CHARACTERIZATION OF DUSTS FROM SECONDARY COPPER PRODUCTION

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Abstract

Various types of waste, including dusts, are produced in the pyrometallurgical production of copper from secondary raw materials. According to the European Waste Catalogue and Hazardous Waste List, dusts from secondary copper production are classified as hazardous waste. In secondary copper production 3.87 million tons of copper were produced worldwide in 2017. The dusts are produced in the following thermal operations: reduction of the melt in the shaft furnace (shaft furnace dust), converting (converter dust), and pyrometallurgical refining (refining dust). These dusts contain significant amounts of heavy metals (Zn, Pb, and Sn) in oxidic forms. The dusts are regarded as secondary raw materials, and it is necessary to look for ways of extracting these heavy metals. The aim of this work was to characterize the individual types of dust and determine their quantitative and qualitative composition. The content of heavy metals in copper shaft furnace dust is (52.16% Zn, 19.33% Pb), in copper converter dust (32.40% Zn, 14.46% Pb), and in refining dust (32.99% Zn).

Keywords: Secondary copper, Dust, SEM EDX analysis, XRD analysis, AAS analysis

1. Introduction

The global demand for copper is in continuous expansion; around 16.5 million tonnes of copper were produced by smelters in 2018. Consequently, this production is accompanied by increasing amounts of dust/sludge, slag, and waste water which represents a serious risk to the environment and human health. It seems that this trend will remain unchanged in the coming years. The total world production of refined copper reached 23.9 million tonnes in 2018 [1, 2]. Secondary copper production grew by 6 %, while primary production rose by 2.3 % in the first quarter of 2018 [3]. Future global copper demand is expected to keep rising due to copper's indispensable role in modern technologies. Unfortunately, increasing copper extraction and decreasing ore grades intensify energy consumption and generate higher environmental impacts [4].

Traditional copper primary production uses chalcopyrite-pyrite concentrates as the raw material, but copper scrap and other secondary materials are recycled into different furnaces. The main primary processing route is the smelting of sulphide concentrate to Cu_2S-FeS matte followed by the converting of matte to blister copper that is fire-refined and electrorefined. Dusts are generated during all stages of primary copper production and the mass of dust can be as much as 10 % of the mass of input concentrate. These dusts are collected by heat recovery boilers, electrostatic precipitators, or baghouses. Common practice has been to recycle these dusts to the smelter to recover the copper content. The recycle of dust also decreases furnace capacity, which hurts productivity. Dusts from concentrate roasting and smelting contain high copper (20 %) and sulphur levels (10 %) and low levels of lead, antimony, and arsenic (roasting: 2.5 % Pb, 0.26 % Sb, 1.4 % As; smelting: 3 % Pb, 0.05 % Sb, 1.88 % As). On the other hand, dusts from converting and slag cleaning have lower copper levels (converter: 8.3 % Cu; slag cleaning: 1.96 %), and higher levels of lead, antimony, and arsenic (converter: 20.2 % Pb, 0.21 % Sb, 4.51 % As; slag cleaning: 16.6 % Pb, 0.92 % Sb, 11.5 % As). As a result, direct recycle of the roaster and smelter dusts is more feasible, and the incentive to treat converter and slag cleaning dusts to remove impurities is higher [5, 6].

The production of copper from secondary raw materials is a physicochemical process occurring at high temperatures and involving melt, slag, gas phase, and furnace lining. The whole production process consists

of several operations, the most important being:

1. Reduction of Cu, Sn, Pb oxides and separation of these components from the rest of the batch, with most of the batch composed of Cu in metallic form,

2. Zn separated to the off-gases and captured in oxidized form in the filtration station,

3. Transfer of unwanted components into slag,

4. Converting of black copper and removal of Ni, Sn and Sb,

5. Pyrometallurgical refining,

6. Electrolytical refining [7].

The production of copper is accompanied by the formation of various kinds of waste such as dusts, sludges, and slags [8, 9]. Dusts from copper production mainly contain oxides of zinc, lead and tin, but also copper [10]. The high content of Zn, Pb, Cd and Sb in these dusts would cause considerable technological problems in direct recycling, which does not allow direct use of dusts in the production of copper [11, 12]. These metals are brought into the production cycle mostly from copper scrap (brass, bronze) and waste electrical and electronic equipment (WEEE). According to the European Waste Catalogue and Hazardous Waste List, copper shaft furnace (CSF) dusts, copper converter (CC) dust, and copper anode (CA) dust are classified as hazardous waste [13]. Fig. 1 shows a scheme of pyrometallurgical copper production from secondary raw materials [14, 15].

