

# MODIFICATIONS OF THE CHEMICAL COMPOSITION AND MICROSTRUCTURE OF FLASH SMELTING COPPER SLAGS IN THE PROCESS OF THEIR REDUCTION

Received – Prispjelo: 2014-01-30  
Accepted – Prihvaćeno: 2014-06-20  
Preliminary Note – Prethodno priopćenje

Blister copper smelting in a flash smelting furnace results in generation of slag that contains high amounts of copper, iron and lead. Most commonly, this material is subjected to reduction with coke in an electrical furnace. In the present paper, results of investigations on reduction of slag with another reducer, i.e. anthracite dust, are discussed. Each experimental slag was analysed for its microstructure, chemical composition and phase composition. Based on the results, a decopperisation level of the study material was estimated. It was shown that anthracite dust might be considered as an alternative for currently used reducers.

*Keywords:* copper, reduction, flash smelting, microstructure, slag decopperisation

## INTRODUCTION

In many pyrometallurgical processes, slags of highly diverse chemical composition are generated. Slags with poor metal contents are basically used in highway engineering, cement industry and chemical industry, while slags with higher metal contents are returned to metallurgical processes or processed with the aim of recovering their metal components. Almost continuously, investigations targeting higher metal recovery from these materials are conducted in many research sites. This regards slags from both steelmaking processes and non-ferrous metal production [1-7]. An example of slag with very high metal content is flash-smelting slag generated during blister copper smelting. Most commonly, this material is subjected to reduction with coke in an electrical furnace. Results of a study on reduction of this type of slag with anthracite dust are discussed below. Each experimental slag was analysed for its microstructure, chemical composition and phase composition.

## RESEARCH MATERIALS

As the initial test material, industrial slag obtained during copper blister flash smelting at KGHM “Polska Miedź” was used. Its chemical composition is presented in Table 1.

Anthracite dust was used as carbon reducer. Its selection resulted from an attempt to find a carbon-bearing material that would be alternative to breeze coke

Table 1 **Chemical composition of the investigated slag**

Component	Content / %mass
Cu	11,6
Pb	3,25
Fe	10,63
Zn	1,31
S	0,03
CaO	13,28
SiO <sub>2</sub>	31,84
MgO	5,08
Al <sub>2</sub> O <sub>3</sub>	8,95

which is used in the industrial practice for the purposes of the discussed technology. It should be noted that various types of alternative fuel, produced based on waste fine-grained carbon materials and biomass, are increasingly often applied in energy and metallurgical industries [8-13].

## RESEARCH METHODOLOGY

Each experimental slag was analysed for its microstructure, chemical composition and phase composition. The first analysis was performed with the use of a HITACHI – 3 400 N scanning microscope (Scanning Electron Microscopy - SEM) fitted with a Thermo Noran energy dispersive x-ray spectrometer (EDS) and an electron probe microanalysis (EPMA) system. The investigations were performed under low vacuum conditions due to poor electrical conductivity of the samples. To illustrate structural morphology, images obtained from a secondary electron (SE) detector, environmental secondary electron detector (ESED) and backscattered electron (BSE) detector were utilised. The phase composition analysis was carried out by means of the x-ray

T. Rzychoń, T. Matuła, B. Chmiela, J. Łabaj - Silesian University of Technology, Katowice, Poland  
K. Rogóż – KGHM „Polska Miedź”, Lubin, Poland

diffraction (XRD) method using a JEOL JDX-7S diffractometer as well as a lamp with a copper anode ( $\lambda_{CuK\alpha} = 1,54178 \text{ \AA}$ ), powered by 20 mA, 40 kV current, and a graphite monochromator. To record the results, a 0,05° step method was applied with a time register of 3 sec within 10 to 90° 2θ. The investigations were conducted using powder samples. Moreover, the AAS method was used for determination of lead, copper and iron contents in the slag.

