WU QIANG, XIAO JUNHUI
ZHANG YUSHU, CHEN CHAO
CHEN ZHIQIANG, DING WEI
LIANG GUANJIE
and
HUANG WENXIAO

Phase evolution and cobalt and sulfur content of complex cobalt-sulfur concentrate during oxidative roasting

Oxidation roasting is the most effective method for treating sulfur in pyrite, Study the calcination temperature and time on cobalt and sulfur during oxidative roasting. After oxidizing roasting of a cobalt ore concentrate in a concentrator in Sichuan, the sulfur in the sample was basically removed, so that the cobalt grade increased from about 6% to about 9%. The results show that the desulfurization effect is best at 900°C and calcination for 2.5 hours. The grade of cobalt is also increased by about 50% compared to that before roasting. In the phase transformation analysis of the specific calcination process, it is concluded that from the beginning of 500°C, pyrrhotite, magnetite and hematite are formed in sequence, and the talc gradually disappears during the temperature increase, and the magnesium iron tip is formed in parallel. The spar, a small amount of chromium forms a zinc spinel in the form of a lattice substitution, and a part of the cobalt-magnesium element is lattice-substituted into the chromite to form cobalt magnesium chromite ore and cobalt chromite. After 600°C, there is a significant change in the spectrum. At this time, some hematite, maghemite and magnetite are formed. Until the 900°C map tends to be stable, pyrite and pyrite (FeS$_2$) are largely converted into hematite and maghemite (Fe$_2$O$_3$), but some magnetite (Fe$_3$O$_4$) still exists.

Messrs. Wu Qiang, Xiao Junhui, Chen Zhiqiang Ding Wei, School of Environment and Resource of Southwest University of Science and Technology, Mianyang 621010, China; Xiao Junhui, Sichuan Engineering Lab of Non-metallic Mineral Powder Modification and High-value Utilization (Southwest University of Science and Technology), Mianyang 621010, China; Sichuan Key Laboratory for Comprehensive Utilization of Vanadium and Titanium Resources (Panzhihua Institute of Vanadium and Titanium) Panzhihua 617000, Sichuan..Institute of Multipurpose Utilization of Mineral Resources, Chengdu 610041, China; The State Key Laboratory of Refractories and Metallurgy (WuHan University of science and technology), Wuhan, 030192 China; Key Laboratory of Radioactive and Rare Scattered Minerals, Ministry of land and Resources, Shaoguan 512026, China); Zhang Yushu and Chen Chao, Institute of Multipurpose Utilization of Mineral Resources, Chengdu 610041, China; and Liang Guanjie and Huang Wenxiao, Key Laboratory of Radioactive and Rare Scattered Minerals, Ministry of land and Resources, Shaoguan 512026, China). Corresponding author: xiaojunhui33@163.com

1. Introduction

As an important strategic material, cobalt plays a pivotal role in the development of the country's economy [1]. It is a key raw material for producing various high temperature and corrosion resistant alloys, hard alloys, super-hard materials, magnetic materials, catalysts and other materials [2]. It is widely used in aviation, aerospace, electrical, mechanical manufacturing, chemical, ceramics and other industries [3, 4]. Cobalt-sulfur concentrate is the most important raw material for cobalt extraction in the industry [5, 6]. The cobalt-sulfur concentrate mainly contains pyrite, pyrrhotite, and some gangue minerals such as talc, quartz and chlorite. Pyrite is the most important mineral of sulfur in cobalt-sulfur concentrates [7, 8]. Jorgensen and Moyle (1982) studied the oxidation of pyrite in the air [9]. They found that hematite was directly formed on the surface of pyrite particles at 404°C, (α-Fe$_2$O$_3$), when the temperature rises, pyrrhotite occurs in the middle of pyrite and hematite, which continues to be oxidized and eventually converted to hematite [9].

In the process of extracting cobalt from cobalt-sulphur concentrate, it is sometimes necessary to oxidize or sulfate sulphides to remove part or all of sulphur. This process is often carried out as a separate oxidation roasting process in metallurgy. Therefore, it is of practical significance to clarify the transformation process of vulcanization drill in oxidation roasting. During the calcination of sulfides, the interaction between metal sulfides and oxygen in the gas phase, the removal of part or all of sulfur, is related to the calcination conditions. The composition of the final product of roasting depends on temperature, partial pressure of oxygen (concentration), roasting time and the nature of sulfide itself. Theory and practice show that temperature is the key factor to determine the reaction, and the concentration of oxygen is also an important link to affect the direction and speed of reaction.

