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ANALYSIS OF COPPER LOSSES THROUGHOUT WEAK ACID EFFLUENT FLOWS GENERATED DURING OFF-GAS TREATMENT IN THE NEW COPPER SMELTER RTB BOR

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Abstract

The previous inadequate treatment of off-gas in RTB Bor in Serbia has resulted in serious pollution of the environment and the possibly high losses of copper through the effluent flows. The project of New Copper Smelter RTB Bor, besides the new flash smelting furnace (FSF) and the reconstruction of Pierce-Smith converter (PSC), includes more effective effluent treatment. Paper presents an analysis of the new FSF and PSC off-gas treatment, determination of copper losses throughout generated wastewaters and discussion of its possible valorization. Assumptions about the solubility of metals phases present in the FSF and PSC off-gas, obtained by the treatment process simulation, were compared with the leaching results of flue dusts. Determined wastewaters characteristics indicate that the PSC flow is significantly richer in copper, mostly present in insoluble metallic/sulfide form, while the FSF flow has low concentration of copper in the form of completely soluble oxide/sulfate. The possible scenario for the copper valorization, considering arsenic and lead as limiting factors, is the separation of the FSF and PSC flows, return of the metallic/sulfide solid phase to the smelting process and recovery from the sulfate/oxide liquid phase.

Keywords: Copper smelter, off-gas treatment, arsenic, lead.

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Introduction

RTB Bor in Serbia is an integrated copper mining and smelting complex considered to be one of the most important producers of copper and precious metals in Central Eastern Europe. Active copper production in RTB Bor, dating since 1903, was accompanied by devastation of the resources and the environment (pollution of water, air and soil, low level of energetic efficiency) [1]. The reduction of liquid and gaseous effluents is expected after the completion of modernization and reconstruction project in late 2013/ spring 2014 [2]. The Project includes replacement of the old roaster/reverberatory furnace with more efficient autogenous smelting of sulfide concentrates in a floating state - Outokumpu Flash Smelting Furnace [3]. RTB Bor has been waiting for autogenous smelting technology for over 70 years since the first initial tests of concentrate smelting to matte and slag without fuel were conducted in the same RTB Bor (former Société Française des Mines des Bor) just before the World War II [4].

The pyrometallurgical copper extraction in the New Copper Smelter RTB Bor from sulfide concentrate ($CuFeS_2$, FeS_2, Cu_2S and FeS) will consist of concentrate drying, autogenous smelting in a flash smelting furnace (FSF) and matte converting process in a Pierce- Smith converter (PSC). The products of copper sulfide concentrate smelting in the FSF are (i) molten sulfide matte (62% Cu), (ii) molten oxide slag (1.4% Cu) and (iii) off-gas (32.3% SO_2). Main oxidation reactions occurring in the FSF are [5]:

$$2CuFeS_2 + \frac{13}{4}O_2(g) \rightarrow \underbrace{Cu_2S \cdot \frac{1}{2}FeS}_{\text{matte}} + \frac{3}{2}FeO + \underbrace{\frac{5}{2}SO_2(g)}_{\text{in off-gas}} \tag{1}$$

$$2FeO + SiO_2 \rightarrow \underbrace{2FeO \cdot SiO_2}_{\text{slag}} \tag{2}$$

The process of matte converting takes place in the PSC during two periods [5] (i) the FeS elimination, the “slag blow” period:

$$2FeS + 3O_2(g) + SiO_2 \rightarrow \underbrace{2FeO \cdot SiO_2}_{\text{slag}} + \underbrace{2SO_2(g)}_{\text{in off-gas}} \tag{3}$$

(ii) the blister copper forming, the “copper blow” period:

$$Cu_2S + O_2(g) \rightarrow \underbrace{2Cu^0}_{\text{blister copper}} + \underbrace{2SO_2(g)}_{\text{in off gas}} \tag{4}$$

Generation of SO_2 during the FSF and PSC processes is essential disadvantage of conventional copper extraction from sulfide ores [6]. Beside SO_2, off gas may also carry substantial levels of copper and impurities (such as arsenic, zinc, lead, bismuth and iron) in the form of dust and volatile phase. Previous inadequate treatment of off-gas in RTB Bor resulted in sever environmental pollution [7, 8], as well as potentially high copper losses.

