Characterisation of the sintering behaviour of Waelz slag from electric arc furnace (EAF) dust recycling for use in the clay ceramics industry

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Abstract

Waelz slag is an industrial by-product from the recovery of electric arc furnace (EAF) dust which is mainly sent to landfills. Despite the different chemical and mineralogical compositions of Waelz slag compared to traditional clays, previous experiments have demonstrated its potential use as a clay substitute in ceramic processes. Indeed, clayey products containing Waelz slag could improve mechanical and environmental performance, fixing most of the metallic species and moreover decreasing the release of some potential pollutants during firing.

However, a deeper understanding of the complex phase transformations during its thermal treatment and the connection of this behaviour with the end properties is desirable in order to explain the role that is played by the Waelz slag and its potential contribution to the ceramic process. For this purpose, in the present study, the chemical, mineralogical, thermal and environmental behaviour of both (i) unfired powdered samples, and (ii) pressed specimen of Waelz slag fired up to different temperatures within the typical range of clay based ceramic production, has been studied. The effect of the heating temperature on the end properties of the fired samples has been assessed.

In general, an increase of the firing temperature promotes sintering and densification of the products and decreases the open porosity and water absorption which also contributes to the fixation of heavy metals. On the contrary, an increase in the leaching of Pb, Cr and Mo from the fired specimens is observed. This can be attributed to the creation of Fe and Ca molybdates and chromates that are weakly retained in the alkali matrix. On the other side, at temperature above 950 °C a weight gain related to the emission of evolved gases is observed. In conclusion, the firing temperature of the ceramic process is a key parameter that affects not only the technical properties but also strongly affects the leaching behaviour and the process emissions.

Keywords

Waelz slag; Ceramic products; EAF dust recycling; Industrial ecology; Sintering behaviour

1. Introduction

The term industrial ecology (IE) is used to describe a novel approach to the production of consumer goods, the design of industrial processes and the definition of corporate strategies aimed at achieving sustainable development. The key concept behind IE is that processes and industries are interacting systems rather than isolated components and that each of these components generates a range of by-products that may be used by other components as a feedstock for their production cycles (Gibbs and Deutz, 2007, Yuan and Shi, 2009 and Costa et al., 2010). IE promotes the change of linear processes into cyclical processes such that the waste or by-product from one industry is used as input for another; this process is called closed-loop recycling.

The Waelz process is a commercial method for recovering volatile metals from electric arc furnace (EAF) dust, a hazardous waste according to the European Waste Catalogue (10 02 07*), and is referred to as the best available technique in the BREF Document of Non Ferrous Metals Industries (IPPC, 2001). During this process, which is used to produce Waelz oxide, a large amount of an industrial by-product, called Waelz slag or Waelz iron product, is generated. Approximately six million metric tons of electric arc furnace (EAF) dust is generated on an annual basis worldwide, whereas only an estimated 2.5 million metric tons is recycled, mainly in the United States, Europe, Thailand and Japan (Global Steel Dust, 2012). In Spain, approximately 125,000 tons of EAF dust is treated annually, generating approximately 70,000 tons of Waelz slag (Vegas et al., 2008). Although Waelz slag is usually classified as non-hazardous waste (10 05 01 identification code in the European Waste Catalogue), its disposal in landfill sites implies high economic and environmental costs. The Waelz process is a rapidly growing recycling method. Three new plants have been opened in 2012, two in Turkey and one in South Korea, by the Befesa Zinc company (Befesa, 2012). Therefore, the amount of Waelz slag needing to be disposed of is increasing, and the study of the potential applications of this material is important.

The Waelz process (Fig. 1) is designed to separate zinc and lead from other materials by reducing, volatilising and oxidising these elements. The materials placed in the kiln consist of EAF dust, other secondary raw materials and coke fines. The normal operating temperature inside a Waelz kiln is approximately 1200 °C. Inside the kiln, the solid materials are first dried and then heated by the countercurrent flow of hot gas and by contact with the refractory lined

walls. The residence time of the material in the rotary kiln is between 4 and 6 h depending on the inclination, length and rotation speed (IPPC, 2001).