2. Sample properties and research methods

2.1 SAMPLE PROPERTIES

This test sample is from the cobalt-sulfur concentrate with an average cobalt content of about 0.6% in the production process of a mineral processing plant of a mining and metallurgical company in Sichuan. The sample mainly contains sulfide ore, pyrite, pyrrhotite, ilmenite. The main gangue minerals are talc, chlorite, olivine, serpentine, cobalt-containing minerals such as cobalt oxide, cobalt sulfide and a small amount. The sulfur in the sample is mostly present in pyrite and cobalt sulfide, and the sulfur in the sample can be effectively removed by means of oxidative baking [10-12].

The laser particle size analysis of the sample, D10: 9.81um, D50: 46.83um, D90: 125.2um particle size analysis results show that about 75% of the sample has a particle size of less than 180 mesh. The main chemical composition analysis of the sample is shown in Table 1, the original ore particle size composition analysis is shown in Fig.1 and the original ore XRD pattern is shown in Fig.2.

2.2 RESEARCH METHODS

Since the cobalt-sulfur concentrate contains a part of pyrite, the pyrrhotite can effectively remove the sulfur in the sample by the oxidative roasting method [13, 14]. The roasting of the sample is carried out in a tubular electric furnace. 10g of cobalt-sulfur concentrate is placed in the corundum boat, and then the corundum boat is placed in the center of the tubular electric furnace at the specified temperature. After a specified time, it is taken out, cooled to room temperature, and weighed. The desulfurization rate of the samples was analyzed
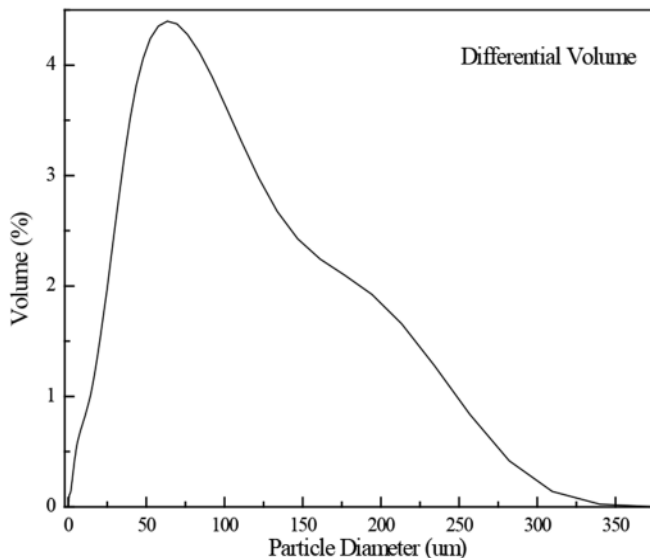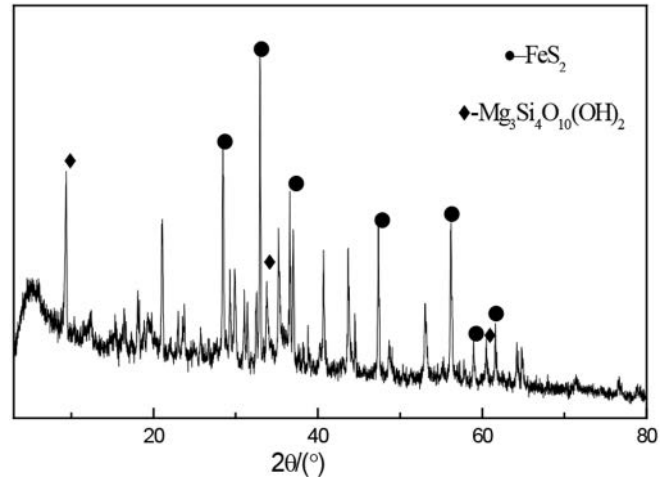

Fig.2. XRD pattern of theraw ore

at different temperature times to explore the effect of cobalt on the roasting conditions.

3. Results and analysis

3.1 INFLUENCE OF OXIDATIVE ROASTING TEMPERATURE

In the process of oxidative roasting, temperature is the most important influencing factor [15]. The temperature directly affects the progress of the calcination reaction and the reaction rate. If the temperature is too low, the reaction does not proceed or the reaction rate is slow, which is not conducive to production and the temperature is too high [16]. The equipment requirements are also improved accordingly. Between temperature, equipment and reaction rate requires research on the temperature and explore a suitable temperature condition, which has positive significance for actual production.

Fig.3a is an XRD diffraction pattern of cobalt-sulfur concentrate calcined at different temperatures for 0.5 hours. At 400°C, there are diffraction peaks of talc and pyrite. As the calcination temperature increases, the characteristic peak of talc gradually disappears. At 500°C, the characteristic peak of weaker hematite appeared, but at this time, the characteristic peak of hematite appeared at 600°C, and the diffraction peak of hematite increased with the further increase of temperature.

