Efficiency of use of collecting agents for increase of extraction values by copper, gold and silver flotation from complex slags of copper-smelting production

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Abstract
The article presents the results of the study of the possibility of using additional collecting agents of BTF series (dialkyldithiophosphates) to increase the extraction of copper, gold, silver from difficult copper smelting slag. The characteristic of used reagent modifications is given. The results of open and closed laboratory flotation experiments are presented; the influence of the pH pulp on extraction of metals is traced. The reasons of increase of copper extraction when applying BTF are analyzed, the optimal ratio of primary and secondary collector is determined.
Keywords: INDUSTRIAL RAW MATERIALS, COPPER, COPPER SLAG FLOTATION, PYRITE, RECYCLE WATER, THE PH OF THE PROCESS, COLLECTING AGENTS, DIALKYLDITHIOPHOSPHATES, EXTRACTION INCREASE

Introduction

Non-ferrous metal industry is the largest producer of waste the main volume of which falls on the slag accumulating over the years in areas of processing enterprises. However, formed slag is a valuable mineral raw material and can be used in the national economy. The Urals region is the main part of the "Copper Belt" of Russia.

Difficult copper smelting slags are characterized by [1] prevalence in the structure of splice of copper sulfide, iron oxide, iron sulfide size of less than 0.044 mm. They are involved in the processing under the conditions of a systematic underutilizing of enrichment plants processing copper and copper-zinc ores especially in the southern Urals. The size of inclusions of the copper-containing mineral phases in the sulfide splices is 1-3 microns. A characteristic feature is the inclusion of an aggregate copper sulfide inside the splice.

Technology used in the flotation is a universal method of enrichment of raw materials of natural (mineral resources) and man-made (mining and metallurgical waste) origin containing non-ferrous metals. It provides the most complete and least expensive extraction of copper from easy specimen slag in copper-smelting production [2]. However, extraction of copper by flotation from difficult slag does not exceed 60% [2], and sometimes even losses of cop -

per with flotation tailings prevail over the extraction of copper in concentrate. The acute issue is extraction of gold and silver, which are carried as an asset (in operation) of the metallurgical enterprise especially from converter slag. Thus, the problem of increasing the extraction of copper, gold, silver despite the continuously ongoing researches in this area continues to be relevant.

A promising solution to these problems is the use of dialkyldithiophosphates. BTF grade reagents containing substances of this chemical class are selected for studies, because of their availability and a number of specific features of the flotation action proven to be effective additional collectors in flotation with xanthogenate in the copper-zinc [3] and copper-pyrite [4] ores increasing the extraction of precious metals. BTF reagents are highly resistant, highly soluble in water and easy to handle.

Converter and dump slags of one of the Southern Urals enterprise are studied and referred by our proposed typification to fayalite-magnetite-pyrite type. The content of the sulfide phase in average is 7%, 0.5% are presented by bornite, and the rest - by pyrite. Copper is located in metal alloys, α_{avCu} varies from 1.40% to 85.08% therein. In addition, metallic copper buckshots of different size are present in slags with α_{Cu} up to 98%. The copper occurs as an impurity in pyrite and pyrrhotite (to 3.23%), in oxide phases (magnetite, ferrite), in fayalite and sodium aluminosilicate. The main copper phases are chalcocite-bornite solid solution (α_{avCu} – 73.15%), bornite (α_{cpCu} – 56.09%), sulfide Fe-Cu solid solution (α_{avCu} – 54.91%), sulfide Fe-Cu-Zn solid solution (α_{avCu} – 16.83%).

The studies of slag flotation showed that the area of effective extraction of copper is pH = 5.0 – 7.5, and maximum values have been obtained at pH = 5.5. That is, the flotation proceeds in the range of pH critical for a stable state of the main collector – potassium butyl xanthate o(PBX). This necessitates the use of an additional collector sustainable to more acidic environment. From BTF reagents for experiments following modifications: BTF 163 BTF 1614, BTF 1624 BTF-1522, BTF 1541 BTF-1552 have been selected. The products are produced according to TU 2452-001-51848149-00 under the brand name “Flotoreagent BTF.” The whole technological process is developed and approved by CJSC “Mechanobr Orgsintez-reagent”, St. Petersburg under the guidance of V. I. Riaboy Doctor of Engineering Sciences, Professor. The characteristic of reagents is shown in Table 1. The table is based on materials [3,4].

