

Effect of sulfur content on copper recovery in the reduction smelting process

Long Wu¹, Hongyang Wang², Kai Dong^{2,*}

¹ Central Research Institute of Building and Construction Co., Ltd, MCC Group, Beijing, China, 100082

² University of Science and Technology Beijing, School of Metallurgical and Ecological Engineering, Beijing, China, 100083

*Corresponding authors: dongkai0015@163.com (K. Dong)

Abstract

This work discussed the advantages of reducing copper in molten copper slag with low S content. FactSage calculated the distribution of copper at equilibrium under different sulfur content. The effect of sulfur content on copper recovery under different oxygen partial pressures was pointed out. The effect of sulfur content on copper recovery in the actual reduction process was explored through experimental research. Under the condition of low sulfur, the Recovery of copper and the stability of the experiment have an ideal results.

Keywords: Copper recovery, Thermodynamic equilibrium, Reduction experiment

1. Introduction

Reduction smelting is one of the methods to recover copper from copper smelting slag[1, 2]. Compared with flotation, the reduction smelting method can directly treat molten copper slag and has better adaptability for raw material[3-5]. At present, this recovery process is mainly to add reducing agents such as pyrite (sulphide) and anthracite to the molten pool[6, 7]. After a long heat preservation time, the matte is separated from liquid slag for Recovery. The limited metal recovery rate is one of the main problems that the smelting reduction method has not been widely used. Flotation is still the main method to treat smelting slag in copper smelters[8, 9]. Hongyu Tian's review summarized various processes[10]. The main methods to improve the metal recovery rate of smelting reduction are as follows: 1) the metal recovery can be effectively improved by adding a large amount of reducing agent[11, 12]. 2) Long-time high-temperature insulation and proper stirring are conducive to improve the settlement of metal droplets in slag. The electrocapillary phenomenon in the molten pool cannot be ignored.[7, 13] 3) Reducing the dissolution of copper in slag is conducive to improving the Recovery of copper[14-16]. The metal recovery was improved by adding CaO and other flux[4, 17]. Based on adding a large amount of reducing agent, the settlement of metal droplets and reducing the dissolution of copper in the slag are the key to improving the metal recovery further.

The reason for this work is that it is difficult to ensure a stable experimental result when we do the reduction smelting-separation experiment of copper slag. Under the same experimental conditions, an error of up to 10% will be obtained. In the high temperature smelting experiment, the volatilization of sulfur in the form of SO_2 or S_2 is inevitable and uncontrollable[18]. Sulfur content affects thermodynamic equilibrium, phase form of products, and separation between slag and metal during smelting.

Yun Wang also pointed out the influence of sulfur content on reducing Ni containing slag in previous

research[19, 20] , and put forward the idea of oxidation desulfurization and reduction for copper recovery[20]. Previous studies have also tried to remove sulfur from copper slag by oxidation[21]. Although the oxidative desulfurization process will increase the amount of reducing agents in the reduction process, it has certain advantages in metal recovery and process stability.

From the perspective of droplet deposition, it was evident that density, viscosity, and interfacial tension affect separation[22]. The basic physical parameters of the slag, metal, and matte are summarized in Table 1. The sulfur content in the initial slag affects the sulfur content in the reduced product phase. According to the Cu-Fe-S phase diagram[23], When the sulfur content of the metal system is different, the received metal phases are different.

Table 1. Physical parameters of slag, metal, and matte

	Density	Viscosity	Surface tension
Metal	7.1–8.0 g/cm ³ [24]		1.1–1.5 N/m (1200–1500 °C) [25]
Matte	4.13–4.98 g/cm ³ [26]		0.32–0.38 N/m (1200 °C)[26]
Slag	3.5–4.0 g/cm ³ (20–40 mol% SiO ₂ at 1400 °C) [27]	0.07–0.14 Pa·s; Fe/SiO ₂ = 1.67 (1200–1300 °C)[27, 28]	0.5–0.4 N/m (20–40 mol% SiO ₂ at 1400 °C) [29]
			Interfacial tension
Interfacial tension between metal and slag			0.96–1.67 N/m (estimated data)[30]
Interfacial tension between matte and slag			0.04–0.09 N/m; Fe/SiO ₂ = 1.0–1.65 (1600 °C)[31]