Fig.3-b is an XRD diffraction pattern at temperature conditions for 1 hour. At 400°C, there are still obvious diffraction peaks of talc and pyrite in the sample. When the temperature rises to 500°C, talc and the characteristic peak of pyrite still exists. At this time, some diffraction peaks of hematite have appeared. After 600°C, the XRD pattern mainly shows the diffraction peak of hematite, and the diffraction peak of talc almost disappears at 900°C.

Fig.1 Laser particle size distribution of sulphur-cobalt concentrate

TABLE 1: MAIN CHEMICAL COMPONENTS OF THE SAMPLE (W/%)

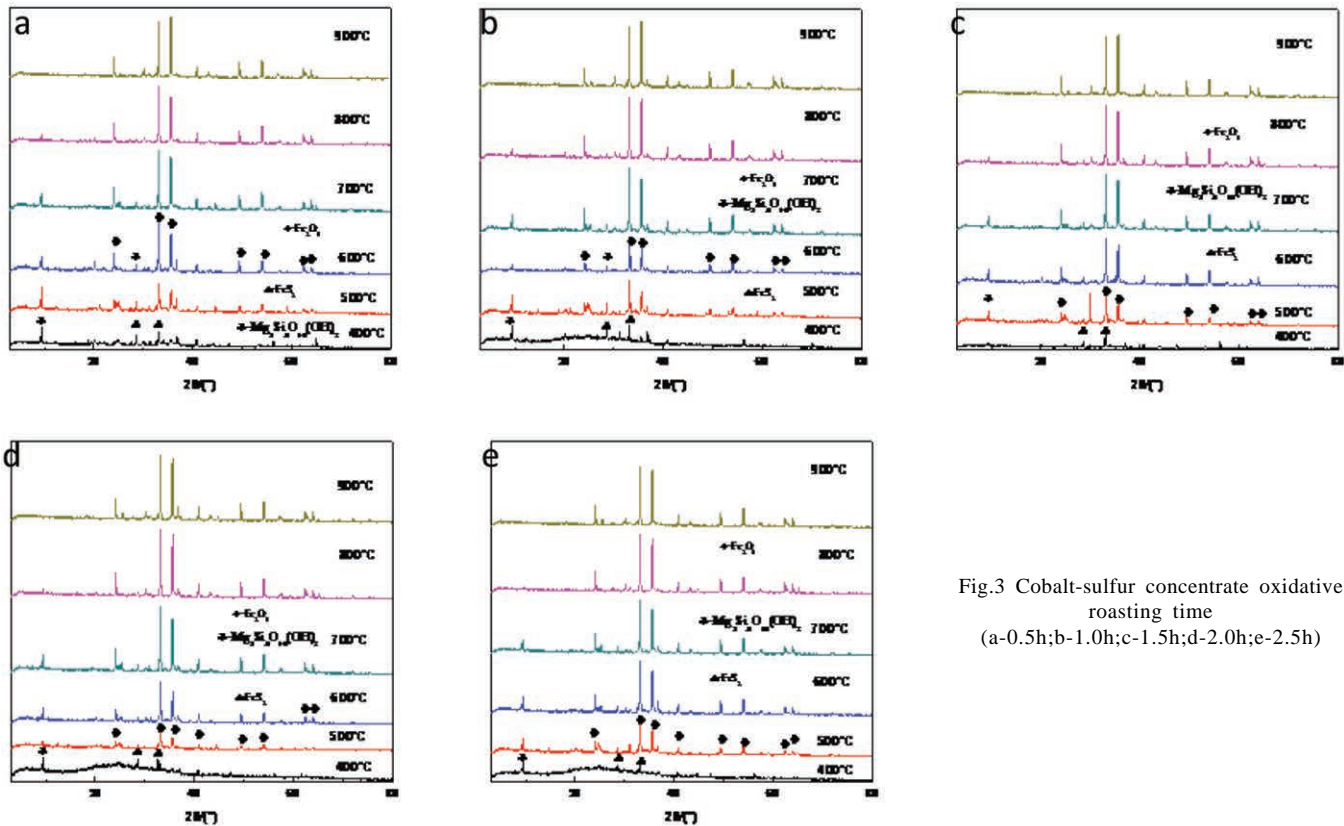| Fe	S	Cu	Co	Ni	Zn	MgO	CaO	SiO_2	Al_2O_3
33.92	25.85	0.79	0.67	1.79	0.18	5.61	0.83	7.68	4.14

Fig.3 Cobalt-sulfur concentrate oxidative roasting time
(a-0.5h;b-1.0h;c-1.5h;d-2.0h;e-2.5h)

Fig.3c is an XRD pattern of cobalt-sulfur concentrate calcined at different temperatures for 1.5 hours. At 400°C, the diffraction peak of pyrite is mainly exhibited. After 500°C, the characteristic peak of hematite begins to appear. The temperature rises further and the characteristic peak intensity increases continuously, indicating that the rate of pyrite conversion to hematite is faster, and the hematite content also increases sharply. Under various temperature conditions, the characteristic peaks of talc are continuously weakened at 900°C. It completely disappears at 900°C.

