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Hydrometallurgical Treatment of Copper Shaft Furnace Dust for Lead Recovery

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Fine-grained fraction (<53 µm) of industrial copper shaft furnace (CSF) dust was characterized in terms of chemical and phase compositions as well as leaching behaviour of lead (zinc) in sodium hydroxide solutions. The leaching was carried out in solutions of 1, 2, 3 and 4 M NaOH at temperatures of 20 and 80 °C and a solid to liquid ratio of 20. The purpose of the leaching study was to confirm the theoretical assumption and at the same time to determine the influence of NaOH concentration and temperature on lead transfer into the solution. The obtained results showed that lead was leached out from the dust sample with the highest extraction of almost 60 % in 2 M NaOH solution after 15 minutes at 80 °C. Zinc extraction of almost 58 % was achieved at 4 M NaOH in 15 minutes at 80 °C.

Keywords:

Lead – Zinc – Copper shaft furnace dust – Leaching

Hydrometallurgische Behandlung von Kupferschachtofenstaub zur Bleirückgewinnung

Eine feinkörnige Fraktion (<53 µm) Kupferschachtofenstaub industrieller Herkunft wurde bezüglich chemischer und Phasenzusammensetzung sowie des Laugungsverhaltens von Blei (Zink) in Natriumhydroxidlösungen charakterisiert. Die Laugung wurde in 1-, 2-, 3- und 4-molarer NaOH-Lösung bei Temperaturen von 20 und 80 °C und einem Fest/Flüssig-Verhältnis von 20 durchgeführt. Der Grund für die Laugungsuntersuchungen war, die theoretische Annahme zu bestätigen und gleichzeitig den Einfluss von NaOH-Konzentration und Temperatur auf den Bleiübergang in die Lösung zu bestimmen. Die Ergebnisse zeigten, dass Blei mit dem höchsten Ausbringen von fast 60 % in 2-molarer NaOH-Lösung nach 15 Minuten bei 80 °C aus der Staubprobe gelaugt wurde.

Schlüsselwörter:

Blei – Zink – Kupferschachtofenstaub – Laugung

Traitement hydrométallurgique de la poussière de cuivre des fours à cuve pour la récupération du plomb

Tratamiento hidrometalúrgico de polvo del horno de cuba para cobre para la recuperación del plomo

1 Introduction

Lead is the softest of the technically important base heavy metals. It is easily rolled and moldable, so it is possible to produce wire rod and tubes as well as sheets and foils. Lead consumption is linked to the manufacture and use of lead-acid batteries and it is estimated to account for 85 % of production (Figure 1) [1]. EU countries produced 343,900 t of lead concentrate in 2014; the main producers being Poland (1.5 %), Sweden and Turkey. Total world mine production in 2015 was reported as 5.0 mill. t [2, 3]. World refined lead metal production in 2015 represented 10.7 mill. t (see Figure 1). China was the world's largest producer of mined lead and the world's largest producer of refined lead in 2015 [2, 3].

