WAELZ SLAG BASED CONSTRUCTION CERAMICS: EFFECT OF THE TRIAL SCALE ON TECHNOLOGICAL AND ENVIRONMENTAL PROPERTIES

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Abstract The construction industry has already begun the transition to circular economy and intensive research has been conducted over the last decades at laboratory scale to assess the potential use of waste in ceramic applications. However, industrial trials to prove its scale up have been performed to a lesser extent. This work studies the effect of trial scale on the technological and environmental properties of high quality ceramic products incorporating Waelz slag (WS), an industrial by-product from the recovery of electric arc furnace dust (EAFD). To this aim, three groups of ceramics have been produced varying the WS content and the process parameters, moulding water and pressure, at laboratory and industrial scale. Preliminary laboratory scale tests were used to optimize WS content and process conditions using the software GAMS (General Algebraic Modeling System). Optimum ceramic products were processed at both laboratory and industrial scale and tested for their technological and environmental properties. Results from the laboratory and industrial trials were compared to evaluate the scale effect on the ceramic properties. The introduction of WS in clay bricks seems to be easily scaled-up for additions of WS ≤ 10%wt, but higher percentages of WS promotes relevant differences in the properties of the laboratory and industrial bricks.

Keywords: Waelz slag, ceramic building material, scale up, environmental assessment, technology properties.

Introduction

The construction industry has already begun the transition to circular economy and intensive research has been conducted over the last decades at laboratory scale to assess the potential use of waste in ceramic applications. However, industrial trials to prove its scale up have been performed to a lesser extent [1–3]. This research aims to apply the principles of the circular economy by the use of Waelz slag (WS), an industrial by-product from the recovery of electric arc furnace dust (EAFD), in the production of ceramic bricks. WS contains the non-volatile components of the original EAFD, primarily iron (~50-60%) and calcium (~15%) oxides. Contrary to EAFD, WS is classified as a non-hazardous waste according to the European List of Waste (code 10 05 01) [4] due to its lower heavy metal concentration. However, occasionally it could be considered as a potentially hazardous waste and it is disposed of in landfills at increasing economic and environmental costs [5, 6]. An attractive alternative to disposal is its use as alternative material in the construction sector [7]. Ceramic processes, apart from the heterogeneity of raw materials and products requirements, are also considered as good potential receptors for the recycling of wastes due to the different roles that they can play in the ceramic process: fluxing agents, fillers, clay substitutes, body fuels, pore formers and other properties affecting wastes. These roles are directly related to the chemical and mineralogical composition of the materials. On the other hand, the different roles that the wastes may play in the ceramic process, make possible to obtain ceramic products fulfilling the quality requirements established by the recent Construction Products Regulation (CPR)[8]. One of the new key issues of the CPR is the requirement on sustainability, especially the sustainable use of natural resources and the reduction of life-cycle impacts [9–13]. Furthermore, the CPR addresses health and environment aspects of the ceramic products, including the potential release of dangerous substances to soil and water during entire lifecycle useful life and at the end of its life.

Previous studies looking for reusing alternatives for WS have provided relevant information about: (i) the sintering behaviour of WS[14]; (ii) the technological and environmental properties of ceramic products containing WS and WS combined with other wastes[15]; (iii) the mathematical models that describe the technological [16] and environmental [17] behaviour of ceramic products containing WS in mixtures with other wastes and, (iv) the acid gas emissions from ceramic processes containing WS and WS mixed with other wastes [17, 18].

Results from all these previous investigations demonstrate that the content of WS in the initial mixture and the firing temperature of the ceramic process are key parameters that affect not only the technological properties but also have a strong effect on their environmental performance. High contents of WS in the mixtures produce ceramic products with increased bulk density, open porosity, and flexural strength when compared with the natural clay but, lower water absorption, weight loss and linear firing shrinkage. In general low firing temperature decrease emissions of acid gases [18, 19], and immobilizes most of the heavy metals present in the WS but do not immobilize neither the Cr nor Mo present in the WS, whose leaching becomes controlled by soluble salts formation [17]. However, to the best of our knowledge, the influence of the moulding parameters (water and pressure of moulding) on the final properties of waste-based ceramics has been studied to a lesser extent. The aim of this research is basically to assess the feasibility of recycling WS in the production of facing bricks, a high temperature process,

through laboratory testing and validation at industrial trials. The reason to select facing bricks for this study is that the market of bricks focuses mainly to be used in external walls. These bricks require high technological, environmental and aesthetic properties, so they are resistant to the weather, with no significant leaching of heavy metals caused by the rain.

This paper introduces an experimental investigation at laboratory scale using extreme firing conditions to study the effect of various substitution rates of WS at different moulding conditions (pressure and moulding water) on the technological properties of the ceramic products. An optimization step to select the best moulding conditions and the optimal WS content in the mixture was also conducted. A second lab-scale trial simulating the industrial firing cycle, as well as an industrial trial were performed using the selected products. The technological, chemical and environmental behaviour of these products were assessed and the feasibility of the scale up of the process was evaluated by comparison of results obtained in the lab and industrial scale trials.

Materials and methods

Materials

The clay employed in this work was supplied by the industrial brickwork *Cerámicas de Cabezón* located in Cantabria (Spain). The WS, commercialised as Ferrosita®, was supplied by Befesa Zinc Aser, Abengoa Group, from its Electric Arc Furnace Dust recycling plant (Erandio, Basque Country, Spain). The raw materials were characterized in terms of chemical composition. The particle size of the raw materials (clay and WS) was set below 500μm, in order to avoid the encapsulation of the WS into the ceramic matrix.

The chemical composition of the raw materials (clay and WS) was determined at Activations Laboratories (Canada). Content in major oxides (Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, MnO, Na_2O) were determined by fusion-inductively coupled plasma (FUS-ICP; Thermo Jarrel-Ash ENVIRO II equipment). The contents in Cd, Cu, Mo, Ni, Pb, and Zn were determined using total digestion and ICP (Perkin Elmer SCIEX ELAN 6000). Contents of As and Cr and Cl were determined by non-destructive instrumental neutron activation analysis (INAA). Content in Ba was measured by means of INAA/FUS-ICP while ion selective electrode (ISE) was used in the case of F (Fluorine automatic analyzer from Mandel Scientific). The total content of S was analysed by combustion and infrared detection (IR) (Eltra CS-800 infrared cell).