Fig. 1. Waelz process of Befesa Zinc Aser, Asua-Erandio (Basque Country, Spain).

The slag produced in the kiln is discharged continuously from the end of the furnace into a quench system. It contains all of the non-volatile components of the raw material (the EAF dust), which are primarily iron and calcium oxide. To use this material, Waelz slag has been investigated as a base material in road construction (Vegas et al., 2008), for use in sports grounds and dikes (Barna et al., 2000) and as natural aggregates in concrete mixtures (Sorlini et al., 2007). Additionally, it can be reprocessed to add more value to the iron content, which is currently under research and development (Global Steel Dust, 2012).

To promote closed-loop recycling, this alternative raw material has been used in ceramic processes. The introduction of waste or by-products into brick manufacturing can not only reduce energy usage, gaseous emissions and raw material consumption, which are some of the main environmental problems associated with the ceramic industry (IPPC, 2007), but can also improve the properties of the products.

Waste of Thermal Process, belonging to group LER 10 of the European Waste Catalogue, such as fly ash, bottom ash, metallurgical slag and foundry sand, have been studied for use in the ceramic industry.

Different authors have assessed the feasibility of the use of these materials as secondary raw materials based on their physical and mechanical properties (Pérez-Villarejo et al., 2012,

Karamanova and Avdeev, 2011, González-Corrochano et al., 2009, El-Mahllawy M, 2008, Jonker and Potgieter, 2005 and Acosta et al., 2002). Some papers have included a leaching test to determine the environmental risk of the new fired product (González-Corrochano et al., 2012, Quijorna et al., 2012, Alonso-Santurde et al., 2011, Bantsis et al., 2011, Fernández-Pereira et al., 2011, Quijorna et al., 2011, Alonso-Santurde et al., 2010, Asokan et al., 2010, Little et al., 2008, Singh et al., 2007 and Çoruh and Ergun, 2006).

Regarding Waelz slag, one study has reported its environmental characterisation as a raw material using leaching tests (Barna et al., 2000), but the thermal behaviour of this material was not determined. Additionally, previous studies have investigated foundry sand and Waelz slag individually and in combination for use in clay bricks (Quijorna et al., 2012, Quijorna et al., 2011, Alonso-Santurde et al., 2011 and Alonso-Santurde et al., 2010). These investigations demonstrated the feasibility of using both waste materials. Foundry sand has advantages because of its high level of silica. The addition of Waelz slag improved the physical and mechanical characteristics of the bricks and reduced the sintering temperature because this slag includes glass network modifying species. However, the leaching data showed an increase in the mobility of Cr, Mo, Pb and Ba (Quijorna et al., 2011).

Previous studies have demonstrated the suitability of Waelz slag to produce commercial lights bricks and block ceramics through pilot (Quijorna et al., 2012) and industrial (Quijorna et al., 2011) trials. Alternative products can be obtained by incorporating Waelz slag into ceramic matrices, improving the technical properties, reducing the cost of firing due to its fluxing characteristics, fixing most of the metallic species and decreasing the release of some potential pollutants during firing.

This work goes one step further towards a better understanding of the role played by the Waelz slag and its potential contribution to the ceramic process. For this purpose a complete characterization of both unfired powdered samples and pressed specimen of Waelz slag fired up to different temperatures within the typical range of clay based ceramic production, was undertaken in terms of chemical and mineralogical composition, thermal behaviour and leaching behaviour.

This characterization study is expected to increase awareness on the particular behaviour of Waelz slag during ceramic processes in order to be used as alternative raw material in other fired clay products. For this purpose, the effect of the heating temperature on the end properties of the sintered samples has been determined. The Waelz slag has been chemically, thermally and mineralogically characterized using thermogravimetric analysis (TGA) coupled with differential thermal analysis (DTA), X-ray diffraction (XRD), X-ray thermodiffraction

(XRT) and scanning electron microscopy (SEM). Additionally, the physical properties of fired bodies produced from Waelz slag have been carried out. Finally, the environmental behaviour during the firing process of manufacturing clay-based ceramic materials has been studied with an emphasis on its critical elements, Cr, Mo and Pb.