In order to increase process efficiency and reduce environmental impact, the New Copper Smelter RTB Bor will include more efficient treatment of off-gas and its further processing in a sulfuric acid plant (SAP). The FSF off-gas is treated in the waste heat boiler (WHB) and the electrostatic precipitator (ESP). During cooling in the WHB the oxide flue dust, suspended in SO_2 off-gas, will transform to sulfates:

$$MeO + SO_2(g) + \frac{1}{2}O_2(g) \rightarrow MeSO_4 \tag{5}$$

Flue dust from the FSF recovered in the WHB and ESP will be re-circulated to the smelting process. Off-gas from the ESP is transported to wet scrubber and cooling tower for wet gas cleaning. The solution from the scrubber and liquid phase formed during condensation in the cooling tower for the FSF off-gas treatment are the first source of weak acid effluent from the New Copper Smelter. The off-gas that exits the PSC will be cooled and treated in an evaporative cooling chamber (ECC). Dust collected in the ECC will be returned to the smelting process. Similar to the FSF wet gas cleaning, off-gas from PSC, will be further cooled and treated in a wet scrubber and a cooling tower. The purified FSF and PSC gases from cooling towers are mixed and sent to a wet electrostatic precipitator (WESP). Suspension created in the scrubber and cooling tower for the PSC off-gas and liquid formed in the WESP represent the second source of weak acid effluent from the New Copper Smelter. Technological scheme of the New Copper Smelter and off-gas cleaning processes is presented in Fig. 1. Generated weak acid effluents represent wastewaters from the copper smelter that will be processed in an effluent treatment plant (ETP). These wastewaters are characterized by high content in free sulfuric acid and heavy metals such as Cu, Ni, Zn, Fe, Pb, As, Bi, and Sb [9]. In the ETP, the FSF and PSC wastewaters will be neutralized with lime while heavy metals will precipitate as hydroxides and form wastewater treatment sludge [10]. Copper and other valuable metals collected in the wastewater treatment sludge represent irreversible loss from the copper smelting process.

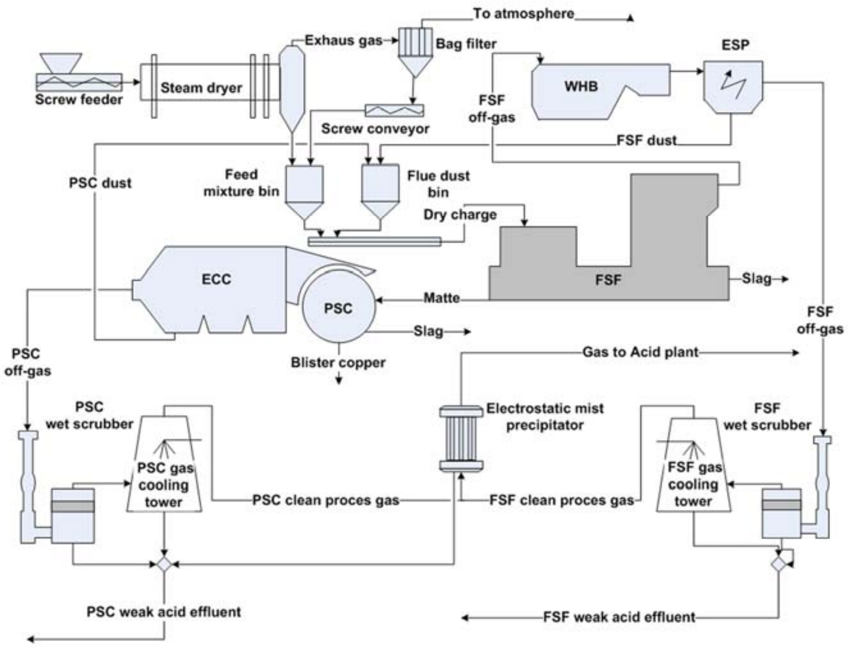

Fig. 1. Technological scheme of the New Copper Smelter and off-gas cleaning processes

The aim of the presented study was to analyze copper losses through the effluent flows (wastewaters) generated during the treatment of off-gas in the New Copper Smelter. The off-gas treatment simulation was done in Outotec's HSC Chemistry 6.1 software package [11] based on designed process condition in order to determine quantities and phases of metals in the form of volatiles and dust in off-gas flows. The composition of generated wastewaters is estimated using the simulation output which was compared to results of the smelter flue dust leaching. The copper losses are determined on the basis of the obtained effluents flows composition. The paper also considers possible methods for copper valorization from wastewaters in the New Copper Smelter in order to increase process efficiency. Authors have not encountered such approach to the analysis of off-gas treatment and losses of copper in the available literature. Testing plan scheme is presented in Fig 2.

