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## The effect of CaO and MgO addition and cooling rate on stability of slag obtained after jarosite and neutral leaching residue treatment in the Waelz process

Dragana Radovanovic <sup>1</sup>, Zeljko Kamberovic <sup>2</sup>, Zoran Andjic <sup>3</sup>, Milisav Ranitovic <sup>1</sup>, Branislav Markovic <sup>4</sup>

<sup>1</sup> Innovation Center of the Faculty of Technology and Metallurgy in Belgrade, University of Belgrade, Karnegijeva 4, 11020 Belgrade, Serbia

<sup>2</sup> Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11020 Belgrade, Serbia

<sup>3</sup> Innovation Center of the Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia

<sup>4</sup> Institute for Technology of Nuclear and Other Mineral Raw Materials, University of Belgrade, Franse d'Eparea 86, 11000 Belgrade, Serbia

Corresponding author: [divsic@tmf.bg.ac.rs](mailto:divsic@tmf.bg.ac.rs) (Dragana Radovanovic)

**Abstract:** Jarosite and neutral leaching residue (NLR) are the greatest environmental problems of hydrometallurgical zinc production due to their high quantity and hazardous content. Pyrometallurgical processes, such as the Waelz process, could be applied to recover valuable metals present in this waste. The paper investigates the possibility of forming environmentally stable Waelz slag after the Waelz process of jarosite and NLR. Waelz slag, obtained using CaO as a conventional alkaline additive in the Waelz process, showed high As and Sb release after the EN 12457-4 standard leaching test. Multiphase equilibrium composition calculations indicated that As and Sb were present as volatile and migratory species in the slag. In order to obtain Waelz slag with more stable matrices that would encapsulate and immobilize pollutants, MgO additions to CaO and different cooling conditions of the slag were further investigated. The efficiency of modification in additives composition and cooling conditions was assessed by EN 12457-4 leaching test and chemical and microstructural characterization (XRF and SEM-EDS analyses) of the Waelz slags. The results show that addition of MgO does not reduce the efficiency of the process, even more it increases leaching resistance of the slags. Concentrations of all investigated metals (As, Ba, Cu, Mo, Pb, Sb, Zn) after the leaching test were below defined limits for non-hazardous waste. Microstructural analyses revealed that MgO remained inert during Waelz process, and thus favoring the formation of amorphous stable structure, which was enhanced by increased cooling rate. All investigated Waelz slags with MgO additions are suitable for further use or safe disposal.

**Keywords:** Jarosite, Waelz slag, arsenic, antimony, leaching test, microstructure

### 1. Introduction

About 90% of the world zinc production is obtained by the hydrometallurgical processes. Conventional method for processing of zinc sulfide ore is the Roasting-Leaching-Electrowinning process (RLE) that includes (1) the ore concentrate roasting to obtain zinc oxide (calcine), (2) the calcine leaching, (3) the purification of solutions after the leaching and (4) the electrolytic recovery of zinc (Moors and Dijkema, 2006). During the RLE process, the calcine leaching is conducted in several steps. The first step is neutral leaching at a pH of 4-4.5 and temperature of 50°C. Zinc present as zinc ferrite (ZnFe<sub>2</sub>O<sub>4</sub>) (5-30% of total Zn in calcine) remains insoluble under these conditions. In the next leaching step, the stable zinc ferrite dissolves under more extreme conditions: concentrated acids and temperatures above 90°C. Hot acid leaching leads to a significant dissolution of iron, as the main

impurity in raw material. The obtained solution is purified by precipitation of iron in the form of jarosite, goethite or hematite (Basturkcu and Acarkan, 2017). Jarosite precipitates by introducing ammonium or other monovalent ions to form an insoluble iron compound  $((\text{MeFe}_3(\text{SO}_4)_2(\text{OH})_6$  wherein  $\text{Me} = \text{K}^+, \text{NH}_4^+, \text{H}^+, \text{Na}^+, \frac{1}{2}\text{Pb}^{2+}$ ). It is estimated that 2 Mg of produced zinc leads to the formation of around 1 Mg of jarosite. Jarosite is a hazardous waste due to the presence of soluble elements, such as Cd, Pb and As. Because of its high quantity and hazardous content, jarosite residue is considered to be the greatest environmental problem in the primary production of zinc (Moors and Dijkema, 2006; BAT, 2014). The best available techniques recommended for the treatment of residues from the hydrometallurgical zinc production are pyrometallurgical processes (for residues that do not contain a higher amount of zinc ferrite and precious metals) and compaction and Jarofix process for jarosite residue (BAT, 2016).