Fig.3d is roasting for two hours. At 400°C, there are only two major diffraction peaks of talc and pyrite. At 500°C, the characteristic peak of hematite appears. The other peaks disappeared as the temperature increased, and finally the diffraction peak of hematite remained. At 800°C, there is still a small amount of talc present and not completely disappeared.

Analysis of Fig.3e shows thatat 400°C-500°C, the change trend is not large, mainly the diffraction peaks of pyrite and pyrrhotite, and the map is obvious after 500°C. The change shows that there is a significant phase transition process under this temperature condition, and the characteristic peaks of hematite and maghemite appear. The diffraction peak of magnetite appears at 600°C, which is known to be in the process of oxidative roasting. The pyrite mainly transforms into hematite and maghemite, and a small part of it becomes magnetite. When it continues to rise to 700°C, the talc phase becomes magnesia spinel, and a small amount of zinc the form

of lattice substitution forms a zinc spinel. At 900°C, the spectrum tends to be stable, at which time the pyrite is basically converted to hematite, but there is still some partially incompletely oxidized magnetite.

3.2 INFLUENCE OF OXIDATION ROASTING TIME

In the oxidative roasting process, time is a key influencing factor. When the time is too short, the reaction is incomplete during the roasting process [17]. Some samples are mixed with the calcined sample, which makes it difficult to further sort the subsequent tests. However, the roasting time is too long, although the reaction is complete, it will cause waste of energy consumption and increase the cost of roasting. It can be seen that the investigation of the time in the roasting of cobalt-sulfur concentrate is particularly important.

Fig.4.(a-f) are XRD patterns of different calcination time of cobalt-sulfur concentrate under fixed single temperature conditions. It can be seen that under the same temperature condition, the increase of roasting duration has little effect on the change trend of the map, and the spectrum remains basically the same. There is a significant change in the temperature increase. From 400°C to 500°C, the diffraction peaks of pyrite, pyrrhotite and talc are mainly present in the spectrum. At 600°C, the diffraction peak of talc is weakened, and the diffraction peaks of hematite, maghemite, iron-magnesium spinel and magnetite appear, and a small amount of cobalt enters the chromite ore in the form of lattice substitution. When the temperature reaches 900°C, the
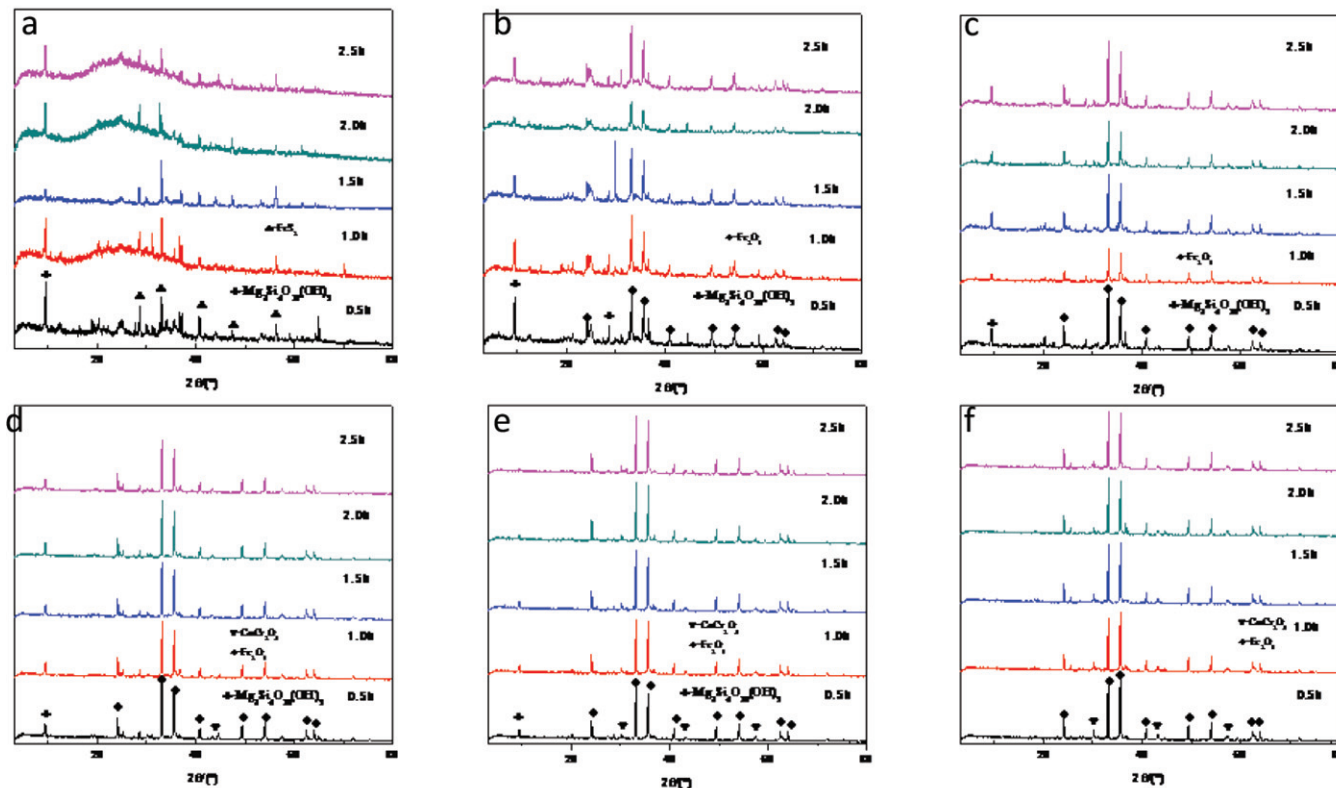
Fig.4. Cobalt sulfur concentrate oxidized roasting temperature
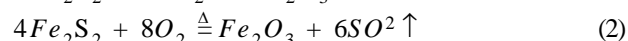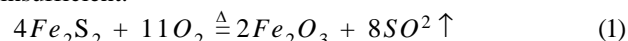(a-400°C, b-500°C, c-600°C, d-700°C, e-800°C, f-900°C)