Experiment

Flotation experiments were carried out according to used earlier schemes of copper-containing slag processing at the concentration plant Sibai branch of OJSC “UGOK”, using recycled water on the equipment of research laboratory. The permanent experimental conditions include: weight of copper slag Q = 700g; grinding fineness – 98.5% of the class -0,044mm; % solid pulp for flotation – 28%, content of free CaO in the recycled water 450-480g/m^3; time of roughing flotation – 20 min. BTF series reagent are supplied into the process as an additional collector consecutively after potassium butyl xanthate (PBX).

Table 1. Characteristics of BTF reagents

Grade of BRF reagent	Type of flotated ores	Foa-ming	Selectivity	Action
163	Cu- Zn , Cu- Ni, Cu- Mo, Cu- FeS, Au- containing, polymet.	remarkable	Relatively high selectivity of action	Provides an increase in the extraction of non-ferrous, rare and precious metals from sulphide ores
1614				
1624				
1522	Cu- Zn , Cu- Ni, Cu- Mo, polymetallic	Mo-derate	Belongs to a type of enough selective collectors	According to the collective capacity exceeds flotoreagent BTF-1541. Increases extraction of Au, Ag and platinoids. Increases extraction both thin and large classes of sulfide minerals. Helps to improve the flotation of oxidized forms of sulfide minerals
1552				

1541	Cu- Zn , Cu-Ni, polymetallic	weak	Selective when separation of pyrite and when separation of sulfide minerals of non-ferrous, rare and precious metals	Provides a high quality of copper and zinc concentrates in the flotation of copper-zinc ores maintaining or increasing the extraction of copper and zinc

Variable conditions of the experiments:

- pH of the medium in grinding and in floatation, which was achieved by supplying to the process of actual highly alkaline recycled water with (pH) = 11 and recycle water conditioned to pH = 7, process water at pH = 7.

- expenditure of the collector, consumption of the frothing reagent, the consumption ratio of potassium butyl xanthate (BPX) and the BTF consumption.

The flotation scheme includes the following: copper "head", recleaning of the copper head, roughing flotation, recleaner flotation to final tailings. Supplying of the collector (a combination of collectors) is carried in each operation fractionally.

Results and discussion

During the experiment when the flotation of converter and dump slags of the same enterprise the identical extraction dependences of copper and precious metals to the flotation regimes were obtained. The paper presents the results obtained in the flotation of copper converter slag in the open cycle (Table 2-6).

Table 2 shows that the maximum extraction of copper in concentrate was 84.05% and the minimum losses with final copper tailings – 15.95% achieved at pH 6.5- 6.8 in grinding and pH 5.5-6 in flotation on one and the same consumption of BPX. Reducing of process pH increases the product yield from the "head". Flotation rate and overall yield increase at constant quality of the concentrate. But at the same time flotation at pH=7 on a "clean" process water is not active.

Table 2. Flotation results of difficult converter slag at different values of pH process