2. Materials and methods

Waelz slag (brand name Ferrosita®) was supplied by Befesa Zinc Aser (Abengoa Group), an EAF dust recycling plant located in Erandio (Basque Country, Spain).

A representative batch of Waelz slag was collected in a $>500\text{ }\mu\text{m}$ sieve to determine the chemical composition of the slag. Additionally, a set of fired Waelz slag specimens were prepared by mixing the as-received slag with water (3%) to study the feasibility of introducing Waelz slag into ceramic processes. The samples were moulded by uniaxial pressing (1472 kg cm^{-2}) using a Mignon SS/EA (Nanetti) and fired at different temperatures (850, 900, 950, 1000, 1050 °C) in a muffle furnace using a heating rate of $6\text{ }^{\circ}\text{C min}^{-1}$ and a dwell time of 60 min. Elemental analysis was performed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) with an ARL Fisons 3410 spectrometer, and the major oxide composition was determined using X-ray fluorescence in Activations Laboratories (Canada).

X-ray powder diffraction data were collected on a D8 Advance automatic diffractometer in the Bragg-Brentano geometry and were used to evaluate the mineralogical composition of the unfired and fired bodies of the Waelz slag (850–1050 °C). $\text{CuK}\alpha 1$ radiation ($\lambda = 1.5406\text{ }\text{\AA}$) was used with a fixed counting time of 8 s in the $10^{\circ} \leq 2\theta \leq 90^{\circ}$ range with steps of 0.03° in 2θ . The qualitative analyses of the raw Waelz slag and the Waelz slag fired compounds were performed using the Diffracplus EVA program (DIFFRACplus Basic. V5 Evaluation Program for XRD analysis).

Scanning electron microscopy (SEM) was performed using a Jeol JSM-5800 LV to assess the textural and pore characteristics of the unfired and fired bodies of the Waelz slag (850–1050 °C) and to study the evolution of this material as a function of temperature. The surface of the sample was treated with a gold coating to improve the obtained images.

The thermal behaviour of the raw Waelz slag was investigated by thermogravimetric analysis (TG) coupled with differential thermal analysis (DTA) using a Setaram Setsys Evolution Thermogravimetric analyser. The slag was placed in an alumina crucible. The flowing conditions were 20 mL min^{-1} in air up to 1050 °C with a ramp rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Additionally, time-resolved X-ray thermodiffractometry was carried out in air using a D8 Advance automatic diffractometer equipped with a variable-temperature stage (Anton Paar

high-temperature oven-camera HTK1200) and a ceramic sample holder. The powder patterns were recorded in steps of 8 s while increasing the temperature at a rate of 15 °C min⁻¹ from room temperature to 1000 °C.

The physical properties of the fired Waelz slag specimens were assessed according to the following standard procedures: BET surface area (nitrogen adsorption using a Micromeritics ASAP 2000); open porosity (mercury intrusion porosimetry using a Micromeritics AutoPore IV 9500); firing shrinkage, weight gain during firing and bulk density (UNE-EN 772-13).

Equilibrium leaching tests (UNE EN 12457-1 and 2) have been carried out to determine the environmental behaviour of the unfired and fired slag. According to the Landfill of Waste Directive 2003/33/CE (OJEC, 2003), the Ba, Cd, Cr, Cu, Mo, Ni and Zn concentrations in the leachates have been analysed using ICP emission spectrometry (Perkin Elmer Plasma 400), and the As, Hg, Pb, Sb and Se concentrations in the leachates have been analysed using atomic absorption spectrometry (Perkin Elmer 1100B). Ion chromatography (Dionex DX 120) has been used to analyse the concentrations of F⁻, Cl⁻ and View the MathML source in the leachates.