Ceramic processing

The methodology used in this work is shown in Figure 1. Three different experiments were carried out in this research:

- A first group A) from a preliminary laboratory trial under extreme firing conditions where the WS content was varied from 0 to 50%, the values of the moulding water content were 3, 6 and 9% and the values of the pressure used at moulding stage were 50, 100 and 200 bars. Mixtures were homogenised and pressed using a hydraulic press (Nanetti, Mignon SS/EA). This first group (A) of pressed specimens with cylindrical shape (40 mm diameter and 14 mm thickness) were dried in a muffle furnace at 100ºC during 24 hours and then fired up to 1000ºC with a firing rate of 6ºC/min and a dwell time of 60 minutes, as described in Cheeseman et al., [20];

- In a second laboratory trial, group B) selected mixtures (with WS contents down to 20%) where pressed using a hydraulic press (Nanetti, Mignon SS/EA) at optimum moulding conditions, 6% of moulding water content and a pressure of 100 bars. Pressed specimens (second group) with cylindrical shape (40 mm diameter and 14 mm thickness) were dried in a muffle furnace at 100ºC during 24 hours. Once dried, those pieces were fired simulating industrial firing cycles in a laboratory electric furnace up to 1020ºC with a firing rate of 1.4ºC/min and a dwell time of 210 minutes;

- Mixtures for industrial proof, group C) were prepared by mixing the selected mixtures containing clay and WS (up to 20%) with higher quantity of moulding water (16-20% depending on the WS content) in order to achieve the desired plasticity values (1.4±0.1kg/cm^2) that requires the extrusion moulding method. Subsequently, the mixtures were extruded using a pilot scale extruder (Verdés, 050-C) to produce specimens with rectangular shape, (150mm*30mm*20mm). Extruded samples (third group) were dried in an industrial drying room at 100ºC for 24 hours and then fired using an industrial brick kiln up to 1020ºC at a firing g rate of 1.4ºC/min and a dwell time of 210 minutes (commercial firing cycle employed for the manufacturing of facing bricks).

Properties of the ceramic products

The technological properties of the fired specimens were assessed according to standard procedures. Linear firing shrinkage (LFS) was measured with a precision calliper, water absorption (WA), as specified by UNE 67027, open porosity (OP) by mercury intrusión porosimetry using a Micromeritics AutoPore IV 9500 porosimeter, weight loss during firing (WL) as specified by UNE 772–13, bulk density (BD) was calculated from the weight/volumen ratio as specified by UNE-EN 772–13:2001 and 3-point flexural strength (MOR) as specified by UNE-EN 843–1.

Firstly, the technological properties of the first group A) were assessed, then the WS content and the moulding parameters (water content and pressure of moulding) were optimized using the software GAMS (General Algebraic Modeling System). Optimum mixtures that produce ceramic products with suitable technological properties were selected for further experiments at laboratory, group B), and industrial scale, group C).

The environmental properties assessed were the release of potentially toxic species during their use and leaching of heavy metals after disposal in landfill sites. The environmental behaviour of the fired specimen during its useful life was assessed using the diffusion leaching test NEN 7345 [21] on monolithic materials takes 64 days. During this time the concentrations of the studied pollutants in the leachant were measured at specified times. The cumulative emission values at the end of the test per unit mass over 64 days (E_{64}) in mg/m^2 were calculated and these values were compared with the threshold limits stablished by the Dutch Building Materials Decree [22]. The environmental behaviour of the fired specimen at the end of life was assessed using compliance leaching tests simulating open (EN12457-1) and closed landfill (EN12457-2) conditions on granulated materials milled to below 4 mm to promote contact and leaching of trace elements. Compliance leaching tests were performed using deionized water with liquid/solid ratios L/S=2 and L/S=10, respectively and 24 h stirring [23]. At the end of the test, samples were filtered and the leachates analysed. The pH was measured and pollutants concentrations in the leachates were determined and compared with the regulatory threshold

limits established for close and open landfill conditions [24]. In three leaching tests, concentration values for Ba, Cd, Cr, Cu, Mo, Ni and Zn were determined using ICP Emission Spectrometry (Perkin Elmer Plasma 400), concentration of As, Hg, Pb, Sb and Se by Atomic Absorption (Perkin Elmer 1100B) and concentration values of F-, Cl- and $SO_4^=$ were determined by Ion Chromatography (Dionex DX 120).

Results and discussion

Characterization of raw materials

Table 1 shows the major oxide composition of the raw materials (clay and WS) and the total content of main elements. The clay consisted primarily of silica (SiO_2) (63.6%) and alumina (Al_2O_3) (17.2%) and lower amounts of iron oxide (expressed as Fe_2O_3) (6.1%) and potassium oxide (K_2O) (3.1%), as well as traces (<1.0%) of other oxides like MgO, TiO_2, Na_2O and CaO. The content in sulphur of the clay is 0.196%, while the content in metals (Ba, Zn, Cr, Ni, Pb, Cu, As, Mo and Cd) was found in percentage below 0.1%.

On the contrary, WS consists mainly of Iron oxide (expressed as Fe_2O_3)(52.7%) and CaO (20%), which can act as fluxing agents during firing, favouring the development of a liquid phase and lowering the sintering temperature [14]. WS present lower concentration of (SiO_2) (8.97%) and alumina (Al_2O_3) (2.91%) and higher concentrations of manganese oxide (MnO) (5.08%), magnesium oxide (MgO) (3.11%) when compared with the clay. Other oxides, such as Na_2O, K_2O, TiO_2 and P_2O_5 were detected at concentrations below 1.0%. The content in zinc (Zn) (>1%), sulphur (S) (0.71%), lead (Pb) (>0.5%), copper (Cu) (0.41%) and chromium (Cr) (0.38%) were found above 0.1%, while the content in Ba, Ni, Mo, As and Cd were reported below 0.1%.

On the other hand, the analysis of crystalline phases, has been carried out in previous studies using XRD [14], was qualitative, the intensity of the peaks provided an approximate idea of the contribution of each of the phases in the material. The phase with the greatest contribution is wustite (FeO), followed by calcium silicate (Ca_2SiO_4) and the combined oxide of iron and calcium (Fe_2O_3 $(CaO)_2$). Other phases in a minor proportion are magnetite (Fe_3O_4) and calcium oxide (CaO).