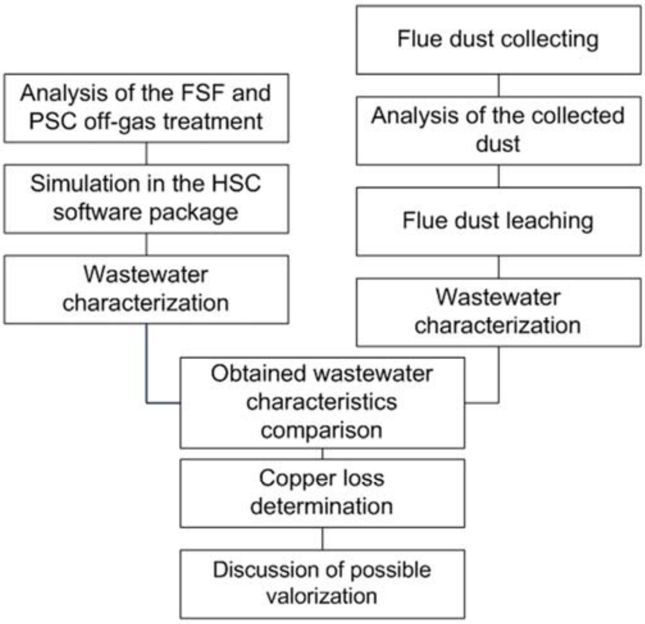

Fig. 2. Testing plan scheme

Experimental

Annual processing capacity of the New copper Smelter RTB Bor is 400 000 tones of copper concentrate and the production of 80 000 tons of anode copper. The projected content of copper and impurities in the concentrate mix for the New Copper Smelter is presented in Table 1.

Table 1. Copper concentrate mix composition*

New concentrate mix, tones per year	400 000
Main components, %	
Cu	20.79
Fe	29.76
S	34.70
SiO_2	7.55
Al_2O_3	2.45
Impurities, %	
Ni	0.01
Co	0.02
As	0.04
Pb	0.08
Sb	0.01
Bi	0.02
Zn	0.27

*Basic design project New Flash Furnace and Sulfuric Acid Plant RTB Bor, Serbia

Products of the concentrate smelting are matte, slag and off-gas bearing SO_2 and flue dust (Reactions 1 and 2). Flue dust in the FSF off-gas consists of small particles of unreacted concentrate or flux, droplets of matte and slag and volatilized elements in the concentrate [5]. In the PSC, matte is converted to blister copper, slag and SO_2 (Reactions 3 and 4). Besides SO_2, the PSC off-gas carries suspended particles of unreacted matte, slag and blister copper in the form of dust and volatiles. Designed characteristics of the FSF and PSC off-gas flows are presented in Table 2.

*Table 2. Designed characteristics of the FSF and PSC off-gas flows**

	Flow	Acid content, wt%	Metals content, wt%				
FSF	4.8 m^3/h	18.9	Cu	Fe	Zn	As	Pb
Volatiles	22.0 kg/h				8.8	31.7	13.5
Solids	5.8 kg/h		24.4	24.5	1.12	0.54	0.43
PSC	3.9 m^3/h	6.12	Cu	Fe	Zn	As	Pb
Volatiles	3.9 kg/h				0.8	22.5	10.1
Solids	95.6 kg/h		23.5	5.9	6.2	5.1	9.0

*Basic design project New Flash Furnace and Sulfuric Acid Plant RTB Bor, Serbia

The equilibrium phase composition of metals in the FSF off-gas that exits the furnace and in the WHB, as well as in the PSC off-gas in the ECC after slag and copper blow periods are determined in Outotec's HSC chemistry 6.1 software [11] based on designed off-gas flows, metals content and process temperature.

Prediction of weak acid effluent characteristics

In this study the characteristics of weak acid effluent flows obtained using two different methods will be compared in predicting the degree of dissolution of metals into the liquid effluent during the off-gas treatment. *The first method*: Characteristics of wastewaters from the New Copper Smelter were determined based on the equilibrium phase composition of metals in the FSF and PSC off-gas flows obtained by simulation in the HSC software package. It was assumed that 100% of all metals in the gas phase would be dissolved, except lead. Also, it was assumed that the metal oxides and sulfates were completely soluble in acid (except for lead oxide and sulfate), while the metallic and sulfide phases remained completely insoluble in weak acid effluents. Based on these assumptions, characteristics of wastewater from the FSF and PSC were determined. *The second method*: In order to determine the real degree of metals dissolution in weak acid effluents, dusts from electro-filters of smelting process (the old roaster/reverberatory furnace) and converting process (PSC) were collected, analyzed and leached for 28 h. Dusts were collected from each operation, approximately 100 grams in weight of individual samples, 3 times per day over a 7-day period. Individual samples were combined for each operation into one composite sample. Chemical compositions of the reverberatory furnace (RF) and PSC dusts were determined by standard volumetric methods. Mineral composition of RF dust was determined using an Ital Structures APD2000 X-ray diffractometer in a Bragg–Brentano geometry under the following conditions: CuKα radiation (λ = 1.5418 Å) and step-scan mode, range 5–60° 2θ, step-width 0.02 °, step-time 0.50 s. Leaching of dusts was performed under conditions that correspond to conditions in effluents: 18.9 %wt. H_2SO_4 at 54°C for the FSF flow and 6.12 %wt. H_2SO_4 at 57°C for the PSC flow. Based on leaching results and assumption that 100% of all metals in the gas phase would dissolve, except lead, characteristics of wastewaters from the FSF and PSC were determined.

