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Extraction of Lead from Hydrometallurgical Processing of Copper Shaft Flue Dust †

Michaela Ruzickova *, Martina Laubertova, Jarmila Trpcevska, Alexandra Kollova, Zita Takacova and Tomas Vindt

Institute of Recycling Technologies, Faculty of Materials, Metallurgy and Recycling, Technical University of Košice, Letna 1/9, 04200 Kosice, Slovakia; martina.laubertova@tuke.sk (M.L.); zita.takacova@tuke.sk (Z.T.)

* Correspondence: michaela.ruzickova@tuke.sk; Tel.: +421-55-602-2416

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Abstract: Pyrometallurgical copper production is carried out in thermal aggregates. Input waste materials with a copper content between 5% and 99% Cu are treated in the individual aggregates. In a shaft furnace, except for molten black copper, slag and shaft flue dust (SFD) are produced as waste. SFD is emitted from the melt and then is captured by fabric filters. This kind of SFD is defined as 'hazardous waste' according to the European Waste Catalogue. SFD contains an attractive quantity of valuable metals like Zn, Sn and Pb. This work focuses on the hydrometallurgical treatment of SFD from secondary copper production with the aim of obtaining usable lead-based products.

Keywords: copper dust; hydrometallurgical processing; lead precipitation; shaft flue dust

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1. Introduction

In recent years, the sales of electric vehicles have increased, which has also resulted in increased copper consumption in the automotive industry. In 2022, 22 million tons of refined copper were produced [1–5]. Due to its indispensable role in modern IT and emerging electromobility, copper production is expected to continue to rise. Increasing copper production will also result in increasing production of solid wastes such as dusts and slags [6]. Shaft flue dust (SFD) from secondary copper production mainly contains oxides of zinc, lead, tin and copper. In 2020, secondary copper production in Slovakia produced a total of 3573.57 t of dust [7]. In recent years, hydrometallurgical methods seem to be appropriate for the treatment of SFD because of the possibility of processing fine-grain-size waste; the selectivity of this method is also significant.

In a study on hydrometallurgical processing, the authors [8–10] used SFD as an input. This input waste was leached using the alkaline leaching agent sodium hydroxide (NaOH) [8] or sulfuric acid (H_2SO_4) [9,10]. In this way, between 88 and 99.6% of Pb was converted into solution. The authors [11] carried out the leaching of SFD with the aim of transferring the maximum amount of Pb and minimum amount of Zn into the solution, under the following optimal conditions: 1 M NaOH, 80 °C and liquid to solid ratio (L:S) = 20. After the metals were transferred into the solution, the extraction was followed. Several procedures can be used, such as precipitation [9,10] or cementation [8]. The authors [8] obtained Pb in the form of cementation precipitate as a final product. By these methods, more than 96% of Pb was removed from the solution. Pb-free solution was subsequently utilised in order to obtain another marketable product [9,10].

The topic of this work is to verify the proposed process of SFD treatment experimentally; SFD leaching was used as the first step of the treatment. A precipitation process is proposed for the recovery or removal of Pb from solutions after leaching. Zn^{2+} containing solution refined from Pb was used for further processing to obtain Zn in metallic form or a Zn compound. Based on the theoretical knowledge, the study of hydrometallurgical treatment of leaching and the characterization of the material from previous research [12], NaOH as a leaching agent was proposed. The solubility of ZnO and PbO present in SFD is assumed at these conditions: 1 M NaOH, 80 °C and pH = 14. This is evident from the thermodynamic study E-pH diagram shown in Figure 1 [12]. The leaching process is probably carried out according to the chemical reactions (1) and (2):

$$\begin{gathered}PbO_{(s)} + 2NaOH_{(aq)} = Na_2PbO_{2(aq)} + H_2O,\\ \Delta G(80\ ^\circ C) = -35.775\ kJ\cdot mol^{-1}\end{gathered} \tag{1}$$

$$\begin{gathered}ZnO_{(s)} + 2NaOH_{(aq)} = Na_2ZnO_{2(aq)} + H_2O.\\ \Delta G(80\ ^\circ C) = -72.159\ kJ\cdot mol^{-1}\end{gathered} \tag{2}$$

