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THE MAIN REASONS FOR INCREASED COPPER LOSSES WITH SLAGS FROM VANYUKOV FURNACE

The article examines the factors affecting to the loss of copper with slags during autogenous smelting of copper concentrates at the Balkhash copper smelting plant (BCP). The composition of concentrates processed in the Vanyukov furnace was analyzed. Slag formation during alloying FeO with ores containing approximately the same amount of SiO$_2$ was studied. The fluxing ability of silicate ore used in charge smelting at BCP has been determined. A scanning electron microscope (SEM) was used to study the distribution of elements in the slag and the main reason for the low fluxing ability of the ores used at BCP was revealed.

Keywords: Vanyukov furnace, chemical composition, autogenous smelting, copper loss, X-ray investigation

INTRODUCTION

Over the past decades, in copper pyrometallurgy have found wide application autogenous processes, such as flash smelting or processes: Outokumpu, Mitsubishi, Noranda, El-Teniente, Aizasmelt, Ausmelt and smelting in the Vanyukov furnace. The last of the above processes is used at BCP and distinguished by high specific productivity, the ability to process relatively poor in copper sulfide concentrates of any granulometric composition, using blast with high oxygen content. However, along with the above advantages, the process has a number of disadvantages, one of which is high copper losses with slag.

Slags play an important role in pyrometallurgical processes. If earlier slag was regarded as waste, now it is a secondary resource, since the favorable physical and mechanical characteristics of copper slag make it possible to use it for the production of products such as cement, aggregate, ballast, abrasive, roofing granules, glass, tiles, etc. Therefore, the integrated use of recycled materials is becoming increasingly popular [1-3].

Today, the deterioration of the composition of the raw material base, the entry into production of concentrates with a copper content of 12 to 23 % with a high content of undesirable impurities such as zinc, arsenic, lead, and violation of the technological mode of the process of separating matte and slag, leads to an increase in copper losses with slags, which in turn requires their further impoverishment.

There are known many methods for depletion of slags. In practice, methods of natural depletion of slags

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from copper-smelting production in electric furnaces [4], depletion with various reducing agents such as aluminum-containing waste [5], waste cooking oil [6], carbon flotoconcentrate [7], or a combination of a reducing agent and a sulfidizing agent [8].

Despite the fact that a huge number of slag depletion options have been developed, they all have a number of disadvantages, and only partially solve the problem of slag depletion and lead to significant irreversible losses of metal with slag. Therefore, ways to reduce the loss of copper with slag in the process of autogenous smelting are becoming increasingly important today.

RESEARCH METHODOLOGY

The samples of the slags were obtained from Vanyukov furnace in Balkhash Copper-Smelting Plant. They were subjected to chemical, X-ray phase, mineralogical, and X-ray fluorescence analysis. X-ray phase analysis was carried out on a DRON-3M diffractometer using Co-Kα radiation, with an Fe filter, heating rate 2 K/min, X-ray fluorescence multi-element automated analysis was carried out on a wave-dispersive combined spectrometer Axios. Also was used SEM with analyzer a Jeol JXA-8230 to study the distribution of elements in slag samples.

RESULTS AND DISCUSSION

The involvement in the production of Eastern Kazakhstan concentrates with an increased zinc content (Table 1) caused a change in the physicochemical properties of the slag, which led to an increase in copper losses during the smelting of the charge.

It is generally accepted that the loss of metals in slags has 2 reasons: chemical dissolution of metals and

Table 1 **Composition of concentrates supplied to Vanyukov furnace at BCP, by main components/ mas. %**

Concentrate supplier	Cu	S	Fe	SiO$_2$	Zn
1	2	3	4	5	6
ZhGOK	17,0	35,9	30,2	4,2	4,0
VKMHK	23,0	29,2	25,8	8,9	3,4
Belous OF	18,0	32,9	24,3	4,0	9,7
Aktogai	22,0	28,0	25,7	14,7	-
Bozymchak	23,0	20,1	19,2	16,9	0,6
Bozshakol	16,0	33,0	28,8	7,6	0,2
Nikol.OF	12,0	25,0	17,0	26,6	7,1
KOF (Cu c-te)	12,3	35,0	28,3	11,0	5,2
KOF (pyrite)	1,3	38,0	31,1	13,8	5,0
NUR OF	20,0	28,0	26,9	15,0	0,4
BOF	18,2	24,9	21,6	11,9	0,5