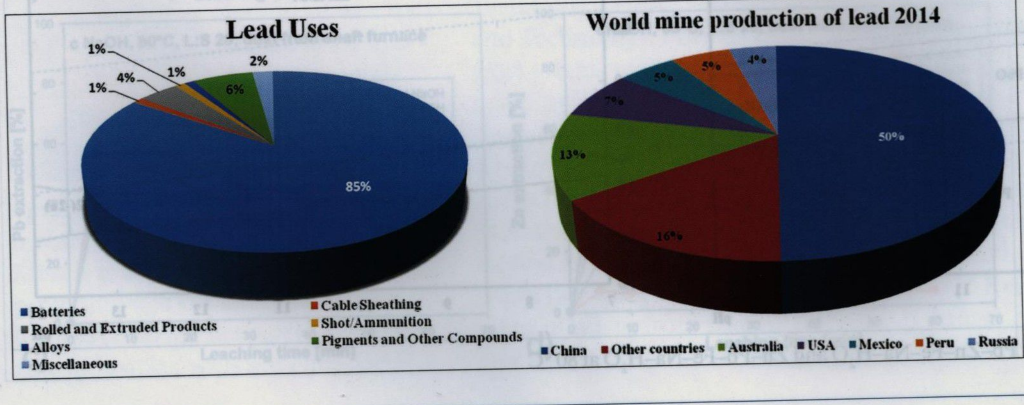


Fig. 1: Lead uses in 2012 and world mine production of lead 2014

2 Lead production from secondary sources

The balance between primary and secondary lead production has shifted since 1998, and in 2011 secondary sources accounted for more than 77 % of EU lead production [4]. Recovery of lead from residues and from flue-dusts from copper smelting is possible. According to the European Waste Catalogue (EWC) and Hazardous Waste List CSF dust is classified as a hazardous waste from copper thermal metallurgy [5]. The CSF copper shaft furnace dust (content of 45 to 60 % Zn) in the Slovak company producing secondary copper was processed hydrometallurgically to zinc sulphate [6]. A flue dust from the secondary copper production serves as a feed material for pyrometallurgical lead and zinc recovery. Under reducing conditions, zinc is volatilised and recovered as oxide, while lead and tin are produced in the form of an alloy [4]. Hydrometallurgical processes are an alternative approach in obtaining and refining of metallic lead. These processes offer the advantage that, unlike traditional smelting operations, harmful lead fume and sulphur-containing gases are not evolved (although in modern plants, pollution control systems can reduce emissions to a low level). Hydrometallurgical methods are generally regarded by the industry as a much cleaner solution in contrast to pyrometallurgy, and may become more important in the future [7, 8].

3 Thermodynamics

Thermodynamic calculations for the chosen leaching systems were carried out using the software HSC Chemistry 7.1 [9]. Lead is present in the CSF in the form of various oxides, sulphates or fluorides, but mainly as PbO and $PbSO_4$ phases, whereas zinc is primarily in the form of ZnO [10, 11]. Leaching of lead and zinc from CSF dust can be described by reactions (1), (2) and (3). Figure 2 shows the Eh-pH diagrams of the systems Pb–Fe–Na–Zn–H_2O and Zn–Fe–Na–Pb–H_2O at 80 °C. Lead is in the Eh-pH diagram in the ionic form above pH 13. Zinc forms the ionic form $ZnO_{2(-2a)}$ only in a very narrow region with the low potential (Eh) in the area of water stability. On the other hand, in the presence of iron a solid phase $Zn-Fe_2O_4$ is also probable. This means that for lead leaching in NaOH solutions pH above 13 and the temperature 80 °C is required. Moreover, for zinc dissolution even more specific conditions are desired. Therefore, the aim of this work was to experimentally verify the possibility of lead and zinc dissolution from the dust into the solution by means of alkaline leaching.

$$PbO + NaOH \rightarrow Na^+ + HPbO_2 \qquad \Delta G^0_{80°C} = -31{,}124\ \text{kJ/mol} \qquad (1)$$

$$PbSO_4 + 2Na_{(+a)} + 3OH_{(-a)} \rightarrow HPbO_{2(-a)} + Na_2SO_4 + H_2O \qquad \Delta G^0_{80°C} = -41{,}354\ \text{kJ/mol} \qquad (2)$$

$$ZnO + 2NaOH \rightarrow ZnO_{2(-2a)} + 2Na_{(+a)} + H_2O \qquad \Delta G^0_{80°C} = -62.857\ \text{kJ/mol} \qquad (3)$$

4 Experimental

4.1 Material and methods

The copper shaft furnace (CSF) dust sample placed at disposal by the Slovak copperworks was used for the leaching experiments. The CSF dust is a waste from pyrometallurgical production of secondary copper. The CSF dust sample was collected during a 10-days' period from the smelting operation. The as-received sample was re-weighed and subjected to coning quartering and dividing sample preparation methods to obtain a representative sample of CSF dust. Elemental composition of the material was determined using classical wet analysis by means of Atomic Absorption Spectrometry (AAS, Varian AA-20++) (Table 1). These results showed that the highest content in the sample had Zn and Pb (52.16 % and 19.33 % respectively). The CSF dust sample was subjected to morphology observation by optical microscopy using the digital microscope Dino-Lite ProAM413T (Figure 3). The sample consisted of two grain-size fractions, coarse and fine rather spherical grains, and grains of larger size were covered by smaller ones. Bulk of the waste occurs in the size range below 53 µm.

