# The effect of particle size reduction of waste material on heavy metals release

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#### Introduction

Mineral resources extraction and its processing in a production process is indispensably entailed with generation of waste. Among the most diverse groups of industrial waste are metallurgical wastes. They are formed as a by-product of various technological processes and characterize by a heterogeneous structure and chemical composition. Formerly, metallurgical waste was not subjected to recycling, but they were stored on slag heaps. Amended legislation concerning environmental protection forced owners of production facilities to undertake actions aimed at prevention of environmental pollution. The increase of people's awareness of the hazards that may cause industrial waste has contributed to the progressive elimination of waste piles and heaps in order to use the waste as raw materials in other industrial branches. Whereas, the waste that cannot be reused because of the high degree of pollution - mainly by heavy metals is deposited on reasonably designed and protected waste landfills. For determining the method on waste neutralization, research study on elution of heavy metals is being performed. Every research test is a source of relevant information on the content of heavy metals in the waste, on possibilities of their release and migration to the environment [1].

Heavy metals that are present in the environment can be in various forms. Poorly soluble forms are most common in soil environment, and in aqueous environment are soluble ones. They create various mineral and organometallic compounds [2]. Mobility of heavy metals in the mass of stored waste is influenced by environmental conditions, water content, and precipitation of metals in the form of an isolated salt. Whereas, the release of certain heavy metals from solids may be conducive to lowering the pH of the environment, in which the waste is placed, on temperature changes, and from oxidation and reducing conditions, fragmentation of the material, and on the organometallic complex solubility increase [3, 4]. Due to weathering and abrasion of materials, size reduction of their grains can be caused, and in consequence, varying amounts of dissolved constituents could be eluted from them.

#### **Material and Methods**

The effect of grain size reduction on the level of leaching of heavy metals was tested by using the slag formed in the rotary furnace at the department of lead refinery in a zinc smelter. The waste was characterized by different grain size. The largest share had a fraction <0.56 mm (55%). Remaining grains consisted of 10%: 0.56  $\div$  1 mm, 12%: 1  $\div$  2.8 mm, 5%: 2.8  $\div$  4 mm, 4%:  $\div$  5.6 mm, 14%:  $\div$  5.6 mm.

The analysis of the content of leachable heavy metal forms was based on the standard PN-EN 12457-2: 2006 [5] and on its modification. According to the standard, a waste fraction with grain size < 4 mm was prepared. Another test specimen was a waste of reduced grain size to <0.125 mm, prepared by grinding a portion of waste, and then sieving it through a sieve with mesh size

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0.125 mm. In the fraction of < 4 mm metallic grains can be observed which are residues from the process. Deionized water with the pH of 7.2 was used to prepare water extracts made of waste of grain size < 0.125 mm and < 4 mm. In addition, in order to analyse the effect of the acidic medium on the release level of heavy metals from test waste fractions, water extracts were prepared by using a liquid with a lowered pH value. For this purpose, nitric acid (V) was added to the water in the amount allowing reduction to pH 4 of the liquid eluent. Water extracts were shaken for 24 hours, and after filtering, the concentrations of Pb, Zn, Cu, Cd, Ni and Cr were measured according to the method of atomic absorption spectrometry with atomization in the flame, by using Solaar 6M spectrometer.

#### **Results and Discussion**

Table I summarizes the average results of selected heavy metal concentrations in water extracts. Metallurgical slag was characterized by a high content of soluble forms of heavy metals (except chromium). On the basis of the requirements for waste disposal by landfills for a given type of waste set out by the Regulation of the Minister of Economy [6], the test waste was classified to the category of hazardous waste. Based on the obtained results, the effect of waste grain size reduction on the rate of release of heavy metals can be observed. Both in acidic and neutral environments, higher concentrations of zinc, copper, cadmium and nickel in the fraction < 4 mm than in fraction < 0.125 mm were observed. The greatest variation was designated for release of nickel.

Table I
Leaching of heavy metals from metallurgical slag of fractions with
various grain sizes

Heavy metal	Leaching (pH 7.2) [mg/kg]		Leaching (pH 4) [mg/kg]	
	Grain size	Grain size <0.125 mm	Grain size	Grain size <0.125 mm
Pb	27.9	29.6	29.2	31.6
Zn	1663	744	1717	765
Cu	25.6	14.1	25.8	16.9
Cd	77.3	28.1	60.1	26.2
Ni	48.8	6.7	50.7	6.8
Cr	<0.1	0.13	<0.1	0.12

Concentrations of this element in aqueous extracts in the sample with fine grain were over 7-time lower than in the case of a grain size < 4 mm. It is suspected that presence of solidified, previously melted metal forms in the waste had the greatest impact on the results. Lower content of other heavy metals in water extracts of waste fractions < 0.125 mm could be influenced by the sample preparation process. Probably, not all grains of the waste were completely fragmented when being milled.