Table 2 **Chemical composition of flux ores in Kazakhstan/ mas. %**

№ of flux	Content of components/ mas. %				
	SiO$_2$	Al$_2$O$_3$	CaO	MgO	Fe
1	65,7	17,50	0,70	0,18	3,4
2	65,5	13,95	1,70	1,30	3,3
3	65,2	11,30	3,45	0,43	3,3

mechanical capture of metal droplets [9-12]. It was also revealed that the content of silica in the slag is the most important technological parameter of the melting process in the PV furnace. Many indicators of charge processing, the stability of the process and also the loss of copper with slag depend on its value.

Table 1 shows that the content of iron sulfide in the charge is insufficient to maintain the heat balance of the furnace since the bulk of the heat during smelting comes from the oxidation of FeS ($5,7 \cdot 10^6$ kJ / t), therefore, fed additional coal (0,5 – 0,9 t/h) and pyrite concentrate KOF (≈ 3 %).

Technological calculations for the smelting of raw materials with a content in the charge: copper from 4 to 16 %, sulfur – 31 %, and silica – 15 %, when using a silicate flux containing 70 % SiO$_2$, showed that with a decrease in the content of copper in the charge, its losses increase, as the volume of the resulting slags increases, both due to the slag-forming components of the concentrates, and a significant increase in the proportion of silicate flux in the charge for slagging oxidizing FeS [13].

The kinetics of dissolution of silica in oxide and oxide-sulfide melts has been previously studied by many scientists. In [14] by the method of a rotating quartz disk, in the temperature range 1 200 – 1 350 °C in the FeO-FeS (5, 10, 25 % FeS) and FeO-FeS-SiO$_2$ systems, it was found that the dissolution rate of quartz increases with increasing temperature and mixing intensity and decreases with increasing FeS content and even more - with increasing Cu$_2$S content.

When 3 – 5 % CaO is added to the oxysulfide melt of iron, the rate of dissolution of SiO$_2$ increases, and with the content of 8 % CaO in the melt, the content of magnetite in it decreases 1,8-3,1 times [15]. However, a further increase in % CaO leads to a decrease in the rate of dissolution of SiO$_2$. When 10 % Al$_2$O$_3$ is added to the

FeO - FeS system, the dissolution rate of quartz decreases, and a further increase in the amount of Al$_2$O$_3$ in the system leads to the formation of herzenite FeO - Al$_2$O$_3$. Replacing FeO with Fe$_3$O$_4$ (from 4,55 to 16,3 %) leads to a noticeable decrease in the rate of assimilation of quartz by the melt. In the FeO-FeS-SiO$_2$ system, the dissolution rate of quartz decreases with an increase in FeS concentration, and increases with the addition of 3 – 8 % CaO.

The negative effect of aluminum oxide on the dissolution of quartz in various oxide-sulfide melts was confirmed in [16 - 17]. When studying the phase formation in the FeO – silicate ore system, the process of slagging was studied using various fluxes, used mainly at BCP and containing approximately the same amount of SiO$_2$, but differing in the content of Al$_2$O$_3$ and CaO (Table 2).

Based on the results of X-ray phase and petrographic analysis, it was revealed that the basis of all three ores is α-quartz.

Besides α-quartz, ore No. 1 contains: andalusite Al$_2$SiO$_5$, anorthoclase (K, Na) AlSi$_3$O$_8$, pyrophyllite Al$_2$Si$_4$O$_{10}$ (OH)$_2$, muscovite, kaolinite, and single grains of hematite and iron hydroxides.

Ore No. 2, in addition to α-quartz, contains: andesine CaAl$_2$SiO$_8$, muscovite KAl$_2$[Si$_3$AlO$_{10}$](OH)$_2$, calcite CaCO$_3$, pyrite, kaolinite Al$_4$Si$_4$O$_{10}$(OH)$_8$, hypersthene (Mg, Fe) OSiO$_2$.

In ore No. 3, in addition to α-quartz, calcite, muscovite, iron hydroxides, and single grains of pyrite are also determined.