Proposed treatments, compaction and Jarofix process, lead to the stabilization of jarosite residue and its environmentally safe disposal (BAT, 2016). However, the significant amounts of metals contained in jarosite (Zn, Pb, Cu and Fe) are permanently lost. Pyrometallurgical processes could be applied for jarosite treatment in order to valorize metals present in this waste. The Waelz process is a pyrometallurgical method usually used for treatment of Zn/Pb bearing waste, such as the electric arc furnace dust (EAFD) from steel production and neutral leaching residue (NLR) from Zn production (Mombelli et al., 2015). The Waelz process includes the reduction, the vaporization and oxidation of zinc and lead. The Zn/Pb materials are mixed with a reducing agent (coke) and flux (lime, quartz or other additives) in the specific ratio, homogenized, pelletized and sent to a rotary kiln furnace. The process is carried out at high temperatures (1200-1400°C) in the reducing atmosphere. Zn, Pb, Cd and potentially present rare metals (such as In) vaporize and transform to oxides at an outlet of the kiln. Products of the process are Waelz oxide and slag. Waelz oxide is an impure mixture of zinc and lead oxides and other volatile components of a charge. The other non-volatile components, primarily iron and calcium oxide, remain in the furnace forming the Waelz slag (Quijorna et al., 2014). Prajsnar et al. (2015) investigated the influence of temperature, time and quantity of flux (lime) and reducing agents on the efficiency of the Waelz process of Zn/Pb raw materials. They found that an increase in process temperature in the range from 1000 to 1200°C and lime addition from 0 to 12% resulted in decrease of zinc and lead content in Waelz slag, e.g. it led to a higher yield of Zn and Pb in the Waelz oxide. Stopić and Friedrich (2009) recommended operation temperature for the Waelz process to be higher than 1100°C in order to provide extraction of ZnO from zinc ferrite. Also, Mombelli et al. (2015) recommended the operation time to be no longer than 1 h for the Waelz process. A long process time could cause oxidation of metal sulfides encapsulated in a glassy matrix of the Waelz slag. The newly formed metal oxides are not fixed within the matrix, and can be easily dissolved in water.

The Waelz slag can be used as a material in civil engineering, e.g. for road construction (BAT, 2014). In order to characterize the slag as a safe raw material, it is necessary to determine its physicochemical stability, especially in contact with water. Proper modifications of the kiln charge lead to an optimal chemical composition of the slag allowing the stabilization of toxic elements (As, Pb, Cd) (Mombelli et al., 2016). Slag is chemically defined by its index of basicity (BI), which is calculated as a ratio of alkali and acid oxides  $((\text{CaO}+\text{MgO})/(\text{SiO}_2+\text{Al}_2\text{O}_3), \%)$ . Slag rich in lime content ( $\text{BI} > 1$ ) is the alkaline slag, while slag with high silica content is referred as the acid slag ( $\text{BI} < 1$ ). Operation under alkaline conditions, resulting in formation of alkaline slag, is preferred in practice. The reason for this is a longer operating period of the kiln refractory and a higher yield of zinc. However, acidic slag is characterized by increased chemical stability and reduced leaching of metals. Barna et al. (2000) investigated the influence of physicochemical and mineralogical characteristics of different Waelz slags on pollutants release. Alkaline slags have shown to be more sensitive to changes in the pH value of solutions and less stable to metals leaching. Although having a lower acid neutralization capacity, which depends on the amount of basic oxide in the material, the acidic slags showed a lesser degree of metals leaching. Mineralogically, the alkaline and acidic slags differ significantly. Alkaline slag is characterized by a calcium silicate matrix. Some calcium silicates present in matrix that possess hydraulic properties, react and dissolve in water, releasing hazardous components to the environment. Mombelli et al. (2014) identified principal calcium silicate phases that react with water and thus are responsible for the release of elements. As the polluting elements are generally bound to

the silicates, the two possible ways to avoid their leaching are a decrease in either the amount of silicates, or in their solubility. In the work of Mombelli et al. (2016), the authors recommended the MgO content of 5-7%, Al<sub>2</sub>O<sub>3</sub> 7-10% and CaO content less than 30% in order to ensure the slag stability. Daugherty et al. (1983) showed that the acidic operation condition (BI<1) produces a glassy, amorphous structure of the slag matrix. Formation of an amorphous matrix depends on the chemical composition and cooling rate of the slag (Tossavainen et al., 2007). Rapid water cooling of the slag may result in an amorphous structure of the matrix which encapsulates the metal oxides, reducing their solubility. Water cooled slag has the same structural constituents as the air-cooled slag, but an order of magnitude smaller (Mombelli et al., 2015). The higher cooling rate prevents nucleation of the calcium silicate crystals, and thus provides an amorphous structure. This fact causes an increase in the stability of the slag and reduces metals leaching. Tossavainen et al. (2007) found that the slag with BI > 1 can also form a glassy structure after rapid cooling as a result of higher MgO content. They investigated characteristics of four different types of steel slags under different cooling conditions, and found that a ladle slag, the one with the highest MgO content, had showed the highest tendency of forming a glassy structure.

This work is a part of a study of a new jarosite and NLR treatment process aiming at the valorization of the valuable metals present in this waste. The objective of this research was the formation of environmentally stable slag after Waelz process of jarosite and NLR, with high leaching resistance, suitable for further use or safe disposal. The work investigates the influence of CaO as a conventional alkaline additive in the Waelz process on leaching behavior of pollutants, especially As and Sb. Furthermore, the work investigates the influence of different MgO addition to CaO and cooling rate on stability of the obtained Waelz slags. The efficiency of modification in additives composition and the cooling condition was experimentally demonstrated by the leaching test and SEM-EDS analyses of the Waelz slags.

## 2. Materials and methods

### 2.1 Jarosite residue and NLR

Jarosite residue and NLR (Zn/Pb materials) used in this research originate from the zinc production and processing in Zorka Šabac Non-Ferrous Metallurgy Plant, located in the north-west part of the Republic of Serbia, 90 km away from the capital Belgrade. The amount of Zn/Pb materials, deposited in the Šabac tailings pond, is estimated at over 300,000 Mg of jarosite, and 100,000 Mg of NLR containing significant amount of Zn and Pb, as well as the precious (Cu and Ag) and minor metals (In). Jarosite and NLR were sampled at different points of the tailings pond (354 drill holes, in the range of 0.5-3.5 m depths with a step of 0.5 m). The samples were homogenized and dried to the constant weight at 105°C in order to determine moisture content. Jarosite and NLR contained 25.5 and 30.3 mass% of moisture, respectively. The determination of chemical and mineralogical composition included X-Ray Fluorescence (XRF), X-ray powder diffraction (XRD) and Thermogravimetric and Differential Thermal Analysis (TG-DTA) analyses. Table 1 presents the composition of the Zn/Pb materials.

