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 form. The dusts are considered 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 represent 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 Cu2S-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 physico-chemical 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]. Dusts from copper production mainly contain oxides of zinc, lead and tin, but also copper [9]. 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 [10, 11]. 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 [12]. Fig. 1 shows a scheme of pyrometallurgical copper production from secondary raw materials [13, 14].
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 [13]. 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) [12 – 15]. 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 [16]. 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 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).

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 is a risk of material loss during charging and the process itself.
Fig. 2: Particle size distribution of all three dust types

Tab. 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                            |

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%. From this reason, dusts from secondary copper production can be considered as valuable secondary raw material.

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

| Sample      | Pb    | Zn    | Fe   | Cu   | Ca   | Cl\(^{-}\) | Si    | Sn    | As   | Ni  |
|-------------|-------|-------|------|------|------|-----------|-------|-------|------|-----|
| CSF dust    | 19.33 | 52.16 | 0.30 | 1.51 | 0.02 | 7.09      | 17.76 | < LoD | < LoD | < LoD|
| CC dust     | 14.46 | 32.40 | 0.11 | 0.92 | 0.13 | 28.37     | < LoD | < LoD | < LoD | < LoD|
| CA dust     | 10.82 | 27.80 | 0.72 | 7.51 | 0.21 | 15.60     | 0.08  | 1.49  | 0.08 | 0.02 |

LoD – limit of detection
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 (PbSO₄), 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 [17 – 19]. In the pyrometallurgical treatment, a reduction could be used followed by evaporation of zinc and lead [20].

![X-ray diffraction (XRD) patterns of CSF dust a), CC dust b) and CA dust c) (Fig. 3)](image)

| Ref. Code | Compound Name           | Chemical Formula |
|-----------|-------------------------|------------------|
| 00-036-1451 | Zinc Oxide              | ZnO              |
| 01-089-7356 | Lead Sulfate            | Pb(SO₄)          |
| 00-041-1373 | Lead Iron Oxide         | PbFe₁₂O₁₉        |
| 00-033-1476 | Zinc Sulfate Hydrate    | ZnSO₄,H₂O        |
| 01-072-1393 | Lead Oxide Sulfate      | Pb₂OSO₄          |
| 01-076-0606 | Calcium Carbonate       | Ca(CO₃)          |
| 00-026-0311 | Lead Chloride Fluoride  | PbClF            |
Tab. 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$_2$OSO$_4$             |
| 00-052-0772 | Lead Oxide             | Pb$_5$O$_8$               |
| 01-075-0573 | Lead Chromium Oxide    | PbO$_3$PbCrO$_4$          |
| 03-065-4374 | Copper Tin             | Cu$_3$Sn                  |
| 00-033-0757 | Lead Iron Oxide        | PbFe$_9$O$_{10}$          |
| 01-070-3394 | Calcium Titanium Oxide Silicate | Ca(TiO)(SiO$_4$) |
| 01-083-2118 | Lead Oxide Fluoride Chloride | Pb$_2$OFCl               |
| 00-031-0995 | Potassium Chromium Oxide | K$_3$CrO$_4$            |

Tab. 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)$_{68}$.$(H_2$O)$_4$       |
| 00-030-0473 | Copper Chloride Hydroxide                   | Cu$_2$Cl(OH)$_3$                               |
| 01-074-2184 | Zinc Tin Oxide                               | Zn$_2$SnO$_4$                                   |
| 00-037-0500 | Zinc Chlorate Hydrate                        | Zn(ClO$_4$)$_2$.6H$_2$O                          |
| 01-070-5323 | Tin Chloride                                 | SnCl$_4$                                        |
| 01-076-0922 | Zinc Hydroxide Chloride Hydrate              | Zn$_5$(OH)$_6$Cl$_2$H$_2$O                       |
| 00-033-1470 | Zinc Chlorate Hydrate                        | Zn(ClO$_4$)$_2$.6H$_2$O                          |

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, a 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 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).
Fig. 4: Particle morphology of samples a) CSF dust, b) CC dust and c) CA dust

Fig. 5: Scanning electron micrograph of the CSF dust particles SEM a), EDS b)
Fig. 6: Secondary electron image of the CSF dust region and distribution of elements

Fig. 7: Scanning electron micrograph of CC dust particles with SEM a), EDS b)

Fig. 8: Scanning electron micrograph of CA dust particles with SEM a), EDS b)
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.

Tab. 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   | 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 |

Conclusion

Various kinds of dust are generated during secondary copper production, and 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 [21].

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