PYROMETALLURGICAL RECOVERY OF VALUABLE METALS FROM Zn-Pb SLAGS

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Abstract

Slags formed during pyrometallurgical extraction of zinc and lead contain numerous metals, and can provide a valuable source of these. Metal recovery from Zn-Pb slags can be accomplished using a pyrometallurgical method consisting in recovering materials at sufficiently high temperatures by transferring them to specific condensed phases (including metallic alloys) or the gas phase with subsequent condensation. The paper presents the results of research on the chemical and phase composition of products and waste generated during the pyrometallurgical processing of refining slags from the Zn-Pb metallurgy. It was found that there was a significant content of metallic lead in the product - sinter, with a very high share of silicate and oxide phases in the waste.

The chemical and phase composition of the tested materials proves the correct course of the pyrometallurgical processing of slags, and the high lead yield indicates the correct selection of its recovery technology, which is the basis for continuing research on the processing of refining slags using the pyrometallurgical method.

Keywords: Pyrometallurgy, zinc, lead, slag, metals, recovery

1. INTRODUCTION

Metallurgical slags resulting from zinc and lead production processes are characterised by a diversity of technical parameters, chemical and mineral composition, which in turn depend on the type of feedstock used, the technological process applied and its course. As metallurgical slags represent one of the most diverse groups among waste materials from metallurgical processes, they should be treated individually. Slags formed during metallurgical extraction of zinc and lead have varying chemical and mineral composition and contain considerable amounts of various chemical elements, among them toxic metals, and contain significant amounts of metals and semi-metals, the predominant ones being: Si, Al, Ca, Ma, Zn, Pb. Among the slags of Zn-Pb metallurgy, refining slags can be distinguished, characterised by much higher contents of Zn, Pb and Cu, with significantly lower concentrations of Si, Al, Ca, Mg [1-5].

The mineral composition of Zn-Pb metallurgical slags is dominated by multiphase crystalline conglomerates formed by high-temperature processes. Typical mineral constituents in these slags are: Zn and Fe oxides and Fe hydroxides, Zn, Pb, Fe and Cu sulphides, Pb sulphates and hydrated Zn, Ca, Cu sulphates, Zn silicates, silicates of the olivine group, melilites $(Ca,Na)_2(Al,Mg)[(Si,Al)_2O_7]$, Pb and Zn carbonates, spinels and multicomponent metal alloys of Pb, Zn, Cu, Fe, As, Sb [6-11]. One type of metallurgical slags are those, which are formed in the process of refining crude lead obtained by pyrometallurgical extraction of Zn and Pb. These slags contain numerous strategic and scarce metals, and can provide a valuable source of these.

The choice of the technological process for recovering metals from metallurgical waste, including slag, depends mainly on its mineralogical and chemical composition. Due to the variety of forms of metal occurrence in slags, it is extremely difficult to identify the optimal technological process for their processing.

One of the main methods of metals recovery from refining slags is pyrometallurgical processing of slags at high temperatures (thermal metallurgy), in various types of furnace, including shaft, muffle, rotary, electric furnaces [12-14]. The products of the process include metallic sinter and waste: slags, dross, dust. The authors' detailed study of the chemical composition and identification of the phase composition of materials formed during pyrometallurgical processing of refinery slags provides a basis for assessing the efficiency of the metal recovery process and for indicating the route of possible further recycling thereof.

2. PYROMETALLURGICAL PROCESSING OF REFINERY SLAGS

In order to determine the feasibility of zinc and lead recovery from refining slags, laboratory-scale process tests were performed in a resistance pit furnace at 1200 °C. The furnace charge consisted of refining slag, coal and limestone $CaCO_3$ in a ratio of 10:5:1. The slag samples were ground and averaged before the actual processing (**Figure 1**) [15].