Table 1: Chemical composition of CSF dust sample [%]

Pb	Zn	Fe	Cu	Ca	Cl^-	Si	Sn	As	Ni
19.33	52.16	0.30	1.51	0.02	7.09	17.76	<LoD	<LoD	<LoD

LoD – limit of detection – AAS method

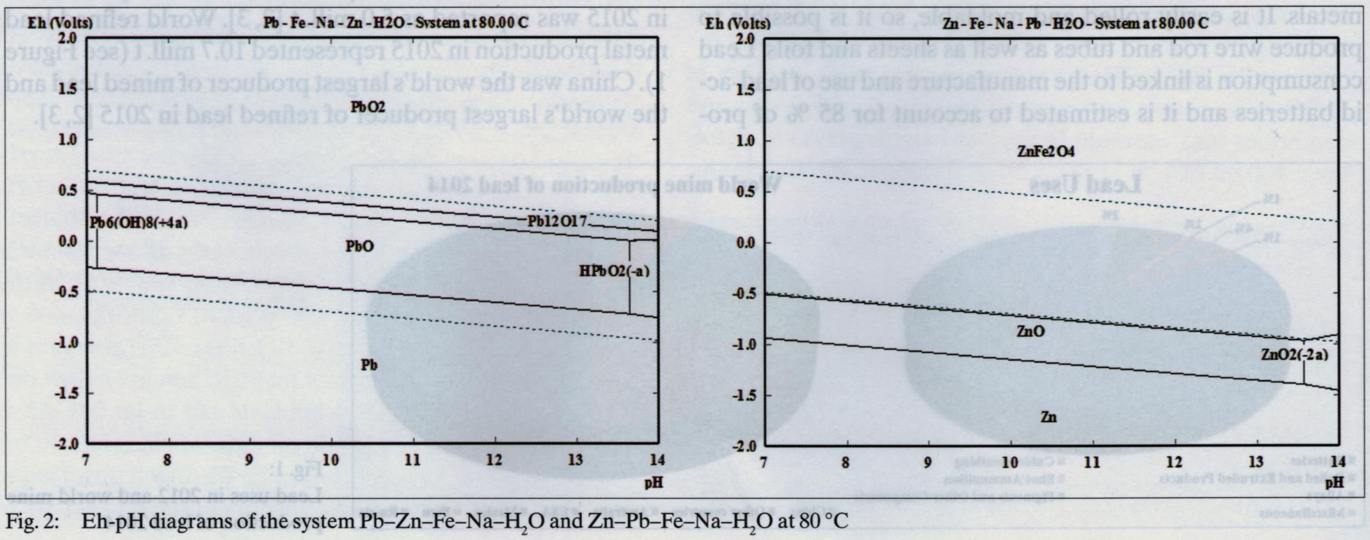


Fig. 2: Eh-pH diagrams of the system Pb–Zn–Fe–Na–H_2O and Zn–Pb–Fe–Na–H_2O at 80 °C