diffraction peaks of talc and pyrite disappear, and the phase becomes hematite and erythromagnetite and a small amount of magnetite which is not completely oxidized. The talc forms iron-magnesium spinel, and cobalt is depositedin chromite.

3.3 Effect of calcination on sulfur reduction

Sulfur is a harmful element in metal smelting, which seriously affects the quality of metal finished products [18]. Studying the desulfurization conditions under different conditions has an effect on practical applications. Experimental conditions: The calcination time was 0.5; 1; 1.5; 2; 2.5 hours, and the calcination temperature was from 400°C to 900°C.

It can be seen from Fig.5 (a-e) that the calcination time is the same, the sulfur content gradually decreases with the increase of temperature, and the desulfurization rate exceeds 80% in the range of 400°C - 600°C, and the sulfur content further increases from 700°C to 900°C. The reduction of the desulfurization rate is slowed down, and the sulfur in the sample is substantially completely removed at 900°C, and the desulfurization rate is close to 100%. Under different calcination times, the overall desulfurization trend is generally the same. With the increase of roasting time, the desulfurization situation does not change much, indicating that temperature is the most important factor in desulfurization, and roasting time has certain influence on

desulfurization but not the most important factor. The following chemical reactions occur in pyrite at high temperatures. Pyrite is converted to hematite in the presence of sufficient oxygen, and is oxidized to magnetite when oxygen is insufficient.

$$4Fe_2S_2 + 11O_2 \stackrel{\Delta}{=} 2Fe_2O_3 + 8SO_2 \uparrow \qquad (1)$$

$$4Fe_2S_2 + 8O_2 \stackrel{\Delta}{=} Fe_2O_3 + 6SO_2 \uparrow \qquad (2)$$

3.4 Effect of calcination temperature on cobalt content

It can be seen from Fig.6 that as the temperature increases, the cobalt mass fraction increases continuously, and the cobalt content increases rapidly at 400°C - 500°C. At 700°C - 900°C, the growth rate of cobalt becomes slower, 800°C- At 900°C, only weak changes tend to be stable. When the cobalt content is almost unchanged at 400°C, the loss rate at this time is also basically zero, and the change trend of the sample burnout rate is positively correlated to the change trend of the cobalt mass fraction.

