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# Assessment of the Harmfulness of the Slags from Copper Smelting Processes, in an Aspect of their Management

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## Abstract

There are two methods to produce primary copper: hydrometallurgical and pyrometallurgical. Copper concentrates, from which copper matte is melted, constitute the charge at melting primary copper in the pyrometallurgical process. This process consists of a few stages, of which the basic ones are roasting and smelting. Smelting process may be bath and flash. Slag from copper production, on the end of process contain less 0,8%. It is treat as a waste or used other field, but only in a few friction. The slag amount for waste management or storage equaled 11 741 – 16 011 million tons in 2011. This is a serious ecological problem. The following slags were investigated: slag originated from the primary copper production process in the flash furnace of the Outtokumpuja Company in HM Głogów 2 (Sample S2): the same slag after the copper removal performed according the up to now technology (Sample S1): slag originated from the primary copper production process in the flash furnace of the Outtokumpuja Company in HM Głogów 2, after the copper removal performed according the new technology (Sample S3). In practice, all tested slags satisfy the allowance criteria of storing on the dumping grounds of wastes other than hazardous and neutral.

**Keywords:** Innovative technology, Slag copper, Leaching, Environmental protection

## 1. Introduction

Due to significant amounts of fly –ashes generated in power plants, as well as copper slag, investigations on the possibility of utilising mixtures of these two wastes as materials for building roads, were undertaken. It was found that the mixture containing 30% of fly–ash and 70% of copper slag is suitable for being used as the pavement base [1].

Copper slag, classified as a waste, creates environment problems, and therefore when it is reused (in such case it is classified as a sustainable material), it brings benefits for the environment, such as e.g.:

- Saving of natural resources of sands, rocks, stones when it is used as an additive at concrete productions,
- Since previously the majority of copper slag was stored on dumping grounds, what created geological and environment

problems, its management will significantly limit this storage.

Copper slag as by-product is mostly dumped in landfills, thus creating a geo-environmental problem. The application of copper slag causes increases of the compression and tensile strength as well as density and other concrete parameters [2].

Sustainable materials are those which provide environmental, social and economic benefits and in the meantime protecting public health and environment over their whole life cycle.

There are two methods to produce primary copper: hydrometallurgical and pyrometallurgical. Copper concentrates, from which copper matte is melted, constitute the charge at melting primary copper in the pyrometallurgical process. This process consists of a few stages, of which the basic ones are roasting and smelting. Smelting process may be bath and flash. The sulphides and oxides of iron and copper are basically in charge. The most often the smelting process is carried out in electric furnaces, where the slag reaction with coke breeze or electrodes occurs and in effect, the neutral slag of a very small copper content is obtained. Secondary copper is produced by pyrometallurgical processes. At smelting of the secondary raw materials the reduction atmosphere is applied. Slag from primary copper contents around 1% Cu. [3].

Copper slag, the glassy material, produced during the matte smelting and copper conversion is a waste material as landfill or sold cheaply, when contain < 0,8 % copper [4].

Large amounts of wastes generated by industries are stored on dumping grounds, which creates problems for humans and for the environment. For many years such by-products as silica fumes, fly-ashes, and slag were considered as wastes. Intensive investigations on possibilities of the management of these by-products, performed in the last years, significantly limited the amounts stored on dumping grounds.

## 2. Matte smelting

Slag from copper production has many interesting mechanical properties [5, 6]. In the suspension furnace the copper blister, and postprocess slags are usually formed. They contain from 1.6-2 % Cu (anode slag) up to 35 % Cu (converter slag) [7].

These slags are directed to the electric furnace as charge materials. The waste materials stored currently on slag dumping areas or converted for road sub-crusts, contain at least 0.6 % of copper, achieving often 0.8 % and even 1 % Cu. It has been estimated that for every ton of copper production about 2,2 - 3 tons of slag are generated. Assuming that the annual copper production in Europe (in 2011 year) equaled 5 337 million tons, the slag amount for waste management or storage equaled 11 741 – 16 011 million tons [8]. This is a serious ecological problem. Presently the slags from the copper production are mainly used for a copper recovery or as an abrasive material [9]. Investigations of the copper slag influence on the environment indicate that it is not hazardous or toxic and therefore can find a wide application [10]. The copper slag was removed from the list of dangerous wastes US EPA.[11]. The slag from the copper production is the replacement of aggregates in concrete and probably also as the cement replacement [12].