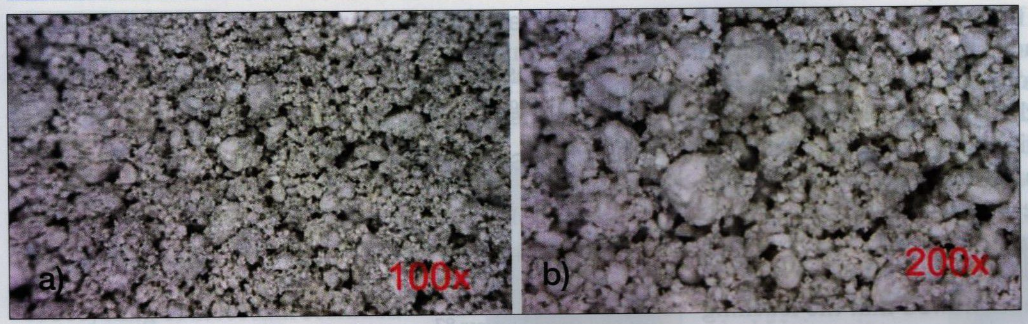
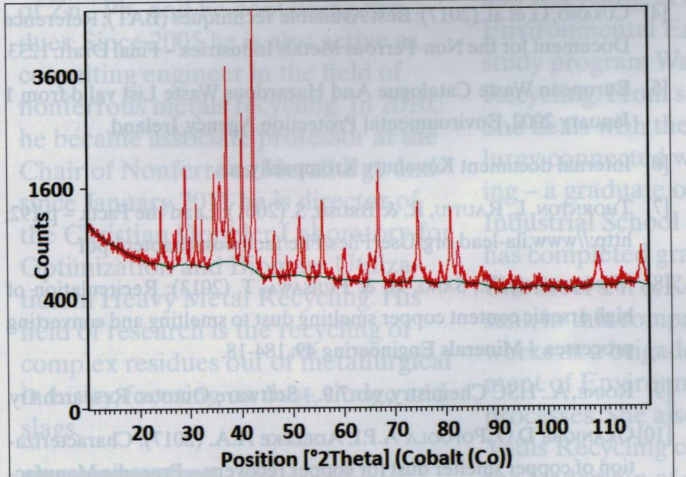


Fig. 3: Particle morphology of the CSF dust sample a) 100×, b) 200×

From the chemical analysis (see Table 1) it is obvious that the sample contains also metals such as Sn, As and Ni which were under the detection limit of AAS method.



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	$ZnSO_4 \cdot H_2O$
01-072-1393	Lead oxide sulfate	Pb_2OSO_4
01-076-0606	Calcium carbonate	$Ca(CO_3)$
00-026-0311	Lead chloride fluoride	$PbClF$

Fig. 4: XRD pattern of the copper shaft furnace dust sample

This sample contents some chlorides. X-ray diffractometer X-PANalytical X'Pert PRO MRD (Co-Kα) was used for qualitative phase analysis. Diffraction pattern of the sample is shown in Figure 4.

4.2 Leaching

Leaching of the CSF dust was carried out in a plastic beaker immersed in a water bath at the temperatures 20 and 80 °C. Sodium hydroxide solutions (400 cm^3) of various concentrations (1 to 4 M) were used as the leaching medium. The experiments were carried out at one liquid to solid (L/S) ratio 20. The suspension was agitated with a mechanical stirrer at constant rate (400 rpm). Leaching time was 60 min. During the process, samples of the leachate were taken in defined time intervals to determine the concentration of metal ions by AAS.

5 Results and discussion

Kinetic curves of leaching dust are shown in Figure 5 (a-d). From the kinetic curves of lead leaching (Figure 5 a, c) it is clear that the highest extraction of lead into the solution was achieved in 2M NaOH within 15 minutes at the temperature of 80 °C. The highest extraction of lead into the solution (40 %) at 20 °C was achieved in 1M NaOH within