No op	Denomination	Yield ,%	β^{Cu}, %	ε^{Cu}, %	Conditions
1	Cu «head»	2.97	22.43	33.07	$pH_{grinding}$=11.0-11.5 $pH_{flotation}$= 12.0-12.5 BPX Collector 400g/t
	g Cu concent.	8.31	9.08	37.47	
	Foam contr.	2.23	3.05	3.38	
	∑g Cu concent	**13.51**	**11.02**	**73.92**	
	Final tail.	86.49	0.61	26.08	
	Initial slag	100	2.01	100	
2	Cu «head»	3.85	24.75	47.31	$pH_{grinding}$ = 9.0-9.3 $pH_{flotation}$ = 8.0-8.5 BPX Collector 400g/t
	g Cu concent	9.71	6.38	30.75	
	Foam contr.	3.41	1.78	3.01	
	∑g Cu concent	**16.97**	**9.62**	**81.07**	
	Final tail	83.03	0.46	18.93	
	Initial slag	100	2,01	100	
3	Cu «head»	4.20	23.12	48.2	$pH_{grinding}$ = 6.5 -6.8 $pH_{flotation}$ = 5.5- 6.0 **BPX Collector 400g/t**
	g Cu concent	10.10	6.4	32.08	
	Foam contr.	3.30	2.3	3.77	
	∑g Cu concent	**17.6**	**9.62**	**84.05**	
	Final tail	82.4	0.39	15.95	
	Initial slag	100	2.01	100	

4	Cu «head»	1.74	19.65	16.97	Process water pH 7.0 BPX Collector 400g/t
	g Cu concent	7.01	12.01	41.79	
	Foam contr.	3.59	4.35	7.75	
	∑g Cu concent	**12.34**	**10.86**	**66.52**	
	Final tail	87.66	0.77	33.48	
	Initial slag	100	2,01	100	

Analysis of the results (Figure 1) of comparative series of flotation experiments using the additional collector BTF on the actual recycled water at a pH in grinding of 11.0-11.5 and pH in flotation of 12.0-12.5 has revealed that the supply to the flotation process of any additional modification of the studied reagents can significantly reduce the total consumption of the collector. This increases the yield of product from "head" and the yield of the total concentrate.

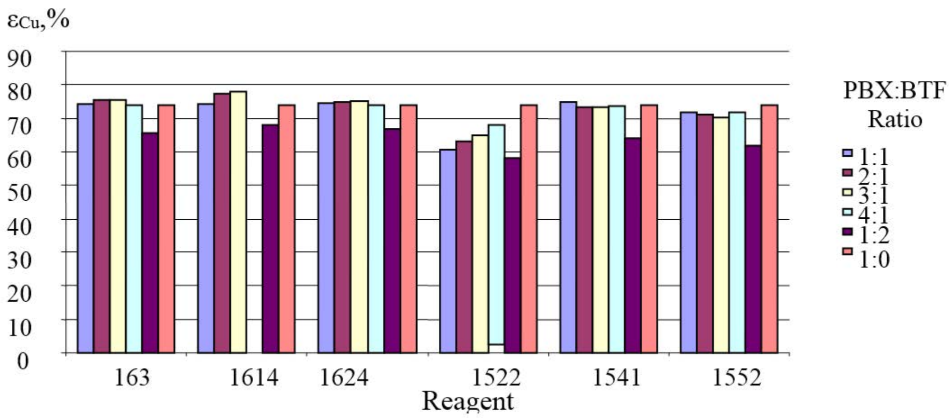

Figure 1. Extraction of copper in concentrate at different ratios of main and additional collectors

The best indicators of flotation obtained using BTF 163 and BTF 1614. The optimum ratio of potassium butyl xanthate (PBX) and BTF was 3: 1. In this case the copper extraction of 77.85% was obtained by using a combination of PBX + BTF1614 when the overall consumption of 300 g/t, i. e. the total collector consumption reduced by 100 g/t (Table 3).

Table 3. Results of copper converter slag flotation while reducing the total consumption of collectors

No op	Product	Yield,%	β^{Cu}, %	ε^{Cu}, %	Conditions
5	∑g Cu concent	**13.95**	**10.9**	**75.61**	pH $_{grinding}$=11,0-11,5 pH $_{flotation}$= 12,0-12,5 Collector PBX+BTF 163 ∑300 g/t
	Final tail	86.05	0.57	24.39	
	Initial slag	100.0	2.01	100	
6	∑ g Cu concent	**14.53**	**10.75**	**77.85**	pH $_{grinding}$=11,0-11,5 pH $_{flotation}$= 12,0-12,5 Collector PBX+BTF 1614 ∑300 g/t
	Final tail	85.47	0.52	22.15	
	Initial slag	100	2.01	100	

The results of flotation experiments using the maintenance mode of specified pH value in grinding and in flotation, with supply of established optimal combination of collectors (PBX: BTF1614 = 3: 1), with changing the total consumption of reagents are given in Table 4.