Complex problems in metallurgy arise from the formation of metal-bearing waste with varying chemical and mineralogical compositions in different states. The formation of dust is a part of the copper production process, and refers to the dust collected during the melting of copper in shaft furnace [14]. Solid particles carried out by the gas are trapped in the separation system. Dusts are characterized by their highly hydrophobic nature, and thus also by excessive dusting during transport. The sludge is characterized by poor sedimentation and thus high moisture content of the material after partial drainage. The most significant quantities of dust in secondary production of copper are generated by dry cleaning of gases in the shaft furnace (shaft dusts, converter dusts) and pyrometallurgical refining (anode dusts) [13 – 16]. The chemical composition of these secondary raw materials varies, and depends mainly on the quantity, quality, type, and type of scrap. Even a slight change in operating conditions could result in a change in dust composition [17]. These dusts are characterized by considerable heterogeneity of grain size, chemical, and mineralogical composition.

In considering these facts, the main aim of this research was the characterization of dusts produced in secondary copper production to determine their composition and mineral phases, as an indispensable preliminary step towards choosing the best available technology for recovery of metals.

2. Particle characterisation
2.1 Sample collection

Copper shaft furnace (CSF) dust, copper converter (CC) dust, and copper anode (CA) dust samples supplied by a Slovakian copperworks were used for the experiments. The CSF, CC, and CA dusts are waste material from pyrometallurgical production of secondary copper. The CSF, CC, and CA dust samples were collected during a ten-day period from the smelting operation. The as-received samples were re-weighed and subjected to coning, quartering, and dividing sample preparation methods to obtain representative samples of CSF, CC, and CA dust. The bulk of the waste material occurs in the particle size range below 53 μm.

2.2 Analysis methods

Particle size analysis was performed using the laser diffraction method on a Malvern Mastersizer 2000E (Malvern Instruments, United Kingdom, precision: ±1 %) with a Scirocco2000M dry sample feeder. The density of each sample was determined using a Micromeritics AccuPyc II 1340 gas pycnometer (Micromeritics Instrument Corporation, USA, accuracy: ± 0.02 % of nominal cell volume).

The chemical composition of the CSF, CC, and CA dust samples was determined using classical wet analysis by means of atomic absorption spectrometry (AAS) on a Varian Spectrophotometer SpectrAA20+ (Varian, detection limit: 0.3 – 6 ppb).
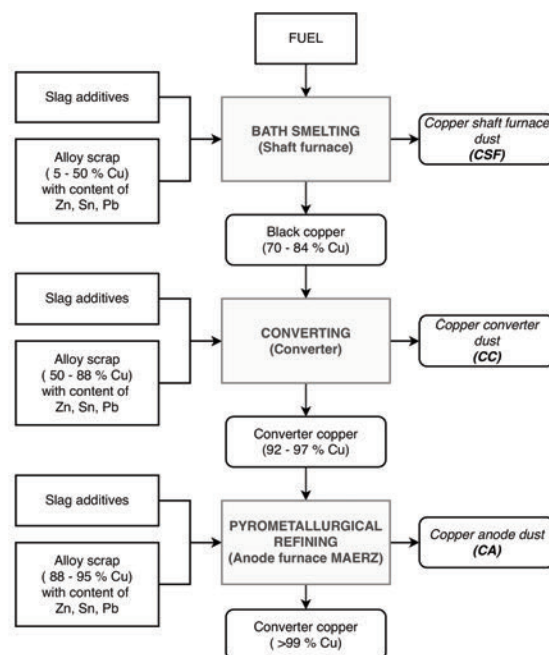

Figure 1. *Flow chart of the pyrometallurgical copper process*

The phases present in homogenized samples of CSF, CC, and CA dust were identified by means of X-ray diffraction phase analysis (XRD). The samples were prepared according to the standardized Panalytical backloading system, which provides nearly random distribution of the particles. The samples were analysed using a Philips X´Pert PRO MRD (Co-Kα) diffractometer (Philips, Netherlands). The phases were identified using X´Per HighScore plus software.