As expected, the jarosite residue mainly contains jarosite (NH<sub>4</sub>Fe<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>) and/or plumbojarosite (PbFe<sub>6</sub>(OH)<sub>12</sub>(SO<sub>4</sub>)<sub>4</sub>), as well as franklinite (zinc ferrite, ZnFe<sub>2</sub>O<sub>4</sub>). NLR includes mainly franklinite and anglesite (PbSO<sub>4</sub>). The material also contains quartz (SiO<sub>2</sub>).

### 2.2 The Waelz process

In this work, CaO and MgO (p.a.) were investigated as additives in the Waelz process of jarosite residue and NLR. Prior to mixing with Zn/Pb materials, CaO and MgO were calcined for 1 h at 1000°C. In order to obtain the maximum homogenization, the all used materials were sieved to obtain a size fraction of <math> < 500 \mu\text{m}</math> prior to mixing. Mixtures of Zn/Pb materials (75% jarosite and 25% NLR) with 12% of additives and 30% of coke in the form of pellets were processed in a short laboratory rotary kiln for 1 h at a constant temperature of 1200°C. The Waelz slag, obtained using CaO as the only additive, was labeled as a referent slag for further investigation. In order to gain more stable Waelz slag, the MgO addition (25% and 50% mixture with CaO) and different cooling rate (on air and in water) were analyzed. Sample identification and relative experimental conditions are presented in

Table 2. Chemical compositions of the obtained slags were determined by the X-Ray Fluorescence (XRF) analyses performed by the use of a Thermo Scientific Niton XL3t analyzer.

Table 1. Composition of jarosite and NLR, mass %

Component	Jarosite residue	NLR
$\text{NH}_4\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2 / \text{PbFe}_6(\text{OH})_{12}(\text{SO}_4)_4$	54.87	
$\text{ZnFe}_2\text{O}_4$	29.53	84.19
$\text{PbSO}_4$		5.39
$\text{SiO}_2$	6.89	4.76
$\text{CaO}$	0.84	0.66
$\text{Al}_2\text{O}_3$	1.98	1.09
$\text{MgO}$	0.04	0.13
K	0.26	0.08
Na	0.10	0.03
S	8.96	1.97
Cu	0.52	1.05
As	0.33	0.31
Sb	0.02	0.02
Ag	0.02	0.02
In	0.01	0.02

Table 2. Sample identification and relative experimental conditions, mass %

Sample	Zn/Pb material		Additives		Coke		Cooling rate
	Jarosite residue	NLR	CaO	MgO	in pellets	to furnace	
Ca100	75	25	100		10	20	on air
Mg25A	75	25	75	25	10	20	on air
Mg25W	75	25	75	25	10	20	in water, 30 min.
Mg50A	75	25	50	50	10	20	on air
Mg50W	75	25	50	50	10	20	in water, 30 min.

### 2.3 The Waelz slag stability analyses

The Waelz slag leaching resistance was analyzed by performing a standard leaching test EN 12457-4 (2002): bottles, containing 100 g of granulated slag (<10mm) and deionized water (liquid to solid ratio, L/S 10), were rotated for 24 h. This is a mild leaching procedure often used to determine the long-term effects of leaching. Solutions after the leaching test were filtered through the blue-ribbon filter papers. Samples were acidified with nitric acid ( $\text{HNO}_3$  p.a.) to  $\text{pH} < 2$  prior to the metal content determination on a Varian Vista 715 ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) device. Triplicate assays were carried out. Microstructure of the obtained Waelz slag was studied using a Scanning Electron Microscopy (SEM) JEOL JSM-5800 at 20 kV. Prior to the SEM analyses the slag samples were crushed to 2mm diameter particle size. The chemical composition of the samples was analyzed using an Energy Dispersive Spectrometer (EDS) Isis 3.2, with a SiLi X-ray detector (Oxford Instruments, UK) connected SEM, and computer multi-channel analyzer.

### 2.4 Multiphase equilibrium composition calculations

In order to investigate the leaching behavior of minor metals present in the Waelz slag (As and Sb) and interpret leaching test results, equivalent composition of the slag during the Waelz process was determined using the Outotec HSC Chemistry software. The results are presented in the form of temperature - equivalent mass composition diagrams.

### 3. Results and discussion

#### 3.1 The Waelz slag

Compositions of the obtained Waelz slags are presented in Table 3. The main component of the slags is Fe in the form of oxides hematite ( $\text{Fe}_2\text{O}_3$ ) or magnetite ( $\text{Fe}_3\text{O}_4$ ). Hematite is one of the products of jarosite thermal decomposition (Frost et al., 2005; Ju et al., 2011), while magnetite ( $\text{Fe}_3\text{O}_4$ ) is formed due to the partial hematite decomposition (Kerolli-Mustafa et al., 2016) and thermal decomposition of zinc ferrite (Stopić and Friedrich, 2009). Zn and Pb are present in a reduced amount compared to the Zn/Pb material, confirming the efficiency of the Waelz process. Cu is present in certain amount, probably in a sulfide form, as well as As and Sb. High content of CaO and MgO is a result of addition of these oxides as additives in Waelz process, while  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  have already been present in the initial Zn/Pb material. BI, as the ratio of alkaline and acid oxides, is the same for all the three slags due to the same amount of alkaline additives (12%), but with different CaO/MgO content. The obtained slags belong to the alkaline slags with  $\text{BI} > 1$ .