Prediction of copper losses and scenarios for its valorization

Copper losses are calculated according to obtained characteristics of the FSF and PSC weak acid flows. Limiting conditions for the further treatment of effluents in order to recover copper are content of impurities, primarily arsenic and lead [12, 13]. For that reason the leaching of arsenic and lead from the RF and PSC dusts under various conditions was investigated: H_2SO_4 concentration of 5, 10, 15 and 20 %wt., leaching for 28 h at 20, 35, 50 and 65°C. In all systems liquid to solid ratio was 10. Scenarios for the possible copper valorization were analyzed on the basis of copper distribution between solid and liquid phases in effluent flows and leaching characteristics of As and Pb from solid phase. The latest researches on copper recovery from smelter effluents available in literature were also discussed.

Results and discussion

Equilibrium phase compositions in the FSF and PSC off-gas flows

Sulfur-oxygen potential diagram for Cu, Fe, Zn, Pb, As – O – S system at 1300°C is presented in Fig. 3. Conditions that correspond to the processes in the FSF and PSC are also marked.

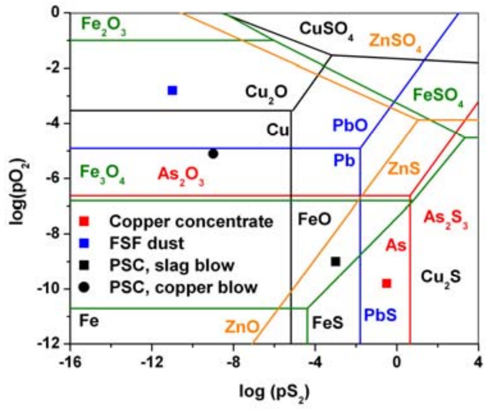

Fig. 3. Sulfur-oxygen potential diagram for Cu, Fe, Zn, Pb, As – O – S system at 1300^{o}C

Metals enter the smelting process in the form of sulfide concentrates. Flue dust suspended in off-gas from the FSF, as products of smelting, is mainly composed of metals oxides. Equilibrium compositions of metals in the FSF off-gas at the outlet of the furnace are presented in Fig. 4.

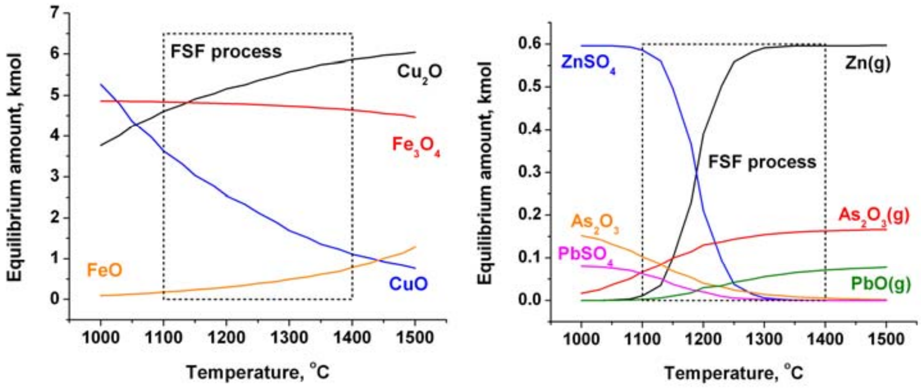

Fig. 4. Equilibrium composition of metals in the FSF off-gas at the outlet of the furnace

In the flue dust at the outlet of the furnace, copper will be in the form of Cu_2O and CuO, iron as oxides Fe_3O_4 and FeO. Arsenic, zinc and lead will be partially present in the gas phase, whereas sulfatization of Pb and Zn begins at this stage. The sulfatization process continues in the WHB where copper and iron are transformed to sulfates, Fig. 5.

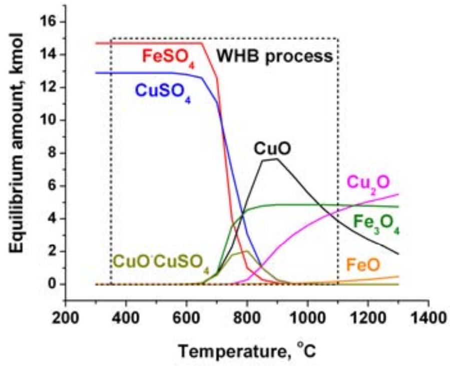

Fig. 5. Equilibrium composition of copper and iron in the WHB

Over 99% of the FSF flue dust will be recovered in the WHB and ESP. Projected off-gas flow to the FSF wet scrubber contains 6 kg/h of dust and 22 kg/h of volatiles.

Matte ($Cu_2S{\cdot}½FeS$) is converted to blister copper and slag during oxidation processes in the PSC: FeS oxidizes to FeO and Fe_3O_4 (the slag blow period) and Cu_2S to metallic copper (Cu) by more intense oxidation during copper blow period. The PSC off-gas, containing dust particles and volatiles, is sent to the ECC for de-dusting and cooling. Equilibrium composition of metals in the ECC after slag blow and copper blow periods are presented in Fig. 6. Metal phases whose quantities were less than 0.05 kmol after the copper blow period were not shown in Fig. 6.

