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Original scientific paper

The possibilities of the utilization of the polymetallic concentrate Čoka Marin

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Abstract: This paper presents the results of calculations of the composition of composite concentrates used as the charge in the Copper Smelter in Bor, from the aspect of the behavior of zinc, lead, arsenic, cadmium and mercury. These elements have extremely harmful effects on the environment and human health; hence it is crucial to comply with legal values of their emission into the environment.

Keywords: copper smelting; impurities; concentrate; ecology; distribution.

INTRODUCTION

Zinc, lead, arsenic, cadmium and mercury are toxic for most living organisms on the Earth. Even very small concentrations of these elements (expressed in ppm) have serious toxic effects.[1] The behavior and distribution of harmful elements in the production process in the Copper Smelter in Bor, have been observed for many years by the experts of Copper Institute (now Mining and Metallurgy Institute Bor).[1] These elements are major pollutants in the environment and have negative effect on the quality of the produced copper and sulfuric acid, which necessitates the continuous monitoring of their content in the starting raw materials. Based on previous studies in the Copper Smelter from the reverberatory furnace, with the gas phase, more than 50 % arsenic, 40–50 % lead and 41 % zinc present in starting charge are emitted into the atmosphere, while the rest is deposited in the slag.[2] During smelter treatment of concentrate, 48.7 % of the mercury is emitted with gases during roasting, and 47.3 % into the gases during smelting.[2]

Marin with a lot of impurities presents a demanding charge that could be treated using the existing technology in the reverberatory furnace only if the allowed limits of any harmful elements in starting mixture are not exceed. In this way, the risk of environmental accidents would be reduced to a minimum.

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The increased industrialization has been followed all over the world by the extraction and redistribution of mineral substances from their natural deposits. Passing through the processes of treatment and use, the mineral raw materials arrive *via* waste water, gases, dust and waste dumps into the air, water and land, and, thus, indirectly into the food chain.[3]

Lead is a typical accumulative poison. It causes the prevention of hemoglobin synthesis, neurological problems (aggressive and destructive behavior), kidney damage and even permanent brain damage.[4]

Zinc is one of the micro-elements necessary for the proper functioning of the body functioning, but in excessive doses can lead to problems in growth and reproduction.[1]

Arsenic, a metalloid that can enter into the body through the lungs and gastrointestinal tract, has negative influence on the process of protein coagulation, and could form complex compounds with co-enzymes.[5]

Cadmium is also an accumulative toxin that adversely affects important enzymes; causes bone disease and kidney damage. Inhalation of dust and gases containing cadmium leads to lung failure due to the accumulation of water in them.[6–8]

Mercury enters into the body by ingestion and inhalation and transfers *via* the blood to the brain where could pass through the blood–brain barrier and causes insomnia, depression and irritability. It also leads to kidney damage.[9] It is only temporarily deposited in the body and a large part is eliminated through the digestive system.

The sampling method for copper concentrates is defined by the SRPS Standard BG-3:451.

The technological analysis of a concentrate includes the determination of content the required elements for process optimization and technological process management, while the environmental analysis involves the determination of the contents of Pb, Zn, As, Sb, Cd, Se, Hg and Cl, which are used to perform an environmental assessment of the concentrate.

Lead and zinc are usually present in the copper ore in the form of PbS and ZnS, arsenic is present in the form of Cu_3AsS_4, FeAsS and Cu_3AsS_4 minerals,[10] while mercury is present in the form of HgS and cadmium in the form of CdS.

The associated elements in a copper concentrate are distributed during smelting according to their physico–chemical properties and are concentrated in the intermediates and products of the pyrometallurgical treatment. The behavior of each element depends on several factors, the most important of which are: the form in which they are present in the raw materials, the technological parameters of the applied process, their inter-relationship with other elements, the concentration of certain elements, *etc*. The parameters of the distribution each element can only be reliably determined by raw material treatment using the specific technology.[11]

A block diagram of copper concentrate treatment, including treatment of the off-gases and sulfuric acid production, is given in Fig. 1.