4. Discussion

(1) When the calcination temperature is 600°C, the XRD pattern changes significantly, indicating that the pyrite has undergone obvious material transformation. According to the map analysis, at 600°C, pyrite and pyrrhotite have some parts. It has been transformed into hematite and maghemite, and as the temperature is further increased, the intensity of the
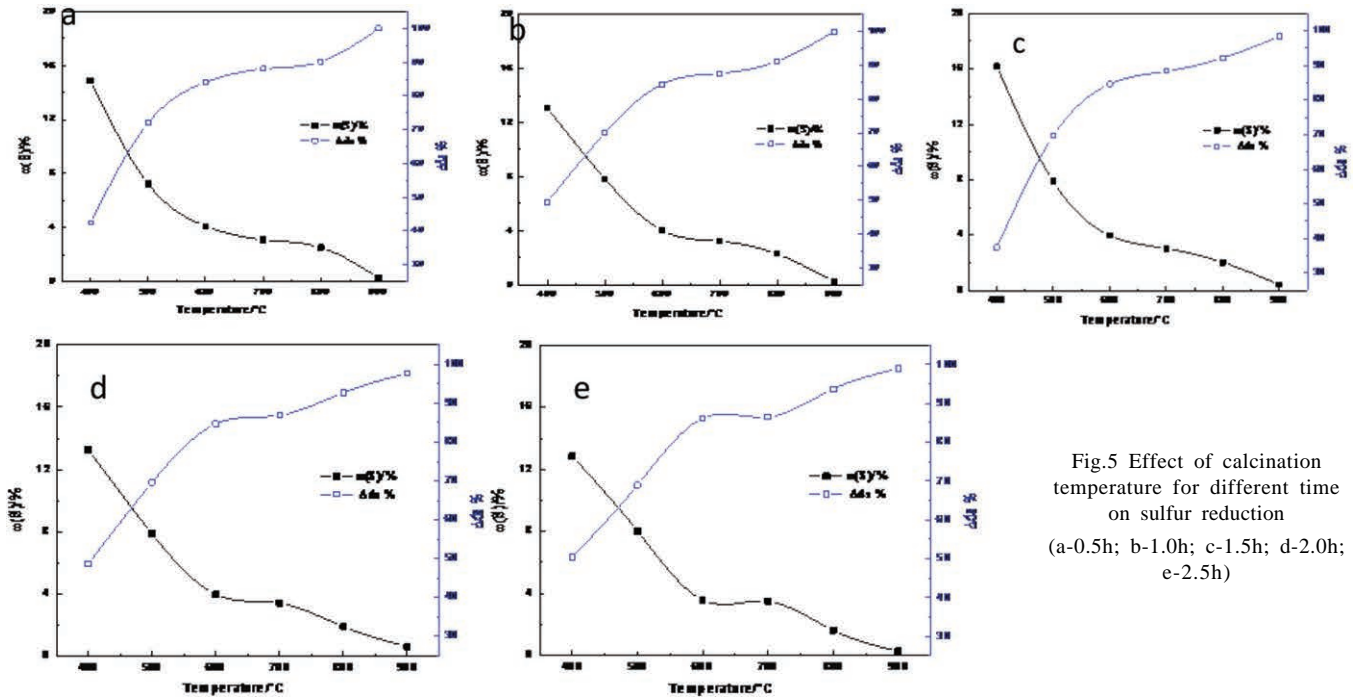
Fig.5 Effect of calcination temperature for different time on sulfur reduction
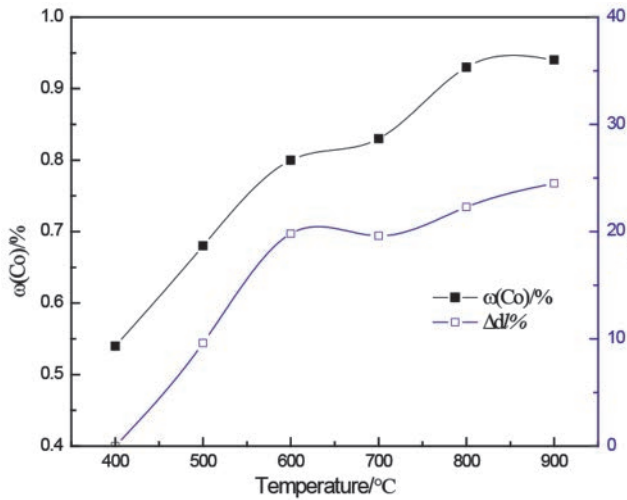
(a-0.5h; b-1.0h; c-1.5h; d-2.0h; e-2.5h)

Fig.6 Effect of calcination temperature on cobalt content

iron and magnesium elements are lattice-substituted into chromite ore to form iron-magnesium chromite ore and cobalt-chromium iron ore.

(3) At 400°C-600°C, the desulfurization rate is faster in the oxidizing roasting process. The desulfurization rate is slowed down at 700°C-900°C, but some sulfur is still detached. At 900°C, the sulfur is basically removed completely after 2.5 hours of roasting.

(4) During the calcination process from 400°C to 900°C, the sulfur in the pyrite and a small amount of CoS are oxidized to SO_2, so that the loss on ignition increases, and the grade of cobalt increases significantly from 0.6% due to the reduction of sulfur content. The left and right increased to about 0.95%.

(5) SEM analysis of raw ore and calcined samples, the original ore as a whole is in the form of a block. Some fine

diffraction peak of hematite is more obvious, and the rate of formation of hematite is also increasing.