The CSF and CC dust samples were subjected to morphology observation by optical microscopy using a Dino-Lite ProAM413T digital microscope (AnMo Electronics Corporation, Taiwan). Each sample was subjected to scanning electron microscopy (SEM) analysis along with energy dispersive spectrometry (EDS). The morphology and microstructure of the samples were studied using a MIRA3 FE-SEM (TESCAN, USA, resolution: 1.2 nm at 30 kV; 2.3 nm at 3 kV) scanning electron microscope (REM). This equipment also enabled multi-elemental semi-quantitative analysis also using EDS.

Leachability testing was performed according to the European standard EN 12457-1:2002. This standard deals with compliance testing in the leaching of granular waste materials and sludges.

3. Results and discussion
3.1 Particle size analysis and density measurement

Fig. 2 shows the particle size distribution of all three dusts. From the curves it follows that the distribution of particles is bimodal and trimodal. The local maximum in the area of large particles reflects with the highest probability a tendency to particle agglomeration. The local maximum in the small particle area below 1 μm indicates the proportion of small particles. The results of density measurement are presented in Table. 1. Copper converter dust and copper anode dust have very similar density values.

Problems of fine-grained material occur especially during transport. Transport must therefore be carried out in closed containers or dusts are pre-treated by pelletizing. However, low granularity is an advantage in hydrometallurgical processing, where a large surface of material is required. It is even less advantageous in pyrometallurgical processing, where there is a risk of material loss during charging and the process itself.

3.2 Chemical composition

The content of major and trace elements in the samples studied are shown in Table 2. These results show that the highest content of Zn and Pb occurs in the samples of CFS and CC dust. The CSF dust contains 52.16 % Zn and 19.33 % Pb as major elements. It also has 1.51 % Cu, 0.3 % Fe, 0.02 % Ca, 7.09 % Cl,$^-$ and 17.76 % Si. The CC dust is characterized by its content of 14.46 % Pb and 32.40 % Zn. In addition, 28.32 % Cl$^-$, 0.13 % Ca, 0.11 % Fe, and 0.92 % Cu are present in the sample. Furthermore, Si, Sn and As (< LoD – limit of detection) are the main trace elements. The content of Zn in the CSF dust is almost twice that in the CC and CA dusts. Proportions of 10.94 % Pb, 32.99 % Zn, 7.57 % Cu and 1.67 % Sn are present in CA dust.

From the chemical composition follows that dusts contain similar or higher contents compared with primary raw material, where the lead content is about 15 %, the zinc 10 %, and the copper content is about 1 %. For this reason, dusts from secondary copper production can be considered as valuable secondary raw material.

Table 1. Density of samples

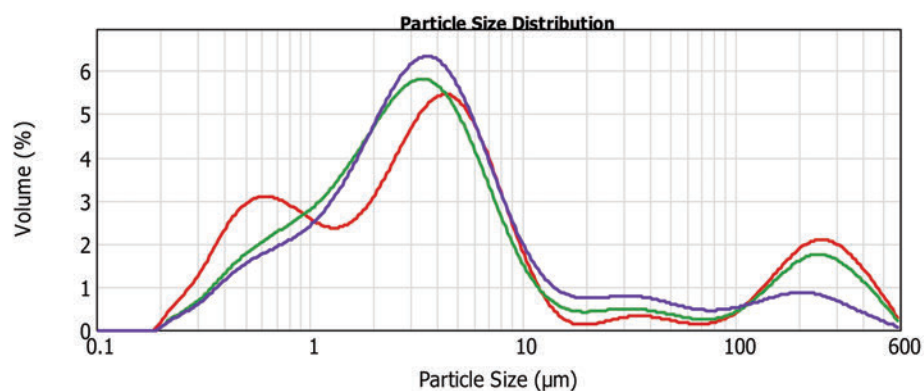| Sample	Average density [g.cm^{-3}]	Standard deviation [g.cm^{-3}]
copper shaft furnace dust (CSF)	4.5623	0.0212
copper converter dust (CC)	3.4165	0.0071
copper anode dust (CA)	3.4145	0.0049

Figure 2. Particle size distribution of all three dust types

3.3 Phase determination

Both CSF and CC dusts contain zinc oxide (ZnO) as the principal mineral according to the diffraction pattern (Fig. 3). Lead is present in CSF dust in the form of various oxides, sulphates or fluorides, but mainly the mineral phase, lead sulphate ($PbSO_4$), whereas zinc occurs primarily in the form of zinc oxide (ZnO). The mineralogical composition of these dusts is shown in Table 3, Table 4 and Table 5.

