Beneficiation research on a low grade linnaeite ore with hematite-pyrite type

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Abstract. Mineralogy and separation experiments were carried out for a low-grade linnaeite ore (0.052%), which belonged to limonite-hematite-pyrite type complex mineral. Under the grinding fineness of 80% - 0.074 mm, linnaeite concentrate which contained cobalt grade of 0.51%, recovery rate of 80.99%, sulfur grade of 23.79%, recovery of 88.03% was obtained by closed-circuit processes of one roughing, two scavenging and one cleaning, which used sulfate acid (4500 g/t) and copper sulfate (300 g/t) as activator, sodium silicate (1000 g/t) and CMC (30 g/t) as inhibitor, ethyl xanthate (100 g/t) and butyl xanthate (100 g/t) as collector, 2# oil (40 g/t) as forther in roughing, no agent in cleaing and first scavenging, used ethyl xanthate (50 g/t) and butyl xanthate (50 g/t) as collector, 2# oil (20 g/t) as forther in second scavenging.

1 Introduction

Cobalt is one of the important strategic mineral in the world, it has high temperature resistance, corrosion resistance, high strength and strong magnetic etc, which are often used to make hard heat-resistant alloy, magnetic alloy, tungsten carbide substrate or adhesive, which widely used in power battery, ceramics, electric machinery, machinery, chemicals, aviation and aerospace industries, it is of special significance in the national economy and social development. Cobalt is difficult to form an independent economic deposit, most of which is associated with copper, nickel and pyrite deposits, the reserves of land resources are relatively small.

In this paper, the hematite-pyrite type cobalt sulfide ore was studied. Although the total iron of the ore reached 23.93%, more than 90% of it was iron oxide mineral, which was difficult to be used. The grade of other metallic elements was low and had little use value, and only sulfur and cobalt had certain use value. Since cobalt mainly existing in pyrite and is replaced by isomorphism, the carrier of cobalt in recovered samples

must be pyrite, but the content of cobalt in pyrite is low and it is difficult to obtain qualified cobalt sulfide concentrate. Therefore, this paper mixed the cobalt sulfide mineral with other sulphides to obtain mixed concentrate.

2 Ore properties

2.1. Sample chemical analysis

The results of multi-element analysis and phase analysis of raw ore can be found in Table 1, Table 2.

According to Table 1 and Table 2, although the total iron of the mine reaches 23.34%, more than 90% of the ore is iron oxide mineral, which is difficult to utilize, and other metal elements are of low grade and have little value in utilization. Cobalt as an important metal element required for new energy batteries can be used as a combined recovery of cobalt sulfur concentrate without separation recovery value.

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

Component	TFe	Co	CaO	SiO ₂	Al ₂ O ₃	MgO	S
Content	23.93	0.052	3.72	36.18	7.30	2.18	2.19
Component	P	Cu	Pb	Zn	As	Au ^a	
Content	0.036	0.019	0.14	0.18	0.005	0.20	

^a unit: g/t

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Table 2. Results of iron phase analysis (%).

Mineral name	Fe ₃ O ₄	Fe ₂ O ₃	FeS ₂	Fe _n S _{n+1}	FeCO ₃	FeSiO ₃	TFe
Iron content in iron phase	0.21	19.27	2.28	0.11	0.25	1.22	23.34
Distribution	0.90	82.56	9.77	0.47	1.07	5.23	100

2.2. Ore composition and structure

The metallic minerals in the sample are mainly hematite, limonite, followed by pyrite, gangue minerals are quartz, clay minerals, carbonate minerals, a small amount of tourmaline, tululite, etc.

Cobalt-bearing minerals: cobalt-bearing minerals are small pyrite or pyroxenite inclusions (particle size < 0.02 mm) encased in pyrite, followed by isomorphism in pyrite. A few are filled in hematite fissures (which can be recovered by strengthening fine grinding).

Hematite: grey-white, it-shaped crystal; granular, a few leaf-shaped, particle size 0.001 x 0.05 mm, content 45-48%.

Limonite: grey microstrip light blue, fibrous-cryptocrystalline aggregate, aggregate size 0.005 x 0.35 mm, with brownish red internal reflection color, distributed between hematite and gangue mineral particles, metasomatic hematite, the metasomatism residual inclusions containing hematite in some aggregates contain 35-40%.