Table 3. Chemical composition of different Waelz slags with calculated BI, mass %

Component	$\text{Fe}_2\text{O}_3$	CaO	MgO	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	Cu	Zn	Pb	As	Sb	BI
Ca100	58.06	24.38	0.11	11.09	2.99	0.54	1.02	0.42	0.086	0.051	1.7
Mg25	56.36	18.10	5.71	10.78	2.91	1.55	1.75	0.41	0.067	0.045	1.7
Mg50	66.43	9.67	8.75	8.34	2.25	1.53	0.73	0.05	0.244	0.037	1.7

#### 3.2 The Effect of CaO as an additive on the Waelz slag stability

The Waelz slag sample Ca100, obtained using CaO as the only additive, was subjected to the EN 12457-4 standard leaching test, and the results are presented in Table 4.

Zn and Pb are metals with a high content in jarosite residue and NLR. Their concentrations in a solution after leaching are well below the maximum allowed concentration (MAC) for the non-hazardous waste: 1.0 mg/kg of Pb and concentration of Zn below detection limit. The reasons for low concentrations in solution are: (1) low content of Zn and Pb in the Waelz slag due to the effective Waelz process, and (2) Zn and Pb that remained in the Waelz slag were probably in the form of stable zinc ferrite (Stopić and Friedrich, 2009) and metallic lead (Frost et al., 2005), respectively. The measured concentration of Ba (1.3 mg/kg), Cu (0.03 mg/kg) and Mo (2.1 mg/kg) were also well below the MAC for the non-hazardous waste. Concentrations of As and Sb in solutions after the EN 12457-4 test were higher than MAC, 3.6 and 2.9 mg/kg, respectively. Content of these elements in Zn/Pb material is very small (Table 1). In order to investigate As and Sb behavior during the Waelz process of Ca100 mixture, the multiphase equilibrium composition calculations with Outotec HSC Chemistry software were applied. The results are shown in Fig.1.

The arsenic-containing minerals typically occur in the base metal ore and enter the metallurgical processes as impurities. The pyrometallurgical mineral processing, including roasting, converting and smelting of arsenic-bearing ore, can mobilize the stable arsenic. In these processes, arsenic is usually present as arsenite (As(III)) or arsenate (As(V)) inorganic oxyanions, where arsenite is more toxic and soluble than arsenate (Nazari et al., 2016). Arsenic species are removed from solution after the hot acid leaching (RLE process) by precipitation along with jarosite residue.  $\text{AsO}_4^{3-}$  is incorporated into a jarosite structure by substitution of  $\text{SO}_4^{2-}$  in lattice (Patiño et al., 2013). Mills et al. (2009) investigated a thermal decomposition of arsenian plumbojarosite. They found that arsenic forms an apatite-type phase,  $\text{Pb}_5(\text{AsO}_4)_2(\text{SO}_4)\text{O}$ , at temperatures up to 860°C. At temperatures above 860°C, crystalline hematite and lanarkite,  $\text{Pb}_2\text{O}(\text{SO}_4)$  coexist with an amorphous phase. It can be concluded that arsenic vaporized, or was contained in the amorphous phase. Flores et al. (2016) studied thermal and chemical decomposition of the ammonium-arsenic jarosite, and found that most of arsenic retains absorbed on hematite particles in an amorphous compound at elevated temperatures and alkaline conditions. Hu et al. (2015) stated that the physical adsorbed arsenic (both in the form of As(III) and As(V)) is easily released at high temperatures (>1050°C), and forms various kinds of arsenites/arsenates with the present inorganic compounds (Ca, Fe, Al). Fig.1 shows that some of arsenic species vaporize at 1200°C during the Waelz process, while a part of arsenic remains in the Waelz slag as alkali-arsenites.

Arsenites are readily soluble in contact with water, as evidenced by the As concentration above the MAC for the non-hazardous waste in solutions after EN 12457-4 test. Antimony is similar to arsenic in its chemical properties and toxicity, and is typically found as sulfide ( $Sb_2S_3$ ) and oxide ( $Sb_2O_3$ ) (Multani et al., 2016). Sb is also incorporated as co-precipitates in the jarosite residue, but in contrast to As, Sb(V) substitutes Fe(III) within jarosite structure. There are a few data in literature on the behavior of antimony during thermal treatment of jarosite (Multani et al., 2016; Karimian et al., 2017). Karimian et al. (2017) investigated Sb and As behavior during jarosite transformation under reducing conditions, and concluded that Sb is much less strongly sorbed to the new formed Fe solid phases than As. The results presented in Fig. 1 confirmed the statement of Multani et al. (2016) that elemental antimony is fairly volatile at temperatures  $>500^\circ C$ . As such, Sb should mostly be contained in the Waelz oxide. Its retention in the slag is probably due to a short operation time of the Waelz process.