The presence of oxides, sulphates and chlorides suggests that these dusts could be treated hydrometallurgically by multi-stage leaching (acidic and alkaline) with subsequent recovery of marketable products [18 – 20]. In the pyrometallurgical treatment, a reduction could be used followed by evaporation of zinc and lead [21].

3.4 Morphology of samples

Fig. 4 shows pictures of the CSF, CC and CA dusts with 50x magnification. Morphological analysis showed that the samples consisted of two grain-size fractions, coarse and fine, rather spherical grains. This fact was confirmed by particle size analysis, which confirmed two groups of particles: bigger particles *(-600 +100 μm)* and smaller particles *(-10 +1 μm)*. Grains of larger size were covered in smaller ones. It is probable that powder particles can form various agglomerates and agglomerate.

The morphology of copper shaft furnace dust particles observed by means of SEM is documented in Fig. 5a). Fig. 5b) documents the EDS analysis of copper shaft furnace dust particles from the area shown in Fig. 5a). From this analysis it follows that elements

Tabble 2. *Content (%) of elements in samples, LoD – limit of detection in AAS methods*

Sample	Content [%]									
	Pb	Zn	Fe	Cu	Ca	Cl⁻	Si	Sn	As	Ni
CSF dust	19.33	52.16	0.3	1.51	0.02	7.09	17.76	< LoD	< LoD	< LoD
CC dust	14.46	32.4	0.11	0.92	0.13	28.37	< LoD	< LoD	< LoD	< LoD
CA dust	10.82	27.8	0.72	7.51	0.21	15.6	0.08	1.49	0.08	0.02

LoD – limit of detection
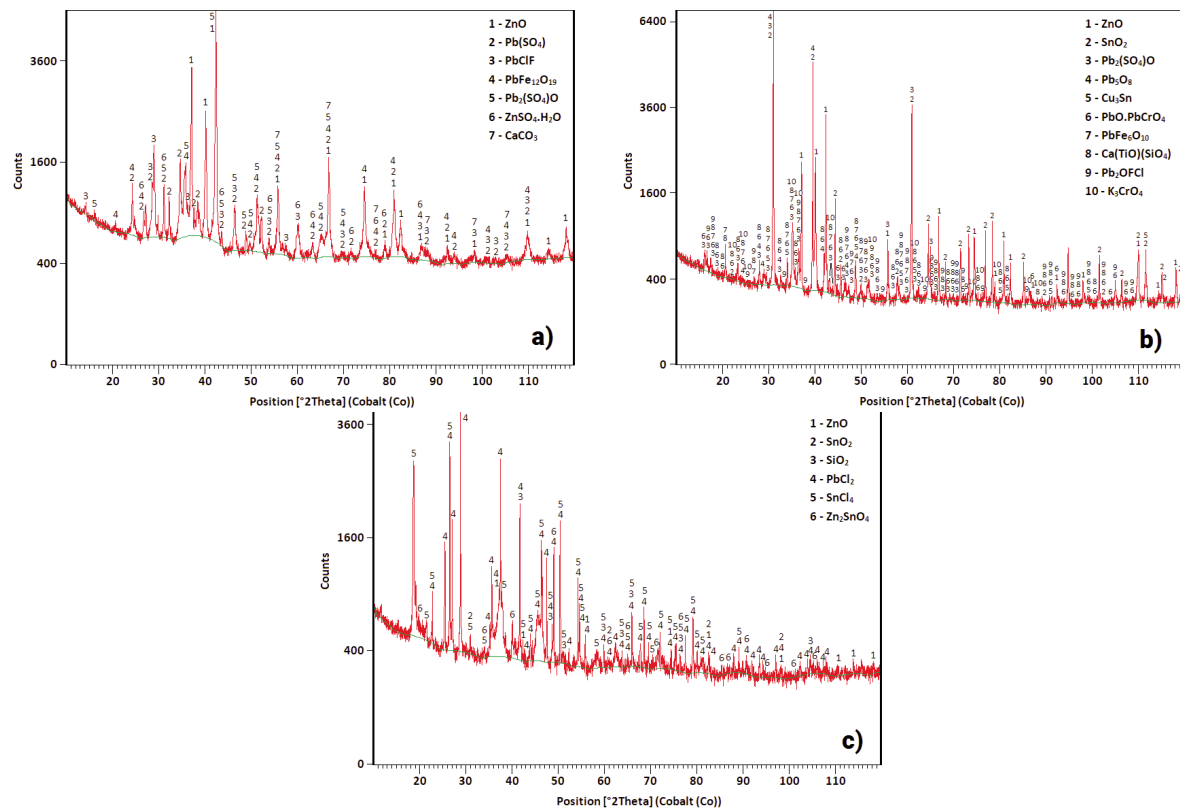
Figure 3. *X-ray diffraction (XRD) patterns of CSF dust a), CC dust b) and CA dust c)*