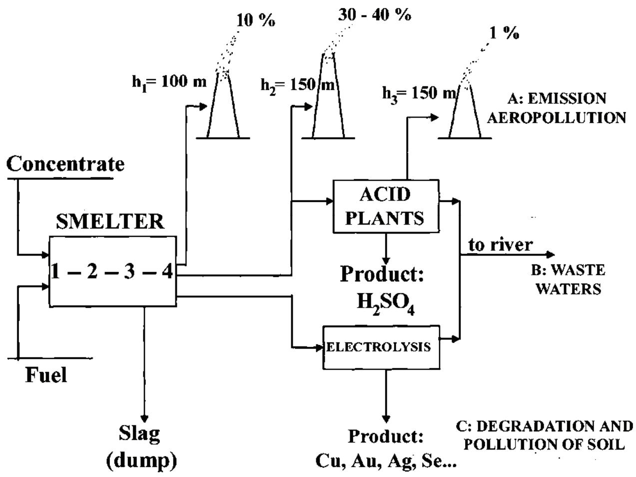


Fig. 1. Block diagram of copper concentrate treatment with pollution sources (1 – roasting; 2 – smelting; 3 – converting; 4 – flame refinement).

The distributions of zinc, lead and arsenic in the output products (anode copper, slag, sludge and water, gas) were calculated based on their emission in the period from 1991 to 1997.[12]

For the cadmium and mercury distribution, there are no available data about their emission, hence a critical analysis of the available data on their distribution through the output products of the copper concentrate treatment[2,3,13] was performed. The obtained distributions of Zn, Pb, As, Cd and Hg, determined as given above, are presented in Table I.

TABLE I. Distribution of Pb, Zn, Hg, Cd and As in the reverberatory furnace in %

Phase	Pb	Zn	Hg	Cd	As
Batch	100	100	100	100	100
Anode copper	1.95	0.05	0	1.37	2.44
Slag	63.76	54.39	5	8.45	12.06
Sludge and water	4.73	4.49	31.6	5.18	34.31
Gas	29.63	41.08	63.4	85	51.19

RESULTS AND DISCUSSION

Monitoring of the contents of impurities in the raw mixture

Using the polymetallic ore from the deposit "Čoka Marin", the collective concentrate (7.92 % Cu, 26 g t^{-1} Au, 127.2 g t^{-1} Ag, 3.92 % Zn, 1.1 % Pb, 0.98 % As, 0.0011 % Cd, 12.1 g t^{-1} Hg) is produced. This concentrate should be combined with the already used concentrates for the preparation the mixture in reverberatory furnace (the composition in relation to the contents of the impurities is given in Table II), in such a way that the composition of obtained concentrate mixture meets the allowed limits for the content of zinc, lead, arsenic, cadmium and mercury. The compositions of used imported concentrates (1--ASSAREL and 2-ELATZITE) are given in Table III. The allowed limits for the contents of zinc, lead, arsenic, cadmium and mercury, estimated based on the prescribed contents of these metals in the output gases of Copper Smelter, are listed in Table IV, from which it is possible to conclude that these impurities in the composite concentrate have to be significantly lower than in the concentrates delivered in the reverberatory furnace and used for the preparation of the mixture.

TABLE II. Input contents of impurities in the copper concentrate formed from the mixture (the amount of concentrate Čoka Marin was varied within the limits of 0–10 wt. %)

Concentrate	Weight (dmt)	Content, %				
		Zn	Pb	As	Cd	Hg
Bor	36050	0.68	0.15	0.19	0.0025	0.000104
Krivelj	86265	0.06	0.009	0.012	0.0027	0.000018
Majdanpek	47510	0.52	0.16	0.01	0.0026	0.000023
Import	30000	0.03	0.2	0.02	0.0025	0.00008
Čoka Marin	–	3.92	1.1	0.98	0.011	0.00121

TABLE III Composition of the used import concentrates (ratio 1:1)

Concentrate	Content, %				
	Zn	Pb	As	Cd	Hg
1	0.04	0.4	0.009	0.0025	0.00006
2	0.02	0.03	0.03	0.0025	0.0001

TABLE IV Allowed limits of the contents of heavy metals (Zn, Pb, As, Cd and Hg; internal limits applied in the Copper Smelter in Bor, based on the allowed values of these elements in the output gases)

Element	Individual concentrate, %	Composite concentrate, %
Zn+Pb	3	1.5
As	0.2	0.1
Cd	0.01	0.0025
Hg	0.0005	0.0002

Using the percentage amounts and the weight of the concentrates from Table II, the calculation was realized based on the obtained data for the contents of Zn, As, Pb, Cd and Hg in the domestic and imported concentrates. A detailed analysis of the results is shown in Figs. 2a–2d.

