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COMPREHENSIVE UTILIZATION OF COPPER CONVERTER SLAGS BY HYBRID BENEFICIATION TECHNOLOGY AND INDUSTRIAL APPLICATION

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Introduction

In China, most copper pyro-metallurgical slag still has high content of copper and iron. Properties of copper slag depend on copper concentrate, smelting process and cooling system, et al[1-3]. The treating processes are mainly as follows:

- obtain the copper concentrates and discard tailings into pond[4]
- as raw materials in the production of cement, concrete and pavements[5]
- used in corrosion rust remove[6]

Though some good results have been achieved, the low level of comprehensive utilization and the weak circulation hasn't change notably.

In 2010, Dajiang Group expanded its beneficiation plant from 100,000 t/a to 200,000 t/a. During early production period, the properties of slag were different from the previous Noranda slag. The grade of copper in converter slag is 5%～8%, with high distribution of copper and cuprous oxide and low copper matte. As a result, the recovery efficiency is low. A hybrid beneficiation process was explored to solve the problem.

Experiments

Properties and phase composition of converter slag

The converter slag was formed in the matte blowing process, with grey and black appearance and partly black-green, hard and crisp characteristic, compact structure, and a density around 4.25. The main compositions are magnetite (Fe_3O_4) and fayalite ($2FeO{\cdot}SiO_2$). The main valuable elements in slag are Cu and a small amount of Co and Ag. Most Copper exists in sulfide, some in metal and oxide, and others in copper ferrite. The phase analyses of slag were shown in Table 1-8. The microscopic analyses and XPS analyses were shown in Figure 1-3.

Table 1: Phase analysis of converter slag /%

Composition	CuS	Cu	Cu_2O	$Cu_2O{\cdot}Fe_2O_3$	Sum
Content	51.34	39.81	4.53	4.32	100

Table 2: Main compositions of converter slag /%

Composition	Cu	Fe	Pb	Zn	S	SiO_2	CaO	Al_2O_3	MgO
Content	8.84	43.76	1.04	2.02	1.21	21.67	1.93	2.71	1.27