Table 3. Mineralogical composition of CSF dust

Ref. Code	Compound Name	Chemical Formula
00-036-1451	Zinc Oxide	ZnO
01-089-7356	Lead Sulfate	$Pb(SO_4)$
00-041-1373	Lead Iron Oxide	$PbFe_{12}O_{19}$
00-033-1476	Zinc Sulfate Hydrate	$ZnSO_4.H_2O$
01-072-1393	Lead Oxide Sulfate	Pb_2OSO_4
01-076-0606	Calcium Carbonate	$Ca(CO_3)$
00-026-0311	Lead Chloride Fluoride	$PbClF$

Table 4. Mineralogical composition of CC dust

Ref. Code	Compound Name	Chemical Formula
00-041-1445	Tin Oxide	SnO_2
01-089-7102	Zinc Oxide	ZnO
00-037-0516	Lead Oxide Sulfate	Pb_2OSO_4
00-052-0772	Lead Oxide	Pb_5O_8
01-075-0573	Lead Chromium Oxide	$PbOPbCrO_4$
03-065-4374	Copper Tin	Cu_3Sn
00-033-0757	Lead Iron Oxide	$PbFe_6O_{10}$
01-070-3394	Calcium Titanium Oxide Silicate	$Ca(TiO)(SiO_4)$
01-083-2118	Lead Oxide Fluoride Chloride	Pb_2OFCl
00-031-0995	Potassium Chromium Oxide	K_3CrO_4

