raw ore heavy flotation combination.

Table 8. Test results of raw ore refloating combined whole process (%).

Product name	Yield	S grade	Sulfur removal rate
Aluminum concentrate	80.60	0.40	4.42
Sulfur concentrate	19.40	35.94	95.58
Raw ore	100.00	7.29	100.00

As can be seen from the test results in Table 8, after the refractory ultra-high sulfur bauxite raw ore is treated in the whole process and the sulfur concentrate and aluminum concentrate obtained

in each process are combined, a comprehensive aluminum concentrate with a yield of 80.60 % and a sulfur content of 0.40 % and a comprehensive sulfur concentrate with a yield of 19.40 % and a sulfur content of 35.05 % can be obtained, and a good desulfurization index is obtained. The low sulfur content of aluminum concentrate can meet the raw material requirements of alumina production and realize the comprehensive utilization of ultra-high sulfur bauxite.

4. Conclusion

1. An ultra-high sulfur Bauxite raw ore in Zunyi contains 52.86 % Al_2O_3 , 11.91 % SiO_2 and 7.29 % sulfur; The useful mineral is diaspore, and the main sulfur bearing mineral is Pyrite. The dissemination relationship between Pyrite and other minerals in the ore sample is complex, and the degree of ore acidification is serious, so it is difficult to select ultra-high sulfur Bauxite.

2. For refractory ultra-high sulfur Bauxite with a sulfur content of 7.29 %, comprehensive aluminum concentrate with a yield of 80.60 % and a sulfur content of 0.40 % and comprehensive sulfur concentrate with a sulfur content of 35.94 % can be obtained through the full process closed-circuit test of "raw ore grading desliming & gravity flotation combined desulfurization". The aluminum concentrate has a low sulfur content, which can meet the requirements of raw materials for alumina production and realize the comprehensive utilization of ultra-high sulfur Bauxite. The Sulfur concentrate can be used as a raw material for producing sulfuric acid.

3. The successful development of the key process technology of heavy flotation combined desulfurization of refractory ultrahigh sulfur Bauxite can not only solve the problem of comprehensive utilization of refractory ultrahigh sulfur Bauxite, alleviate the existing ore supply crisis of alumina enterprises, but also solve the environmental problems caused by acidification of ore storage yard, with good economic and environmental benefits.

5. Acknowledgement

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6. References

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