From the perspective of sulfide dissolution in slag, reducing sulfur solubility in copper slag is one of the key means to reduce copper loss. The copper loss in slag is profoundly discussed in the literature [14]. The study of sulfide dissolution points to a possibility, that is, under the reduction condition, by controlling the sulfur content of the slag matte system, the dissolution of copper sulfide in slag can be significantly reduced, and then the recovery rate can be improved. Therefore, the sulfide thermodynamical dissolution of slag and the settlement of metal(matte) droplets jointly affect the recovery rate. The difference in sulfur content in the reduction process can be explained qualitatively, as

0.00	4.50	0.00	0.00	95.50	0.00	4.00	50.81	12.70	1.98	0.000
1.00	3.60	0.00	0.00	95.50	0.20	4.00	50.76	12.70	1.98	0.050
2.50	2.25	0.00	0.00	95.50	0.50	3.99	50.68	12.70	1.98	0.125
5.00	0.00	0.00	0.00	95.50	1.00	3.98	50.56	12.70	1.98	0.250
5.00	0.00	0.45	1.38	93.84	1.49	3.97	50.47	12.70	1.98	0.375
5.00	0.00	0.89	2.75	92.20	1.98	3.97	50.39	12.70	1.98	0.500
5.00	0.00	1.33	4.13	90.55	2.48	3.96	50.30	12.70	1.98	0.625
5.00	0.00	1.77	5.50	88.91	2.97	3.95	50.22	12.70	1.98	0.750

Table 4 Composition for reduction experiment and calculation, wt%

Cu ₂ S	Cu ₂ O	FeS	FeO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	Σ
0.00	4.50	0.00	62.25	3.48	25.66	4.12	100.00
1.00	3.60	0.00	62.19	3.47	25.63	4.11	100.00
2.49	2.24	0.00	62.09	3.47	25.60	4.11	100.00
4.98	0.00	0.00	61.94	3.46	25.53	4.10	100.00
4.97	0.00	1.37	60.76	3.39	25.49	4.02	100.00
4.96	0.00	2.73	59.60	3.33	25.45	3.94	100.00
4.95	0.00	4.09	58.43	3.26	25.40	3.86	100.00
4.94	0.00	5.44	57.28	3.20	25.36	3.79	100.00

2.2. Thermodynamic calculation method

FactSage 7.1[34] is used for thermodynamic calculation. Under the actual reduction conditions, the sulfur content in slag matte and P_{S2} in gas phase system cannot be ignored [35, 36]. During factsage calculation, the gas phase system can be idealized, and it is considered that the total sulfur content in slag and matte remains fixed under the reduction system. The difference between the actual condition and the ideal equilibrium calculated by FactSage is shown in Figure 2.

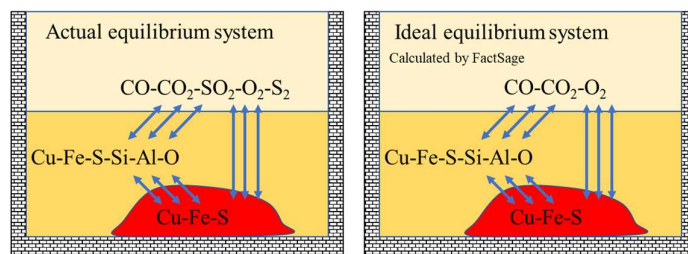


Figure 2 difference between the actual equilibrium and the ideal equilibrium calculated by FactSage

The temperature of thermodynamic calculation was set at 1400 °C, which can ensure the complete liquid

phase of slag and provide a better fluidity in the experimental process[21]. After inputting the initial slag composition with different sulfur content in Table 3 into FactSage, set the gas phase composition in equilibrium calculation to include CO₂, CO, and O₂. The partial pressure of S₂ in the gas was set to dormant phase. The partial pressure of oxygen rang from 10⁻⁸ to 10⁻¹⁰[37].

2.3. Experimental method

Carbon reduction experiments with different initial sulfur content were used to verify the point of view in this paper. Using high-purity graphite powder as reducing agent, it is assumed that under the reduction condition, the copper iron oxide in the slag is reduced to Cu and Fe, and the reduction product is co, at this time, C/O = 1. The C/O is set as 0.1 and 0.2 in the experiment, and the ratio of reducing materials is shown in Table 5. Because the blending of copper oxide is different under different sulfur content, the addition of graphite powder is not invariable.