The loss on ignition (LOI) is associated with the presence of clay minerals, hydroxides, organic matter and volatile components. It can be an important parameter to be considered during ceramic processing, with implications in the development of OP, LFS and MOR [16]. The LOI of the clay (6%) corresponds primarily to the loss of crystallisation water and organic matter. The negative LOI value of WS, which amounted up to ~3.7% of the original mass, indicates a weight gain during firing. This could be attributed to the iron oxidation during the thermal treatment, mainly present in the WS as wustite (FeO) to produce magnetite (Fe_3O_4) [14, 15].

Preliminary laboratory trial (group A)

The effect of process parameters on the ceramic properties was studied. Figure 2 shows the dependence of the ceramic properties (weight loss, bulk density and linear firing shrinkage) of the first group of fired products (group A) obtained in a preliminary lab-trial at extreme conditions on three process parameters: WS content, water content and moulding pressure.

In general, the moulding pressure does not show a significant influence in any of the properties of the ceramic products. On the contrary, weight loss (WL) and linear firing shrinkage (LFS) increase with the water content and decrease with the introduction of WS. It is observed that ceramic products with WS content above 30% suffer negative LFS or expansion. These results are attributed to (i) the presence of inert compounds that do not react during firing which does not contribute to the sintering mechanisms, mainly by a viscous type flux vitrification [25] and, (ii) the oxidation of the crystalline phase wustite (FeO) contained in the WS into magnetite (Fe_3O_4) during the firing process [14]. 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).

The Bulk density (BD) of the ceramic products decreases with the water content and it increases with the WS content. This is attributed to the higher density of the WS mainly due to its high iron content (52,7 %). The water absorption (WA) of the ceramic products increases with moulding water content which contributes to higher WL increasing the OP of the products and thus the WA. On the contrary, the evolution of WA is mainly to increase until WS 20% and then decreases with the content of WS. It is due to WS is constituted of hematite, Fe_2O_3, a refractory material that difficult the sintering mechanisms and thus increasing the open porosity which has a direct effect on the WA. However, when the content of WS is higher the LFS of the material is negative, reducing the porosity, increasing the density of the material and reducing the WA [26].

The next step was the optimization of process parameters using software GAMS. The mathematical expressions that relates the physical properties and WS and water content have been obtained by the software TableCurve 3D (Systat software Inc, 2010). The properties BD, LFS and WL can be easily described through linear polynomial equations (with $r^2 > 0.9$) that show the correlation between each property (P) and the WS and moulding water (W) contents. On the contrary, more complex mathematical models are needed in the case of WA. The polynomial coefficients (a-g) of these equations (models) are shown in Table 2. The more complex behaviour of WA was also observed in previous works [16] where more complex equations were needed to model and predict its behaviour as a function of the raw materials content [27].

$$P = a + b * WS + c * W \qquad eq.1$$

$$P = a + b + WS + c * WS^2 + * d * WS^3 + e * WS^4 + f * WS^5 + g * W \qquad eq.2$$

The validity interval of these equations is W between 3 and 9% and WS from 0 to 50%.

Equations 1 and 2 were used to calculate the maximum value of WS content that can be introduced in the ceramic mixtures without detriment of the ceramic properties. The optimization software package used was the General Algebraic Modelling System (GAMS) which is a high-level modelling system for mathematical programming problems and, the problem has been solved within a relative tolerance of 0.01% from the global optimal value.

Table 3 shows the results of the optimization step as well as the lower and upper bounds considered as the technical limits of the physical properties. In order to obtain ceramic products suitable for the intended uses, the ceramic properties must meet the established quality standards. The usual value of BD for facing bricks is in the range 2-2.15g/cm^3. High quality

bricks typically exhibit LFS values below 8% [28, 29] and WA below 16 %. The typical WL on heating for clays used in the manufacture of commercial bricks has been reported to be between 5 and 15% [28,30]. Higher WL values are associated with higher energy consumptions in the firing process and also to higher emission values (CO_2 and volatile organic compounds) while lower weight loss values are found in high density ceramics. Clays with low content in carbonates usually show values of WL close to the lower limit (5%), while high content of carbonates in the clay increases the WL during firing.

Results from the optimization process (Table 3) show that up to 21.5% in weight of WS can be successfully introduced in the ceramic mixture without detriment in the resulting ceramic properties. The use of larger amounts of WS must be avoided due to detrimental changes in the bulk density of the products.

Laboratory simulation of selected mixtures (group B)

Selected mixtures containing up to 20% of WS were pressed at the optimum conditions (6% of water moulding content and 100 bars) simulating the industrial firing cycle of facing bricks at laboratory scale. The technological (WL, WA, LFS, OP, BD and MOR) and environmental (leaching of potential hazardous pollutants during the life use and end of life stages) properties of the ceramic products were assessed.

Figure 3 shows the effect of the WS content on the ceramic properties (weight loss, bulk density and linear firing shrinkage, open porosity and flexural strength) of the second group of pressed specimens. In the same way to the results found in the preliminary lab-trial, both firing shrinkage (LFS) and weight loss (WL) of the ceramic products decrease with the WS content which has a significant effect in the bulk density (BD) that also increases with the WS content. As expected from the prelaminar lab test, the water absorption (WA) and open porosity (OP) of these ceramic products increase with the WS content. On the contrary, the modulus of rupture (MOR) decreases with the WS content. Mechanical strength is strongly dependent on the microstructural characteristics of the fired ceramic. Results indicate that the additions of WS introduce pore or cracks into the ceramic microstructure. This detrimental effect is presumably due to the fact that the WS particles act as major flaws in the ceramic microstructure, concentrating the stresses during the mechanical testing.

The results of the environmental behaviour of ceramic bodies during its useful life using the Dutch diffusion leaching test is summarized in Table 4. It shows the E_{64}value which represents the accumulated concentration of potentially hazardous pollutants (in mg/m^2) calculated from data obtained from samples extracted at specific times during the diffusion leaching test. The results show a high mobility of alkaline, alkaline earth, fluorine, chlorine and sulphate ions. It can be notice that, the reference sample, without WS also presents high E_{64} values for Na, Cl and F. Ceramic products containing 20% of WS show higher mobility of $SO_4^{=}$, and slightly higher of Ca.