Table 4 shows that reducing the process pH to 6.8-5.5 has allowed to obtain an increase in the copper extraction by 6.68% with loss in the quality of copper concentrate by 1.48% and desired total consumption of collector decreases by 50% to 200 g / t.

Table 4. Results of copper converter slag flotation with decreasing pH process and combinations of collectors

No op	Denomination	Yield,%	β^{Cu}, %	ε^{Cu}, %	Conditions
8	**∑g Cu concent**	**18.3**	**9.27**	**84.53**	pH $_{grinding}$ = 6.5-6.8 pH $_{flotation}$ = 5.5-6.0 Collector PBX+BTF 1614 ∑200 g/t
	Final tail	81.7	0.38	15.47	
	Initial slag	100	2.01	100	

The study of distribution of the total iron, sulfur sulfide, gold and silver between the concentrate and final tailings when different modes of flotation have shown that growth of extraction of copper, gold, silver, and decrease of losses with final tailings corresponds to the growth of iron and sulfur extraction to the concentrate (Table 5). Consequently, the copper extraction increase is associated with the growth in the extraction in the splices concentrate of copper containing phases with iron sulfide.

Table 5. Results of extraction of copper, sulfur, iron in the concentrate when various modes of flotation

No op	Denomination	Yield, %	β^{Cu}, %	β^{S}, %	β^{Fe}, %	ε^{Cu}, %	ε^{S}, %	ε^{Fe}, %	Conditions
1	**∑g Cu concent**	**13.51**	**11.02**	**5.04**	**40.25**	**73.92**	**35.67**	**12.74**	pH $_{grin}$=11.0-11.5 pH $_{flot}$= 12.0-12.5 PBX 400g/t
	Final tail	86.49	0.61	1.42	43.05	26.08	60.86	87.26	
	Initial slag	100	2.02	1.91	42.67	100	100	100	
2	**∑g Cu concent**	**16.97**	**9.62**	**6.53**	**40.67**	**81.07**	**58.16**	**16.17**	pH $_{grin}$ = 9.0-9.3 pH $_{flot}$ = 8.0-8.5 PBX 400 g/t
	Final tail	83.03	0,46	0.76	43.08	18.93	41.84	83.83	
	Initial slag	100	2.01	1.91	42.67	100	100	100	
3	**∑g Cu concent**	**17.6**	**9.62**	**7.00**	**42.2**	**84.05**	**67.8**	**17.88**	pH $_{grin}$ = 6.5 -6.8 pH $_{flot}$ = 5.5- 6.0 PBX 400 g/t
	Final tail	82.4	0.39	0.7	41.4	15.95	32.2	82.12	
	Initial slag	100	2.01	1.82	41.54	100	100	100	
6	**∑g Cu con-cent**	**14.53**	**10.75**	**5.89**	**39.65**	**77.85**	**45.48**	**13.52**	pH $_{grin}$=11.0-11.5 pH $_{flot}$= 12.0-12.5 PBX +BTF 1614 300g/t
	Final tail	85.47	0.52	1.1	43.1	22.15	54.52	86.48	
	Initial slag	100	2.01	1.88	42.59	100	100	100	
7	**∑g Cu con-cent**	**17.3**	**9.75**	**6.88**	**40.54**	**83.6**	**64.27**	**16.86**	pH $_{grin}$ = 9.0-9.3 pH $_{flot}$ = 8.0-8.5 PBX +BTF 1614 250g/t
	Final tail	82.7	0.4	0.8	41.8	16.4	35.73	83.14	
	Initial slag	100	2.02	1.85	41.58	100	100	100	
8	**∑g Cu con-cent**	**18.3**	**9.27**	**7.03**	**41.12**	**84.53**	**68.92**	**18.2**	pH $_{grinding}$ = 6.5-6.8 pH $_{flotation}$ = 5.5-6.0 PBX +BTF 1614 200 g/t
	Final tail	81.7	0.38	0.71	41.5	15.47	31.08	81.8	
	Initial slag	100	2.01	1.87	41.44	100	100	100	