3. Results and discussion

3.1. Characterisation of the raw and fired Waelz slags

3.1.1. Chemical composition

The major oxide and trace element composition of the raw and fired Waelz slags are shown in Table 1. As shown by this table, the major oxides present in the unfired Waelz slag are iron oxide (expressed as Fe₂O₃) (52.74%), calcium oxide (CaO) (20.03%) and silica (SiO₂) (8.97%), with a total contribution of over 75%. Furthermore, the chemical composition of this slag indicates a high content of network modifier oxides (CaO, MgO, MnO), which could reduce the amount and viscosity of the liquid phase. These compounds have a fluxing effect, reducing the temperature to achieve a sintering density (Little et al., 2008). The negative (−3.69%) loss on ignition (LOI) indicates a gain in mass during the thermal process have a higher contribution than the release of evolved gases. The total content of the trace elements was lead (Pb) (57300 mg kg⁻¹), zinc (Zn) (21900 mg kg⁻¹), sulphur (S) (7100 mg kg⁻¹), copper (Cu) (4100 mg kg⁻¹), chromium (Cr) (3800 mg kg⁻¹) and other minor elements, namely, Ba, Ni and Mo (below 1000 mg kg⁻¹). The chemical composition of the Waelz slag is in agreement with the results from the raw material, which demonstrates that the temperature does not affect the composition of the major oxides. The LOI of the fired samples is positive, showing the total oxidation of the slag and a higher contribution to the loss from the volatiles.

Table 1. Major oxide and trace element composition of Waelz slag.

Major oxides (wt.%)	Raw Waelz slag	850 °C	900 °C	950 °C	1000 °C	1050 °C
Fe ₂ O ₃ ^a	52.74 ± 2.74	44.22 ± 0.02	44.85 ± 1.04	45.75 ± 1.90	42.99 ± 1.55	45.46 ± 1.21
CaO	20.03 ± 2.60	20.33 ± 0.62	19.53 ± 0.57	19.32 ± 0.84	23.28 ± 0.54	20.64 ± 0.25
SiO ₂	8.97 ± 1.01	7.34 ± 0.09	7.72 ± 0.30	8.05 ± 0.74	8.71 ± 0.40	7.34 ± 0.07
MnO	5.08 ± 1.24	3.86 ± 0.19	3.86 ± 0.17	3.89 ± 0.28	4.11 ± 0.16	3.60 ± 0.04
MgO	3.11 ± 0.42	3.87 ± 0.06	3.55 ± 0.08	3.54 ± 0.11	4.02 ± 0.08	3.84 ± 0.05
Al ₂ O ₃	2.91 ± 0.58	2.27 ± 0.01	2.20 ± 0.05	2.35 ± 0.08	2.77 ± 0.06	2.38 ± 0.04
Na ₂ O	0.49 ± 0.26	0.73 ± 0.31	0.84 ± 0.19	0.72 ± 0.26	0.61 ± 0.13	0.30 ± 0.01
P ₂ O ₅	0.45 ± 0.08	0.38 ± 0.02	0.37 ± 0.02	0.38 ± 0.02	0.46 ± 0.01	0.41 ± 0.01
Ti ₂ O	0.21 ± 0.02	0.151 ± 0.01	0.149 ± 0.01	0.155 ± 0.01	0.183 ± 0.01	0.154 ± 0.01
K ₂ O	0.10 ± 0.05	0.23 ± 0.07	0.29 ± 0.08	0.21 ± 0.10	0.19 ± 0.09	0.15 ± 0.08
LOI	−3.69 ± 1.18	1.42 ± 0.58	1.46 ± 0.54	1.17 ± 0.69	1.17 ± 0.52	0.53 ± 0.35
Trace elements (mg kg ^{−1})						
Pb	57.300 ± 260.18	67.400 ± 3.15	64.700 ± 289.69	66.000 ± 439.83	40.400 ± 432.97	63.100 ± 426.10
Zn	21.900 ± 206.14	12.100 ± 12.60	14.200 ± 10.86	11.300 ± 10.36	9710 ± 20.30	8270 ± 9.63
S	7100 ± 40.82	8600 ± 43.48	8030 ± 31.32	7450 ± 50.26	9390 ± 38.25	8090 ± 26.23
F	4400 ± 923.76	3400 ± 424.26	3500 ± 494.97	2800 ± 777.82	3300 ± 530.33	3400 ± 282.84
Cu	4100 ± 916.52	2860 ± 339.41	3180 ± 275.77	3060 ± 219.20	3420 ± 243.95	2950 ± 268.70
Cr	3800 ± 414.77	4990 ± 410.12	5550 ± 544.47	5470 ± 692.96	4230 ± 611.65	3590 ± 530.33
Cl	2200 ± 17.26	3300 ± 777.82	4700 ± 594.54	3100 ± 989.95	2400 ± 502.89	2400 ± 15.84
Ba	910 ± 127.03	6580 ± 40.53	6750 ± 26.11	6070 ± 37.41	6350 ± 37.49	6100 ± 37.56
Ni	430 ± 89.78	642 ± 249.61	692 ± 197.28	701 ± 291.33	390 ± 171.12	361 ± 50.91
Sb	309 ± 59.27	195 ± 68.59	202 ± 57.51	211 ± 61.52	243 ± 51.97	232 ± 42.43
Mo	110 ± 32.56	251 ± 113.14	213 ± 75.90	198 ± 76.37	149 ± 57.28	143 ± 38.18
As	62 ± 8.5	70 ± 2.12	91 ± 8.25	61 ± 12.02	102 ± 11.31	63 ± 10.61
Se	<3	16 ± 0.74	<3	<3	<3	<3
Cd	1.1 ± 0.67	0.6 ± 0.35	0.6 ± 0.64	0.85	0.6 ± 0.78	1 ± 0.71