The environmental behaviour at the end of the useful life where these materials are considered construction and demolition waste and disposed of landfills is presented in Table 5. In this table is summarized the results of the leaching of potentially hazardous pollutants (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Zn, Cl^-, F^- and $SO_4^{=}$) that are above the detection limit of the equipment used. The concentrations of the elements are obtained from the compliance leaching

tests performed simulating closed (EN 12457-1) and open landfill conditions (EN 12457-2) with liquid to solid ratios of 2 and 10 l/kg, respectively. If the relation between liquid to solid ratio and mobility of pollutants is analysed, it can been seen that in general, the higher the liquid to solid ratio, the higher the leaching of pollutants in the compliance leaching tests. As expected from previous analysis, the higher mobility in the ceramic products is observed for $SO_4^=$, Cl^- and F^- due to its higher contents. The range of pH values of leachates are between 9.30 and 10.10, being smaller for L/S ratio 2 [31].

Independently on the liquid to solid ratio, the WS content increases the leaching of Mo, and $SO_4^=$ in the samples mainly. Previous studies showed that the mobility of Mo is not only dependent on the corresponding contents in the initial mixtures but is also related to certain parameters such as: (i) open porosity or specific surface area [14, 32]; (ii) the presence of alkalis and alkaline earth compounds in the mixtures, which allows the oxidation of molybdenum to Mo (VI) to form soluble molybdates that promote Mo leaching and; (iii) the mineralogical composition of the fired products, namely the amount of the glassy phase, which depends on both the major oxides contents and the firing temperature [17, 33].

Industrial proof of selected ceramic products (group C)

The analysis of the technological properties of selected ceramic products (group B) was performanced in the same way as the group B. Figure 4 shows the effect of the WS content on the ceramic properties (weight loss, bulk density and linear firing shrinkage, open porosity and flexural strength) obtained in the industrial trial using natural gas as fuel. A similar behaviour to the ceramics obtained in the second laboratory trial simulating the industrial firing cycle (group B) is observed for the products obtained at industrial scale. The higher the WS content, the lower the firing shrinkage (LFS), the weight loss (WL) and the flexural strength (MOR) but the higher the bulk density (BD), open porosity (OP) and water absorption (WA).

Most of the technological properties of all the industrial products containing up to 20% of WS meets the lower and upper bounds considered as the limit of the physical properties (see Table 3) established for the most restricted use of clay bricks. However, industrial bricks containing 20% of WS show values of BD and WL that do not fall within the lower and upper limits summarized in Table 3. It should be noticed that even the reference sample containing only clay has WL slightly below the lower limit, so the products obtained do not meet this criterion for brick. The application of the products obtained with WS content, can be different to facing brick, uses that requires high density ceramics.

In the same way as group B species, the analysis of the environmental properties of selected ceramic products was carried out for the group C species, during its useful life using the Dutch diffusion leaching test and at the end of the useful life, simulating closed and open landfill conditions.

The results of the diffusion test, E_{64} accumulated concentration value (mg/m^2), of the species as function of WS content are summarized in Table 4. Most of the potential hazardous pollutants are far below this limit, except for anionic compounds (chlorides, fluorides and sulphates), which exceed the limit value and thus might be considered as critical pollutants. However, the reference sample, without WS, already exceeds the limit for chlorides and fluorides. This is due to the high solubility of alkaline and alkaline earth salt. In fact, the addition of WS reduces the

content in chlorides and fluorides but increases the contents in sulphate and calcium salts, probably by the formation of calcium sulfate, due to the high Ca content in the slag, 20%, which can give rise to efflorescents.

Table 5 shows the results of the leaching of potentially hazardous pollutants at the end of its useful life. As it happened in the case of species of group B, the higher the liquid to solid ratio the higher the leaching of pollutants in the compliance leaching tests. Results from these tests were compared to the threshold limits established for waste acceptance at non-hazardous landfills. Results show that the leaching of most of the metals as well as chlorides, fluorides and sulphates anions is far below the acceptable limits for non-hazardous landfills and, only the leaching of Mo in products containing WS are above the corresponding threshold limit for non-hazardous waste. Mo is considered as a critical pollutant whose leaching needs to be further studied. According to Verbinnen and collegues [34], the addition of stabilizing additives to the initial mixture might be able to decrease oxyanions mobility.

Effect of the trial scale on the properties of selected ceramic products

Laboratory and industrial-scale facing bricks containing up to 20 % were compared in terms of the overall technical performance and the behaviour of the critical environmental pollutants during the useful life, $SO_4^{=}$, Cl^- and F^-, and at the end of life, Mo.

Technological properties: In general, the industrial bricks were found to have higher mechanical resistance (MOR), LFS, WA and OP when compared with the laboratory bricks. The higher strength and LFS values of the industrial-scale bricks may be due to better mixing and compaction in the industrial process [35]. In addition, the more oxidizing atmosphere at laboratory scale favours the oxidation of FeO into Fe_3O_4, increasing the volume but favouring the porosity development in a lesser extent than in the industrial kiln, where the reducing atmosphere favours the reverse reaction, increasing the hollow volume. The lower LFS of the laboratory bricks affects the WA which has the same behaviour as OP. Although there is a pronounced increase in OP of the industrial bricks, a lower decrease in the porosity is observed when 20% of WS is introduced, compared to laboratory bricks. This might be attributed to the higher LFS of the bricks obtained at industrial scale.

On the contrary, laboratory bricks show slightly higher values of BD and surprisingly much higher values of WL compared to the industrial bricks. The lower WL of the industrial bricks might be related to the higher initial water content in the samples.

Environmental performance during the useful life stage: Results show that the mobility of F^-, Cl^- and $SO_4^{=}$ during the diffusion leaching tests is slightly higher at industrial scale. The higher porosity of industrial WS-bricks enhances the solubilisation of chlorine, fluorine and sulphur containing compounds during the diffusion leaching tests.