It is possible because heavy metals in the slag are stable and difficult for leaching. The management of copper slag in various economy fields, especially in the cement industry, which is able to utilise large amounts of this material, instead of storing it on dumping grounds, eliminates storage costs and decreases production costs e.g. of cement. In spite of generally positive assessments of the copper slag in the environment, it is necessary to investigate the slag originated from the given technology with regard to a possibility of the hazardous substances, especially metals, elution. The aim of the performed investigations was to determine to which degree the components can be eluted from slag (of a large copper content) obtained directly from the copper smelting, from the same slag but previously subjected to the removing copper process in the electric furnace in the HM „Głogów” and from the same slag but previously subjected to the copper removing process with applying the new technology developed by A. Bydątek et al. (described below). Studies were carried out in an aspect of the economic possibility of utilising waste slag or their storing in the proper dumping ground<sup>1</sup>.

## 3. Method of the removing copper from the slag

In the majority of used - up to know - methods of pyrometallurgical copper recovery from the postprocess slag, including the ones applied in Huta Głogów KGHM, coal in a form of coke or coal briquettes [13-15] together with fluxes. From the authors and others [7, 16-19] experience as well as from theoretical analyses it results, that such form of the carbon reagent is - in relation to reactions occurring within the slag phase - very low efficient. Solid coal reacts only with gaseous components of the atmosphere and, in practice, does not dissolve in the slag and does not react with its components. As result of introducing carbide reagents or carbide-forming metals with carbon or carbides into the slug, carbon ions {C<sup>2+</sup>} and {C<sup>4+</sup>} are formed. Therefore the Authors developed special mixtures - for removing copper from the slag - containing carbon, carbide and carbide-forming metals reducers, stimulators of ionic reactions in the slag and fluxes correcting its properties. Such mixtures more efficiently influence with the slag, and due to it the copper recovery is more efficient [20, 21]. In the first stage of the process of removing copper from the slag under laboratory and semiindustrial conditions, the charge of the flash furnace slag was put into the furnace of 300 kg capacity. Then the technological addition in a coke form in the amount (calculated versus the slag mass) of 5 %, cyanamide containing 60 % of calcium cyanamide in amount of 1 % and fluxes in a form of Na<sub>2</sub>O in amount of 5 %, oxide and haloid fluxing agents and calcium phosphate Ca<sub>2</sub>P<sub>2</sub>O<sub>5</sub> in the total amount of 3 %.

Into the decanter with melted slag aluminium carbide Al<sub>4</sub>C<sub>3</sub> refined to the granulation 1-30 mm in amount of 1 % versus the

<sup>1</sup> There are three kinds of dumping grounds in Poland, classified according to the allowable boundary elution values of components. These are: dumping grounds of neutral wastes, dumping grounds of wastes other than hazardous and neutral, dumping grounds of hazardous wastes.

slag mass, and the alloy composed of 85 % Fe<sub>3</sub>C, 4 % P, remainder Fe, refined to the granulation 20 -100 mm in a total amount of 1 % versus the copper mass subjected the reduction from slag, are introduced.

## 4. Materials and Methods

The following slags were investigated:

- Slag originated from the primary copper production process in the flash furnace of the Outtokumpuja Company in HM Głogów 2 (Table 1). (Sample S2).
- Slag originated from the primary copper production process in the flash furnace of the Outtokumpuja company in HM Głogów 2, after the copper removal performed according the up to now technology (Table 1). (Sample S1).

Table 1.

The chemical composition of slag slurry in HM "Głogów 2" before and after the removing copper process (S1)

Component, % mas.											
SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Cu <sub>2</sub> O	PbO	FeO	ZnO	As <sub>2</sub> O <sub>3</sub>	
Before removing copper (sample S2)											
33.94	15.60	4.94	10.00	0.75	2.39	14.01	3.29	10.37	1.41	0.254	
After removing copper (Sample S1)											
41.20	23.11	7.65	12.34	2.23	2.55	0.73	0.76	11.58	0.54	0.007	

Table 2.