Table 5 Ingredients of copper slag reduction experiment with different initial sulfur content

S/Cu	Quality of synthetic slag	Cu ₂ O	Fe ₂ O ₃	FeO	Graphite	C/O
0.000	100	4.50	3.48	62.25	2.31	0.2
0.050		3.60	3.47	62.19	2.29	
0.125		2.24	3.47	62.09	2.26	
0.250		0.00	3.46	61.94	2.22	
0.375		0.00	3.39	60.76	2.18	
0.500		0.00	3.33	59.60	2.14	
0.625		0.00	3.26	58.43	2.09	
0.750		0.00	3.20	57.28	2.05	
0.000	100	4.50	3.48	62.25	1.15	0.1
0.050		3.60	3.47	62.19	1.14	
0.125		2.24	3.47	62.09	1.13	
0.250		0.00	3.46	61.94	1.11	
0.375		0.00	3.39	60.76	1.09	
0.500		0.00	3.33	59.60	1.07	
0.725		0.00	3.26	58.43	1.05	
0.750		0.00	3.20	57.28	1.03	

The experiment was carried out in a high-temperature tubular furnace. Argon was used as the shielding gas. The mixed material was put into an alumina crucible and heated to 1400 °C at the rate of 10°C/min. After holding for 60min, cool the temperature to below 1100 °C at the rate of 20 °C / min under argon to completely solidify the sample. Because the sulfur content in the molten pool could not be kept stable during the experiment, and the complete separation could not be guaranteed during the metal settlement, three repeated experiments were carried out for all parameter experimental groups.

2.4. Test and conversion methods

After melting and heat preservation, large pieces of metal settle at the bottom of the crucible. After crushing the sample to large pieces, slag/matte separation can be realized. After cutting and polishing the received metal samples, the composition of Cu, Fe and S in the metal was analyzed by chemical method.

Take the slag sample in the middle of the crucible for chemical analysis, and detect the contents of Cu, Fe, S and SiO₂ in the slag.

After the detection, the SiO₂ content is obtained, because the fixed ratio between Cu/Fe/SiO₂ is guaranteed, the mass of each phase and the distribution of each element can be converted according to the detected composition.

The metal recovery rate is defined as:

$$\eta = M_{Cu \text{ in matte(metal)}} / M_{Total \text{ Cu}}$$

$M_{Cu \text{ in matte(metal)}}$ refers to the mass of copper in the received metal, $M_{Total \text{ Cu}}$ refers to the total mass of copper

The distribution rate is defined as:

$$L_{Cu} = \omega_{Cu \text{ in slag}} / \omega_{Cu \text{ in matte(metal)}}$$

$\omega_{Cu \text{ in slag}}$, $\omega_{Cu \text{ in matte(metal)}}$ refers to the mass content of copper in slag and received matte(metal)

respectively.

Because sulfur inevitably volatilizes during the experiment, S/Cu in the experimental results is converted by the following formula.

$$S/Cu = (\omega_{S \text{ in slag}} \times M_{slag} + \omega_{S \text{ in metal}} \times M_{metal}) / (\omega_{Cu \text{ in slag}} \times M_{slag} + \omega_{Cu \text{ in metal}} \times M_{metal})$$

3. Results and discussion

3.1. Calculation results

The phase diagram of Cu-Fe-SiO₂-O₂-S slag matte metal under different oxygen partial pressures was calculated by using FactSage 7.1 phase diagram function. Under the condition of fixed Cu-Fe-SiO₂ ratio, with the decrease of oxygen partial pressure and the increase of reduction degree, copper metal phase gradually becomes the main metal product. On the contrary, matte phase is the main metal product when the sulfur content is high and the oxidation of the molten pool is strong. Combined with the discussion in Table 1 above, it is unfavorable for slag-metal separation in molten state.