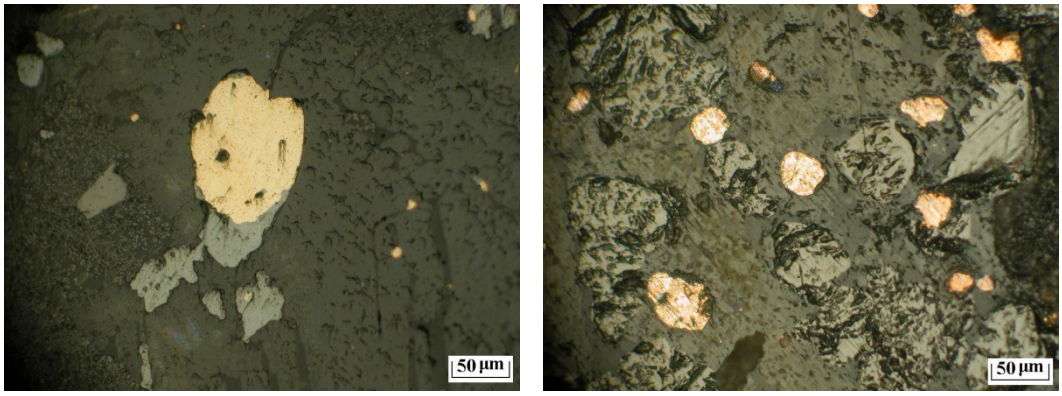

Figure 1: Optical micrograph of matte phase in converter slag

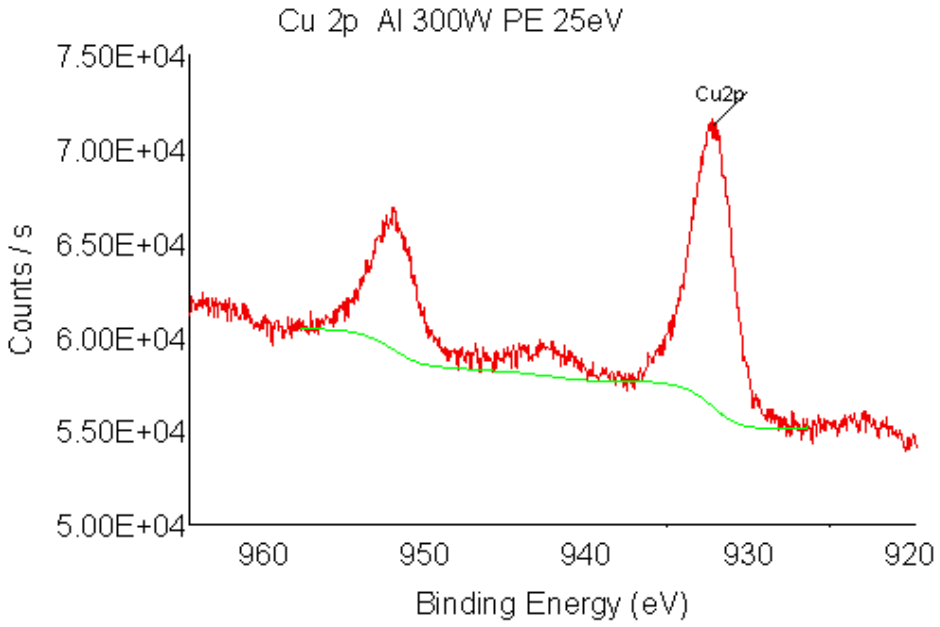

Figure 2: XPS of Cu2P in converter slag

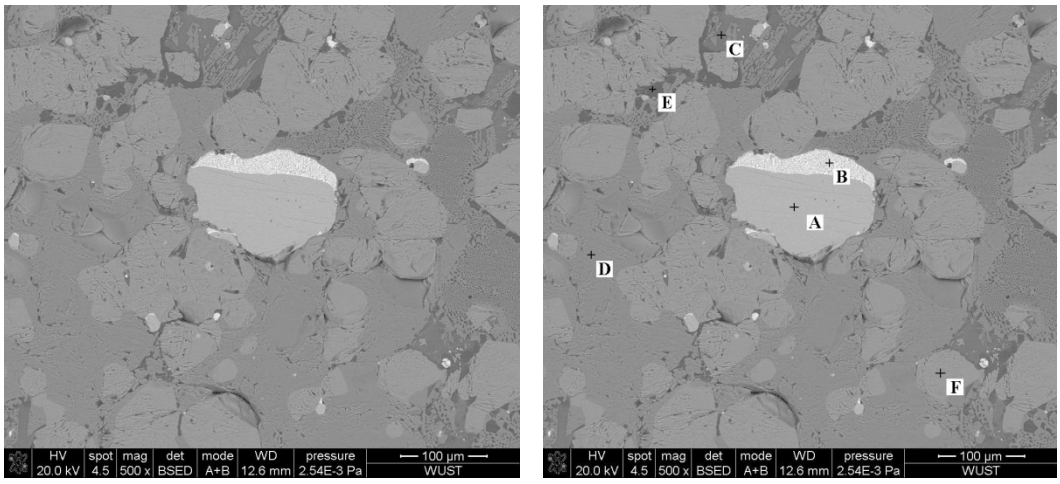

Figure 3: SEM photograph and EDS analysis point

Table 3: EDS analysis of point A in Figure 3

Element	S	Fe	Cu
Wt;%	22.80	6.58	70.62
At.%	36.64	6.07	57.29

Table 4: EDS analysis of point B in Figure 3

Element	S	Fe	Ni	Cu	As	Sn	Sb	Pb
Wt.%	15.40	4.37	0.15	30.07	0.50	0.17	0.55	48.79
At.%	37.45	6.11	0.20	36.90	0.52	0.11	0.35	18.36

Table 5: EDS analysis of point C in Figure 3

Element	O	Na	Al	Si	K	Ca	Fe	Zn	As
Wt.%	40.06	1.19	5.08	34.46	1.29	6.19	10.08	1.20	0.44
At.%	57.39	1.19	4.32	28.12	0.76	3.54	4.14	0.42	0.13

Table 6: EDS analysis of point D in Figure 3

Element	O	Si	Fe	Ni	Cu	Zn	As
Wt.%	26.54	17.19	53.20	0.21	0.16	2.41	0.29
At.%	50.72	18.72	29.13	0.11	0.08	1.13	0.12