Table 4. EN 12457-4 leaching test results of Ca100 sample, mg/kg\*

Element	As	Ba	Cu	Mo	Pb	Sb	Zn	pH
Ca100	3.6	1.3	0.03	2.1	1.0	2.9	<0.05	11.0
MAC**	2.0	100	50	10	10	0.7	50	>6.0

\* Concentrations of Cd, Cr, Hg, Ni and Se were below detection limits for these metals

\*\* MAC- maximum allowed concentration for the non-hazardous waste (Rulebook, 2010)

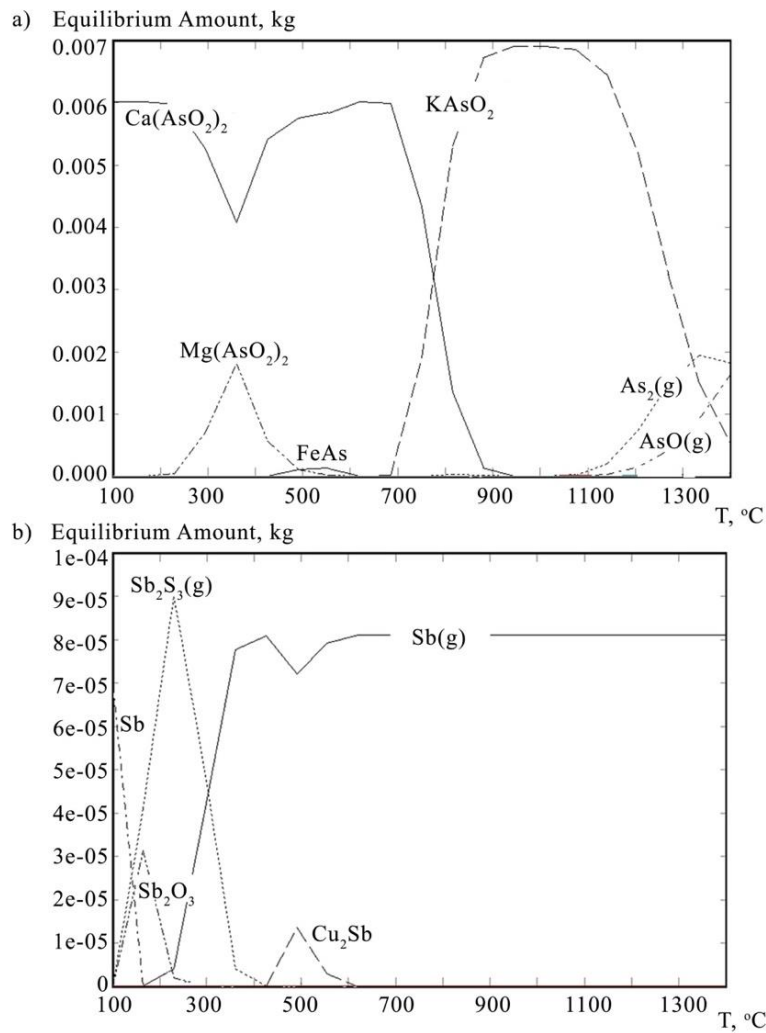


Fig. 1. Equilibrium amount of a) arsenic and b) antimony phases during Waelz process

In the Waelz slag, arsenic and antimony are present as highly mobile species. The method for their immobilization could be the encapsulation within a stable matrix. Encapsulation involves physical

interaction (non-chemical encapsulation), chemical interaction (cement-based and lime-based processes), or thermal interaction (vitrification and thermoplastic polymer encapsulation) between the waste and solidifying reagents in order to isolate the pollutants within an inert compound with a high structural integrity (Conner and Hoeffner, 1998). Ca100 is an alkaline slag due to addition of CaO as a flux in the Waelz process. Alkaline slag is characterized as less stable than acid ones due to calcium silicates present in a matrix which easily react and dissolve in water. In order to analyze the structure of the Waelz slag, Ca100 sample was subjected to a SEM-EDS. SEM image coupled with the EDS analysis of selected specific phases/points of Ca100 slag structure is presented in Fig. 2. The micrograph shows a porous structure of the Waelz slag, obtained by the use of CaO as the only additive, with large elongated and prismatic gypsum crystallites. These gypsum crystallites partially originate from the primary Zn/Pb material, and partially are formed during the Waelz process. According to EDS analyses it can be concluded that the Fe oxides, as the final product of the Waelz process of jarosite and NLR, with poorly formed calcium ferrites and silicates, and unreacted CaO are also present in the slag structure. The porous matrix of Ca100 slag has not succeeded to incorporate and immobilize migratory elements, which resulted in a high As and Sb concentration in a solution after the EN 12457-4 leaching test.

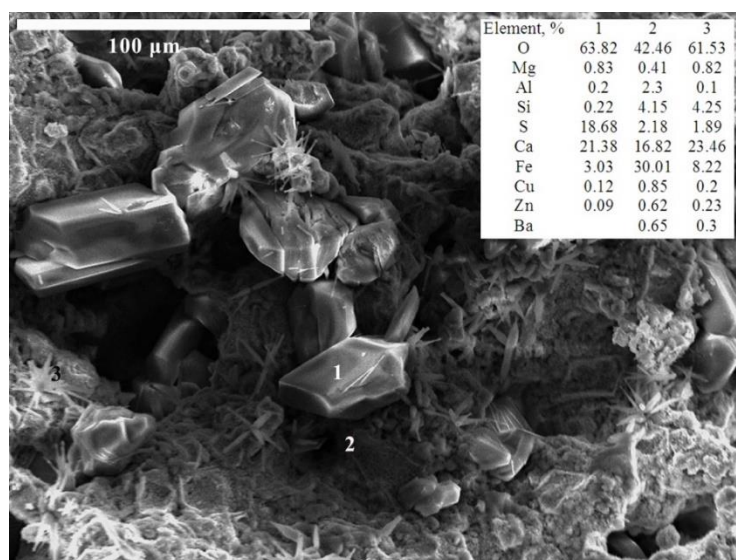


Fig. 2. SEM-EDS analysis of Ca100 sample of the Waelz slag

### 3.3 The Effect of MgO addition on the Waelz slag stability

The aim of MgO addition was a modification of charge composition in order to obtain the stable Waelz slag suitable for further use or safe disposal. More stable acid slags are characterized by an amorphous structure which could also be formed within the structure of alkaline slags increasing the cooling rate (Tossavainen et al., 2007). Due to this reason, the effect of cooling conditions on the Waelz slag stability was investigated. The slags obtained with two different MgO contents in additives (25% MgO + 75% CaO and 50% MgO + 50% CaO) were cooled on air and in water for 30 min. The slags were subjected to the EN 12457-4 leaching test and the results are presented in Table 5.