Environmental performance during the end-of-life stage: As shown in Table 5, Mo is the main pollutant whose mobility is above the threshold limit for non-hazardous materials when WS is added to the clay. Mo leaching values tends to be higher at industrial scale. Again, the higher OP of the industrial products compared to those obtained at laboratory scale might play a key role contributing to their higher Mo leaching.

The characteristics of the industrial bricks confirm substantially the results achieved during the laboratory testing. However, differences in the properties of the bricks obtained at laboratory

and industrial-scale could be attributed to disparities in test methods: (i) moulding process (pressure versus extrusion) that also requires introducing significant differences in the content of the moulding water (6% versus 16-20%) to obtain the plasticity necessary for the extruder, (ii) the kiln environment (electrical versus natural gas), (iii) the cooling rate (natural versus controlled).

The results suggest that the use of WS as alternative raw materials in the production of facing bricks is feasible and could be transferred to the industrial sector for large scale production, taking into account a maximum recommended percentage of 10 % of WS. Higher WS contents strongly affect the reproducibility and scale-up of the laboratory trials due to relevant differences on most of the technological, chemical and environmental properties of the laboratory and industrial bricks.

Conclusions

The present paper assesses the use Fe-rich Slag as a clay substitute for the production of facing bricks at laboratory and industrial scale. Three trials varying the process conditions and the Waelz slag (WS) content have been performed.

A similar behaviour of technological and environmental properties has been observed at laboratory and industrial scale with the introduction of WS. However, ceramic bodies obtained at industrial scale have a higher increase of open porosity (OP) than those obtained at laboratory scale. This difference could be due to differences in the atmosphere of the kilns. The oxidizing atmosphere of the electric oven used at laboratory scale favours the oxidation of FeO in Fe_3O_4, that increase the volume of solid mass; while the reducing atmosphere of industrial facilities promotes the inverse reaction increasing the hollow volume.

Based on these analyses, it can be concluded that WS could be used as alternative raw material on the facing bricks production cycle with high performance up to certain amounts whithout significant detriment on the technological properties of the final products. In addition, the introduction of WS in clay bricks seems to be easily scaled-up for additions of WS $\leq$10%. The addition of 20% of WS promotes relevant differences in the properties of the laboratory and industrial bricks. The main technical limitation of the use of 20% of WS is the increase in the weight loss (WL) whose value does not fall within the lower and upper limits. From the environmental point of view, only Mo is considered as a critical pollutant at the end of life stage (landfill), not, on the other hand, during the useful life stage. The difference in behavior can be attributed to the fact that in one scenario the test is performed on monolithic material and in the other on granular material milled below 4 mm. While the anions, only, according to the limits proposed by BMD, not currently regulated, its behaviour presents a limitation in its utilization stage, due to the formation of salts on the surface of the products, called eflorescences. Further studies are being performed to evaluate the potential benefits of the use of additives to decrease the Mo leaching from the ceramic products for non-hazardous waste landfill, as well as avoiding the presence of efflorescents on the surface, and in this way not limit the scenarios of use of the products final ceramics

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FIGURE CAPTIONS

Figure 1. Experimental methodology scheme used in this work.

Figure 2. Mechanical properties, linear firing shrinkage (LFS, weight loss (WL), bulk density (BD) and water absorption (WA), of the first group of pressed ceramics obtained in the preliminary lab-trial performed at extreme firing conditions (up to 100ºC, at 6ºC/min, 1h dwell time), as function of the Waelz slag (WS) content, moulding pressure and water content.

Figure 3. Mechanical properties, (LFS, weight loss (WL), bulk density (BD) and water absorption (WA), mechanical strength (MOR) and open porosity (OP), of the second group of pressed ceramics obtained in the second lab-trial simulating the industrial firing conditions of facing bricks, as function of the Waelz slag (WS) content.

Figure 4. Mechanical properties, (LFS, weight loss (WL), bulk density (BD) and water absorption (WA), mechanical strength (MOR) and open porosity (OP), of the third group of extruded ceramics obtained in the industrial trial (facing bricks process), as function of the Waelz slag (WS) content

TABLE CAPTIONS

Table 1. Major oxides and traces elements composition (Wt.%) of the clay and Waelz slag (WS)

Table 2. Coefficients and r2 values of the equations of the technological properties (bulk density, wáter absorption, linear firing shrinkage and weight loss), of products obtained in the first groupof pressed ceramics obtained at extreme firing conditions (up to 100ºC, at 6ºC/min, 1h dwell time) in laboratory trials, as function of the Waelz slag (WS) content and moulding water content.

Table 3. Optimum values obtained from the optimization program as well as the lower and upper limits according to brick quality standards.

Table 4. Cumulative concentration (E_{64} mg/m^2) of the second group of pressed ceramics obtained in the second lab-trial simulating the industrial firing conditions of facing bricks, as function of the Waelz slag (WS) content and the third group of extruded ceramics obtained in the industrial trial (facing bricks process), as function of the Waelz slag (WS) content.

Table 5. Concentration (mg/kg) of components (Compliance leaching test) of the second group of pressed ceramics obtained in the second lab-trial simulating the industrial firing conditions of facing bricks and of the third group of extruded ceramics obtained in the industrial trial (facing bricks process), as function of the Waelz slag (WS) content.