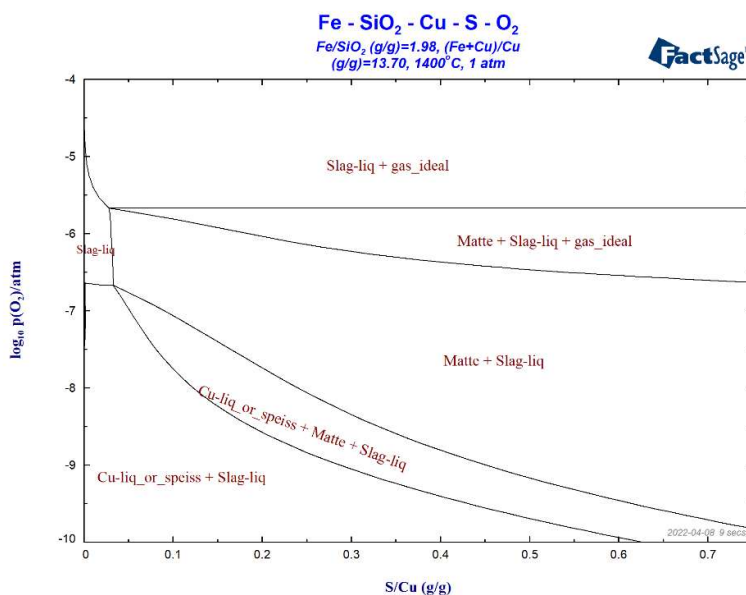


Figure 3 Cu-Fe-SiO₂-O₂-S Phase diagram(Calculated by FactSage)

As shown in Figure 4, as oxygen partial pressure decreased, the amount of the metal phase significantly

increased. However, when the initial S content in the slag decreased, the fraction of the metal phase increased. From the perspective of metal formation quality, the reduction of sulfur content is conducive to the formation of metal phase under low oxygen partial pressure (10^{-10}). However, when the oxygen partial pressure of the molten pool is high, the reduction of sulfur content inhibits the transfer of copper phase matte in the slag to some extent. The addition of sulfide such as pyrite is obviously more conducive to the formation of metal.

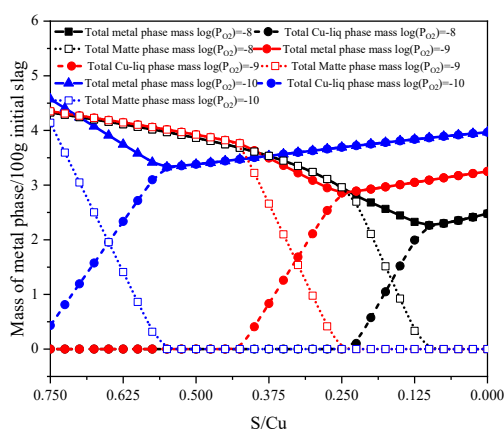


Figure 4. The relationship between the metal and matte mass and S content(Calculated by FactSage)

The decrease of equilibrium oxygen partial pressure reduces the loss of Cu in slag. When the initial sulfur content is high, the gain of oxygen partial pressure is insignificant. When the sulfur content decreases, there is an obvious gain for the decrease of Cu content in slag under low oxygen partial pressure. However, under the condition of higher oxygen partial pressure, the reduction is inhibited by low sulfur, which is related to the phase of the product. The increase of copper content and the decrease of sulfur content in matte lead to the excessive dissolution of oxides in slag[38]. Thermodynamic calculation results show that if the optimal copper recovery rate was expected to achieve, a large number of reducing agents and low sulfur content are conducive.

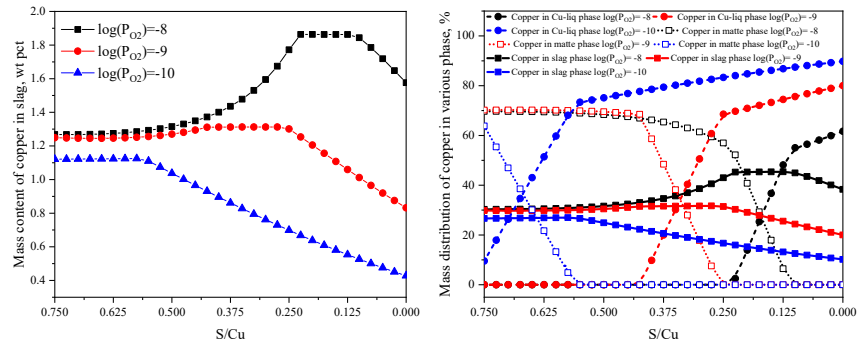


Fig. 5 (a) Cu content in slag under different initial sulfur content (b) mass of copper in each phase under initial sulfur content (Calculated by FactSage)

3.2. Experimental results

Because in the process of reduction reaction, s in the molten pool will inevitably be removed. The initial sulfur content is not exactly the same as the premixed. The sulfur content in matte and slag is obtained by chemical test, and the ratio of total mass of S to total mass of Cu can be converted into the initial sulfur content of the actual molten pool system.