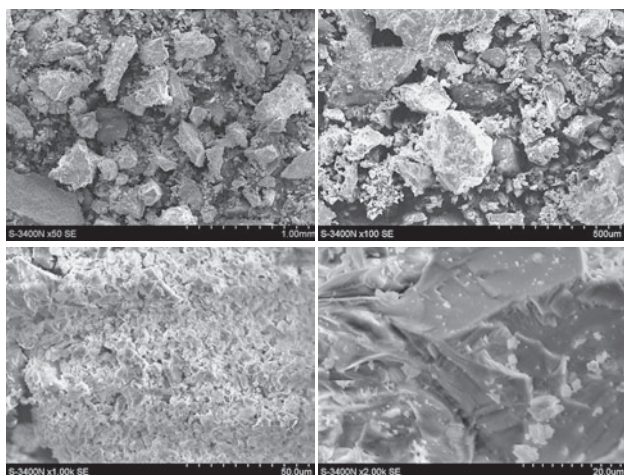


Figure 1 Images of the initial slag microstructure

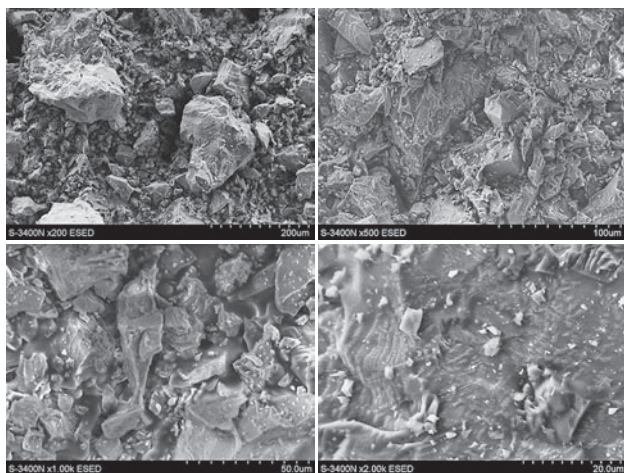


Figure 2 Images of the post-reduction slag

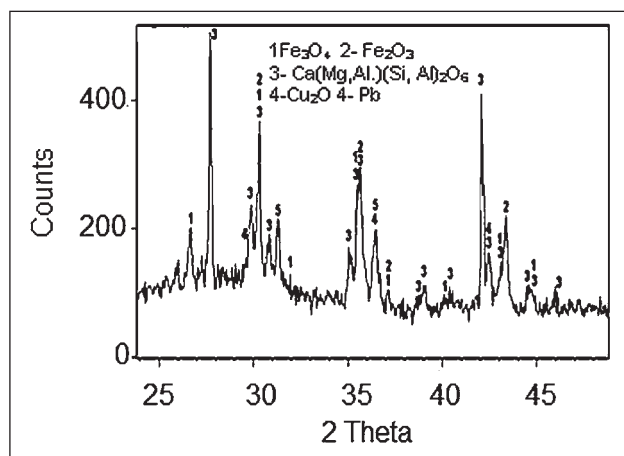


Figure 3 Part of the x-ray diffractogram of the initial slag

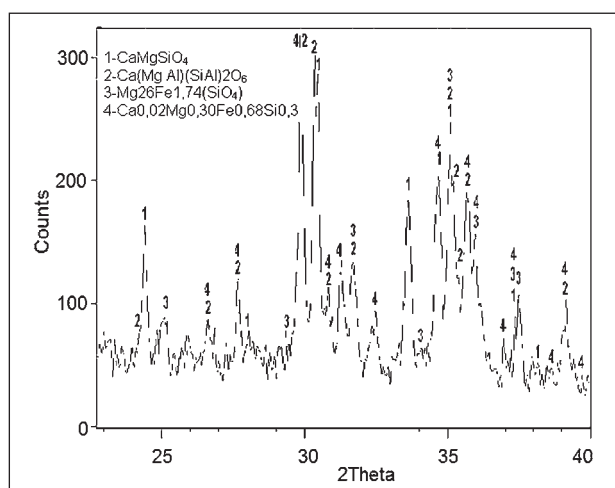


Figure 4 Part of the x-ray diffractogram of the post-reduction slag

### STUDY RESULTS

In Figures. 1 and 2, images of microstructures of the initial slag and the slag following a 5-hour reduction process are presented while Figures. 3 and 4 show EDS spectra for the same slag types.