Table 5. Mineralogical composition of CA dust

Ref. Code	Compound Name	Chemical Formula
00-005-0416	Lead Chloride	$PbCl_2$
00-023-0950	Copper Chloride Hydroxide Hydrate	$Cu_{46}Cl_{24}(OH)_{68}.(H_2O)_4$
00-030-0473	Copper Chloride Hydroxide	$Cu_2Cl(OH)_3$
01-074-2184	Zinc Tin Oxide	Zn_2SnO_4
00-037-0500	Zinc Chlorate Hydrate	$Zn(ClO_4)_2.6H_2O$
01-070-5323	Tin Chloride	$SnCl_4$
01-076-0922	Zinc Hydroxide Chloride Hydrate	$Zn_5(OH)_8Cl_2.H_2O$
00-033-1470	Zinc Chlorate Hydrate	$Zn(ClO_4)_2.6H_2O$
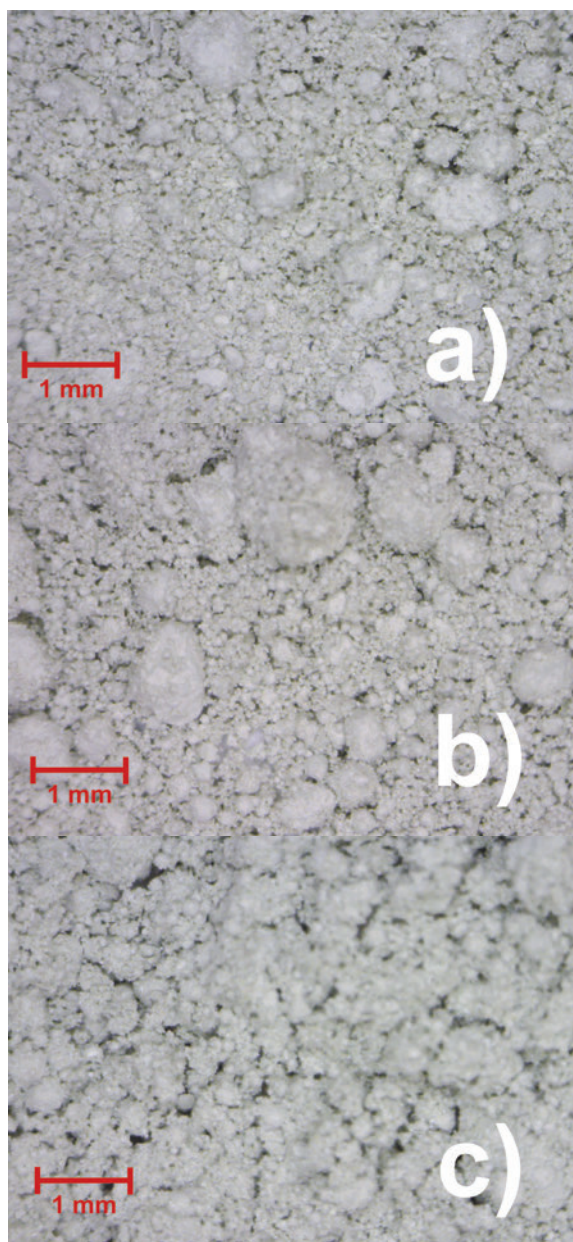
Figure 4. Particle morphology of samples a) CSF dust, b) CC dust and c) CA dust

Zn and Pb predominate in the metal content. Fig. 6 shows the mapping of CSF dust particles. From this observation it appears that lead bound with sulphur is present in two larger particles with a size of about 1 μm.

Fig. 7a) documents the morphology of copper converter dust particles and Fig. 8a) the morphology of copper anode dust. From the EDS analysis shown in Fig. 7b) it is evident that copper converter dust contains zinc, copper, and lead as the main metals, but the chlorine content is also considerable. Similarly, copper anode dust contains zinc, lead, copper, and chlorine, as seen in Fig. 8b).
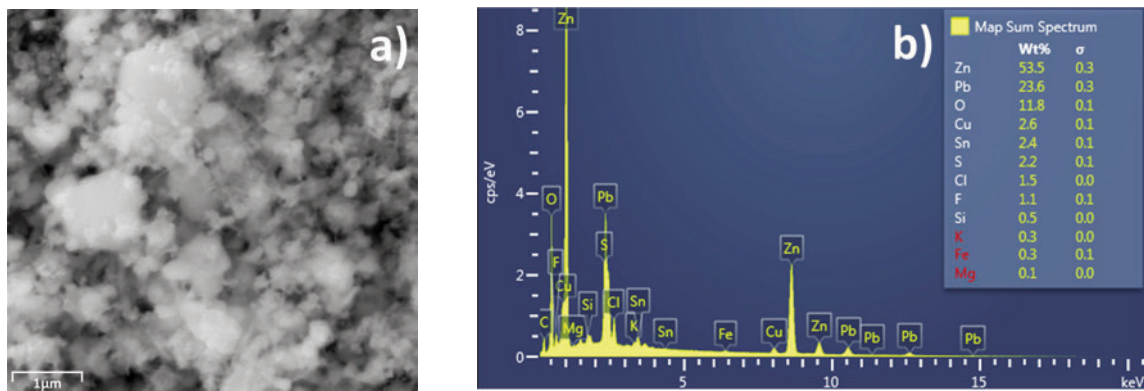
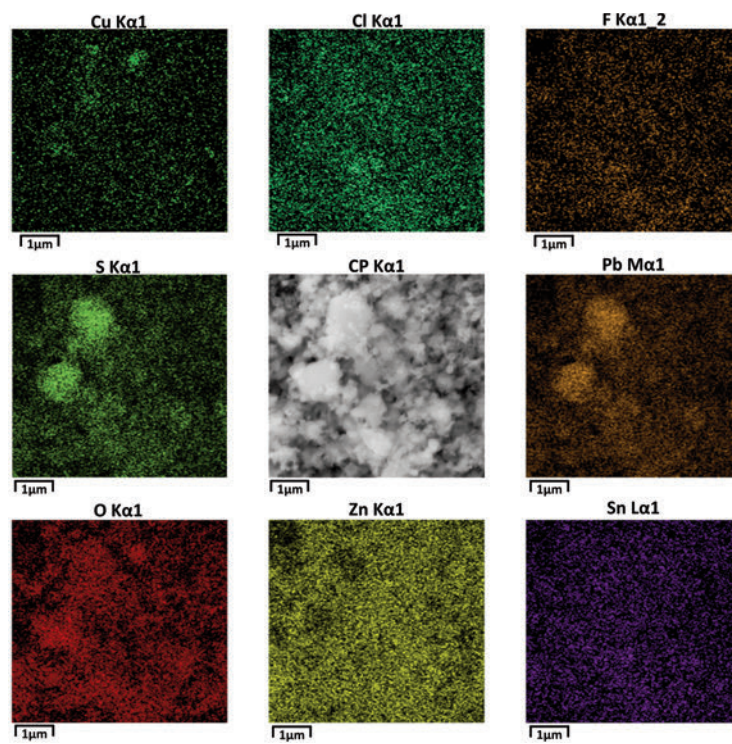*Figure 5. Scanning electron micrograph of the CSF dust particles SEM a), EDS b)*