Table 6. The results of the closed experiments using PBX and combinations of PBX with BTF 1614

No op	Denomination	Yield, %	β^{Cu}, %	β^{Au}, g/t	β^{Ag}, g/t	ε^{Cu}, %	ε^{Au}, %	ε^{Ag}, %	Conditions
9	**∑g Cu concent**	**14.17**	**10.55**	**1.43**	**46.4**	**73.97**	**48.57**	**62.99**	pH $_{grin}$=11.0-11.5 pH $_{flot}$= 12.0-12.5 PBX 400 g/t
	Final tail	85.83	0.61	0.25	4.0	26.03	51.43	37.01	
	Initial slag	100	2.01	0.42	11.5	100.0	100.0	100.0	

10	**∑g Cu concent**	**19.14**	**9.02**	**1.15**	**40.2**	**84.22**	**54.18**	**72.38**	pH $_{grin}$ = 6.5 -6.8 pH $_{flot}$ = 5.5-6.0 PBX 400 g/t
	Final tail	80.86	0.40	0.23	3.45	15.78	45.82	27.62	
	Initial slag	100	2.05	0.41	10.10	100.0	100.0	100.0	
11	**∑g Cu concent**	**15.3**	**9.93**	**1.32**	**44.8**	**79.02**	**48.82**	**64.11**	pH $_{grin}$ =11.0-11.5 pH $_{flot}$= 12.0-12.5 PBX:BTF 3:1 300 g/t
	Final tail	84.7	0.48	0.25	4.53	18.04	51.18	35.89	
	Initial slag	100	1.92	0.41	10.69	100.0	100.0	100.0	
12	**∑g Cu concent**	**18.01**	**9.65**	**1.38**	**42.9**	**85.13**	**60.25**	**72.92**	pH $_{grin}$ = 6.5 -6.8 pH $_{flot}$= 5.5-6.0 PBX:BTF 3:1 200 g/t
	Final tail	81.99	0.37	0.2	3.53	14.86	39.75	27.08	
	Initial slag	100	2.04	0.41	10.59	100.0	100.0	100.0	

Analysis of concentrates and flotation tailings on gold and silver content in various reagent modes showed that when decreasing the process pH and supply of collectors combination the increase in gold and silver extraction in concentrate was observed (Table 6).

Conclusion

The combination of potassium butyl xanthate as the main reagent of collectors and BTF series reagent as an additional in the flotation process of copper smelting slag production in recycle water of the mining and processing enterprise allows increasing the extraction of copper, gold and silver in concentrate when decreasing twice the total consumption of collector compared to the traditionally used reagent mode using only potassium butyl xanthate.

In the alkaline medium (pH> 11), the increase in the extraction of copper in concentrate with the expected decrease in quality of the concentrate was obtained using reagents BTF: 1541,163, 1624, 1614.

The best results were obtained using BTF1614 reagent in combination with potassium butyl xanthate at the ratio: PBX:BTF = 3: 1. In an alkaline medium (pH greater than 11) the increase when extraction to the concentrate was as follows: copper – 5.05% , gold – 0.25%, silver – 1.12%. The copper content in the final tailings was reduced from 0.61% to 0.48%. At the optimum pH of flotation process (pH less than 7 to 6.8-5.5) the increase in the extraction of copper in the concentrate amounted to 11.16 % as a result of the active flotation of copper sulfide splices with pyrite. The increase in extraction of gold and silver in the concentrate were 11.68% and 9.93% respectively. The copper content in the final tailings at the same time reduced to 0.37%.

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