Thus, in the studied ores, one of the main slag-forming substances - silica partially bound with alumina, in ore No. 2 there is also a compound of magnesium with silica - hypersthene. Therefore, it should be expected that the lower the content of "free" silica in the FeO-SiO$_2$ system, the more difficult slag formation will be, since the amount of ore for slagging the resulting iron (II) oxide was calculated based on the chemical composition of the flux in terms of SiO$_2$, taking its activity equal to 1. The more difficult the formation of fayalite is, the easier and more complete the oxidation of iron (II) oxide will be.

The source of FeO was oxalic iron (analytical grade), which, when heated to 850 °C, decomposes into FeO, CO, CO$_2$ and H$_2$O.

A weighed portion of FeC$_2$O$_4$.2H$_2$O and ore was taken from the calculation of the complete slagging of obtained FeO with silica available in the ore, then it was thoroughly mixed, ground and placed in a pre-calcined crucible of much larger size in a thin layer. After that, the crucible was lowered into a preheated furnace. The sampling interval is 1 min, that is, after 1, 2 ... 14 min after lowering the crucible with a weighed portion into the isothermal zone of the furnace. After excavation, the crucible was tempered on a massive iron plate.

Experiments were carried out at a temperature of 1 210 – 1 220 °C to slow down the rate of slag formation. The time of the beginning and end of phase formation with these fluxes in the temperature range 1 210 – 1 220 °C is the same, but slagging and oxidation of iron (II) oxide proceeds in them in different ways.

By X-ray phase analysis, it was possible to determine that during the slagging of FeO and ore No. 1, with the least amount of "free" silica, along with the appearance of fayalite (the base of the sample), magnetite, α-quartz and the maximum, in comparison with the other two fluxes, content of hematite are recorded.

Petrographic analysis also revealed pyroxene of the augite type (Ca, Na) (Mg, Fe, Al) [(Si, Al) $2O_6$] in this sample. When the melt is held for 10 minutes in a given temperature range, augite becomes the basis of the sample instead of fayalite. The rest of the components are also present in the sample.

During slag formation in the system ore No. 2 – FeO, in addition to hematite, magnetite, fayalite and α-quartz (as in X-ray structural analysis), petrographic analysis determines - FeO wustite, iron hydroxides and small sulfide inclusions. After 10 minutes of exposure at 1 210 – 1 220 °C, there appears pyroxene, presumably augite and quartz glass. Iron hydroxides and wustite disappear.

When alloying ore No. 3 with iron oxide (II) in the temperature range 1 210 – 1 220 °C at the beginning of slag formation with a 5 - minute exposure, petrographic analysis determines: magnetite, α-quartz, albite NaAl-Si_3O_8 [2U (-), N ~ 1,530], wustite, fayalite. Then, upon complete melting of the sample and holding it in a given temperature range, the following phases were found in the sample: magnetite, delafossite (the original colored ore No. 3 contains copper), fayalite, augite, α-quartz, hematite, and quartz glass.

Thus, in the interaction of silica fluxes with a high alumina content, along with fayalite, a compound of the augite type (Ca, Na) (Mg, Fe, Al) [(Si, Al) $2O_6$] appears in the slag phase. Moreover, when iron (II) oxide is slagged with ore No. 1, with a maximum Al_2O_3 content, augite appears immediately, at the beginning of the slag phase formation process and, when it is completely formed, becomes the basis of the sample instead of fayalite. With a lower content of Al_2O_3, during slagging of FeO with ores No. 2 and 3, augite is formed later and does not prevail over fayalite in terms of content. Augite is an aluminous pyroxene that melts with difficulty at a temperature of 1 500 °C [18].

It was found that the lower the Al_2O_3 content and the higher the CaO content in the ore with the same silica content, the greater the fraction of the fayalite phase in the slag and the slower the oxidation process of the wustite dissolved in it, which is consistent with the data from [14]. The presence of $CaCO_3$ calcite in ores 2 and 3, which completely dissociates in the temperature range 900 – 1 000 °C with a maximum development at 940 °C, will increase the contact area of slag-forming oxides with FeO and thus accelerate the formation of the slag phase.