The comparison of the results of EN 12457-4 test of Ca100 sample (Table 4) with samples with MgO addition (Table 5) has shown that with increasing MgO content, the pH values of solutions decreases. The reason for this is the decreased concentrations of alkali ions present in solutions, primary  $\text{Ca}^{2+}$  ions. Also, there are minor differences in the pH values between the samples obtained by different cooling rate (Mg25A compared to Mg25W and Mg50A compared to Mg50W). Concentration of Cu and Mo varies between 0.35 and 0.64 mg/kg for Cu and 0.54 and 0.65 mg/kg for Mo. However, these values are well below the maximum allowed concentration for the non-hazardous waste defined for copper and molybdenum, 50 and 10 mg/kg, respectively. Concentrations of Pb were under the detection limits (0.5 mg/kg) in solutions after the leaching of samples with MgO and lower compared to Ca100 sample (1.0 mg/kg). Barna et al. (2000) and Mombelli et al. (2015) also found that Pb release

from the Waelz slag was greater in alkaline conditions, while the release of Zn increased with decreasing of pH value. In this work, the Zn concentration was the highest in a solution of Mg25A sample, but decreased for the rapid cooled samples (Mg25W and Mg50W). It can be concluded that different microstructure, obtained by different cooling conditions, has a greater effect on Zn leaching than the pH value. Concentrations of Ba in solutions increased with increasing MgO content in slags, with no evident impact of slags cooling rate on its release. Mombelli et al. (2016) investigated the effect of MgO on Ba release from the Waelz slag, and found that in both cases, with high and low MgO content, barium release could be enhanced. In slags with low MgO content, Ba is dissolved in a calcium silicate lattice. This phase possesses the hydraulic properties and easily reacts with water, thus, releasing Ba. On the other hand, in slags with high MgO content, magnesium replaces Ca and Ba in a silicate lattice, barium remains in the form of BaO, and as an alkaline oxide, it tends to dissolve in water together with the other alkaline elements. Addition of MgO resulted in a decrease of the As leaching, where the As concentrations in all solutions of slags containing MgO were below the MAC. Also, higher cooling rate of the slags led to the reduced arsenic leaching (Mg25A compared to Mg25W, and Mg50A compared to Mg50W) probably by forming more stable matrices with the amorphous structures. Leaching behavior of antimony is similar to arsenic. Addition of MgO resulted in decreased Sb concentration in solutions after the leaching test below the MAC for the non-hazardous waste, 0.7 mg/kg. The immobilization of Sb was also enhanced in matrices obtained by a higher cooling rate, confirming the effect of slag microstructure on the release of the migratory elements. The lowest concentration of arsenic and antimony has been detected in a solution of Mg25W sample, 0.16 and 0.053 mg/kg respectively.

Table 5. EN 12457-4 test results of the Waelz slag containing MgO, mg/kg

Element/Slag	As	Ba	Cu	Mo	Pb	Sb	Zn	pH
Mg25A	0.54	1.39	0.51	0.65	<0.5	0.19	6.03	8.05
Mg25W	0.16	1.93	0.64	0.61	<0.5	0.053	0.79	8.04
Mg50A	0.62	5.63	0.42	0.55	<0.5	0.13	1.07	7.40
Mg50W	0.41	2.72	0.35	0.54	<0.5	0.087	<0.05	7.41
MAC	2.0	100	50	10	10	0.7	50	>6.0

\*MAC- maximum allowed concentration for non-hazardous waste

In order to investigate the effect of MgO addition and cooling rate on microstructure of the obtained Waelz slag, and thus its stability and resistance to the leaching of migratory elements, the samples were subjected to the SEM-EDS analyses. Fig. 3 shows the micrographs of Mg25A (a) and Mg25W (b), while the micrographs of Mg50A (a) and Mg50W (b) samples are presented in Fig. 4, with the EDS analyses of chemical compositions of selected points. As expected, the major component of slags are the solid iron oxides probably in the form of hematite ( $\text{Fe}_2\text{O}_3$ ) as a product of jarosite thermal decomposition (Frost et al., 2005; Ju et al., 2011), and magnetite ( $\text{Fe}_3\text{O}_4$ ) formed due to the partial hematite decomposition (Kerolli-Mustafa et al., 2016), and thermal decomposition of zinc ferrite (Stopić and Friedrich, 2009). According to EDS analyses it can be concluded that the present CaO formed needle-like calcium ferrites (Fig.3, a and b), and the unvaporized zinc remained in the form of stable zinc ferrites. CuS and BaS are also present in the structure as the original components of jarosite and NLR. Fig. 3 and 4 show an increased formation of amorphous structure obtained by increase of MgO content in the slags: Mg25A (Fig. 3a) compared with Mg50A (Fig. 4, a) and rapid cooling: Mg25A (Fig. 3a) compared with Mg25W (Fig. 3, b) and Mg50A (Fig. 4a) compared with Mg50W (Fig. 4b). The increase of MgO content and cooling rate resulted in a denser structure with smoother surface which appears more consolidate.