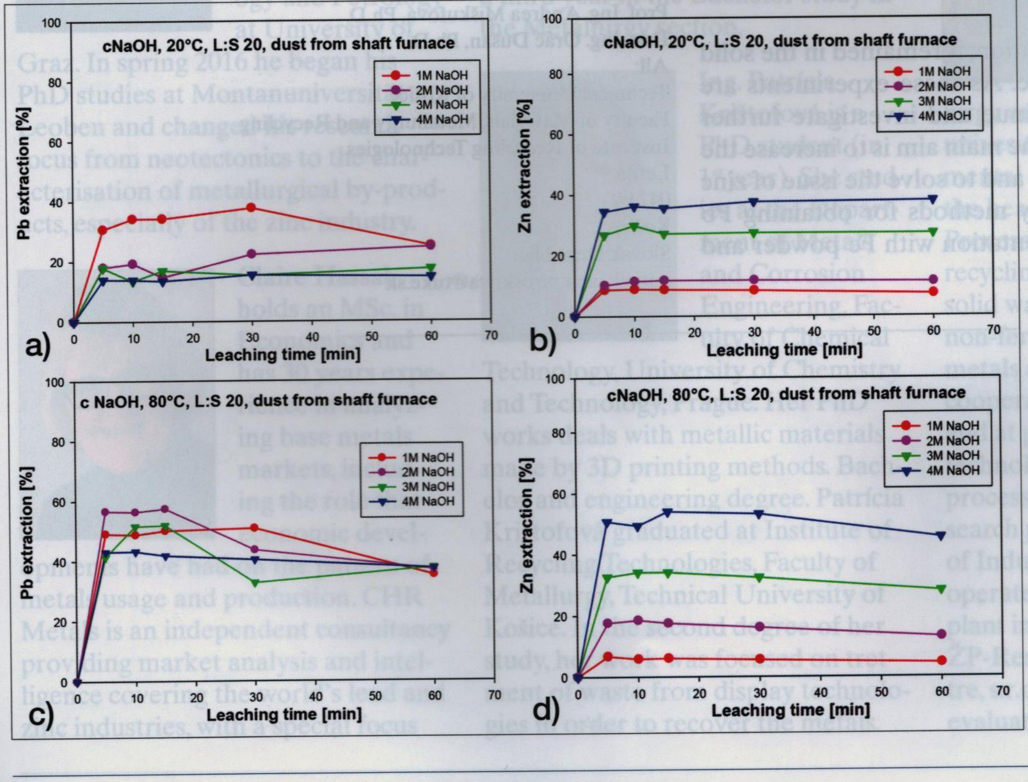


Fig. 5: Kinetic curves of leaching dust in NaOH at 20 and 80 °C

30 min of leaching. Increasing the NaOH concentration did not increase the amount of lead in the solution as predicted from the E-pH diagrams. From leaching curves for zinc (Figure 5 b, d) it can be seen that zinc leaching is more dependent on NaOH concentration than lead. The highest extraction of Zn was achieved in 4M NaOH at both temperatures (Figure 5 b, d). The highest extraction of zinc (around 38 %) was reached at the temperature of 20 °C in 5 min of leaching. The highest extraction at 80 °C (approx. 58 %) was extracted in 15 min. Results showed that the leaching process of CSF dust is quite fast, but the extraction of both metals was not complete. Leaching process stopped after approximately 10 to 15 minutes of leaching. The problem could be the formation of new solid phases during leaching. The temperature has a positive effect on the leaching of lead as well as zinc. As a result of this laboratory research (CSF dust treatment), examining different concentrations of NaOH, it can be argued that in order to maintain the higher extractions of Pb in a solution, lower concentrations of NaOH at higher temperature are satisfactory. In contrast, Zn dissolution requires higher concentrations of NaOH at higher temperature. In order to reach the higher metals extraction even higher temperature are required or at the same time it is suitable to examine and control the possible formation of intermediate products during alkaline leaching (PbO, $Pb_{12}O_{17}$ or $ZnFe_2O_4$).

6 Conclusion

This work confirmed the theoretical assumption that the alkaline leaching of copper shaft furnace dust dissolves Pb into the solution. The optimum extraction of metals (Zn, Pb) to the NaOH solution occured under these conditions:

- for Pb: 80 °C, L : S ratio 20, 2M NaOH (almost 60 %) is achieved;
- for Zn: 80 °C, L : S ratio 20, 4M NaOH (almost 58 %) is achieved.

Iron did not pass into the solution; it remained in the solid phase in the leaching residue. As these experiments are pilot, it is necessary to continue and investigate further parameters of the leaching. The main aim is to increase the yield of lead into the solution and to solve the issue of zinc dissolution. Suitable recovery methods for obtaining Pb from solutions are then cementation with Fe powder and electrolysis.

Acknowledgements

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