The mass of metal harvest fluctuates greatly. This is mainly because the sulfur content in the molten pool is not stable during the experiment. Moreover, in the same holding time, the complete separation of metal cannot be guaranteed, which is an inevitable error in all reduction experiments. When graphite is used as reducing agent, there are obvious boundaries between metal quality. When S/Cu is less than 0.2, the metal mass increases slightly with the decrease of sulfur content. When S/Cu is greater than 0.2, the decrease of sulfur content has an inhibitory effect on the metal mass. High sulfur content is conducive to the formation of matte and indirectly improve the quality of received metal.

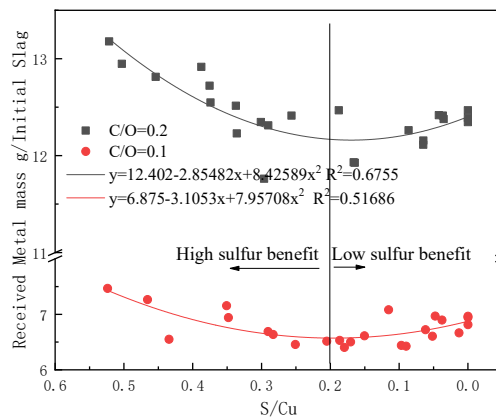


Figure 6 Total mass of received metal

Figure 7 shows the change of residual copper content in slag with the decrease of sulfur content under different carbon blending. When C/O is 0.2, with the decrease of sulfur content, the residual copper content in slag gradually decreases, and the lowest is about 0.35%. Under the condition of high carbon distribution, the regularity is relatively obvious. This is mainly because under the condition of high carbon blending, the main product phase is Cu-Fe alloy, and there is no large number of metal inclusions due to difficult separation. When C/O is 0.1, the residual copper content at high sulfur content is very unstable. With the increase of sulfur content, a large amount of Cu remains in the slag. One part of this is from the metal inclusions that cannot be separated, and the other part is Cu dissolved in the slag. Under the condition of low sulfur, even if the carbon addition is low ($C/O = 0.1$), the copper content in the slag can also be reduced to less than 0.6%. Under the same temperature control and heating conditions, low carbon addition and high sulfur content are injurious to reduce the copper content in tailings.

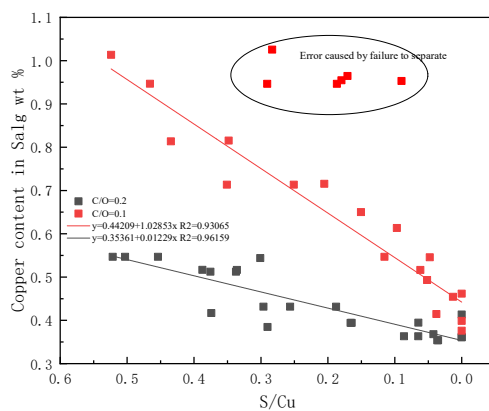


Figure 7 Residual Cu content in slag

The increase of sulfur content reduces the copper grade in the metal phase. When $C/O = 0.1$, the Cu content in matte increases significantly with the decrease of sulfur content. When the sulfur content is low, the copper content exceeds 50%. When $C/O = 0.2$, although the reduction of sulfur content can also improve the copper grade, the copper content less than 30 will produce a lot of difficulties in subsequent utilization. It causes the increase of oxygen consumption, slag amount and copper loss of converting slag in the blowing process.

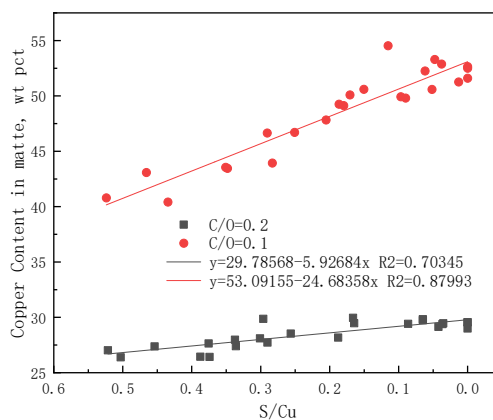


Fig. 8 Cu content in received metal (matte)

The recovery rate and distribution ratios after reduction are shown in Figure 9. When $C/O = 0.2$, the Recovery of copper increases gradually with the decrease of sulfur content. This is similar to the thermodynamic results, and the reduction of sulfur content has little effect on the Recovery of copper.