^aTotal iron (FeO + Fe₃O₄) expressed as Fe₂O₃.

3.1.2. Mineralogical composition

The X-ray powder diffraction pattern of the raw Waelz slag (Fig. 2) has been fitted using the pattern matching routine in the Diffracplus EVA program. Remarkably, the existence of iron in different types of oxides can be seen: FeO (wustite), Fe₂O₃ (CaO₂) (iron calcium oxide) and Fe₃O₄ (magnetite). Moreover, calcium silicate (Ca₂SiO₄) and CaO (lime) can be distinguished,

and, according to the chemical composition of the Waelz slag, other compounds (e.g., alumina or quartz) may appear as overlapping peaks and/or in very low quantities.

Fig. 2. XRD patterns describing the mineralogical composition of Waelz slag.

The presence of wustite (FeO) is somewhat common under standard conditions. The strongly reducing conditions used for the Waelz process in the rotary kiln allow for the presence of this iron oxide in the Waelz slag. Furthermore, the presence of magnetite has been confirmed using a permanent magnet and by observing the sample orientation.

The major crystalline phases present in the Waelz slag bodies fired at different temperatures (850–1050 °C) were also determined by X-ray diffraction. As shown in Fig. 3, the main differences between the Waelz slags is the complete oxidation of wustite into magnetite at 850 °C and the probably breakdown of compounds with silicate and lime into quartz (SiO₂) and calcium oxide (CaO) that begins up to 1000 °C and the peaks appears at 1050 °C. These results are in good agreement with the known chemical compositions of these materials.

3.1.3. Scanning electron microscopy (SEM)

The textural characteristics and the evolution of the surface porosity with the firing temperature have been investigated by scanning electron microscopy (SEM). Fig. 4 shows the SEM observations of the surface of the green pressed body (unfired) and the surfaces of the Waelz slag bodies fired at different temperatures (850–1050 °C). The green body exhibits an extended open porosity characterised by irregularly shaped pores. The use of increasingly high

firing temperatures resulted in the formation of a reduced open porosity in the fired bodies due to an increase in the surface tension of the liquid phase. This tension generates a capillary pressure that tends to bring the particles together (Romero et al., 2008). Although the bodies fired at 1000 °C show good sintering characteristics in terms of their visual appearances and physical properties, is at 1050 °C, when the SEM images show the formation of a liquid phase that binds the grains, as described in the following section.

Fig. 3. XRD patterns of the Waelz slag bodies fired at temperatures between 850 and 1050 °C.

Fig. 4. SEM images on the surfaces of the Waelz slag bodies fired at different temperatures (850–1050 °C) and of the green body.