The acid slags are characterized by an amorphous structure due to a high content of silicon that forms a long molecule chains network by polymerization. These chains rearrange slowly into crystals, and thus create an amorphous structure by cooling. Alkaline slag will have the amorphous structure by the rapid cooling of melt and transformation from the liquid to the solid state without forming crystals (Tossavainen et al., 2007). Viscosity of alkaline slags depends on a chemical potential of the primary solid phase. Viscosity of molten slag increases with decreasing temperature and abruptly



increases at a specific crystallization temperature (Lee et al., 2004). Lee et al. (2004) found that the MgO content had a remarkable effect on crystallization temperature that was shifted to higher temperatures with increasing the MgO content in slags. Tossavainen et al. (2007) explained the effect of MgO differently. They found that at 1400°C only 40% of the total MgO content was present in a liquid slag, while the rest was present as the MgO crystals which reduced the BI of the melt, and thus influenced the amorphous structure forming properties in the material. The same can be concluded in this study. Magnesium present in the slags has been detected by the EDS analyses in a very small quantity (< 1%), except in a microstructure of Mg50A sample (Fig.4, a) point 2, where it formed the (Fe, Mg, Ca)-spinel phase. It can be concluded that added MgO remained unreacted, decreasing BI of the rest of the slag (Tossavainen et al., 2007) and, thus, favoring the formation of amorphous structure (Fig. 3 and 4). The amorphous structure encapsulated migratory elements present in the Waelz slag, and reduced their leachability in a contact with water. Modification of additive composition in the Waelz process and cooling conditions of the Waelz slag led to an increase of leaching resistance and stability of the slag.