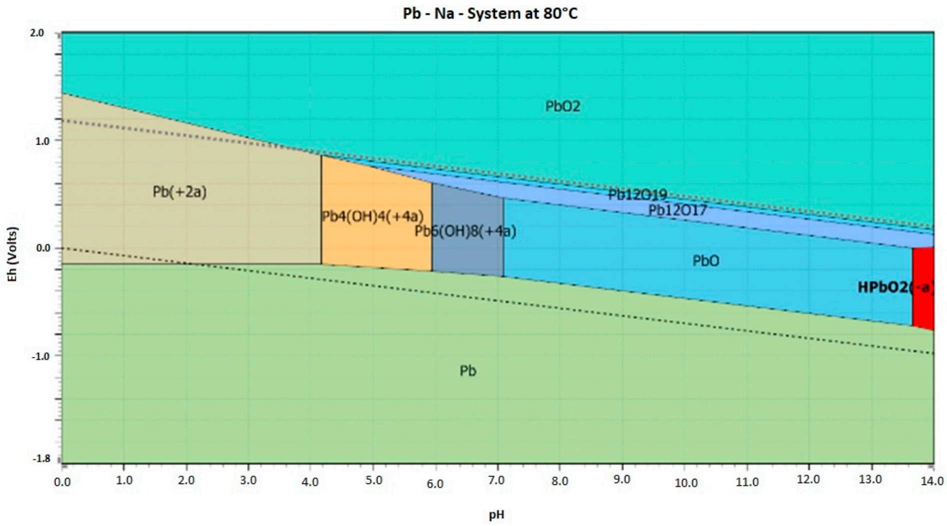

Figure 1. E-pH diagram of Pb-Na-H_2O system at 80 °C [12].

When the leaching process is finished, the process of recovery of the metals or metals compounds from solution can be started via precipitation or cementation. The aim of precipitation is to remove or recover the lead from the solution as a compound usable in another process. A suitable precipitating agent for the process should be selected according to the solubility of the inorganic compounds in water. It is also important to follow further commercial use and consider the harmfulness to the environment of these recovered compounds. Figure 2 shows an E-pH diagram of the system Pb-S-Na-H_2O at 25 °C.

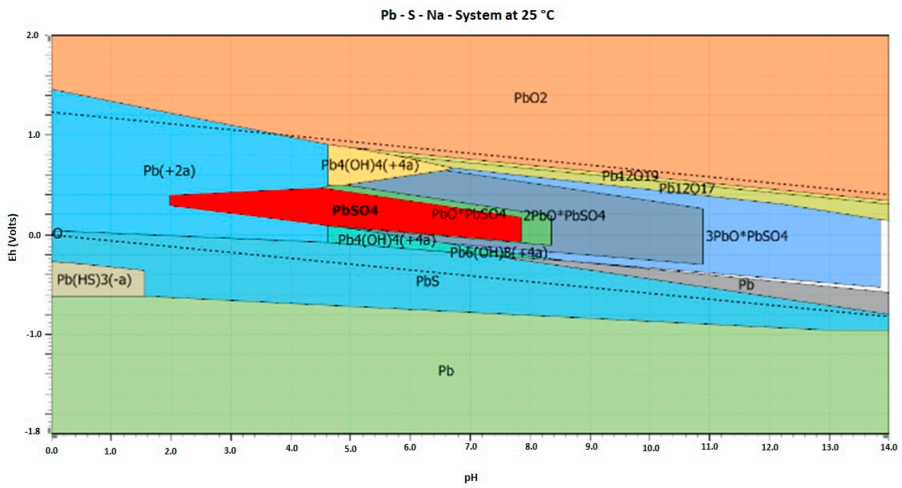

Figure 2. E-pH diagram of Pb-S-Na-H_2O system at temperature 25 °C [12].

Examples of low-solubility compounds are: lead phosphate ($Pb_3(PO_4)_2$), which has been identified as a carcinogen; lead hydroxide ($Pb(OH)_2$), which has been used in the past as a white pigment, but it has been banned due to its harmful effects on human health and its environmental impact; and lead sulphate ($PbSO_4$), which is usually used to produce an active paste for lead–acid batteries. The solubility product (K_s) of lead sulphate ($PbSO_4$) at a temperature of 25 °C and ionic strength I = 0.0 mol·dm^{-3} is 1.514 × 10^{-8} [13]. Based on the properties of the individual compounds, it is environmentally appropriate to use sulfuric acid as a precipitating agent for lead. The solution after lead precipitation containing Zn^{2+} can be treated by crystallization to produce $ZnSO_4 \cdot 7H_2O_{(s)}$ as a next marketable product. Based on a previous study [12], it can be concluded that the precipitation will proceed according to the following reactions (3) and (4):

$$\begin{gathered} Na_2PbO_2 + 2H_2SO_{4(aq)} = Na_2SO_{4(aq)} + 2H_2O + PbSO_4 \downarrow \\ \Delta G^0_{298K} = -573.22\ \mathrm{kJ \cdot mol^{-1}},\ K_s(PbSO_4) = 1.514 \times 10^{-8} \end{gathered} \tag{3}$$

$$\begin{gathered} Na_2ZnO_2 + H_2SO_{4(aq)} = ZnSO_{4(aq)} + 2NaOH_{(aq)} \\ \Delta G^0_{298K} = -196.29\ \mathrm{kJ \cdot mol^{-1}} \end{gathered} \tag{4}$$

The aim of this article is to propose a possible method of SFD treatment by alkaline leaching followed by lead precipitation. By this procedure, it would be possible to obtain usable products from hazardous waste.