The chemical composition of slag obtained in the laboratory melting after the removing copper process

Component, % mas. (sample S3)											
SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Cu <sub>2</sub> O	PbO	FeO	ZnO	As <sub>2</sub> O <sub>3</sub>	
45.50	17.75	5.05	9.73	1.52	8.5	0.45	1.62	13.00	0.37	0.005	

## 5. Leaching Test - Investigation of Results and their Discussion

Table 3 presents the results of leaching slag samples S1, S2 and S3.

The allowable concentrations of substances, corresponding to the criteria (acc. TCLP test -Toxicity Characteristic Leaching Procedure—Regulatory Levels) of the neutral wastes allowance for storing on the dumping grounds of neutral wastes as well as the allowance criteria of wastes other than hazardous and neutral, which are not municipal wastes, for storing on the dumping grounds of wastes other than hazardous and neutral are listed in Table 4.

When comparing the slag from the flash furnace process before removing copper (S2) with the slag after removing copper (S1) performed in HM Głogów, it can be stated that, the majority of parameters determined in filtrates obtains higher values for the raw slag of a high Cu content (Sample S2) than for the slag after removing copper (Sample S1).

It concerns especially such metals as: Mo 0.979 and 0.193 mg/kg ds, respectively; Pb 6.83 and 1.61 mg/kg ds, respectively; As 0.490 and < 0.010 mg/kg ds, respectively; Ba 0.525 and 0.139 mg/kg ds, respectively; Cu 25.3 and 0.249 mg/kg ds, respectively.

- Slag originated from the primary copper production process in the flash furnace of the Outtokumpuja Company in HM Głogów 2, after the copper removal performed according the new technology (Table 2). (Sample S3).

The elution results of slag samples: S1, S2 and S3. (Table 3).

In order to determine the potential threat to groundwater contamination, the solid waste leaching test are performed.

The tests are performed in accordance with Polish standard PNEN12457-4: 2006, basic test [22]. In order to determine the hazard solid waste leaching results obtained they were compared with the limit of substances eluted from wastes stored in dumping site for neutral wastes (acc. to the Polish standards) and toxicity threshold values of the Toxicity Characteristic Leaching Procedure (TCLP) (US EPA)).

Table 3.

The results of the research leaching slag S1, S2 and S3

Parameter	Units	Results of sample testing S1	Results of sample testing S2	Results of sample testing S3
Arsenic	mg/kg ds	< 0.010	0.490	< 0.010
Barium	mg/kg ds	0.139	0.525	0.108
Cadmium	mg/kg ds	< 0.005	0.024	0.010
Chromium – total	mg/kg ds	< 0.030	0.054	< 0,030
Copper	mg/kg ds	0.249	25.3	0.566
Mercury	mg/kg ds	< 0,005	< 0.005	< 0.005
Molybdenum	mg/kg ds	0.193	0.979	< 0.04
Nickel	mg/kg ds	< 0,04	< 0.04	< 0.04
Lead	mg/kg ds	1.61	6.83	0.168
Antimony	mg/kg ds	< 0.50	< 0,50	< 0.50
Selenium	mg/kg ds	< 0.010	< 0.010	< 0.010
Zinc	mg/kg ds	< 0.050	1.36	< 0.050
Chlorides	mg/kg ds	28.0	1.30	290.0
Fluorides	mg/kg ds	1.0	< 1.0	10.0
Sulphates	mg/kg ds	31.0	6900	760.0
Dissolved Organic Carbon (DOC)	mg/kg ds	28.2	26.4	22.0
Total Dissolved Solids (TDS)	mg/kg ds	715	715	5 330

\* ds - dry substance

Table 4.