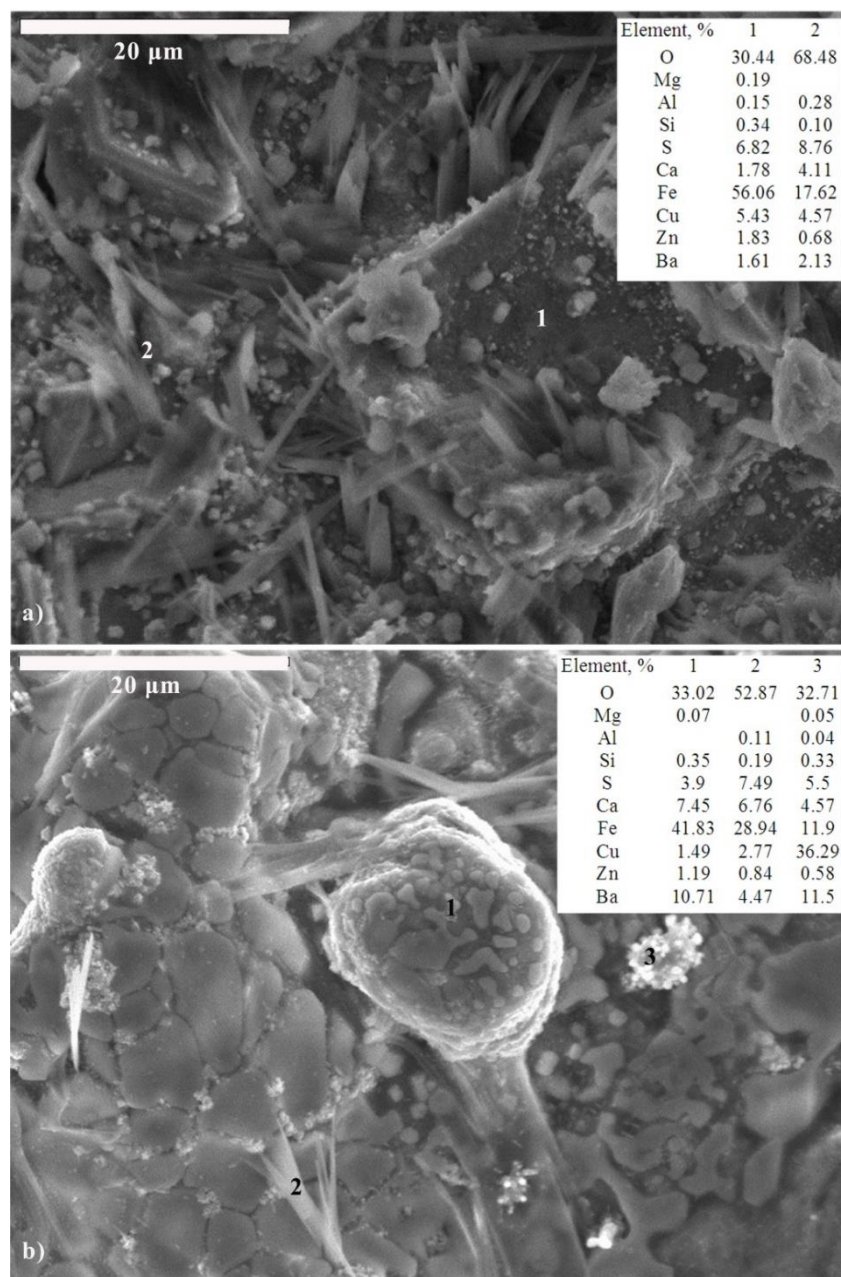


Fig. 3. Results of the SEM-EDS analyses: a) Mg25A, b) Mg25W

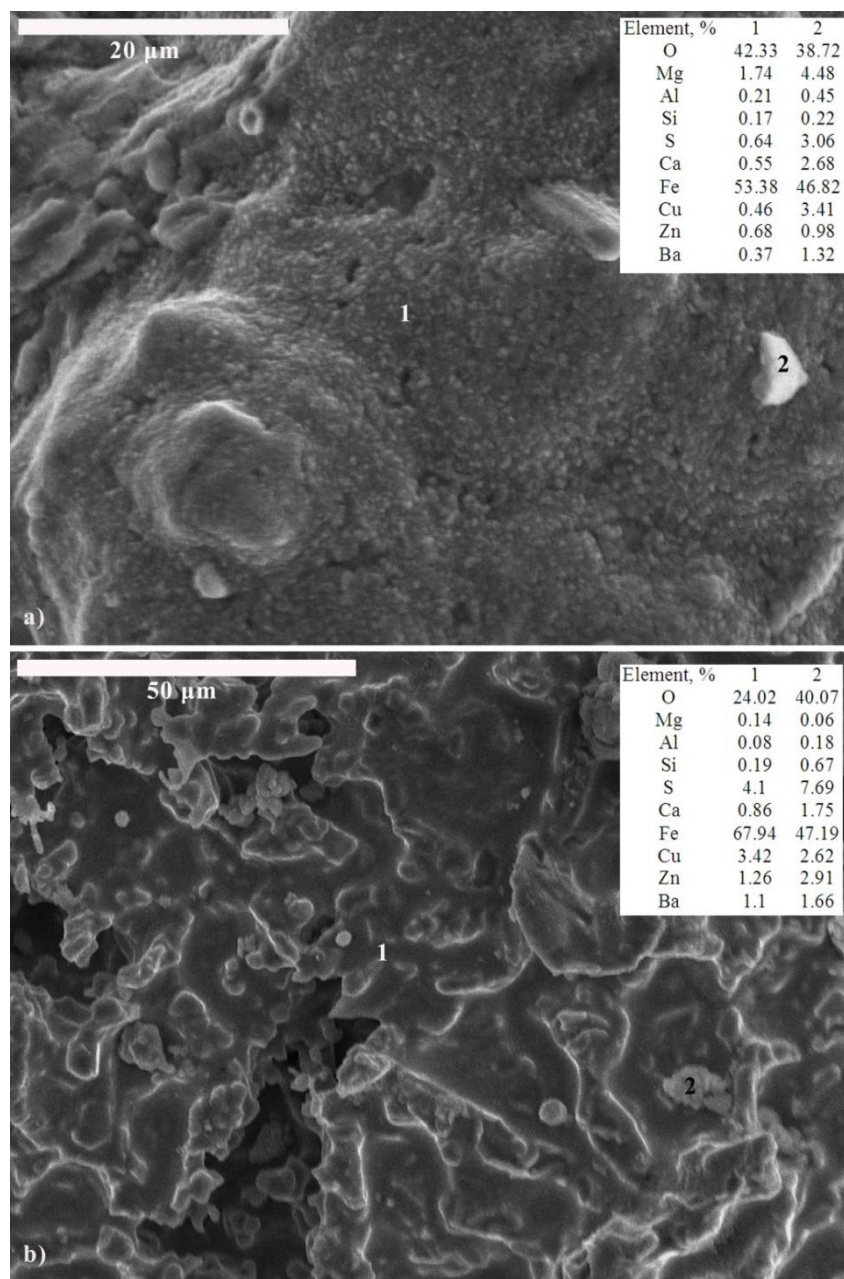


Fig. 4. Results of the SEM-EDS analyses: a) Mg50A, b) Mg50W

#### 4. Conclusions

The Waelz process was applied for jarosite residue and NLR treatment. Different Waelz slags were obtained by varying MgO content in an additive, and by a different slag cooling rate. The main components of the slags are Fe-oxides with low Zn and Pb content, confirming the efficiency of the Waelz process. BI was the same for all the slags due to the same amount of alkaline additives added (12%), but with different CaO/MgO content. A referent slag, Ca100, obtained using CaO as a conventional additive in the Waelz process showed leaching of As and Sb above the maximum allowed concentration for non-hazardous waste after the EN 12457-4 standard leaching test. Concentrations of the other investigated elements (Ba, Cu, Mo, Pb and Zn) were well below the regulation limits. The multiphase equilibrium composition calculations indicated that a part of arsenic content vaporizes during the process, while the rest remained in the form of highly soluble alkali-arsenites. Sb was present as fairly volatile elemental antimony and its retention in the slag is probably

due to a short operation time of the Waelz process. A method for immobilization of such mobile species could be by the encapsulation within a stable matrix. The SEM-EDS analysis of Ca100 slag sample revealed a porous structure of the slag matrix with large gypsum crystallites with poorly formed calcium ferrites and silicates, and unreacted CaO.

In contrast to the referent Ca100 slag, the slags obtained using the additives containing 25% and 50% of MgO showed a reduced leaching of As and Sb below the maximum allowed concentration after the EN 12457-4 test. Concentration of leached Ba, Cu, Mo, Pb and Zn remained well below the regulation limits. Rapid cooling of the slags resulted in a greater decrease in As and Sb leaching, indicating the main role of the slag matrix microstructure in pollutants release. This was confirmed by the SEM-EDS analyses of MgO slags. The addition of MgO and the increased cooling rate led to formation of a denser amorphous structure of the slag matrices, able to encapsulate migratory elements such as arsenic and antimony. The reason for this is MgO that remained inert during the Waelz process reducing BI of the rest of slag content and, thus, favoring the formation of amorphous stable structure.

Modification of additive composition in the Waelz process and cooling conditions of the Waelz slag led to an increase of leaching resistance and stability of the slag. All investigated Waelz slags with MgO additions are suitable for safe disposal or further use in civil engineering.

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