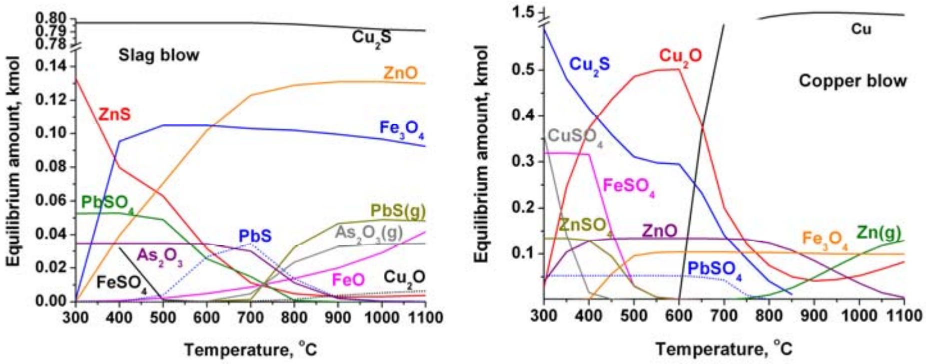

Fig. 6. Equilibrium compositions of metals in the ECC of the PCS

During the PSC off-gas cooling in the ECC after the slag blow period, copper remains in the sulfide form, arsenic as oxide, while iron and lead are transformed to sulfates. At 700°C, arsenic and lead will be partially present in the gas phase. During the cooling after the copper blow period, metallic copper will be transformed to sulfide and sulfate; iron, zinc and lead oxides will be sulfatized, while arsenic remains as As_2O_3. The gas phase at 700°C will also contain zinc in addition to arsenic and lead. Projected dust removal from the PSC off-gas flow in the ECC is 66%. The combined PSC off-gas flow after the slag blow and copper blow periods contains 95 kg/h of dusts and 4 kg/h of volatiles.

Table 3 shows the equilibrium metals form at 700°C in the WHB for the FSF off-gas flow and in the ECC for the PSC off-gas flow before and after solids (dust) removal. Obtained results of the metals distribution between the solid and gas phases and the distribution between soluble sulfate/oxide and insoluble metallic/sulfide phases was used to predict the characteristics of wastewater (the first prediction method).

Table 3. Equilibrium metals form composition in the WHB and ECC at 700°C before and after solids removal, wt. %

	The FSF off-gas			The PSC off-gas					
				Slag blow			Copper blow		
Metal	Form	Before	After	Form	Before	After	Form	Before	After
Cu	$CuSO_4$	100	100	Cu_2S	100	100	Cu	57.3	57.3
							Cu_2S	17.6	17.6
							Cu_2O	25.1	25.1
Fe	$FeSO_4$	100	100	Fe_3O_4	97.2	97.2	Fe_3O_4	97.2	97.2
				FeO	2.8	2.8	FeO	2.8	2.8
Zn	Zn (g)	5.9	96.2	ZnS	8.3	8.3	Zn (g)	0.6	0.8
	$ZnSO_4$	94.1	3.8	ZnO	91.7	91.7	ZnO	99.4	99.2
Pb	PbO (g)	12.8	99.1	PbS (g)	2.8	4.1	Pb (g)	0.5	0.7
	$PbSO_4$	87.2	0.9	$PbSO_4$	28.2	27.8	$PbSO_4$	81.6	81.4
				PbS	65.3	64.4	Pb	4.1	4.0
				PbO	3.7	3.6	PbO	13.8	13.9
As	As_2O_3 (g)	39.5	99.9	As_2O_3 (g)	13.6	19.3	As_2O_3 (g)	11.3	16.2
	As_2O_3	60.5	0.1	As_2O_3	86.4	80.7	As_2O_3	88.7	83.8

RF and PSC dust characteristics

Chemical composition of the RF and PSC dusts is presented in Table 4. Copper and iron are the main metal constituents in both dusts, with the RF dust richer in iron and the PSC dust in copper. SiO_2, which originates from the silica flux, is also present in both of dusts.

Table 4. The RF and PSC dusts chemical composition, wt. %

Dust	Cu	Fe	Zn	As	Pb	SiO_2	Al_2O_3	S
RF	5.94	15.45	1.00	0.50	0.18	38.85	13.22	2.79
PSC	45.04	8.67	3.00	0.09	2.37	13.52	0.75	12.74

XRD analysis of the RF dust showed the presence of two phases: chalcopyrite ($CuFeS_2$) and magnetite (Fe_3O_4). In addition to these phases, the presence of non-stoichiometric sulfides of other metals with general formula $CuFe_{1-x}M_xS$, where M = Zn, As, Pb, Ni is also possible.