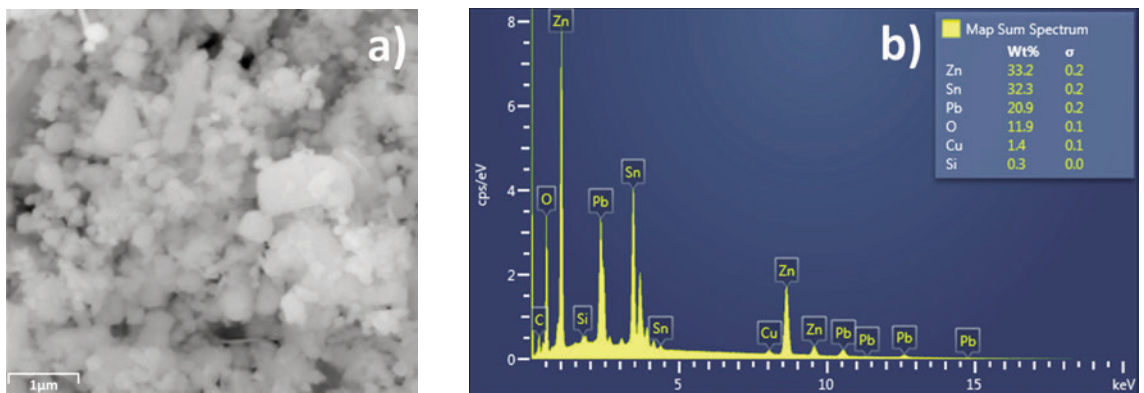*Figure 6. Secondary electron image of the CSF dust region and distribution of elements*

Figure 7. Scanning electron micrograph of CC dust particles with SEM a), EDS b)
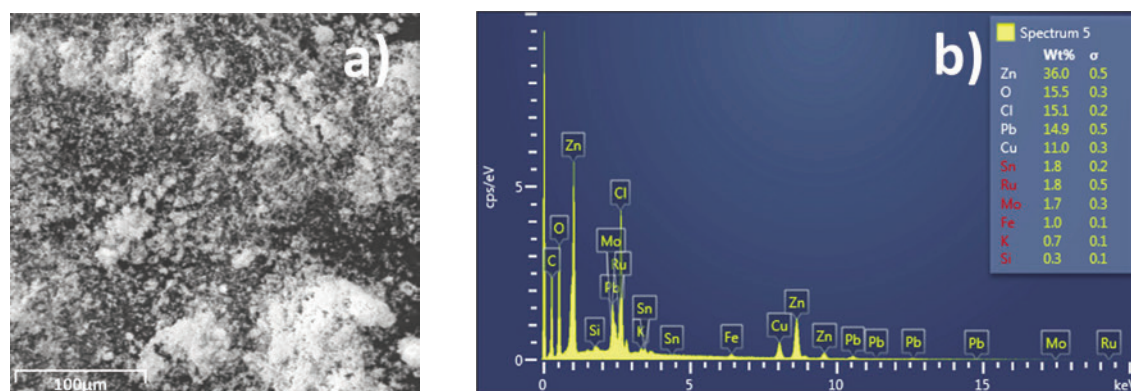
Figure 8. *Scanning electron micrograph of CA dust particles with SEM a), EDS b)*