The changes in the contents of zinc and lead in the concentrate mixture containing varying amounts of Čoka Marin concentrate, within the limits 0–10 %, are presented in Fig. 2a. Analyzing this figure, it is possible to conclude that the combined contents of these two metals did not exceed the allowed limit of 1.5 % (Zn+Pb), even when the maximum 10 % of Čoka Marin concentrate was present in the mixture.

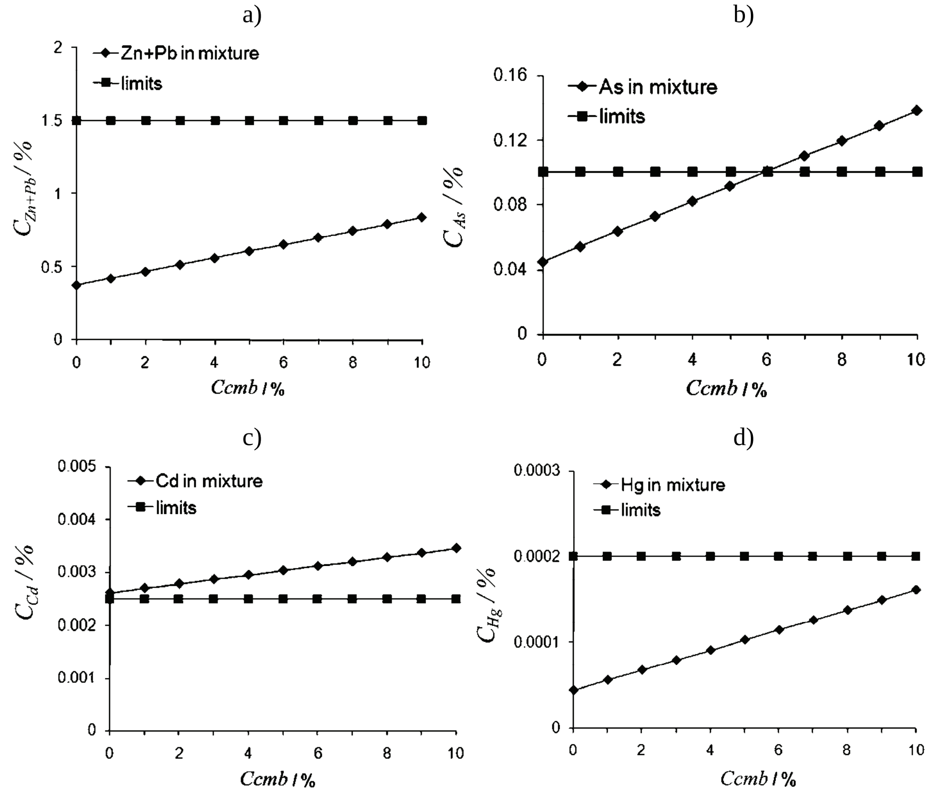


Fig. 2. Change of impurities content in the concentrate mixture depending on the varying contents of Čoka Marin concentrate (a – Zn+Pb; b – As; c – Cd and d – Hg); *Ccmb* – percentage of concentrate Čoka Marin in batch; C_{Zn+Pb} – percentage of zinc and lead in concentrate mixture; C_{As} – percentage of arsenic in concentrate mixture; C_{Cd} – percentage of cadmium in concentrate mixture; C_{Hg} – percentage of mercury in concentrate mixture.

The change in the content of arsenic in the concentrate mixture containing varying amounts of Čoka Marin concentrate, within the limits 0–10 % is shown in Fig. 2b. Analyzing this figure, it is possible to conclude that the content of this element exceeds the prescribed limit of 0.1 % when the amount of Čoka Marin concentrate in the mixture exceeded about 6 %.

The change in the content of cadmium in the concentrate mixture containing varying amounts of Čoka Marin concentrate, within the limits 0–10 %, is presented in Fig. 2c. Analyzing this figure, it is possible to conclude that content of this metal is above the allowed limit of 0.0025 % Cd when more than 2 % of

Čoka Marin concentrate was added to the mixture. Concentrate mixtures containing less than 2.5 % Čoka Marin concentrate met the given ecological conditions for their use.