There was also indicated a slight increase in the level of lead elution from fraction < 0.125 mm. Concentration of this metal in water extracts, being prepared using the eluent at the pH 7.2 and pH 4, were higher from concentrations in water extracts with waste grain size < 4 mm by explicitly 5.7% and 7.6%, respectively. Chromium was more easily eluted in larger quantities from fine fractions of waste. In the case of samples with grain size < 4 mm, the content of this element was recorded below the limit of quantification.

The research tests were carried out by using an eluents with various pH values in order to assess the extent to which heavy metal concentrations will change after the pH level of the eluent will be decreased. This is significant in case of various atmospheric agents (such as Acid rain) effect the waste being disposed in the environment, causing a change in the level of release of pollutants. Based on the research results (Tab. I), higher concentrations of lead and zinc in acid environment were observed than in the pH neutral environment. A similar trend can be also perceived for nickel concentration in the extract from waste with a grain size < 4 mm. Lowering the pH level in the liquid was not so significance for the release of chromium and also copper samples having a grain size of < 4 mm. Whereas, the elution level was increased for copper in fine-grained fraction (of 2.8 mg/kg). Higher concentrations in liquid at pH 7.2 level were determined only for cadmium.

#### **Conclusions**

The tested metallurgical slag was characterized by different leaching level of heavy metals, depending on the degree of fineness of waste. Higher concentrations of zinc, copper, cadmium and nickel were designated in the fraction < 4 mm than in fractions with grain size reduction to < 0.125 mm, both in the acidic and neutral pH water environments. Significant effect of lowering pH of the eluent on increase of release rate of zinc and on decrease of the leaching level of cadmium from waste fraction < 4 mm was observed. In most cases, waste fragmentation influences an increase in the release of heavy metals due to better contact of the eluent with waste grains. However, on the basis of research results presented in the paper it can be stated that this is not a rule. The result obtained in the study of release is probably affected by the form and source of the waste, its chemical and mineralogical composition, and sample preparation, as well. The impact of these factors on the leaching of heavy metals will be the basis for further studies of the authors of the paper.

#### Literature

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## NCBiR ogłosiło terminy naboru wniosków do Programu INNOCHEM

Narodowe Centrum Badań i Rozwoju (NCBiR) wyznaczyło terminy ogłoszenia konkursu i rozpoczęcia naboru wniosków do Programu INNOCHEM. – *Uruchamiany przez NCBiR Program to realna szansa na wzrost konkurencyjności przemysłu chemicznego w Polsce* – mówi dr Tomasz Zieliński, Prezes Zarządu Polskiej Izby Przemysłu Chemicznego, inicjatora Programu. Konkurs w ramach Programu INNOCHEM zostanie ogłoszony 18 grudnia 2015 r., a nabór wniosków będzie trwał od I lutego do I marca 2016 r. Pula środków przeznaczonych na dofinansowanie projektów badawczo-rozwojowych wyniesie ok. I 20 mln zł. INNOCHEM obejmie projekty o charakterze innowacyjnym skierowane m.in. na rzecz wytwarzania podstawowych produktów przemysłu chemicznego (np. produktów rafinacji ropy naftowej, dodatków do paliw i olejów mineralnych, nawozów, wielkotonażowych tworzyw

polimerowych, produktów specjalistycznych). W założeniach Programu pierwszy raz w historii polskiego przemysłu działania badawczorozwojowe będą wsparte w takiej skali. Przedstawiciele branży liczą na to, że Program, oprócz wzmocnienia innowacyjności w polskich firmach przyczyni się również do zacieśniania współpracy między przemysłem a nauką. – Pomoc w finansowaniu projektów B+R dobrze przysłuży się polskiej chemii – ocenia Tomasz Zieliński. – Mamy nadzieję, że obok programu sektorowego będą wprowadzane inne sposoby wzmacniania innowacyjności, np. ulgi podatkowe dla przedsiębiorstw wprowadzających projekty badawczo-rozwojowe. Polska Izba Przemysłu Chemicznego rozpoczęła prace nad studium wykonalności dla INNOCHEMU w zeszłym roku. Studium zostało przyjęte przez NCBiR w grudniu 2014 r., a pozytywnie zaopiniowane w połowie 2015 r. projekty z programu sektorowego INNOCHEM będą finansowane z Programu Operacyjnego Inteligentny Rozwój (PO IR). Programy sektorowe nadzoruje Narodowe Centrum Badań i Rozwoju.(abc)

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