Table 6. *Results of leachability testing*

Sample	Concentration [mg.dm^{-3}]												
	Cu	Ni	Pb	Sn	As	Al	Cd	Co	Cr	Se	Zn	Cl$^-$	SO$_4^{2-}$
copper shaft furnace dust (CSF)	0.6	1.01	59	0	0	0	167.93	0	0	7.8	5255.56	880	0.56
copper converter dust (CC)	0	0	32.53	0	0	0	192.4	0	0	7.2	3890	6100	2.38
copper anode dust (CA)	0.54	0	9.96	0	0	0	13.24	0	0	0	623.67	710	0.39

3.1.5 Leachability testing

The results of leachability tests by the European standard EN 12457-1: 2002, for all three dusts are shown in Table 6. From the results it follows that concentrations are exceeded for copper, lead, cadmium, selenium, and chlorides. According to the limits, all three dusts could be disposed of only in landfills for hazardous waste.

4. Conclusions

Various kinds of dust are generated during secondary copper production as well as their reprocessing produces waste materials which are considered hazardous. According to their high metal content (Zn, Pb, Sn), their disposal does not offer any economic or environmental benefit. In view of this fact, the main objective of this study was to obtain basic information for the re-use of these wastes in different fields. The characterization of three waste materials, copper shaft furnace (CSF) dust, copper converter (CC) dust, and copper anode (CA) dust, generated during reprocessing from secondary copper smelting, was performed as an essential step towards finding applications or treatments for these types of waste. They contain fine particles and are mainly enriched with Zn, Pb and Fe. Zincite (ZnO) is the major mineral phase in which Zn is present in these dusts. Pb was found in the CSF dust as a sulphate (PbSO$_4$). These dusts are an important secondary resource of Zn and Pb, and their reprocessing has both remarkable economic and environmental benefits in contrast to their disposal or incorporation into other products. A hydrometallurgical process appears to be an attractive option for processing these hazardous waste materials [22].

Acknowledgments

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KARAKTERIZACIJA PRAŠINE IZ PRERADE SEKUNDARNIH SIROVINA BAKRA

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Apstrakt

Različite vrste otpada, uključujući i prašine, proizvode se u pirometalurškoj proizvodnji bakra iz prerade sekundarnih sirovina bakra. Po Evropskom katalogu otpada i Listi opasnog otpada, prašine iz prerade sekundarnih sirovina bakra se klasifikuju kao opasan otpad. U preradi sekundarnih sirovina bakra 2017. godine je u svetu proizvedeno 3.87 miliona tona bakra. Prašine se proizvode u sledećim termalnim operacijama: redukcija rastopa u šahtnoj peći (prašina šahtne peći), konvertovanje (konvertorska prašina), i pirometalurška rafinacija (prašina iz rafinacije). Ove prašine sadrže značajne količine teških metala (Zn, Pb, i Sn) u obliku oksida. Ove prašine se smatraju sekundarnim sirovinama, i potrebno je tražiti načine za ekstrakciju ovih teških metala. Cilj ovog rada je bio karakterizacija pojedinačnih tipova prašina i određivanje njihovog kvantitativnog i kvalitativnog sastava. Sadržaj teških metala pri proizvodnji bakra u prašini šahtnih peći je (52.16% Zn, 19.33% Pb), u konvertorskoj prašini (32.40% Zn, 14.46% Pb), i u prašini iz rafinacije (32.99% Zn).

Ključne reči: Sekundarne sirovine bakra; Prašina; SEM EDX analiza; XRD analiza; AAS analiza