Analysis of the PSC dust from RTB Bor [14] has shown that copper is present as sulfide (70-80%) and oxide (20-30%) and iron as Fe_2O_3 and Fe_3O_4.

Wastewater characteristics

Distribution of metals between solid and liquid phase in the FSF and PSC weak acid effluents based on described prediction methods are given in Fig. 7.

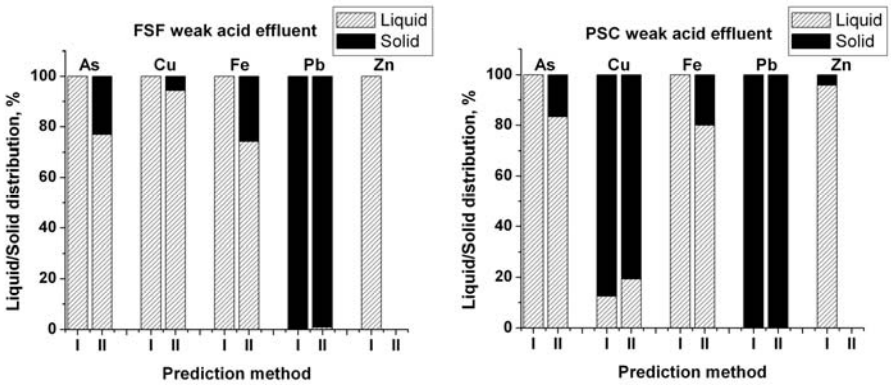

Fig. 7. Distribution of metals between liquid and solid phase in FSF and PSC weak acid effluents based on two prediction methods: I –HSC simulation, II – leaching results

There is a certain difference between two applied methods for the determination of metals content distribution in liquid/solid phase of the FSF and PSC effluent flows. Considerable differences are in predicting the leaching of arsenic and iron. In both flows, it is assumed that 100% of As and Fe, present as oxides, would dissolved, while leaching test results have shown 76.9% (FSF) and 83.3% (PSC) of arsenic extraction and 74.1% (FSF) and 80.1% (PSC) of iron. Leaching of copper in the FSF and PSC weak acid was 94.3% and 19.3% which is very similar to calculated 100% and 12.5%, respectively. Both, leaching results and calculations have shown that more than 99% of Pb remains in solid phase. Concentrations of zinc in leachates were not analyzed. Differences in the methods probably occur due to unreacted particles present in dusts, which were not taken into consideration for the HSC calculation of the equilibrium composition.

The FSF and PSC wastewaters characteristics calculations were done based on designed FSF and PSC off-gas flows content (Table 2) and liquid/solid distribution percent obtained by prediction methods (Fig.7) and presented in Tables 5 and 6.

Table 5. FSF weak acid effluent

Metals	Off-gas flow		Weak acid effluent flow			
			I method		II method	
	Volatiles, %	Solids, %	Dissolved, kg/h	Solids, kg/h	Dissolved, kg/h	Solids, kg/h
Cu	0.0	24.4	1.42	0.0	1.34	0.08
Fe	0.0	24.5	1.43	0.0	1.06	0.37
Zn	8.8	1.12	2.00	0.0	----	----
Pb	13.5	0.43	0.0	2.99	0.0	2.99
As	31.7	0.54	6.99	0.0	6.98	0.01

Table 6. PSC weak acid effluent

Metals	Off-gas flow,		Weak acid effluent flow,			
			I method		II method	
	Volatiles, %	Solids, %	Dissolved, kg/h	Solids, kg/h	Dissolved, kg/h	Solids, kg/h
Cu	0.0	23.5	2.81	19.68	4.34	18.15
Fe	0.0	5.9	5.66	0.00	4.53	1.13
Zn	0.8	6.2	6.48	0.25	----	----
Pb	10.1	9.0	0.00	17.91	0.00	17.91
As	22.5	5.1	5.70	0.00	4.90	0.80

The main difference among the methods is reflected in the distribution of iron content in liquid/solid phases in the FSF flow and the distribution of copper, iron and arsenic in the PSC flow. In the FSF flow, the concentration of dissolved iron, according to the method I, is higher than the Fe concentration determined by the second method, while the concentrations of copper, arsenic and lead are approximate. In the PSC flow, the method II predicted higher concentration of dissolved copper and lower concentration of dissolved arsenic and iron than the method I. Although the applied methods showed some differences in the dissolution of metals in the weak acid effluents, the differences in obtained wastewater characteristics are less considerable.

The copper losses determination

The copper losses, presented in Fig. 8, are determined considering the designed FSF and PSC effluent flows of 4.8 and 3.9 m^3/h, respectively, and their projected characteristics. The calculation was based on the method I. The total copper losses through the FSF effluent flow are 35.1 kg per day as dissolved copper and 535.8 kg/day through the PSC flow which includes 468.8 kg/day of copper as suspended solids and 67.0 kg/day of dissolved copper.