When C/O is 0.1, the promoting effect of low sulfur content is very obvious. Because the separation between slag and matte is difficult, it causes a lot of instability to the reduction experiment. In the actual production process, the instability of copper recovery is also caused by this reason. When the sulfur content decreases to a certain range ($S/Cu < 0.1$), the Recovery of copper is still considerable even under the condition of $C/O = 0.1$. The distribution ratios after reduction are shown in Figure 9(b). When the S content decreased, the Cu distribution ratio decreased significantly, exhibiting an evident trend. The distribution ratio of Cu under different carbon addition can be seen that although the copper grade in matte is higher when $C/O = 0.1$, Cu tends to be distributed in slag due to the influence of sulfur content. Only when the sulfur content is less than 0.2 can L_{Cu} accord with the thermodynamic law of reduction experiment.

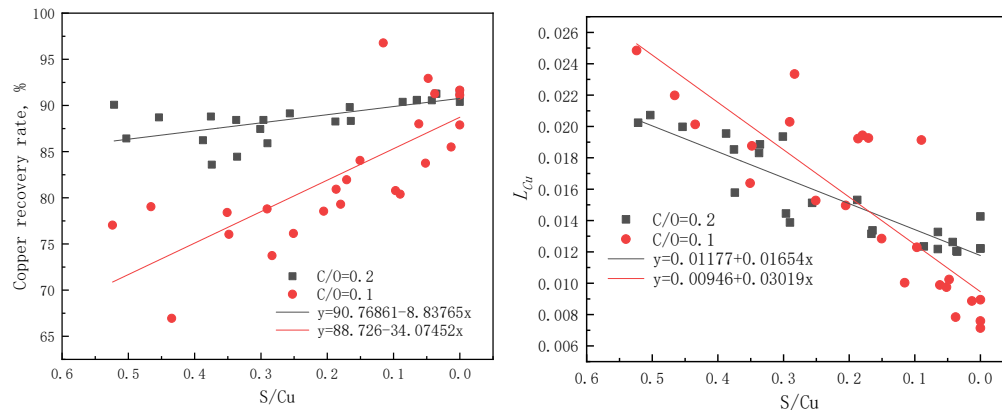


Figure. 9 (a) copper recovery (b) copper distribution ratio

Figure 10 shows the morphology of the slag after reduction and Recovery. As mentioned above, incomplete melting separation at high temperature will inevitably lead to the loss of copper in the slag. Moreover, this loss is uncontrollable. Through the experiment, we can see that with the decrease of S/Cu in the slag-metal-matte system, it can promote the Recovery of copper when a large amount of reducing agent is added. However, this phenomenon is the coupling between thermodynamics and melting separation.

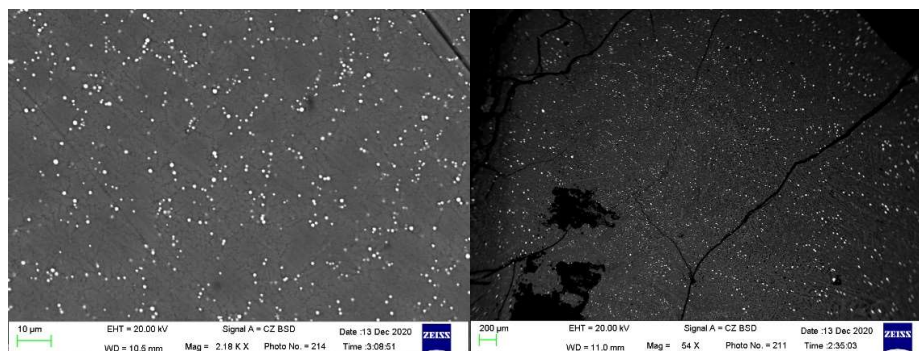


Figure 10 Slag sample after reduction smelting

4. Conclusion

In the reduction smelting process of copper slag, sulfur content is an important factor affecting metal recovery. In the thermodynamic calculation under ideal conditions, the increase of S content is beneficial to the Recovery of Cu at higher oxygen partial pressure. Under low oxygen partial pressure, low sulfur content is more conducive to the Recovery of Cu. Sulfur content affects the types of metal products produced by reduction. Because sulfur will volatilize into the gas phase at high temperature, the sulfur content in the molten pool is not stable, which leads to the uncontrollability of the reduction experiment. At the same time, under the condition of high sulfur content, because matte inclusion in the slag cannot be separated from the slag through sedimentation, the sulfur content increases the metal loss in the slag. The actual recovery experiment is not completely consistent with the law of thermodynamics. Considering the experimental stability and metal recovery, low sulfur content is very beneficial to copper recovery in the reduction process of copper slag.

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