It was noted that at the initial stage, in the first 5 - 6 minutes, in the presence of «free» quartz in the ore-iron (II) oxide system, the rate of slag formation is quite high. Then, with a decrease in the content of «free» quartz in the system, the rate of slag formation slows down.
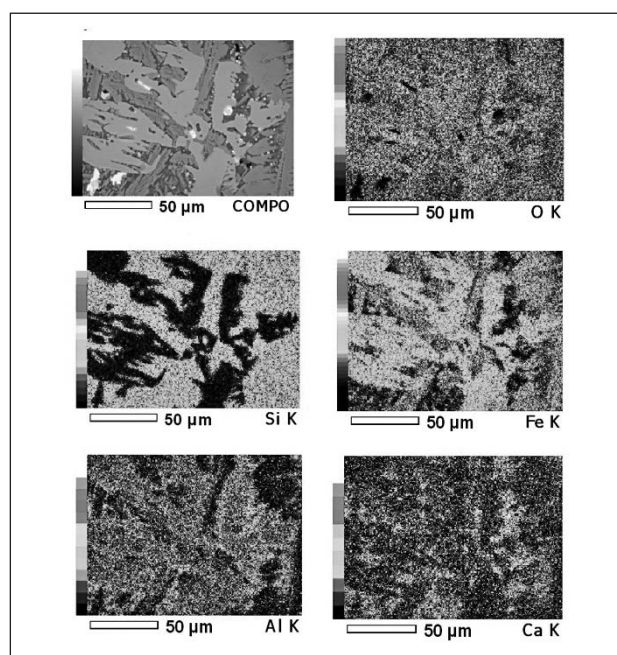

Figure 1 – Distribution of elements in slag

A decrease in the phase of a-quartz will accordingly decrease the rate and completeness of slagging of iron oxide (II). It should be noted that all compounds with silica are stable in the temperature range of 1 210 – 1 220 °C and will negatively affect the kinetics of slagging.

Currently, at BCP, when melting the charge, silicate gold-bearing ore of the reflective class is used. X-ray fluorescence analysis showed that it contains, mas. % : 67,65 SiO_2; 14,56 Al_2O_3; 0,51 MgO; 2,47 CaO; 3,13 K_2O; 2,70 Fe_2O_3. Then its fluxing ability will be:

FA= C_{SiO2} + C_{CaO} – 1,73*C'_{Al2O3} – 0,39*C''_{Al2O3} – 0,75C_{MgO} [17] or

FA = 67,65 + 2,47 – 1,73 * 10,07 – 0,39 * 4,49 – 0,75 * 0,51 = 50,65

that is, about half of the supplied flux is not flux, moreover will require additional heat for heating and melting.

X-ray phase analysis revealed in the ore sample: quartz; albite - $NaAlSi_3O_8$; calcite - $CaCO_3$; grossular - $Ca_3Al_2Si_3O_{12}$; anorthoclase - $(Na,K)(Si_3Al)O_8$ and muscovite - 2M1 - $KAl_2(Si,Al)_4 O_{10}(OH)_2$.

Considering the given phase composition of the flux ore and its transformation upon heating, it can be argued that a rather viscous slag melt (albite, anorthoclase, mullite) will form in the furnace [18] with impregnations of unmelted individual aluminosilicates and quartz. The interaction of quartz with the oxidizing iron of the concentrates will be slowed down, and part of the iron will begin to oxidize to magnetite or hematite, which will contribute to an increase in copper losses both in dissolved and suspended state, due to the strong heterogenization of the slag and its high oxidation potential.

To study the distribution of elements in the slag dump slag was taken from the PV-1 mixer, it's composi-

tion, mas. %: 22,93 SiO_2; 5,10 Al_2O_3; 0,86 MgO; 1,61 CaO; 39,7 Fe; 1,07 Cu; 2,45 Zn; 0,46 Pb; 1,27 S; 0,90 K_2O; 0,65 Na2O. The distribution of some elements in slag is shown in Figure 1.

It can be seen from the presented micrograph that the area rich in silicon is interconnected with the area with the lowest iron content, but the maximum one for aluminum and calcium. The areas rich in iron contain much less silica than the most enriched in aluminum and calcium, which is evident from their color on the micrograph.