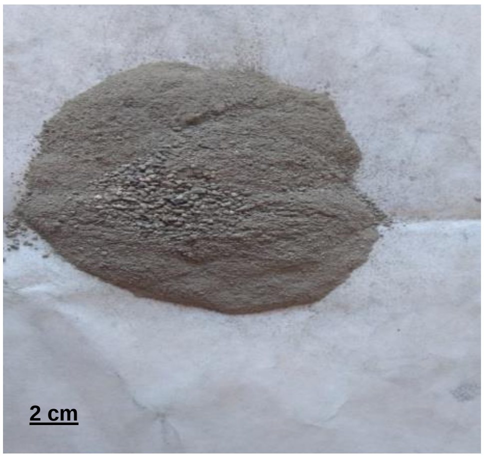

Figure 1 Example of ground and averaged refining slag sample

The process involved the reduction of zinc and lead oxides with coal, followed by the oxidation of zinc to zinc oxide ZnO.

It should be assumed that the following reactions mainly took place in the furnace workspace:

$$2ZnO + C \rightarrow Zn_g + CO_2 \tag{1}$$

$$ZnO + CO \rightarrow Zn_g + CO_2 \tag{2}$$

$$2PbO + C \rightarrow Pb + CO_2 \tag{3}$$

$$PbO + CO \rightarrow Pb + CO_2 \tag{4}$$

$$2Zn_g + O_2 \rightarrow 2ZnO \tag{5}$$

Coal acted as a reducing agent, while limestone acted as a flux, which lowers the melting point of the slag, causing it to liquefy and separate the metallic phase in the form of removable secondary slags. The product of the process was metallic sinter and the main waste was the secondary slag.

3. MATERIALS AND METHODS

The object of the study was metallic sinter (**Figure 2**) and secondary slag produced during an experiment that involved pyrometallurgical processing of slags from lead refining at the Miasteczko Śląskie Zinc Smelting Plant.

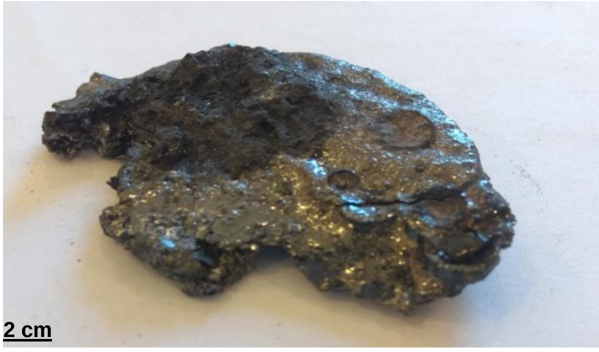

Figure 2 Metallic sinter from slag processing

The phase composition and chemical composition of the analytical samples of slags taken and then appropriately prepared were determined using the following methods [15]:

- X-ray fluorescence (XRF) – chemical composition,
- X-ray microprobe (EPMA) – chemical composition within a micro-area,
- identification of phases by X-ray diffraction (XRD).

The chemical composition of the slag samples was determined by X-ray fluorescence (XRF) using a PANalytical Epsilon 1 spectrometer.

Chemical composition was determined in a micro-area by means of a Joel JCXA 733 X-ray microanalyzer, equipped with an Oxford Instruments ISIS 300 energy-dispersive spectrometer to obtain information on qualitative and quantitative chemical composition within a micro-area of the tested grain. Analysis conditions: focused beam, diameter 1-2 µm, accelerating voltage 20 kV, current $3 \cdot 10^{-9}$ A).

The phase composition was determined by X-ray diffraction analysis(XRD) using a PANalytical AERIS diffractometer with a $Cu_{K\alpha}$ lamp, under the following conditions: voltage 40 kV, current 8 mA, 2theta angle step 0.003°, time 4.84 s, 2theta angle scanning range 7-77°. The proportions of minerals in the samples were determined by the Rietveld method, using Panalytical's High Score Plus software.

4. RESULTS OF RESEARCH

4.1. Chemical composition

The major chemical constituents of the tested slag samples include Na_2O and SO_3, their average concentration being 24.03 wt% and 17.11 wt%, respectively (**Table 1**). Further chemical constituents found in slags include Fe_2O_3 – 12.10 wt%, SiO_2 – 10.44 wt%, PbO – 9.96 wt% and CuO – 9.45 wt%. The average concentrations of other slag constituents, i.e. Al_2O_3, CaO, K_2O, P_2O_5, MnO, TiO_2, are below 3 wt%.