(2) Before 500°C, the XRD pattern remained basically unchanged, indicating that pyrite (FeS_2) at this temperature, the phase transformation process is slow, and the new phase formation is less. There is a significant change after 600°C, indicating that a large number of new phases are formed, mainly hematite (Fe_2O_3), and some cobalt,
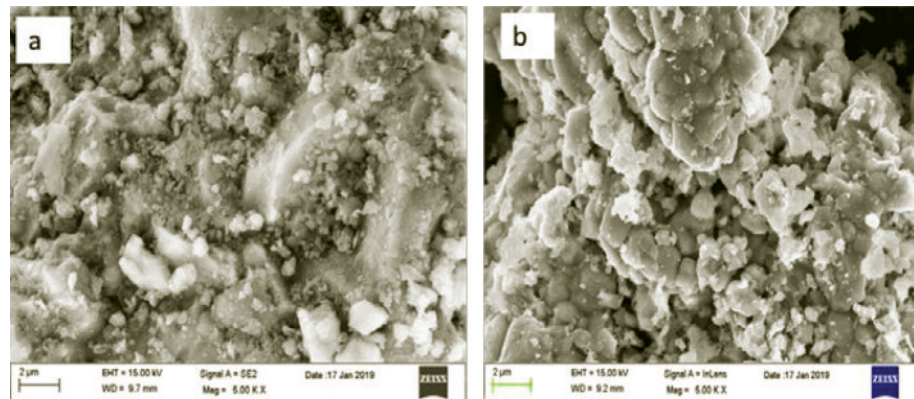

Fig.7 SEM analysis of the spectrum (a-Raw ore, b-Roastingsample)

TABLE 2 ENERGY SPECTRUM MICROANALYSIS OF THE RAW ORE

Element	O	Mg	Si	S	Fe	Co	Ni
Weight%	12.36	1.17	0.73	6.05	5.36	1.13	1.96
Atomic%	65.25	4.06	2.19	15.95	8.11	1.61	2.83

TABLE 3 RESULTS OF ENERGY SPECTRUM MICROANALYSIS OF THE ROASTING SAMPLE

Element	O	Mg	Si	Fe	Co	Ni
Weight%	7.79	0.58	0.36	17.32	0.84	1.03
Atomic%	56.25	2.77	1.47	35.83	1.65	2.02
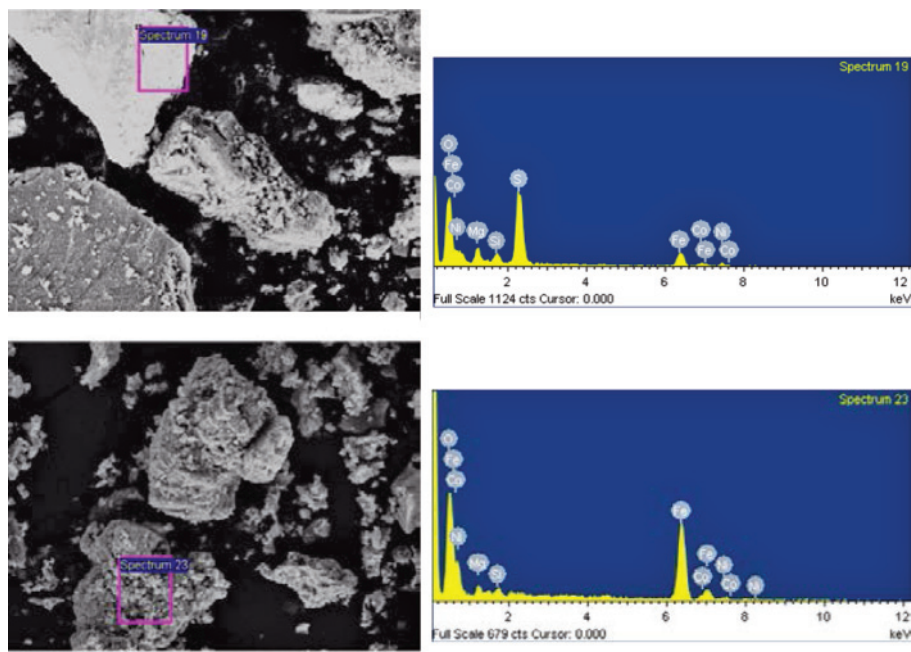
Fig.8 SEM-EDS analysis results of ore and roasting 2.5h sample

particles exist as shown in Fig.7-a. After oxidative roasting, the whole grain appears as shown in Fig.7-b. There are obvious differences in morphology. The part of pyrite in the ore is mainly characterized by pyrite. After 2.5 hours of calcination, it mainly appears as hemispherical spherical morphology. The elemental analysis results of the ore micro-regions are shown in Table 2. The results of the elemental analysis of the calcined micro-regions are shown in Table 3. The ore contains some sulfur and a small amount of cobalt, and the sulfur is substantially completely removed after calcination.