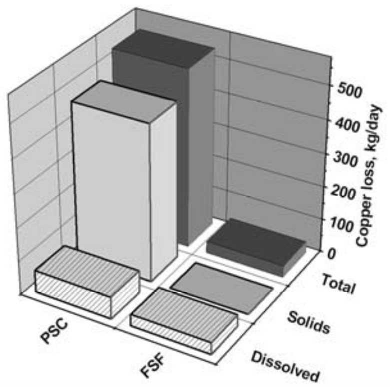

Fig. 8. Projected copper losses through the FSF and the PSC effluent flows, kg/day

There are significant differences in the content and liquid/solid distribution of copper between wastewater flows from the FSF and PSC. The PSC effluent flow is considerably richer in copper content than the FSF, accounting 94% of the total copper losses in both flows. In the FSF weak acid flow, over 94% of the copper is in the soluble form, while in the PSC flow more than 80% of copper remains in solid phase according to both prediction methods.

The copper valorization

Considering a very different nature of flue dusts and generated weak acid effluents, possible scenario for the copper valorization could be the separation of the FSF and PSC effluent flows and their individual treatment. In the FSF flow, copper is mainly present in the liquid phase, while in the PSC flow more than 80% of copper is in the solid form. For that reason the copper valorization could be further performed by separating the solid and liquid phases in each flow. The solid phase can be returned to the smelting process, while the copper from the liquid phase can be extracted using various hydrometallurgical methods.

Before returning the solid phase to the smelting process, the possibility of removing the impurities, particularly arsenic and lead, from copper should be considered. The leachability of arsenic and lead from the RF and the PSC flue dusts under different leaching conditions are presented in Fig. 9.

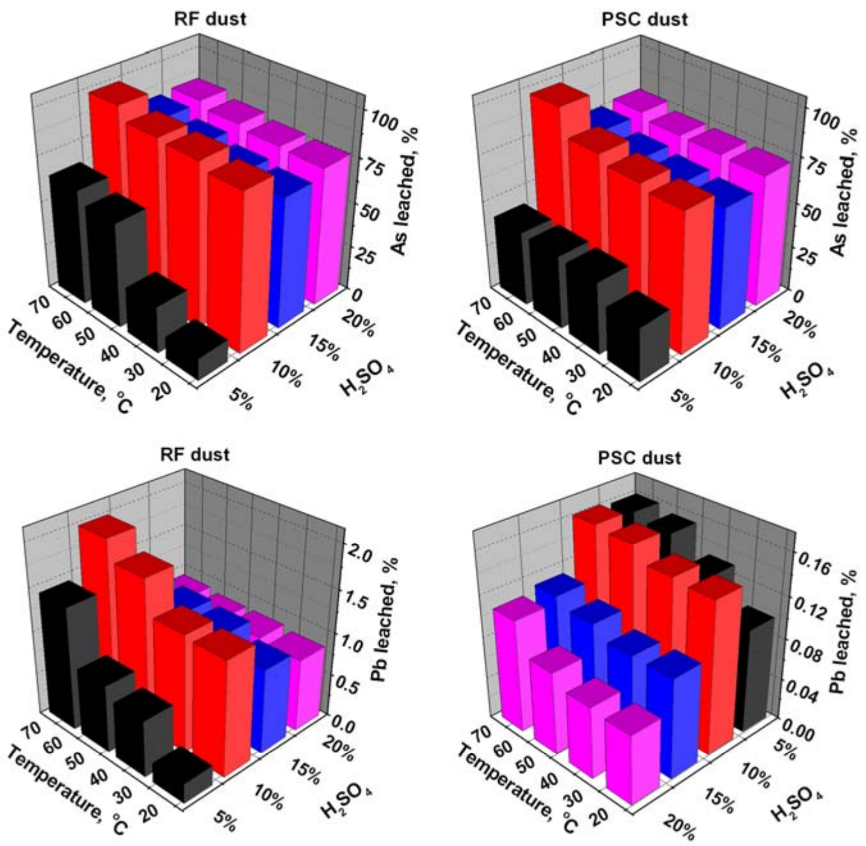

Fig. 9. The arsenic and lead leachability from the PSC and RF flue dusts under various conditions after 28 h of leaching