Pyrite: light copper yellow, semi-autogenous crystal, mostly pentagonal dodecahedral crystal, some of the crystals are fragmentation, particle size 0.02 x 1.2 mm, is star-shaped, pulse-like distribution, content is 8-10%.

Figure 1. Flowchart of grinding fineness test.

3 Experimental results and discussion

3.1. Grinding fineness test

Flotation tests are carried out under different fineness. The test conditions and processes are shown in Figure 1, and the test results are shown in Figure 2.

It can be seen from Figure 2 that with the increase of grinding fineness, the content of cobalt sulfide in concentrate grade increases, and the recovery rate increases at first and then decreases, and reaches the maximum when the grinding fineness reaches -0.074 mm 80%. At this time, the cobalt content of crude concentrate is 0.28% and the recovery is over 41%, which indicates that cobalt sulphide in ore is easier to be separated. At the same time, cobalt is high in sulfur, low in cobalt and low in sulfur, indicating that cobalt is mainly associated with pyrite, and that cobalt is enriched in a sulfur concentrate by strengthening recovery of sulfur.

3.2. Study on the Type and dosage of Activator

At grinding fineness of -0.074 mm 80%, the test conditions were as follows: type and dosage of activator, collector butyl xanthate 200 g/t, 2# oil 40 g/t. The test procedure is shown in Figure 1, and the test results are shown in Figure 3.

Figure 2. Results of grinding fineness test.

Figure 3. Results of activator type and dosage.

As can be seen from Figure 3, the copper sulfate is selected to be better than the alkaline medium in the acid medium, and when the amount of the sulfuric acid is 4500 g/t, the use effect of the copper sulfate mixed with different amounts is not small, and the comprehensive consideration cost is finally determined to adopt the sulfuric acid 4500 g/t and copper sulfate 300 g/t, at the time, the cobalt grade is 0.29%, the recovery rate is 43.12%.

3.3. Study on the types and dosage of Inhibitors

At grinding fineness of -0.074 mm 80%, the test conditions were as follows: the activator is sulfate acid 4500 g/t, copper sulfate 300 g/t, the type and dosage of inhibitor, the collector butyl xanthate 200 g/t, the 2# oil 40 g/t, the test flow as shown in Figure 1, the test results are shown in Figure 4.

From Figure 4, it can be seen that the best effect is obtained by using water glass CMC as inhibitor, when the dosage is 1000 g/t and 30 g/t, the cobalt grade is 0.33%, and the recovery rate is 44.12%.

Figure 4. Results of inhibitor type and dosage.

3.4. Study on the types and dosage of Collector

At the grinding fineness of -0.074 mm 80%, the test conditions were as follows: the activator is sulfate acid 4500 g/t, copper sulfate 300 g/t, the inhibitor is water

glass 1000 g/t and CMC30 g/t, the type and dosage of collector are variable, 2# oil is 40 g/t, the test procedure is shown in Figure 1, the test results are shown in Figure 5.

Figure 5. Results of collector type and dosage.

From Figure 5, it can be seen that the best effect is obtained by using ethyl xanthate butyl xanthate as collector, and the cobalt grade is 0.32% and the recovery rate is 44.36%.

3.5. Scavenging test

At grinding fineness of -0.074 mm 80%, the test conditions were as follows: the activator is sulfate acid 4500 g/t and copper sulfate 300 g/t, the inhibitor is water glass 1000 g/t and CMC 300 g/t, the collector ethyl xanthate

100 g/t and butyl xanthate are 100g/t, the 2# oil is 40 g/t, two scavenging operations (no chemicals added) are carried out, and the test results are shown in Table 3.

As can be seen from table 3, the cumulative recovery rate of the three concentrates reached 84.42% with the total flotation time of 13 min after two scavenging, indicating that the sulfur concentrate is basically recovered by two scavenging, so the two scavenging are finally determined.

Table 3. Results of scavenging times.