3.2. Thermal evolution of Waelz slag with temperature

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the Waelz slag were performed at temperatures up to 1050 °C under air flow (Fig. 5). The decomposition curves reveal a step process. An initial weight loss (<0.2%) from 40 to 100 °C is associated with surface effects due to water from the atmosphere on the surface. The second step is from 200 to 900 °C, in which a weight gain of 3.8% is accompanied by exothermic effects that give rise to marked peaks at 600 and 740 °C. This step could be attributed to the oxidation of Fe(II) to Fe(III), which is in good agreement with the X-ray diffraction data, and to other compounds of Fe(II), for which a weight gain was noted (de Pedro et al., 2005 and Barthelet et al., 2003). At temperatures above 950 °C, an additional weight loss was observed, which was attributed to the emission of evolved gases.

Fig. 5. TGA/DTA analysis of Waelz slag.

The exothermic reaction and the weight gain observed in the thermogravimetric analysis of the Waelz slag have also been investigated using X-ray thermodiffraction. As shown in Fig. 6, the powder patterns exhibit a thermostructural change at temperatures similar to those obtained from the TGA/DTA data. Except for wustite (FeO), none of the different crystalline phases identified in the Waelz slag show a significant change in the range of the weight gain. To follow the iron oxidation process, an analysis of the intensities of the monitored peaks of wustite (FeO) [(2 0 0) at $2\theta = 41.9^\circ$] and magnetite (Fe₃O₄) [(3 1 1) at $2\theta = 35.4^\circ$] has been conducted (Fig. 7). The data show that the structure of wustite (FeO) was maintained up to 250 °C after heating in air, as the intensity of the monitored peak remains essentially unchanged.

The phase transformation of wustite (FeO) into magnetite (Fe_3O_4) started at approximately 250 °C and proceeded through an irreversible process. From 350 to 700 °C, a phase transition was detected as a consequence of the partial change into magnetite (Fe_3O_4).

Fig. 6. Thermodiffractometry analysis of Waelz slag.

Fig. 7. Thermal dependence of the intensities of the wustite (FeO) and magnetite (Fe_3O_4) monitor peaks.

Above 750 °C, the diffraction-monitored peak assigned to wustite (FeO) disappeared, and the oxidation was almost complete. These results are supported by the TGA/DTA analysis, which revealed changes in weight.

3.3. Physical properties of fired samples

Fired samples produced at temperatures between 850 and 1050 °C have been characterised in terms of their visual appearance and physical properties. The fired bodies produced below 1000 °C exhibited an incomplete sintering of their mineral constituents. The structures of samples fired at 1000 and 1050 °C did not show noticeable faults. However, the sample produced at 1050 °C showed small bubbles on its surface, indicative of the difficulty in removing the evolved gases due to the higher viscosity of the amorphous phase.

Fig. 8 illustrates the physical properties of the fired samples, including the BET surface area, open porosity, firing shrinkage, weight gain and bulk density, as a function of the firing temperature in the range of 850–1050 °C. The BET surface areas and open porosity values decrease with increasing firing temperatures. The open porosity presents a minimum value (13 %) at 900 °C, and this value increases again at temperatures above 1000 °C. The lower open porosity values that were observed at higher firing temperatures indicate that the sintering process follows a viscous liquid phase mechanism due to the formation of a glassy phase (Romero et al., 2008). These results are supported by the SEM observations (Fig. 4).

Fig. 8. The specific surface BET area, open porosity, firing shrinkage, weight gain and bulk density as a function of the firing temperature from 850 to 1050 °C.

On the other hand, the results of the bulk density analysis show an increase in the density, which reaches a maximum of 2.8 g cm^{-3} at 1000°C . Thus, the fired samples undergo an expansion and weight gain as they are heated to increasingly high temperatures. Even higher temperatures (1050°C) result in a decrease in the bulk density, which could be due to so-called body bloating, which tends to expand the pores and increase the closed porosity (Romero et al., 2009). The weight gain corroborates the value obtained from the thermogravimetric analysis and the composition analysis. The expansion and weight gain are attributed to the transformation of the crystalline phase wustite (FeO) into magnetite (Fe_3O_4) during the firing process and to the emission of enclosed gases. Fig. 9 shows the polyhedral view of wustite (FeO) and magnetite (Fe_3O_4). As observed in this figure, the unit cell size of crystalline magnetite (Fe_3O_4) is approximately double that of iron oxide (FeO). Consequently, the volume of the unit cell in magnetite (Fe_3O_4) is nearly eight times larger than that in wustite (FeO) (Fjellvag et al., 1996 and Fleet, 1981).