The change of the content mercury in the concentrate mixture containing varying amounts of Čoka Marin concentrate, within the limits 0–10 %, is shown in Fig. 2d. Analyzing this figure, it is possible to conclude that content of this metal in the mixture did not exceed the allowed limit of 0.0002 % Hg, even when the amount of Čoka Marin concentrate was the maximum of 10 %.

Monitoring the content of impurities through the anode copper and pollution sources

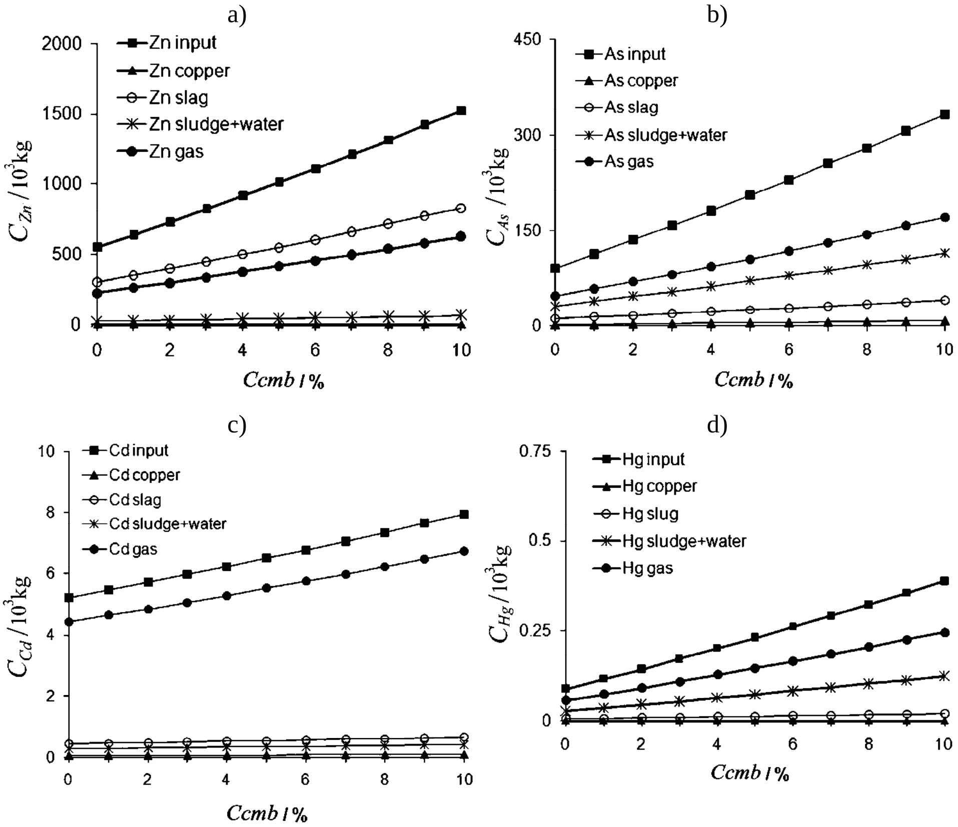
Taking into account the data listed in Table I, which considers only the content of impurities in the mixture, the original calculations are extended. Additionally, the obtained results included a distribution of impurities between the anode copper and the by-products (slag, sludge and water and gas) from the smelting of the copper concentrate, which cause different types of pollution. These are shown in Fig. 3.

The distribution of zinc between the anode copper and the by-products (slag, sludge and water, gas) obtained during the processing of mixtures composed of the copper concentrates listed in Table II is presented in Fig. 3a. Analyzing this Figure, it is possible to conclude that the largest amount of zinc from the process is contained in the slag and, in second place, in the gas phase. The anode copper contains a negligible quantity of zinc.

The distribution of arsenic between the anode copper and the by-products (slag, sludge and water, gas) obtained during the processing of mixtures composed of the copper concentrates listed in Table II is presented in Fig. 3b. Maximum amount of arsenic from process exits in the gas phase and the rest mostly in waste water, while the slag bonds a small amount of this element. The anode copper contains 2.44 % As (Table I).

The distribution of cadmium between the anode copper and the by-products (slag, sludge and water, gas) obtained during the processing of mixtures composed of the copper concentrates listed in Table II is shown in Fig. 3c. The largest part of cadmium from the process exits in the gas phase, while the other by products contain smaller amounts of this element; about 1 %. remains in the anode copper.