Produce name	Yield	Grade		Recovery	
		Co	S	Co	S
Concentration 1	6.97	0.340	17.01	45.57	52.03
Concentration 2	6.69	0.196	9.88	25.22	28.99
Concentration 3	5.32	0.133	3.72	13.63	8.68
Taling	81.02	0.010	0.29	15.58	10.30
Ore	100.00	0.052	2.28	100.00	100.00

3.6. Cleaning test

At grinding fineness of -0.074 mm 80%, the test conditions were as follows: the activator is sulfate acid 4500 g/t and copper sulfate 300 g/t, the inhibitor is water glass

1000 g/t and CMC 30 g/t, the collector is ethyl xanthate 100g/t and butyl xanthate 100 g/t, and the 2# oil is 40 g/g. two cleaning operations (no chemicals added) are carried out, and the test results are shown in Table 4.

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Table 4. Results of cleaning times.

Produce name	Yield	Grade		Recovery	
		Co	S	Co	S
Concentration	3.46	0.60	28.89	39.92	43.84
Middling 1	1.12	0.10	7.62	2.15	3.74
Middling 2	2.30	0.054	4.18	2.41	4.22
Tailing	93.12	0.031	1.18	55.51	48.19
Ore	100.00	0.052	2.28	100.00	100.00

Table 4 shows that after only one cleaning operation, the combined grade of concentrate and ore one is 0.48%, which basically meets the quality requirements of the first grade products of cobalt sulphide concentrate ($\text{Co} \geq 0.45\%$, $\text{S} \geq 27\%$). Considering the selection cost and

process flow, we decide to adopt only one cleaning operation.

3.7 Closed circuit test

The closed-circuit test results are shown in Table 5.

Table 5. Results of closed-circuit

Produce name	Yield	Grade		Recovery	
		Co	S	Co	S
Concentration	8.40	0.51	23.79	80.99	88.03
Tailing	91.6	0.011	0.30	19.01	11.97
Ore	100.00	0.053	2.27	100.00	100.00

As can be seen from Table 5, through the closed circuit process of one roughing, one cleaning and two scavengings, the grinding fineness of -0.074 mm 80%, the activated agent of crude separation is 300 g/t copper sulfate, and the inhibitor is water glass 1000 g/t and CMC 30 g/t, the collector ethyl xanthate 100 g/t and butyl xanthate 100 g/t, 2# oil 40 g/t, cleaning, scavenging one blank flotation, scavenging two using collector ethyl xanthate 50 g/t and butyl xanthate 50 g/t, 2# oil 20 g/t, a better index of cobalt content 0.51%, recovery 80.99%, sulfur 23.79% and recovery 88.03% are obtained.

(50 g/t) as collector, 2# oil (20 g/t) as further in second scavenging.

Acknowledgements

We gratefully acknowledge the financial assistance of Yunnan Provincial Education Department Project (No: 2019J0738), National natural science foundation (No: 51964044), Yunnan Local Colleges Applied Basic Research Projects (No: 2018FH001-051).

4 Conclusions

(1) The main mineral composition of the sample is hematite-pyrite type mineral, hematite, pyrite is other-shaped granular structure, implicit crystal and leaf-like structure: pyrite is distributed in limonite or hematite aggregate as metasomatism residue. The ore structure mainly has strip structure, breccia, and disseminated structure. Although the total iron of this mine is 23.93%, more than 90% are iron oxide minerals, which are difficult to use. Cobalt as the important metal element needed for new energy batteries co-exists with pyrite can be recovered by mixing with other sulphide ores. The grade of other metal elements is lower than that of other metal elements.

(2) Under the grinding fineness of -0.074 mm 80%, linnaeite concentrate which contained cobalt grade of 0.51%, recovery rate of 80.99%, sulfur grade of 23.79%, recovery of 88.03% was obtained by closed-circuit processes of one roughing, two scavenging and one cleaning, which used sulfate acie (4500 g/t) and copper sulfate (300 g/t) as activator, sodium silicate (1000 g/t) and CMC (30 g/t) as inhibitor, ethyl xanthate (100 g/t) and butyl xanthate (100 g/t) as collector, 2# oil (40 g/t) as further in roughing, no agent in cleaing and first scavenging, used ethyl xanthate (50 g/t) and butyl xanthate

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