Table 7: EDS analysis of point E in Figure 3

Element	O	Al	Si	K	Fe	Ni	Cu	Zn	As	Sn
Wt.%	41.58	2.14	45.49	1.71	6.25	0.11	0.14	0.36	0.69	1.52
At.%	57.94	1.77	36.11	0.98	2.50	0.04	0.05	0.12	0.21	0.28

Table 8: EDS analysis of point F in Figure 3

Element	O	Fe	Ni	Cu	Zn	As	Sn
Wt.%	22.52	71.49	0.99	1.24	2.24	1.11	0.41
At.%	50.69	46.11	0.61	0.70	1.23	0.54	0.12

From Table 1-8 and Figure 1-3, it can be seen that during the convert slag forming period, the grade of matte was increasing, eventually turn into white matte, even crude copper and partial cuprous oxide. The content of copper in this batch of the primary ore is a little higher, the content of metal copper of which is obviously higher than the normal. The particles obtained by grinding are coarse, due to the high content of metal copper. So copper can't be recycled completely through flotation. During pilot production period, the content of copper in tailings was about 0.8%, and the highest could reach up to 2%. In order to reduce the content of copper in tailings, experiments were conducted in aspects of intensified grinding, adjusting technological process and gravity concentration.

Flotation tests of converter slag

The flotation tests were performed in a 3L mechanical agitation flotation machine. Batch sample weighed 1000g. Flotation products were weighed after being dried and concentrate grade analyses.

Results and discussion

Grinding tests

The converter slag was crushed and then gone through the 2mm sample sieve. XMQ–67 ball mill was adopted in the grinding process. Each sample was taken at 1000g, and the grinding time was 10min, 15min, 20min, and 25min, respectively. Samples were screened with standard sieve, and copper distribution was analyzed afterwards. The results were shown in Table 9.

Table 9: Effect of grinding time on granularity and copper distribution

Granularity / Grinding time	＋0.074mm		–0.074＋0.043mm		–0.043mm	
	Content	Cu%	Content	Cu%	Content	Cu%
10min	36.32%	7.88	22.34%	10.95	41.34%	8.06
15min	19.80%	9.26	26.87%	9.04	53.33%	8.44
20min	11.03%	13.59	25.36%	8.46	63.61%	7.85
25min	7.01%	19.19	20.70%	8.12	72.29%	7.77

Compared with Noranda slag, the content of –0.074mm of converter slag was 80.2% with the grinding time of 15min, while that was 88.42% for Noranda slag under the same condition. So it can be found that the converter slag was harder to grind than Noranda slag. And many copper particles still can be found after grinding, which has an adverse effect on subsequent froth flotation.

Optimization of operating parameters

Small flotation tests were conducted in this stage. Considering the high Cu grade in the converter slag, stage grinding – stage beneficiation process was adopted in order to achieve the target of "early recovery". According to past production practice, the grinding fineness was determined as –0.074mm account for 70% in the first stage and –0.043mm account for 70% in the second stage. Sodium butyl xanthate was used as collector. $2^{\#}$ oil was used as foaming agent. 1kg ore was taken as sample. XFD–3 single flotation cell was used in the tests. Flotation tests results were shown in Table 10.

Table 10: Results of optimized flotation tests

Product	Weight, g	Productivity %	Cu grade %	Cu amount	Distribution %	Concentrate recovery
Copper concentrate 1	197	19.70	33.58	66.1526	73.3128	92.75%
Middling 1	107	10.70	14.62	15.6434	17.3366	
Middling 2	80	8.00	3.84	3.072	3.4045	
Tailing	616	61.60	0.871	5.3654	5.9461	
Sum	1000	100.00	9.02	90.2334	100.00	

It can be observed in Table 10 that though stage grinding and staged separation process, copper loss in tailings is still considerable high for partial metals were not dissociated completely.

In order to decrease the grade of tailings, copper particles need to be grounded fine enough, so grinding time should be prolonged. The experiment scheme of –0.074mm account for more than 75% in the first stage, and –0.043mm account for 75%-81% were investigated. The results were shown in Table 11.