5. Conclusions

Oxidation roasting has a very good effect on desulfurization and phase transformation of cobalt-sulphur concentrate. At high temperature, the removal of sulphur is almost complete. Pyrite reacts with oxygen at high temperature. There are different change processes under different temperature conditions. This phase transformation process is analyzed. In the range of 400°C-600°C, the desulfurization rate exceeds 80%. At 700°C - 900°C, the sulfur content is further reduced, the desulfurization rate is slowed down, and the basic desulfurization is complete at 900°C. Starting from a certain temperature, there are pyrrhotite, magnetite and hematite in sequence. The talc gradually disappears in the process of increasing temperature, forming magnesium iron spinel in parallel, and a small amount of chromium is formed by lattice replacement. Zinc spinel. After 600°C, there is a significant change in the spectrum. At this time, some hematite, maghemite and magnetite are formed. Part of the cobalt and magnesium elements are lattice-substituted into chromite ore to form cobalt-magnesium chromite ore and cobalt-chromite. Until the 900°C map tends to be stable, pyrite and pyrite (FeS_2) are largely converted into hematite and maghemite (Fe_2O_3), but some magnetite (Fe_3O_4) still exists. The results of the morphology analysis also confirmed that the pyrite roasting was mainly converted to hematite, and the elemental analysis of the microdomain also confirmed that roasting had a significant effect on desulfurization.

References

1. Elmawardy, R., et al., (2011): Does nickel allergy play a role in the development of in-stent restenosis? *Eur Rev Med Pharmacol Sci.,* 15(11): p. 1235-1240.

2. Verma, S.K., D.P. Whittle, and J. Stringer, (1972): Sulphidation of cobalt-based alloys*. *Corrosion Science,* 12(7): p. 545, IN1, 553-552, IN12, 554.

3. Sharma, Y.C., et al., (2009): Nano-adsorbents for the removal of metallic pollutants from water and wastewater. *Environmental Technology.* 30(6): p. 583-609.

4. Teo, A., et al., (2016): Polymeric Biomaterials for Medical Implants & Devices. *Acs Biomaterials Science & Engineering.* 2(4).

5. Sahu, S.K., (2008): Recent Advances in the Extraction of Copper, Nickel and Cobalt. Metallurgy.

6. Crundwell, F.K., et al., (2011): Chapter 32 – Overview of the Extraction of Platinum-Group Metals. Extractive Metallurgy of Nickel Cobalt & Platinum Group Metals, p. 411-413.

7. Fleicher, V.D., S.N. Punukollu, and C.P. Andrewsspeed, (1984): Discovery, geology and genesis of copper-cobalt mineralisation at Chambishi Southeast Prospect, Zambia. *Precambrian Research.* 25(1): p. 119-133.

8. Alard, O., (2011): Pyrite tracks assimilation of crustal sulfur in Pyrenean peridotites. *Mineralogy & Petrology.* 101(1-2): p. 115-128.

9. Jorgensen, F.R.A. and F.J. Moyle, (1982): Phases formed during the thermal analysis of pyrite in air. *Journal of Thermal Analysis.* 25(2): p. 473-485.

10. Zhao, X., et al., (2018): Improving the Desulfurization Degree of High-Grade Nickel Matte via a Two-Step Oxidation Roasting Process. *Metallurgical & Materials Transactions B.* 49(4): p.1-7.

11. Abzalov, V.M., A.V. Sudai, and B.P. Yur'Ev, (2008): Desulfurization in roasting iron-ore pellets. *Steel in Translation.* 38(12): p.1003-1007.

12. Wang, L., et al., (2015): Oxidation roasting of molybdenite concentrate. *Transactions of Nonferrous Metals Society of China.* 25(12): p. 4167-4174.

13. Fan, X., et al., (2013): Study on Iron Recovery and Desulfurization of Pyrite Cinder.

14. Hao, S., et al., (2013): Desulfurization mechanism of calcium salts in direct reduction roasting of pyrite cinder. *Journal of University of Science & Technology Beijing.* 35(8): p. 977-985.

15. Qi, T.-g.Q., et al., (2011): Thermodynamics of chromite ore oxidative roasting process. *Journal of Central South University of Technology.* 18(1): p.83-88.

16. Gan, M., et al., (2014): Reaction behavior of low grade molybdenum concentrates in oxidation roasting process. *Chinese Journal of Nonferrous Metals.* 24(12): p. 3115-3122.

17. Zhang, J.H., et al., (2014): Influencing Factors of Vanadium Slag Roasting with Calcium and Oxidation Kinetics for Roasting Process. *Journal of Northeastern University,* 35(6): p. 831-835.

18. Chichko, A.N., N.V. Andrianov, and A.A. Chichko, (2007): Oxidation of sulfur in the smelting bath of an arc furnace. *Steel in Translation.* 37(7): p. 618-622.