The amount of leached arsenic increased with increasing the leaching time and temperature, which was expected. However, the effect of increasing acid content on the arsenic leaching was varying. The arsenic extraction from the PSC and RF flue dusts was reduced with a further increase of acid content over 10%. The highest arsenic concentration in solution was obtained with 10% H_2SO_4 at 65°C after 28h of leaching. Under these condition 97.5% of arsenic was leached from the PSC dust and 99% from the RF dust. Unlike arsenic, lead remains almost completely insoluble under all tested conditions. Again, the highest leaching was achieved with 10% of H_2SO_4 which was 0.15% of lead leached from the PSC dust and 2% from the RF dust. Analyzing the results of arsenic and lead leaching and copper content in the FSF and PSC effluent flow, the following may be concluded:

a) By separating the solid from the liquid phase in the PSC flow, the solid phase would contain over 99% and 80% of total lead and copper content in this flow, respectively. If the PSC solid phase is returned to the process, total copper losses would be reduced by 82.1%. However, recirculation of dust to the FSF increases the content of impurities (such as arsenic, zinc, lead and iron) in the incoming batch and influences the quality of the process [13, 15]. Content of zinc and lead in the dust will have a limiting effect on the amount of recirculated material to the smelting process, while the content of arsenic in the dust defines the amount of recirculated material to the converting process [12]. Presented leaching results have shown that complete removal of arsenic from the solid phase would be achieved by solid/liquid separation in the PSC flow.

b) By separating the solid from the liquid phase in the FSF flow, the liquid phase would contain over 94% of copper together with dissolved arsenic. Recovery of copper from the solution can be achieved by further treatment of this liquid phase.

Morales et al. [16] studied the leaching of copper flash smelter flue dusts with weak sulfuric acid under atmospheric conditions. Arsenic in the solution after leaching is oxidized to As^{5+} by introducing O_2 to the system and precipitated by iron(III) sulfate as iron(III) arsenate. Copper remains in the solution with zinc and nickel. Copper recovery from the leaching liquid could be achieved by cementation with elemental iron or by electrolysis. In Codelco Norte (EcoMetales) in Chile, the dust leaching process with sulfuric acid is applied followed by return of the solid residue to the furnace, and the solution is sent to the solvent extraction and copper electrowinning process (SX-EW). The procedure is further improved by precipitation of arsenic as crystal scorodite ($FeAsO_4 \cdot 2H_2O$) from the super saturated solution [17]. The copper sulfate solution, obtained after leaching the dust with sulfuric acid, could be used directly as electrolyte in the copper electrorefining process [18]. Arsenic, antimony and other impurities should be removed from the solution before electrolysis due to the possibility of creating highly toxic arsine and stibine [19]. In the work done by Shibayama et al. [20] the dust was first subjected to the pyrometallurgical process which leads to the evaporation of arsenic for over 90%, while the rest is sent to the two-stage leaching process with sulfuric acid. The dissolved copper was recovered by solvent extraction. Recovery of copper from the liquid phase in the FSF and PSC effluent flows by using some of the above procedures would reduce the total copper losses by 17.9%.

The copper valorization from effluent flows, generated during the treatment processes of the FSF and PSC off-gases, depends on its concentration in effluents, the concentrations of other secondary elements, primarily arsenic and lead, and, then, the distribution of copper between the solid and liquid phases. The off-gas composition, including the concentration of copper, directly depends on the quality of the used copper concentrates and applied copper smelting technology.

Conclusion

Off-gases, generated during copper smelting processes, bear certain amount of valuable metals in the form of flue dust and volatiles. Solutions formed in wet scrubbers and cooling towers for the FSF and PSC off-gas treatment represent two sources of weak acid effluents (wastewaters) in the New Copper Smelter RTB Bor through which copper is irreversibly lost from the process. Characteristics of the wastewaters are determined by using two prediction methods. The first method is based on the equilibrium metal form compositions obtained by simulation of the FSF and PSC off-gas treatment process in the HSC software package. It was assumed that metals in oxide/sulfate form, present in dust, would dissolve (except lead) in weak acid together with metals present as volatiles. Metals in metallic/sulfide form would remain in solid phase. The second method is based on the results of the RF and PSC flue dusts leaching under conditions corresponding to the weak acid flows. Results of applied methods mostly differ in predictions of arsenic and iron solubility in both of flows, while the methods gave similar results in leaching of lead and copper.

Obtained wastewaters characteristics indicated that the FSF and PSC flows significantly differ in the content of copper and its distribution between the solid and the liquid phase. The PSC flow is significantly richer in copper, mostly present in insoluble metallic/sulfide form. The FSF flow has a low concentration of copper in the form of completely soluble oxide/sulfate. Daily losses of copper are estimated at over 500 kg of which 93% is lost through the PSC flow with over 80% of copper in the solid form. The possible scenario for the copper valorization from the effluents is the separation of FSF and PSC flows, as well as the separation of solids from the liquid phase. The leaching test results showed 97.5% and 99% arsenic leaching from the PSC and RF dusts, respectively, while lead remained almost completely insoluble. This means that the solid/liquid phase separation would lead to the separation of dissolved arsenic and copper from the solid phase in the FSF flow and removal of dissolved arsenic from solids containing lead and copper in the PSC flow. The return of the PSC solid phase into the production process would reduce the total copper loss by 82.1%. Recent studies on the recovery of copper from the liquid phase containing arsenic are discussed. Prior to copper extraction by using a variety of hydrometallurgical methods, it is necessary to remove arsenic from solution, usually by its precipitation as iron (III)-arsenate.

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