2. Materials and Methods

Hydrometallurgical procedures were carried out using standard leaching apparatus [14]. A sample of SFD with a composition of 44.02% Zn, 14.57% Pb, 1.2% Cu and 1.578% Sn, determined using atomic absorption spectrometry (AAS) on A Thermo ICE 3000 atomic absorption spectrometer, was used for leaching in 1 M NaOH at 80 °C. Lead and zinc are present in SFD in the form of oxides (PbO, ZnO and SnO_2), analysed using X-ray diffraction phase analysis (XRD) on an X-ray diffraction analyser PANalytical.

The initial volume of leaching reagent was 200 mL of 1 M NaOH, the sample weight of the SFD was 10 g at a temperature of 80 °C, and the ratio of liquid-to-solid phase (L:S) was 20. Samples of 5 mL at different leaching times were taken for the determination of Pb and Zn content in the solution using AAS. The results were processed by common mathematical and statistical methods using the following computer technology: Microsoft Office Excel 365, HSC Chemistry, version 10 (modules Reaction Equations and Eh—pH Diagrams). The SFD, as well as the precipitate, was analysed, in addition to the AAS, using scanning electron microscopy (SEM) and X-ray dispersive spectroscopy (EDX).

3. Results and Discussion

During the leaching of SFD in 1 M NaOH, the leaching efficiency of zinc hardly changed with increasing time. On the other hand, the Pb leaching efficiency was the highest already after 10 min of leaching, indicating that the efficiency gradually decreased with the increasing leaching time [11,12].

The SEM analysis (Figure 3a) shows the morphology of the SFD sample. The EDX analysis record of the SFD sample (Figure 3b) shows the zinc, lead and copper content. The morphological study of the solid residue after the leaching of the SFD (Figure 3c) indicated the presence of smaller particles. The EDX analysis (Figure 3d) confirmed a change in the chemical composition, with the removal of significant content of lead. The content of zinc, copper and tin in the solid residue was determined using the EDX analysis.

The next step of the treatment process was the precipitation of lead from the leachate. For the initial precipitation experiments, 0.5 M H_2SO_4 as the precipitating agent at 25 °C was chosen. By gradually increasing the volume of the precipitant, the pH of the solution and the colour of the precipitate was changed. When the solution reached pH = 6, the precipitate was white in colour. This is a visual prediction for the formation of the $PbSO_4$ precipitate. However, this statement needs to be confirmed by quantitative and qualitative analysis. The lead and zinc content in the solution after leaching and after precipitation are shown in Table 1. Figure 4 shows a suggested scheme of the hydrometallurgical treatment of SFD.