Criteria of the neutral wastes allowance for storing on the dumping grounds of neutral wastes as well as the allowance criteria of wastes other than hazardous and neutral, which are not municipal wastes, for storing on the dumping grounds of wastes other than hazardous and neutral

Parameter	Units	The requirements for wastes in the dumping grounds for neutral waste. (basic parameters)	Allowable elution values in the dumping grounds for wastes other than hazardous and neutral	Maximum concentration of contaminants for toxic characteristic US EPA TCLP criteria mg/dm <sup>3</sup>
Arsenic	mg/kg ds	0.5	2	5.0
Barium	mg/kg ds	20.0	100	100
Cadmium	mg/kg ds	0.04	1	1.0
Chromium – total	mg/kg ds	0.5	10	5.0
Copper	mg/kg ds	2.0	50	25
Mercury	mg/kg ds	0.01	0.2	0.2
Molybdenum	mg/kg ds	0.05	10	
Nickel	mg/kg ds	0.4	10	20
Lead	mg/kg ds	0.5	10	50
Antimony	mg/kg ds	0.06	0.7	
Selenium	mg/kg ds	0.1	0.5	10
Zinc	mg/kg ds	4.0	50	250
Chlorides	mg/kg ds	800	15 000	
Fluorides	mg/kg ds	10	150	
Sulphates	mg/kg ds	1 000	20 000	
Dissolved Organic Carbon (DOC)	mg/kg ds	4 000	60 000	
Total Dissolved Solids (TDS)	mg/kg ds	500	800	
Phenolic index		1		

\* ds - dry substance

There is a very large difference in elution from these two slag in the case of sulphates: in the slag of a high copper content the sulphates concentration equals 6900 mg/kg ds, while from the slag after removing copper 31 mg/kg ds is eluted. This is caused by a high sulphates content in the flash furnace slag before the

copper removal. It is the reason of the technology of the process performed in the flash furnace, where sulphide ores during the smelting procedure generate sulphur oxides, while the slag obtained after the copper removal process does not contain so much sulphur. The organic compounds content and the concentration of the total dissolved solids (TDS) were the same in both filtrates. When comparing the composition of slag obtained after the copper removal (S1 and S3) performed under different conditions, small differences can be noticed. Slag S3 (in which the copper removal was performed acc. to the technology of A. Bydalek et al.) contains more SiO<sub>2</sub> and less CaO and MgO, than slag S1. Slag S3 contains nearly twice less Cu, which means, that when such waste slag is stored on the dumping ground less Cu is lost irretrievably. The concentration of eluted Cu was nearly twice higher for slag S3 than for slag S1, while the Pb concentration in sample S1 is 10-times lower than in sample S3. Concentration of chlorides in the filtrate obtained from elution of sample S1 was 10-times higher than in the filtrate from sample S3. There was a very large difference in the total dissolved solids (TDS) in filtrates obtained from slag S1 (715 mg/kg ds) and from slag S3 (5 330 mg/kg ds). Probably this is caused by various additions used in the processes of the copper removal from the slag. **In practice, all tested slags satisfy the allowance criteria of storing on the dumping grounds of wastes other than hazardous and neutral.** Assessing the tested slags with regard to the possibility of their storing on the dumping grounds of neutral wastes it should be stated that the copper removal process significantly decreases metals content in obtained filtrates. In the filtrate obtained from the slag not subjected to the copper removal process significant excesses - of the concentration allowable values in the given dumping ground - of such metals as: lead (12-times), antimony (10-times), copper (12-times), molybdenum (twice) were found, both slag after the copper removal process have in their filtrates only lead (3-times) and antimony (app. 10-times) excesses. The slag after the copper removal process became more environmental friendly and can be (after the proper preparation) stored on dumping grounds of neutral wastes or utilised at roads and bridges building, as the concrete matrix (of course after testing of this waste).

## 6. Conclusions

The performed investigations of elution from the slag from the flash furnace process of obtaining copper from its ore in HM „Głogów”, indicated that:

- The slag before removing copper, as well as the slag from which the copper was removed by various technologies, satisfy the binding criteria of the dumping grounds for wastes other than hazardous and neutral.
- Both slags after the copper removing process (S1 and S3), satisfy the binding criteria of the dumping grounds of neutral wastes and are totally safe for the environment.
- Various technologies of the copper removal from the flash furnace slag do not influence the ecological assessment of the obtained products.

- The slag obtained after the copper removal in the electric furnace, can be safely applied in various economic sectors, including cement and concrete productions.

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