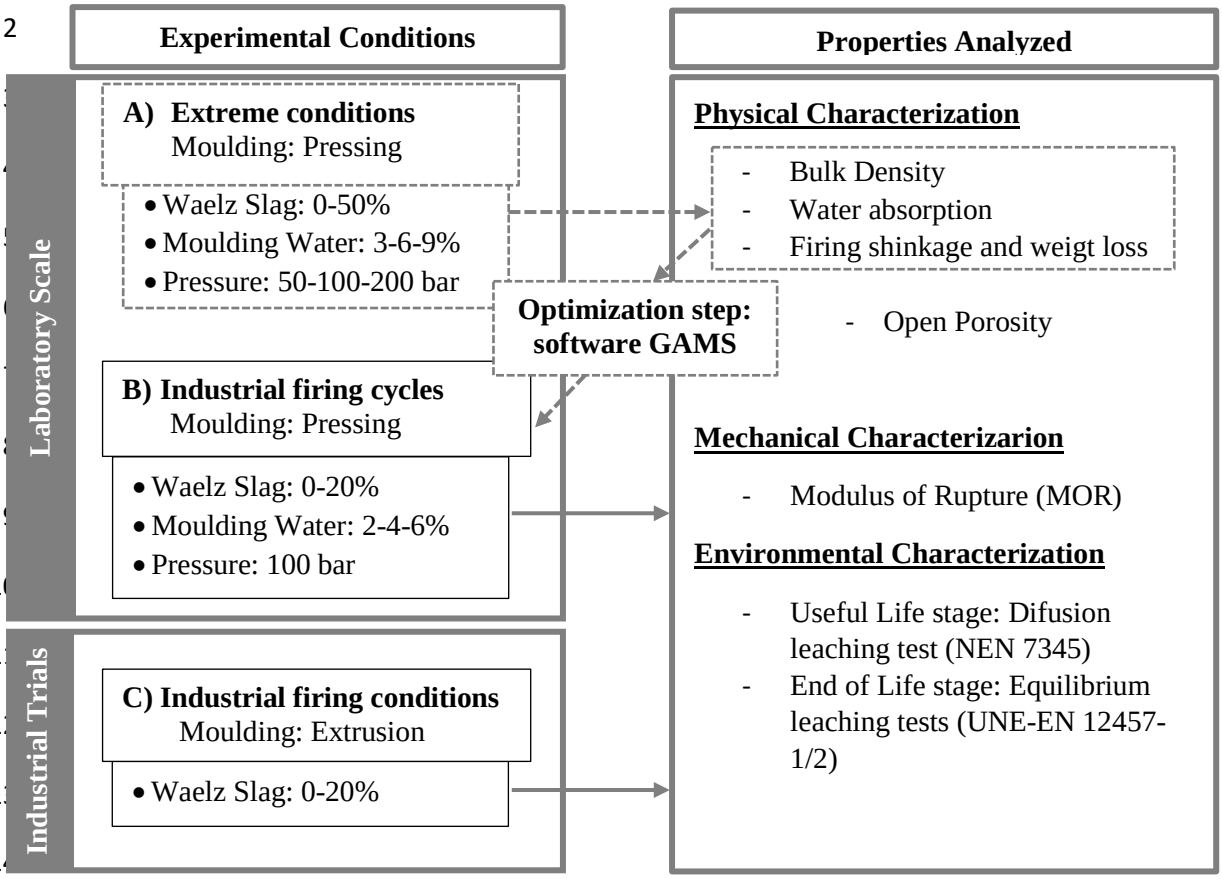

Figure 1. Experimental methodology scheme used in this work.

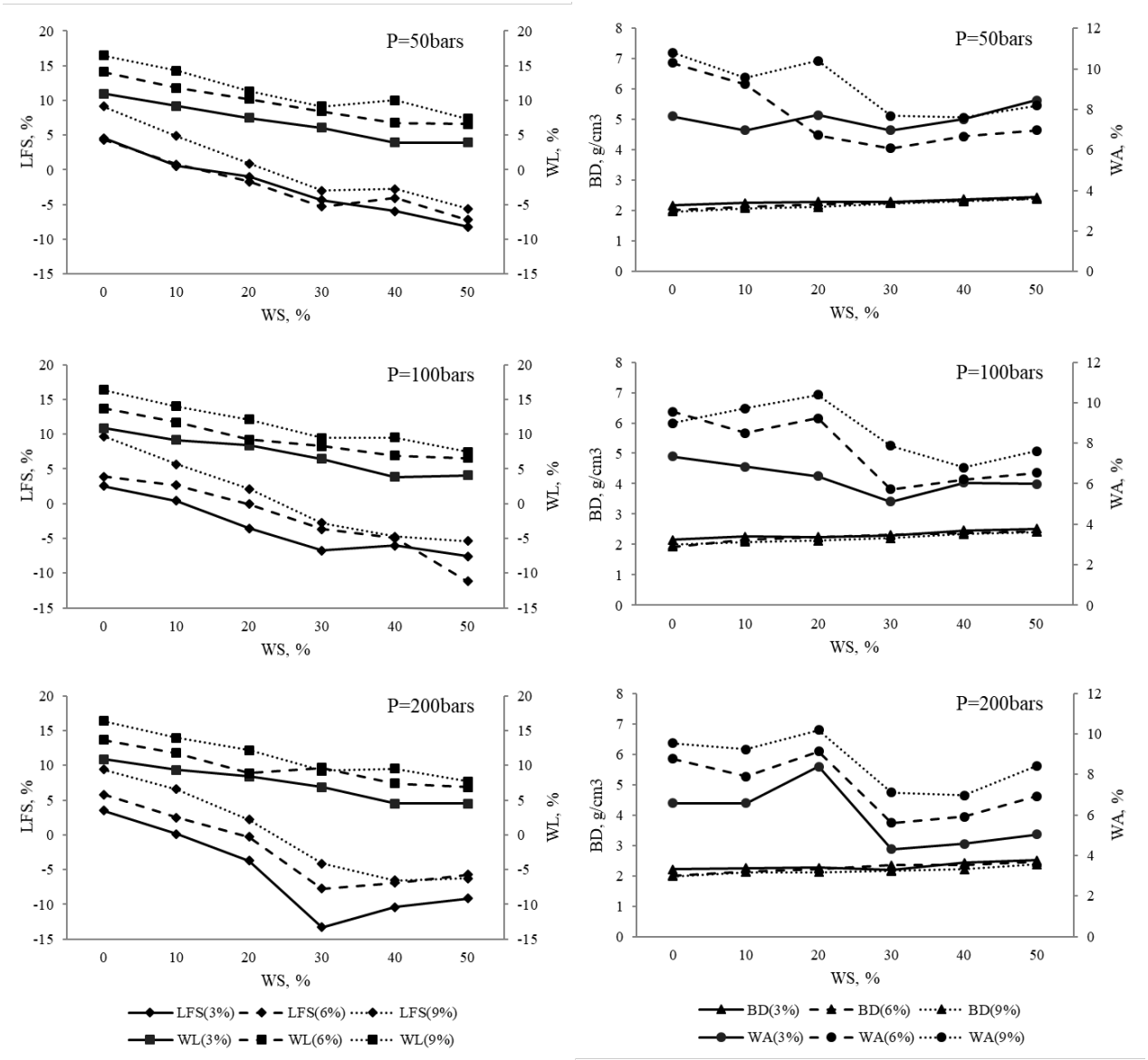

Figure 2. Mechanical properties, linear firing shrinkage (LFS), weight loss (WL), bulk density (BD) and water absorption (WA), of the group A of pressed ceramics obtained in the preliminary lab-trial performed at extreme firing conditions (up to 100ºC, at 6ºC/min, 1h dwell time), as function of the Waelz slag (WS) content (%), moulding pressure (bar) and water content (%).