The distribution of mercury between the anode copper and the by-products (slag, sludge and water, gas) obtained during the processing of mixtures composed of the copper concentrates listed in Table II is shown in Fig. 3d. Mercury is completely removed from the anode copper and the largest part of this element exits with the gases and waste water.



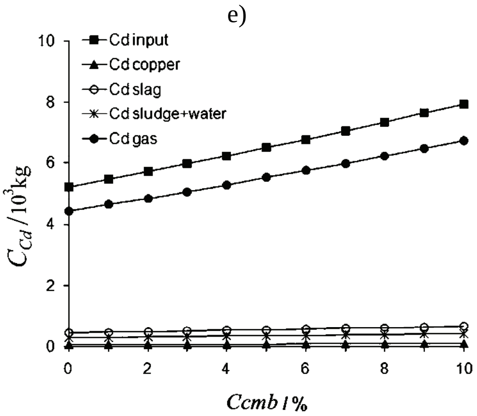


Fig. 3. Distribution of impurities (a – Zn, b – As, c – Cd, d – Hg and e – Pb) between the anode copper and the by-products (slag, sludge and water, gas); *Ccmb* – percentage of concentrate Čoka Marin in the batch; C_{Me} – content of Me (Me = Zn, As, Cd, Hg and Pb) in the concentrate mixture and the products (copper, slag, gas, sludge and water).

The distribution of lead between the anode copper and the by-products (slag, sludge and water, gas) obtained during the processing of mixtures composed of the copper concentrates listed in Table II is presented in Fig. 3e. For the most part, lead remains in the slag, but a significant portion exits in the gas phase, while about 2 % is contained in the anode copper.

Based on the calculation results in the first part of this study, it can be seen that the content of cadmium is the main problem, if the set limits for the contents of impurities are to be met. The use of 0 to 10 % Čoka Marin concentrate in the mixture is not limited by the emission of zinc, lead or mercury into the atmosphere.

Arsenic allows the use of Čoka Marin concentrate up to about 6 % in the mixture.

The cadmium in the Čoka Marin concentrate allows the participation of this concentrate in the mixture only up to about 2.5 %, which limits its practical use and does not allow the high profitability its gold content to be expressed.

The use of Čoka Marin concentrate in the existing process is also limited by the cumulative increase of the content of impurities in the atmosphere during the exploitation. This indicates that the use of this concentrate in other modern processes may be possible under strict control.

Based on the results obtained in this part of the work, the distribution of the impurities (As, Pb, Zn, Cd and Hg) can be monitored through the anode copper and the by-products (slag, sludge and water, gas).

Based on the obtained results, it could be concluded that significant amounts of Zn, As, Cd, Hg and Pb exits with gases and for this reason, special attention should be to paid to the process of capture and purification of the gases and also to the provision of a hermetic gas line.

The waste water carries significant amounts of As and Hg, which necessitates the employment of suitable procedures for its purification.

With the slag, larger quantities of Zn and Pb are removed that necessitates the determination of the form in which these elements exist and that regulations are adhered to for the postponement of such material, to reduce soil degradation.

CONCLUSIONS

Taking into account all the mentioned influences of zinc, lead, arsenic, cadmium and mercury and their content in possible mixtures for smelting in the reverberatory furnace, such a solution cannot be recommended. For the health reasons, it would be better to export this type of concentrate to allow it to be smelted now using appropriate contemporary technology, or to wait for the installation of new technology in the RTB Bor Smelter Plant.

И З В О Д

МОГУЋНОСТ КОРИШЋЕЊА ПОЛИМЕТАЛИЧНОГ КОНЦЕНТРАТА ЧОКА МАРИН СА АСПЕКТА УТИЦАЈА САДРЖАЈА ШТЕТНИХ ЕЛЕМЕНАТА НА ОКОЛИНУ

ЛИДИЈА Д. ГОМИЦЕЛОВИЋ, ЕМИНА Д. ПОЖЕГА и ВЛАСТИМИР К. ТРУЈИЋ

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У раду су изложени резултати прорачуна састава композитних концентрата који се користе као шаржа у Топионици бакра у Бору са аспекта понашања штетних елемената: цинка, олова, арсена, кадмијума и живе. Ови елементи показују веома штетно дејство на околину и здравље људи, тако да је од изузетне важности да се испоштују законом порписане вредности њихове емисије у околину.

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