Table 11: Flotation results of extended grinding time and flotation time

Product	Weight,	Productivity,	Cu	Cu	Distribution	Concentrate

	g	%	grade, %	amount	%	recovery
Copper concentrate 1	215	21.50	30.25	65.0375	71.4007	96.50%
Middling 1	112	11.20	18.54	20.7648	22.7964	
Middling 2	76	7.60	3.42	2.5992	2.8535	
Tailing	597	59.70	0.45	2.6865	2.9493	
Sum	1000	100.00	9.11	91.088	100.00	

From Table 10 and 11, it can be seen that the grade of tailings decreased significantly from 0.871% to 0.45%. However, the grade of 0.45% in the tailing is still higher than the goal of 0.35%. Thus, the extended grinding time of –0.074mm account for 80% and –0.043mm account for 85% were investigated. The flotation results were shown in Table 12.

Table 12: Flotation results of grinding time and flotation time extended further

Product	Weight g	Productivity %	Cu grade %	Cu amount	Distribution %	Concentrate recovery
Copper concentrate 1	199	19.90	29.42	58.55	66.23	96.37%
Middling 1	124	12.40	20.12	24.95	28.22	
Middling 2	69	6.90	3.12	2.15	2.43	
Tailing	608	60.80	0.45	2.75	3.11	
Sum	1000	100.00	8.84	88.40	100.00	

It was shown in Table 12 that the grade of tailings wasn't decline significantly, however the grade of concentrate decline slightly. Then the grinding system of –0.074mm account for 75% in the first stage and –0.043mm account for 75%～80% was feasible.

Gravity – magnetic separation – flotation hybrid beneficiation process

In single flotation tests the lowest tailing grade was 0.45%, is still higher than the target of 0.35%. Considering Cu exists in converter slag is matte and metallic copper, and the specific gravity of metallic copper is heavy and hard to grinded, then the floatability is poor. However, due to its heavy specific gravity and coarse particles, most of metallic copper can be separated from copper compounds by hydraulic classification. In view of the large amount of magnetic iron in mineral, metallic copper can be separated from copper compounds by magnetic separation.

In this stage, the gravity concentration–magnetic separation–flotation hybrid beneficiation process was adopted. Beneficiation tests were conducted under the condition of –0.074mm account for 75% in one stage grinding. Results were shown in Table 13.

Table 13: Results of hybrid beneficiation tests

Product	Weight g	Productivity %	Cu grade%	Cu amount	Distribution %	Concentrate recovery
Flotation raw ore	772.3	77.23	5.90	45.57	52.37	97.82%
magnetic concentrate	227.7	22.77	18.55	42.24	48.55	
Flotation concentrate	193.9	19.39	22.11	42.87	49.27	
Flotation tailings	549.7	54.97	0.345	1.90	2.18	
Raw ore	1000	100	8.7	87.01	100.00	

It can be seen from Table 13 that through the hybrid beneficiation process, two kinds of products were obtained, the grade of tailings decreased from 0.45% to target 0.345%, and comprehensive recovery of copper concentrate increased from 96.50% to 97.82%.

Industrial utilization of converter slag by hybrid beneficiation process

Dajiang Group built a slag production line to treat converter slags with a capacity of 200,000 t/a. The reagent system was 230-270g/t butyl xanthate with 15-22g/t pine oil. After more than a year of industrial application, when the grade of converter slag is 5%-8%, the grade of recovered metallic copper concentrate was 18%-20%, the grade of recovered flotation concentrate was 28%-30%, the grade of discarded tailings was 0.30%-0.35%. The comprehensive recovery was 93%-96%. The industrial results were shown in Table 14.

Table 14: Results of industrial production of rich oxygen blowing converter slag

Product	Productivity	Grade	Distribution
		Cu	Cu
Raw copper concentrate	9-11	18-20	50-55

Flotation copper concentrate	4-6	28-30	39-41
Cu tailings	84-86	0.30-0.35	5-7
Primary ore	100	4-8	100

Conclusions

- Compared with Noranda slag, the grindability of high grade converter slag is poor. To achieve good beneficiation results, the grinding time should be extended to dissociate metallic copper.
- Considering the high specific gravity of metallic copper, satisfactory results were achieved by hybrid combined beneficiation process. When the feeding grade is 5 ～8%, the grade of produced metallic Cu concentrate reaches 18-20%, froth concentrate reaches 28-30%, tailing concentrate reaches 0.30-0.35%, overall recovery reaches 93-96%.

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