The major chemical constituent of the sinter sample is PbO, the average content of which is 55.61 wt%. Minor chemical constituents of the sinter sample include: SO_3 – 21.70 wt%, Fe_2O_3 – 8.07 wt% and Na_2O – 6.42 wt%. The average concentrations of other sinter constituents, i.e. SiO_2, SnO, CuO, Al_2O_3, MgO, CaO, ZnO, K_2O, MnO and P_2O_5 are below 2 wt%.

Table 1 Average chemical composition of the tested slag and sinter samples (wt%)

	SiO_2	**TiO_2**	**Al_2O_3**	**Fe_2O_3**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**
Slag	10.44	0.16	2.99	12.10	0.22	-	0.67	24.03	0.67
Sinter	1.98	0.03	1.08	8.07	0.05	1.08	0.91	6.42	0.10
	SO_3	**P_2O_5**	**SrO**	**BaO**	**ZnO**	**PbO**	**CuO**	**SnO**	**Total**
Slag	17.11	0.37	0.08	-	0.25	9.96	9.45	-	100.00

Sinter	11.70	0.02	-	-	0.39	65.61	1.27	1.29	100.00

4.2. Phase composition

Using X-ray diffraction analysis, it was demonstrated that the predominant crystalline phases in secondary slags formed during pyrometallurgical processing of refinery slags are silicates, iron and sodium silicates, and oxides of copper, iron and calcium. Lead sulphides and iron, copper and iron sulphates are present in smaller quantities (**Table 2, Figure 3**)

Table 2 The percentage of phases in the slag samples analysed.

Phase group	**Phase**	**Chemical formula**	**Mass percentage of constituent** (%)
Silicates and hydrated silicates	Ferripyrophyllite	$Fe_2(Si_4O_{10})(OH)_2$	5.9
	Disodium Catena-disilicate	$Na_2(Si_2O_5)$	8.7
	Ferrierite	$SiO_2 \cdot 0.45H_2O$	4.1
	Quartz	SiO_2	3.8
	Coesite	SiO_2	11.2
Oxides	Lime	CaO	1.8
	Copper(III) Ferrate(I)	$Cu(FeO_2)$	0.7
	Spinel-(Cu,Fe)	$CuFe_2O_4$	3.3
Sulphates and hydrated sulphates	Rhomboclase	$FeH[SO_4]_3$	1.8
	Iron sulphate trihydrate	$FeSO_3 \cdot 3(H_2O)$	3.5
Sulphides	Pyrrhotite	FeS	0.6
	Chalcopyrite	$CuFeS_2$	0.4
	Galena	PbS	1.2
Metals	Lead	Pb	1.5
Amorphous substance	Glass	-	51.5