Fig. 9. Polyhedral view along [010] of the wustite compound FeO (a) and of the magnetite compound Fe_3O_4 (b). The big and small balls are oxygen and iron atoms, respectively.

3.4. Leaching behaviour

The influence of the firing process on the leaching behaviour of Waelz slag has been assessed by the equilibrium leaching tests UNE EN 12457-1 and 2, which simulate closed and open disposal scenarios, respectively. The results (Tables 2 and 3) showed that As, Cd, Cu, Ni, Hg, Sb and Se concentrations were lower than the detection limit in every case. The leachate pH values were in the range 11.84–12.46, i.e., alkaline.

Table 2. Concentration (mg kg⁻¹) of elements in the leachates according to the equilibrium leaching test L/S 2 (UNE EN 12457-1).

T (°C)	Green body	850	900	950	1000	1050
pH	12.46 ± 0.08	11.77 ± 0.06	11.87 ± 0.07	11.88 ± 0.08	11.89 ± 0.01	11.84 ± 0.09
As	<DL	<DL	<DL	<DL	<DL	<DL
Ba	1.01 ± 0.01	0.09 ± 0.03	0.09 ± 0.01	0.12 ± 0.02	0.11 ± 0.01	0.15 ± 0.03
Cd	<DL	<DL	<DL	<DL	<DL	<DL
Cr	0.32 ± 0.03	104 ± 0.02	134 ± 0.04	216 ± 0.04	145 ± 0.03	133 ± 0.03
Cu	0.14 ± 0.02	<DL	<DL	<DL	<DL	<DL
Hg	<DL	<DL	<DL	<DL	<DL	<DL
Mo	2.68 ± 0.02	44.5 ± 0.04	46.41 ± 0.03	64.27 ± 0.05	46.27 ± 0.02	65.8 ± 0.03
Ni	0.206 ± 0.05	<DL	<DL	<DL	<DL	<DL
Pb	131 ± 0.16	<DL	<DL	<DL	<DL	<DL
Sb	<DL	<DL	<DL	<DL	<DL	<DL
Se	<DL	<DL	<DL	<DL	<DL	<DL
Zn	2.28 ± 0.02	0.28 ± 0.02	0.35 ± 0.01	0.48 ± 0.03	0.22 ± 0.04	<DL

Table 3. Concentration (mg kg⁻¹) of elements in the leachates according to the equilibrium leaching test L/S 10 (UNE EN 12457-2).

T (°C)	Green body	850	900	950	1000	1050
pH	12.25 ± 0.01	11.86 ± 0.05	11.86 ± 0.03	11.86 ± 0.02	11.97 ± 0.02	11.90 ± 0.005
As	<DL	<DL	<DL	<DL	<DL	<DL
Ba	113 ± 0.22	1.15 ± 0.20	1.22 ± 0.25	1.15 ± 0.20	1.05 ± 0.23	0.84 ± 0.21
Cd	<DL	<DL	<DL	<DL	<DL	<DL
Cr	7.67 ± 0.61	184 ± 0.57	291 ± 0.67	403 ± 0.63	202 ± 0.67	124 ± 0.59
Cu	0.43	<DL	<DL	<DL	<DL	<DL
Hg	<DL	<DL	<DL	<DL	<DL	<DL
Mo	4.61 ± 0.41	75.1 ± 0.38	83.7 ± 0.43	80.6 ± 0.42	62.2 ± 0.4	80.2 ± 0.45
Ni	<DL	<DL	<DL	<DL	<DL	<DL
Pb	608.75	<DL	<DL	<DL	<DL	<DL
Sb	<DL	<DL	<DL	<DL	<DL	<DL
Se	<DL	<DL	<DL	<DL	<DL	<DL
Zn	4.27 ± 0.42	0.35 ± 0.05	0.91 ± 0.04	0.81 ± 0.04	0.65 ± 0.04	<DL