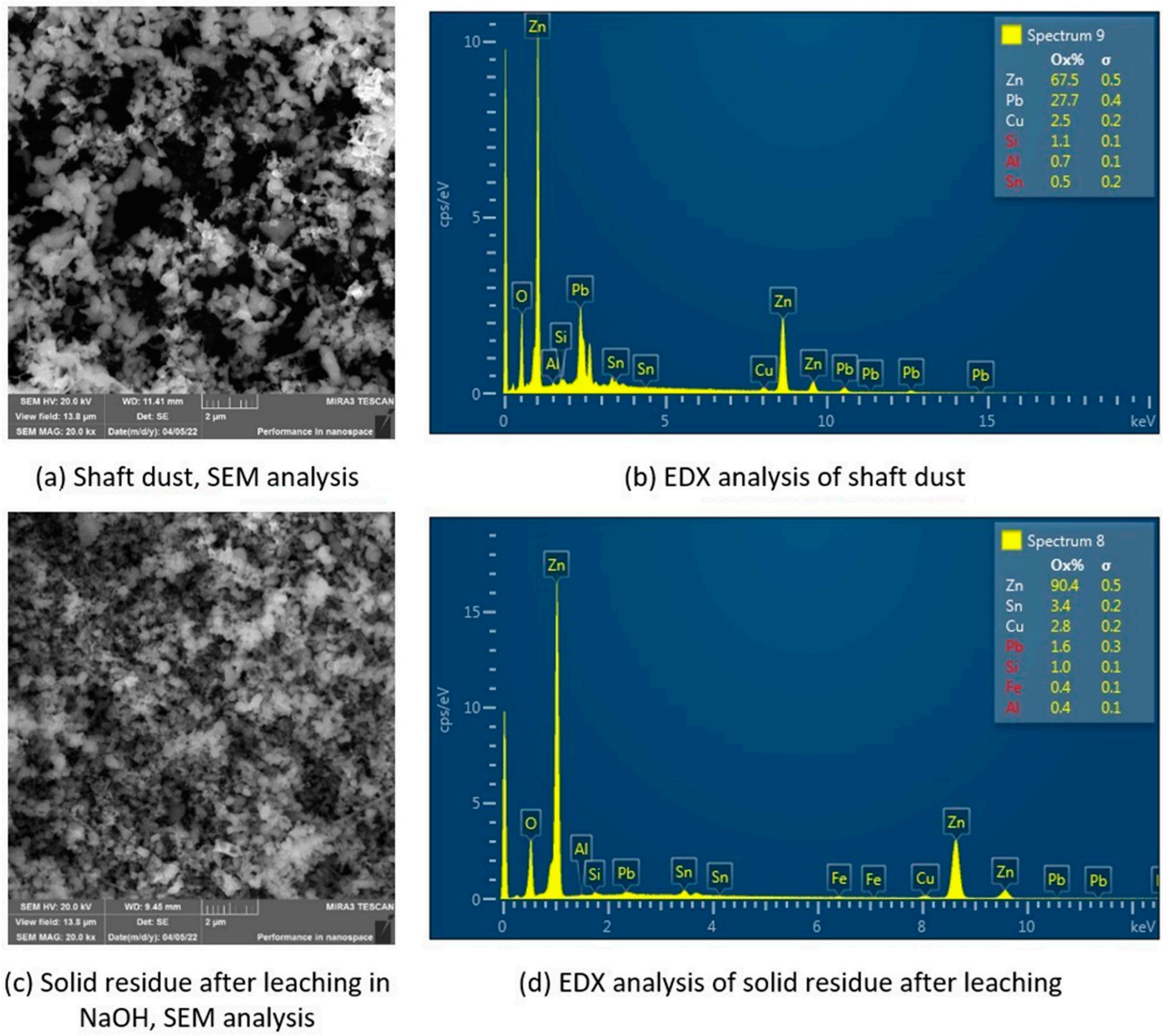

Figure 3. Morphology of SFD and solid residue after leaching, SEM and EDX analysis.

Table 1. Lead and zinc content in solution after leaching and precipitation.

	pH	Pb ($\mu g \cdot mL^{-1}$)	Zn ($\mu g \cdot mL^{-1}$)
Leachate (solution before precipitation)	14	4968	622
Solution after precipitation	7	6.07	283
	3	1.62	589

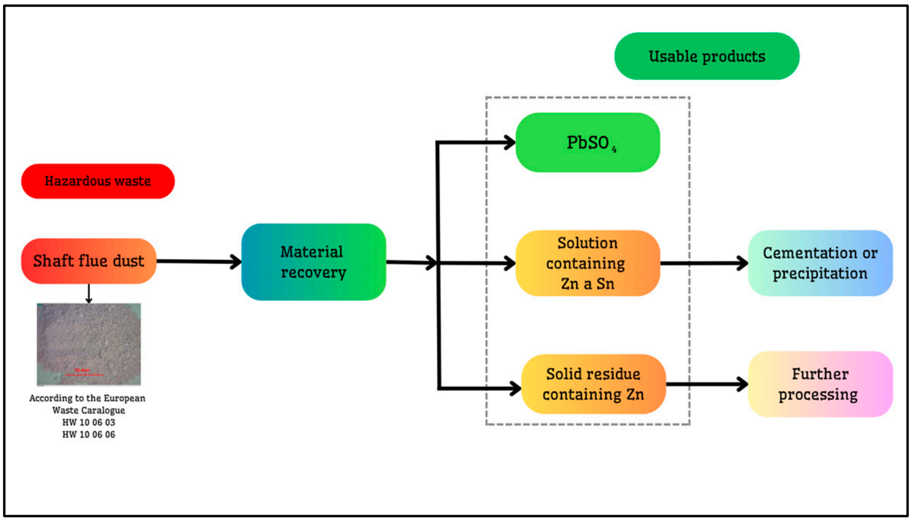

Figure 4. Proposed scheme of possible treatment of SFD.

4. Conclusions

In this work, a procedure for the hydrometallurgical treatment of SFD from secondary copper production was proposed. The following optimal leaching conditions for SFD treatment were confirmed: 1 M NaOH, 80 °C, pH = 14, 400 rpm and L:S = 20. Under these conditions, 98% of Pb was transferred into the solution. Sulfuric acid was chosen as a suitable precipitating agent, assuming the formation of $PbSO_4$. Lead sulphate can be considered as a usable product in the treatment of SFD. Initial experiments confirmed the formation of a white precipitate within the theoretical pH range for lead sulphate formation. The solution after lead precipitation containing Zn^{2+} can be used for further processing to obtain a usable zinc-based product. The proposed method of material recycling of SFD, currently classified as hazardous waste with content of zinc and lead, could provide the development of usable products. This suggests that the hydrometallurgical treatment process will support the circular economy.

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