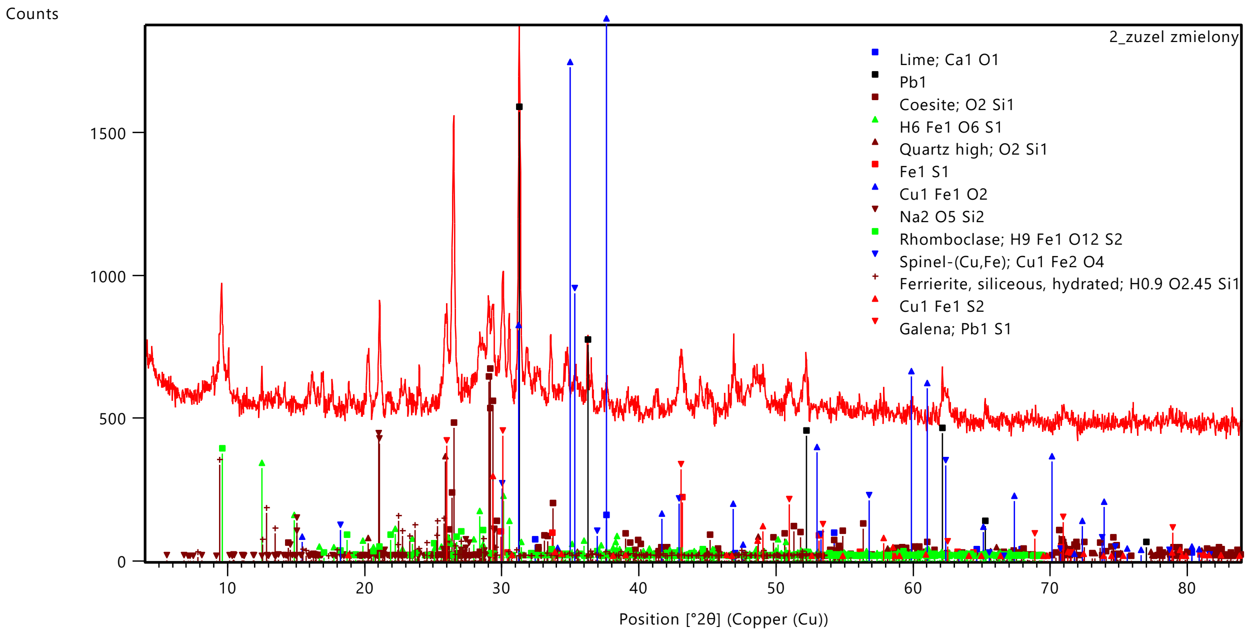

Figure 3 Example of diffractogram of slag sample

In the phase composition of the metallic sinter, Pb predominates with a 70% content, the other components being: glass 19.8%, sulphides 7.6% , oxides 0.8% and crystalline silicates 0.5% (**Table 3**).

Table 3 The percentage of phases in the metallic sinter samples analysed

Phase group	Phase	Chemical formula	Mass percentage of constituent (%)
Silicates	Carnegieite	$NaAlSiO_4$	0.5
Oxides	Magnesium ferrite	$MgFe^{3+}_2O_4$	0.2
	Magnetite	$(Fe_3(Fe^{2+}Fe^{3+})O_4)$	0.6
	Wustite	FeO	-
	Litharge	PbO	1.5
Carbonates	Hydrozincite	$Zn_5[(OH)_3/CO_3]_2$	-
Sulphides	Sphalerite	ZnS	-
	Wurtzite	ZnS	1.6
	Galena	PbS	5.5
	Chalcopyrite	$CuFeS_2$	0.5
Metals	Lead	Pb	70
Amorphous substance	Glass	-	19.8

The examination of the chemical composition in the micro-areas confirmed the presence of the main phases identified by X-ray diffraction and allowed the mineral inventory to be supplemented with trace phases (**Table 4**), which are present in the slags and sinter studied in much smaller quantities, hence their presence was not indicated in the X-ray diffractograms.

The phase composition of the slags revealed, in addition to the main phases identified by XRD, the presence (**Figure 4, Table 4**) of sulphides: pyrite (FeS_2),chalcopyrite ($CuFeS_2$), covellite (CuS), CuS_2 which form individual phases; sulphates contained in multiphase conglomerates: thenardite Na_2SO_4, $FeSO_4$, chalcanthite $CuSO_4$, arcanite K_2SO_4, metallic precipitates (alloys): $Fe_{60}Zn_{11}O_{25}R_4$, where R=Na, Ca, and $Pb_{31\text{-}34}Fe_{28\text{-}29}Cu_{14\text{-}16}O_{18\text{-}19}R_{4\text{-}8}$, where R=Zn, Sb, and metallic elements: Cu, Pb, Cu.

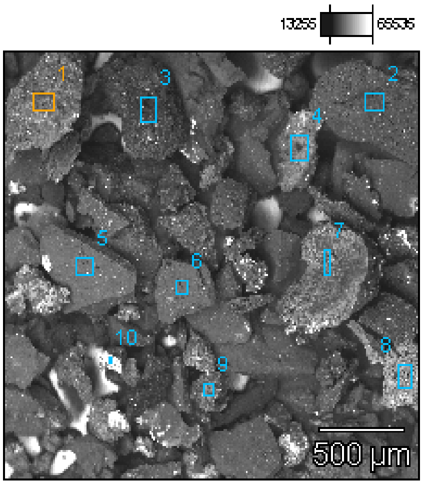

Figure 4 Micro-area with measurement points – an example slag sample (**Table 4**)

In the phase composition of the metallic sinter identified from the micro-area analyses, metallic precipitates (alloys) predominate: $Pb_{53-57}Fe_{8-9}O_{16-22}R_{13-23}$, where R=Na, As, Si, Zn; less often Cu, Sb, and $Pb_{31-34}Fe_{28-29}Cu_{14-16}O_{18-19}R_{4-8}$, where R=Zn, Sb, Na, sulphides Cu_2S and CuS and eventually glass (**Figure 5, Table 5**).