The leaching behaviour of Waelz slag has been previously reported in the work of Barna et al. (2000). These authors concluded that the mobility of metals is controlled by their solubility in the range of pH values studied, 5–12 for the critical metals Zn, Pb and As. In this work, the leaching of As, Cd, Hg, Sb and Se are below the detection limit in both, the green body and the fired samples. The raw Waelz slag presents a high mobility of Zn, Pb and Ba. The thermal process reduces the mobility of Zn and Pb below the detection limit; however, the leaching of Cr and Mo increases.

The mobility of Cr increased at temperatures up to 950 °C, beyond which it decreased, while the Mo mobility does not differ significantly with temperature. The literature has shown that oxyanions can be adsorbed on the surface of amorphous iron oxides that many alkaline wastes contain (Van der Sloot, 2002). Furthermore, the complexation of these compounds has been studied (Cornelis et al., 2008 and Adell et al., 2007) and a relation between the specific surface area and the extension of the complexation process found for View the MathML source (McKenzie, 1983). In his work McKenzie concluded that the decreasing in the specific surface lead to higher Mo leaching. This behaviour, which could be extended to Cr, may be an explanation for the trends observed in this work, since Waelz slag specific surface area decreased during firing from 6.70 m² g⁻¹–1.50 m² g⁻¹.

Furthermore, it has been proved that oxyanionic metals such as Mo and Cr can be found in elemental (X⁰) or hexavalent state (X^{VI}) in alkaline waste (Cornelis et al., 2008). The reducing atmosphere generated during the Waelz process could transform oxyanion into its elemental state and create compounds of low volatility. However, Mo and Cr could react with Ca and Fe during the firing process and generate Ca and/or Fe molybdates and chromates that are weakly retained in the matrix (Hu et al., 2013, Hyks et al., 2009, Cornelis et al., 2008, Xu et al., 2008, Kirk et al., 2002, Paoletti, 2002 and Reich et al., 2002).

4. Conclusions

- Waelz slag was a multicomponent by-product to which iron oxide, calcium oxide and silica contributed over 75 %. Waelz slag had significant amounts of network modifier compounds (FeO, CaO and MgO) that increase the amount of the liquid phase and decrease its viscosity, hence improving sintering and sample densification. The composition was not affected by temperatures from 850 to 1050 °C. Raw Waelz slag bodies had negative LOI values, but fired specimens had positive ones. This indicated that the slag oxidation process was complete and the volatile compounds were released.

- XRD analysis indicated wustite (FeO), calcium silicate (Ca₂SiO₄), iron calcium oxide (Fe₂O₃(CaO₂)), magnetite (Fe₃O₄) and lime (CaO) as main crystalline phases of raw Waelz slag. The firing process transformed FeO into Fe₃O₄ by oxidation at 850 °C and CaSiO₄ was broken down into SiO₂ and CaO at 1050 °C.

- The TGA/DTA analysis showed the exothermic reaction that transformed Fe(II) into Fe(III) at 200–900 °C and the weight loss of the emission of evolved gases, which was confirmed by X-ray thermodiffraction, pointing out that the phase transformation of wustite into magnetite started at approximately 250 °C and above 750 °C was almost complete. Visual

analysis of the fired samples showed the sintering process starting at temperatures about 950–1000 °C. The thermal treatment led to volume and weight increases as consequence of FeO oxidation, as well as decreases of surface area and open porosity of them. This could indicate that the sintering process was produced according to a liquid phase mechanism derived to the formation of a glassy phase. These results were backed by SEM images. The raw Waelz slag presented high mobility of Zn, Pb and Ba. The thermal process reduced the leaching of these metals but increased the mobility of Cr and Mo. This mobility may be due to the reduction of surface area, decreasing the adsorption of these compounds on iron oxides, and the behaviour of Fe and Ca molybdates and chromates formed during the thermal process, weakly retained in the alkali matrix, as Waelz slag.

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