In Tables 2 and 3, contents of primary slag components following various reduction times are presented. Their graphic interpretations are shown in Figures 5-7.

Table 2 Examples of the primary slag component contents following the reduction process

Reduction time / h	Slag component content / %mass			
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
Initial slag	31,84	8,95	13,28	5,08
1	33,56	9,05	23,01	3,99
2	36,88	9,33	20,39	3,86
5	38,77	10,79	16,19	3,96

Table 3 Examples of Cu, Pb and Fe contents in the post-reduction slag

Reduction time / h	Slag component content / %mass		
	Cu	Pb	Fe
Initial slag	11,60	3,25	10,63
1	1,63	2,40	13,11
2	0,71	1,13	11,42
5	0,19	0,17	7,74

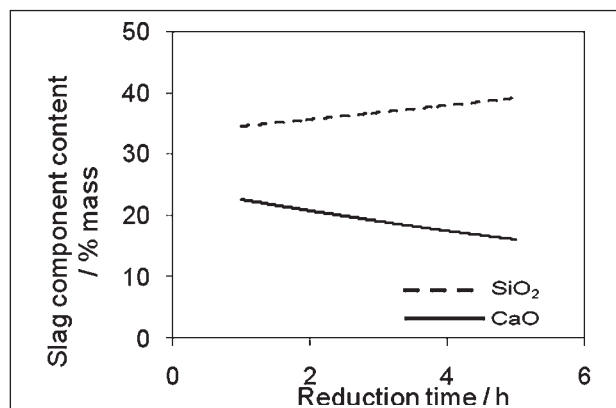
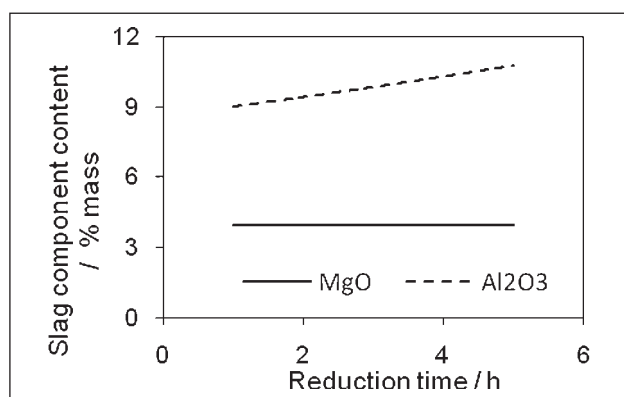
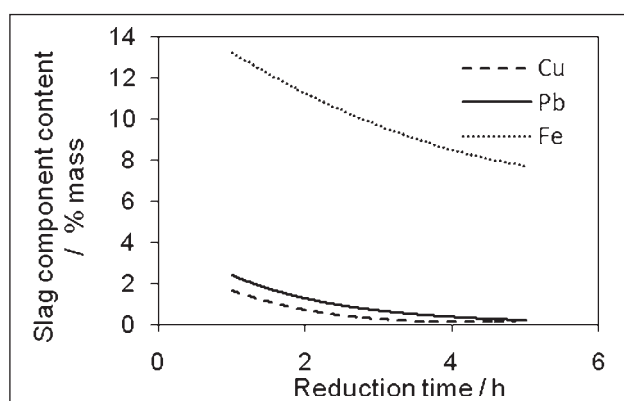


Figure 5 Changes in SiO<sub>2</sub> and CaO contents in the slag during the process of reduction