Table 4 Phase composition of the examined measurement areas of an example slag sample (wt%)

Measurement point	**CuS_2**	**FeS_2**	**PbS**	**Glass**		**Zn**		**Total**
3	54.2			45.8				100.0
4	23.7	20.4	17.4	38.4				100.0
8	5.2	4.1		83.3		7.4		100.0
9	14.5	15.7		69.8				100.0
Measurement point	**$FeSO_4$**	**K_2SO_4**	**$CuSO_4$**	**Na_2SO_4**	**$Pb_{met.}$**	**$Cu_{met.}$**	**Glass**	**Total**
1	16.6	1.9	16.6	35.7			29.2	100.0
2		5.2	31.6	36.4			26.8	100.0
5		6.2	25.0	28.0			40.8	100.0
6		7.9	26.1	21.0			45.0	100.0
7		5.2	37.2	26.3			31.2	100.0
10		7.0	8.2	15.9	20.7	34.9	13.2	100.0

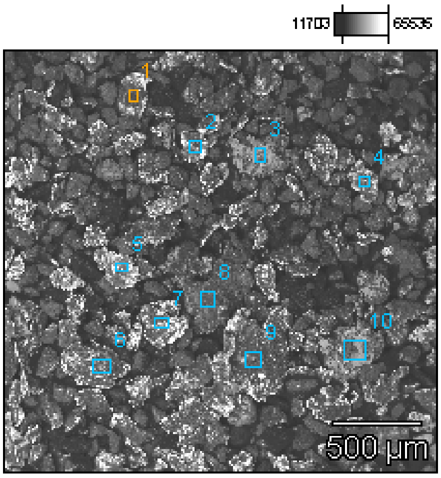

Figure 5 Micro-area with measurement points–an example metallic sinter sample (**Table 5**)

Table 5 Phase composition of the examined measurement areas of an example metallic sinter sample (wt%)

Measurement point	**CuS_2**	**CuS**	**Alloy (Fe+Pb)**	**Alloy (Fe+Pb+Cu)**	**Glass**	**Zn**	**Total**
1	40.6		34.2		25.2		100.0
2	25.7		64.5		9.8		100.0
3		17.4	77		5.6		100.0
4	29.9		58		12.1		100.0
5	36.4		54.6		9.0		100.0

6				91.1	8.9		100.0
7	26.1		62		10.3	1.6	100.0
8	30.8		49.8		19.4		100.0
9	34.3		51.3		14.4		100.0
10		14.9	76.7		8.4		100.0

4. CONCLUSIONS

Based on the research conducted, it can be concluded that:

1. Pyrometallurgical processing of refining slags generates secondary slags in which the phase composition is dominated by silicate phases, i.e. amorphous glass and crystalline silicates. This phase composition, with a predominance of amorphous glass, is typical of iron-rich slags (Fe content > 10%) that cool slowly in air. The highest proportion of silicate phases with high iron content indicates also the separation of metallic phases from the liquid slag in the course of the process.
2. The phase composition of the processing product (sinter), which is clearly dominated by metallic lead, is indicative of the correct course of the process (attaining proper thermodynamic parameters for the reduction reaction) in a resistance furnace atmosphere and the use of appropriate fluxes in the right proportions.
3. The low Zn content of secondary slags and metallic sinter is a result of the oxidation of ZnS during the pyrometallurgical processing of the refining slags and the deposition of zinc in the form of ZnO inside the furnace and on the furnace filters.
4. Tests carried out on the processing of refining slags for the recovery of Pb using the pyrometallurgical method, in which lead recovery efficiencies of 50% were achieved, indicate that this is a rational method, while further trials of processing the resulting sinter using hydrometallurgical methods, such as chemical leaching with sulphuric acid (VI), should be carried out to increase the metal extraction efficiency.

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