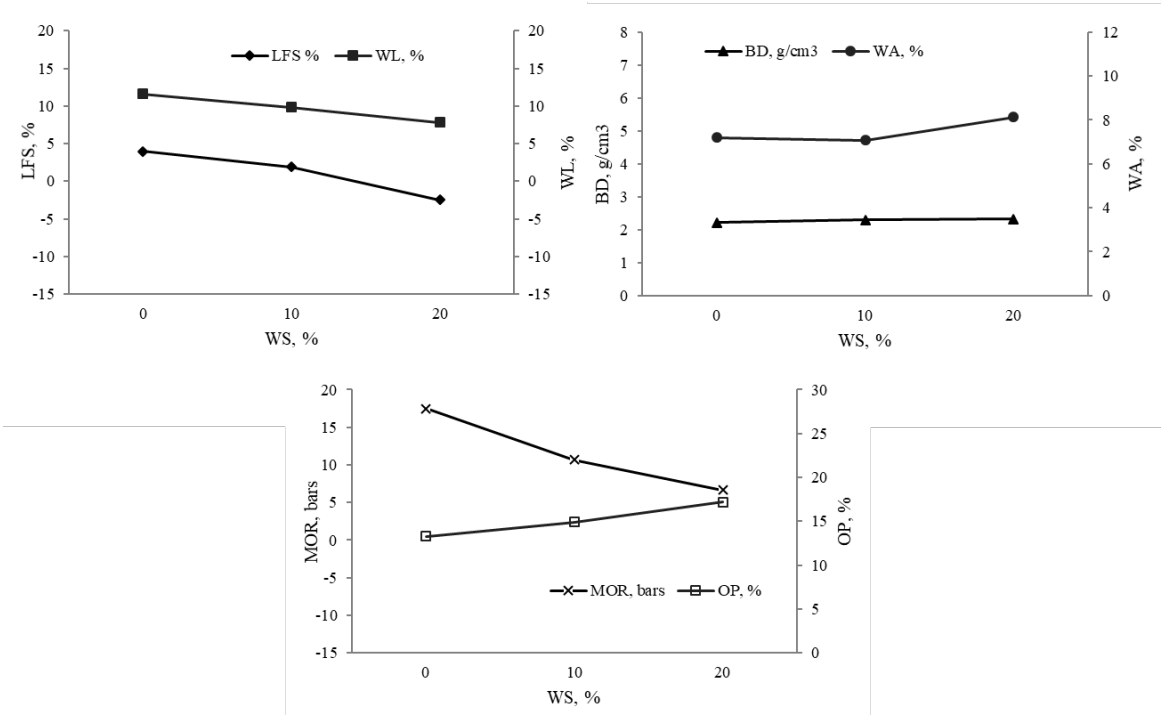

Figure 3. Mechanical properties, (LFS), weight loss (WL), bulk density (BD) and water absorption (WA), mechanical strength (MOR) and open porosity (OP), of the group B of pressed ceramics obtained in the second lab-trial simulating the industrial firing conditions of facing bricks, as function of the Waelz slag (WS) content.

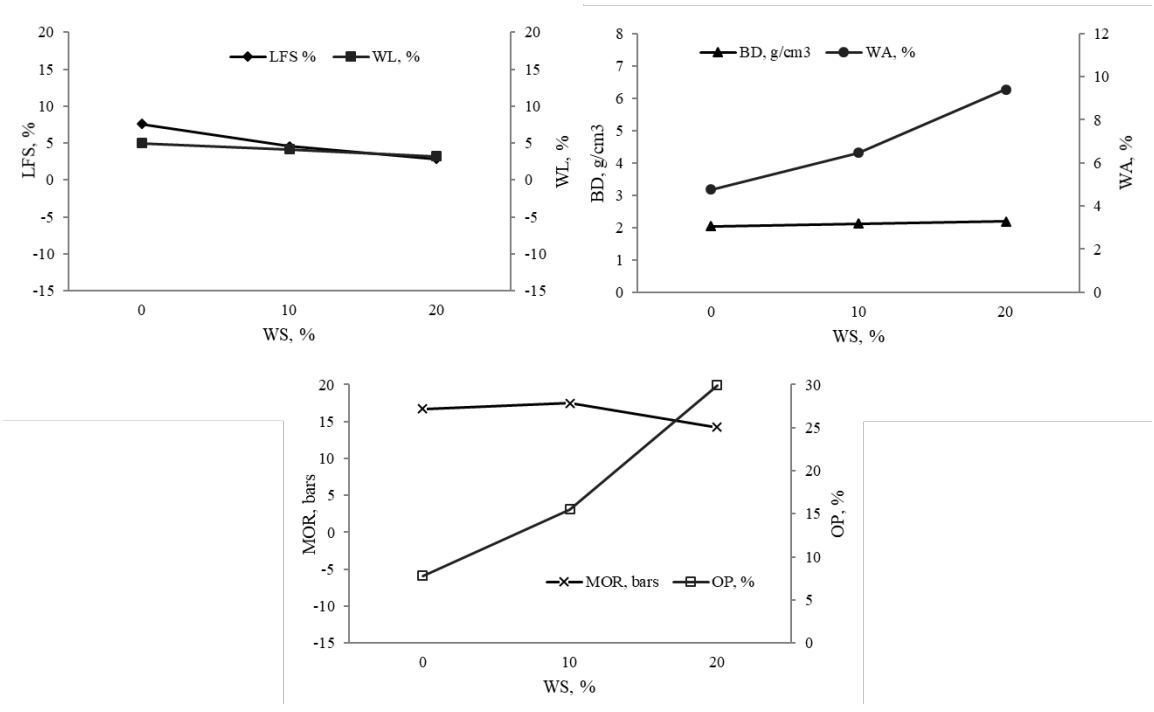

Figure 4. Mechanical properties, (LFS), weight loss (WL), bulk density (BD) and water absorption (WA), mechanical strength (MOR) and open porosity (OP), of the group C of extruded ceramics obtained in the industrial trial (facing bricks process), as function of the Waelz slag (WS) content.