**Figure 6** Changes in  $\text{Al}_2\text{O}_3$  and MgO contents in the slag during the process of reduction



**Figure 7** Changes in lead, copper and iron contents in the slag during the process of reduction

## SUMMARY

The investigations regarding post-reduction slag microstructures showed their diverse morphologies. In the slag, rounded, flat and spherical particles were observed. The analysis of slag sample diffractograms showed that in the slags, iron mainly occurred in the forms of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  while copper was found in the form of  $\text{Cu}_2\text{O}$ . The  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and CaO contents in the slag changed within 31 to 39 % mass, 8 to 11 % mass and 13 to 16 % mass, respectively. During the first stage of reduction, higher iron content was observed compared to the initial value, which means that in the reduction process of the analysed slag, the first reduced compounds were copper and lead oxides. In the study, very high levels of copper and lead reduction were obtained which was confirmed by decreased to less than 0,2 % mass contents of these metals in the slag versus the initial values of 11,6 and 3,25 % mass, respectively.

## Acknowledgements

The study was conducted under the Research Project No. PST1/A5/21/2012, financed by the National Research and Development Centre, Poland.

## REFERENCES

- [1] S. M. A. Basir, M. A. Rabah, Hydrometallurgical recovery of metal values from brass melting slag, *Hydrometallurgy*, 53 (1999) 2, 31-44.
- [2] M. I. Muravyov, N.V. Fomchenko, A.V. Usoltsev, E.A. Vasilyev, T.F. Kondratieva, Leaching of copper and zinc from copper converter slag flotation tailings using  $\text{H}_2\text{SO}_4$  and biologically generated  $\text{Fe}_2(\text{SO}_4)_3$ , *Hydrometallurgy*, 119-120 (2012) 5, 40-46.
- [3] X. Ren, O. Wei, S. Hu, S. Wie, The recovery of zinc from hot galvanizing slag in an anion-exchange membrane electrolysis reactor, *Journal of Hazardous Materials*, 181 (2010) 1-3, 908-915.
- [4] J. Vereš, M. Lovás, S. Jakabský, V. Šepelák, S. Hredzák, Characterization of blast furnace sludge and removal of zinc by microwave assisted extraction, *Hydrometallurgy*, 129-130 (2012) 11, 67-73.
- [5] P. Migas, M. Karbowniczek, Interactions between liquid slag and graphite during the reduction of metallic oxides, *Archives of Metallurgy and Materials*, 55 (2010) 4, 1147 - 1157.
- [6] A. Semykina, V. Shatokha, S. Seetharaman, Innovative approach to recovery of iron from steelmaking slags, *Ironmaking & Steelmaking*, 37 (2010) 7, 536 -540.
- [7] M. Dziarmagowski, M. Karbowniczek, M. Pyzalski et al., Reduction of the converter slag in electric -arc furnace, *Ironmaking & Steelmaking*, 19 (1992) 1, 45-49.
- [8] J. Lipart, T. Matuła, M. Niesler, L. Blacha, J. Filipczyk, Wastes from the coal-enrichment process as alternative reducers for lead smelting from lead-acid accumulator scrap, *Metalurgija*, 52 (2013) 4, 493-496.
- [9] J. Łabaj, M. Słowikowski, W. Żymła, J. Lipart, The research on reactivity of alternative carbon reducers, *Metalurgija*, 52 (2013) 1, 68-70.
- [10] M. Niesler, J. Stecko, L. Blacha, B. Oleksiek, Application of fine-grained coke breeze fractions in the process of iron sintering, *Metalurgija*, 53 (2014) 1, 37-40.
- [11] M. Niesler, L. Blacha, J. Łabaj, T. Matuła, A study on the process of fine-grained plumbiferous material agglomeration, *Metalurgija*, 52 (2013) 4, 521-524.
- [12] J. Hehlmann, W. Szeja, M. Jodkowski, Research on Combustion Process of Polydisperse Coal Mixtures of New Generation with Dominant Share of Quasicoking Coal, *Rocznik Ochrona Środowiska*, 13 (2011) 1, 891-902.
- [13] J. Hehlmann, W. Szeja, M. Jodkowski, Benducki P, Research on Receiving Composite Energetic Biofuel Based on Biomass from Sewage Sludge Fermentation Process, *Rocznik Ochrona Środowiska*, 13 (2011) 1, 921-934.

**Note:** Nowak P. is responsible for English language, Katowice, Poland