That is, the flux used at BCP when melting the charge poorly slags out the oxidizing iron. The bonds between silica and oxides of aluminum and calcium in the ore are not broken, so there is no good interaction between the oxidizing components of the charge and the silica of the flux.

CONCLUSION

The conducted studies had shown the main reasons for increased copper losses with dump slags at BCP:
- low melting temperature, as a result of a decrease in the quality of processed copper concentrates and flux materials;
- insufficient fluxing ability of silicate ore used in charge smelting, which is associated with the preferred use of gold-bearing ores, rich in aluminum oxide, and, for rapid slag formation, requires feeding into the furnace a large excess of it, against the calculated one, to obtain a relatively homogeneous melt. However, an increase in the loading of flux materials, in turn, leads to an even greater deficit of heat and the production of heterogeneous slag melts with a high copper content in them, both in dissolved form and in the form of mechanical suspension. And the output of furnace slag itself will increase, which will further increase the total loss of copper.

Acknowledgments

REFERENCES

[1] I. A. Onaev, Physical and chemical properties of non-ferrous metallurgy slags, Nauka, Alma-Ata, 1972, 118 p.
[2] A. V. Vanjukov, V. Ja. Zajcev, Slags and mattes of non-ferrous metallurgy, Metallurgija M, 1969, 5 p.
[3] S. A. Kvyatkovskii, E. A. Sit'ko, B. M. Sukurov, Metallurgist, 64 (2020), 678-686, https://doi.org/10.1007/s11015-020-01044-2.
[4] P. Coursol, N. C. Valencia, P. Macrey, S. Bell, and B. Davis, JOM, 64 (2012) 11, 1305-1313.
[5] Khojiev, Yusupkhodjayev, Aribjonova, Beknazarova, International Journal of Innovative Technology and Exploring Engineering, 9 (2019), 2831-2837, https://doi.org/10.35940/ijitee.B7200.129219.
[6] Shiwei Zhou, Yonggang Wei, Shuoyao Zhang, Bo Li, Hua Wang, Yindong Yang, Mansoor Barati, Journal of Cleaner Production, 236 (2019), 117668, https://doi.org/10.1016/j.jclepro.2019.117668.
[7] L. Blacha, J. Łabaj, M. Jodkowski and A. Smalcerz, Metalurgija, 59 (2020) 3, 329-332.
[8] X. Yang, Zhang, J., Zhang, Metall Mater Trans B, 49 (2018), 3118–3126, https://doi.org/10.1007/s11663-018-1396-3.
[9] J. C. Fernandez-Caliani, G. Rios, J. Martinez, F. J. Jimenez, Journal of Mining and Metallurgy, Section B: Metallurgy, 48 (2012) 2, 161-171, https://doi.org/10.2298/jmmb111111027f
[10] I. Imris, M. Sanchez, G. Achurra, Mineral Proces. and Extractive Metallurgy, 114 (2005) 3, 135-140, https://doi.org/10.1179/037195505X49769
[11] N. Cardona, P. Coursol, P. J. Mackey, R. Parra, Canadian Metallurgical Quarterly, (2011) 50, 318-329.
[12] J. Yannopoulos, Can Metall Q, (1970) 10, 291-307.
[13] B. K. Kenzhaliev, S. A. Kvjatkovskij, S. M. Kozhahmetov, L. V. Sokolovskaja, Complex use of mineral raw materials, (2018) 3, 45-53, https://doi.org/10.31643/2018/6445.16
[14] I. A. Montilo, S. N. Shin, Cvetnye metally (1969) 1, 44-46.
[15] Zuo Zongliang, Qingbo, Liu Junxiang, Qin Qin, Huaqing Xie, Fan Yang, Wenjun Duan, ISIJ International, 57 (2017) 2, 220-227, https://doi.org/10.2355/isijinternational.ISIJINT-2016-402
[16] N. E. Fokina, I. A. Montilo, Ju. P. Nikitin, Issledovanija shlakovyh rasplavov, Sverdlovsk, (1983) 4.3, 160-162.
[17] V. M. Bobrov, S. M. Kozhahmetov, E. A. Sitko, Cvetnye metally, (2010) 4, 51 - 55.
[18] A. G. Betehtin, Kurs mineralogii, KDU, 2007, pp. 560-561.