Table 1. Major oxides and traces elements composition (Wt.%) of the clay and Waelz slag (WS)

Composition (Wt.%)	**Clay**	**WS**
Fe_2O_3*	6.06	52.74
CaO	0.57	20.03
SiO_2	63.58	8.97
ZnO	0.02	5.10
MnO	0.07	5.08
MgO	0.97	3.11
Al_2O_3	17.16	2.91
PbO	<0.1	2.20
Na_2O	0.63	0.49
P_2O_5	0.12	0.45
TiO_2	0.85	0.21
K_2O	3.08	0.1
TOTAL	93.09	94.09
LOI (1000ºC)	6.03	-3.69
Trace elements (Wt.%)		
S	0.196	0.710
Cl	0.02	0.49
F	0.05	0.44
Cu	0.00221	0.41
Cr	0.00336	0.38
Ba	0.0599	0.091
Ni	0.00324	0.043
Mo	0.00011	0.011
As	0.00203	0.0062
Cd	0.000025	0.00011

Table 2. Coefficients and r^2 values of the equations of the technical properties (bulk density, water absorption, linear firing shrinkage and weight loss), of products obtained in the first groupof pressed ceramics obtained at extreme firing conditions (up to 100ºC, at 6ºC/min, 1h dwell time), in laboratory trials, as function of the Waelz slag (WS) content and moulding water content.

Property (y)	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**r^2**
Bulk Density	2.190	$7.3\ 10^{-3}$	-0.022					0.93
Water Absorption	6.680	-0.810	0.140	$-8.9\ 10^{-3}$	$1.84\ 10^{-6}$	$-1.45\ 10^{-3}$	0.356	0.92
Linear firing Shrinkage	0.810	-0.277	0.715					0.93
Weight Loss	8.970	-0.150	0.714					0.96

Table 3. Optimum values obtained from the optimization program as well as the lower and upper limits according to brick quality standards.

Variables	Lower limits	Upper limits	Optimal values
WS (%)	0	50	21.5
Moulding water (%)	3	9	6
Bulk density (g/cm^3)	2	2.15	2.15
Weight loss (%)	5	15	12.10
Linear firing shrinkage (%)	n.a.	8	1.27
Water absorption (%)	n.a.	16	9.36

n.a. not applicable

Table 4. Cumulative concentration (E_{64} mg/m^2) of the second group of pressed ceramics obtained in the second lab-trial simulating the industrial firing conditions of facing bricks, as function of the Waelz slag (WS) content and the third group of extruded ceramics obtained in the industrial trial (facing bricks process), as function of the Waelz slag (WS) content.

	WS content						
Components	**Second group lab trial**			**Third group industrial trial**			**Limits**
	0%	**10%**	**20%**	**0%**	**10%**	**20%**	**BMD***
Cr	<DL	<DL	<DL	<DL	<DL	<DL	1500
Zn	53	38.3	37.2	54.7	50.3	36.2	2100
Cd	<DL	<DL	<DL	<DL	<DL	<DL	12
Co	15.2	14.8	15.6	13.5	14.1	14.7	n.a.
Ni	<DL	<DL	<DL	<DL	<DL	<DL	525
Ba	<DL	<DL	<DL	<DL	<DL	<DL	6300
Fe	40	41.4	39	38	42.3	37.9	n.a.
Mn	<DL	<DL	<DL	<DL	<DL	<DL	n.a.
Mg	140.4	125.8	78.6	187	185	225	n.a.
Mo	42	35.5	34.6	35.2	37.1	41	150
Al	44.9	35.2	36.8	33.6	36	45.8	n.a.
V	47.4	41.1	41.3	39.9	41.5	48.6	n.a.
Ca	10,183	21,351	34,957	6,481	12,778	24,539	n.a.
Hg	<DL	<DL	<DL	<DL	<DL	<DL	20
Cu	<DL	<DL	<DL	<DL	<DL	<DL	540
Sr	<DL	<DL	<DL	<DL	<DL	<DL	n.a.
Pb	8	6.3	3.7	5.9	6.2	1.1	1275
Se	3.8	3.9	4	3.5	3.7	4.5	15
As	6.7	6.5	6.9	6.6	5.5	5.0	435
Sb	5.5	4.7	4.8	5.4	6.7	5.1	39
Na	494	313	294	672	492	542	n.a.
K	81.8	78.1	63.2	106.7	115.9	138.5	n.a.
F^-	2063	2156	2356	2,834	1,941	1,322	140
Cl^-	46,023	44,457	38,144	46,971	46,552	31,037	30,000
$SO_4^=$	33,692	54,534	75,177	38,376	39,798	65,922	45,000

(<DL) below the detection limits; (n.a.) not applicable; *BMD: Building Materials Decree thresholds

Table 5. Concentration (mg/kg) of components (Compliance leaching test) of the second group of pressed ceramics obtained in the second lab-trial simulating the industrial firing conditions of facing bricks and of the third group of extruded ceramics obtained in the industrial trial (facing bricks process), as function of the Waelz slag (WS) content.

Compounds	Second group lab trial						Third group industrial trial							
	L/S=2			L/S=10			L/S=2			L/S=10			Limits, NHL*	
WSC	0%	10%	20%	0%	10%	20%	0%	10%	20%	0%	10%	20%	L/S=2	L/S=10
As	0.069	0.063	0.039	0.393	0.256	0.171	0.10	0.095	0.071	0.42	0.39	0.34	0.4	2
Ba	<DL	0.466	0.387	<DL	0.61	3.10	0.35	0.37	0.34	0.61	1.22	1.80	30	100
Cr	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.46	<DL	<DL	<DL	4	10
Mo	<DL	4.456	88.33	3.21	5.72	20.92	<DL	6.70	17.46	<DL	10.21	29.41	5	10
Sb	0.0037	0.0099	0.0045	0.021	0.036	0.022	0.013	0.016	0.013	0.024	0.027	0.038	0.7	0.7
Se	0.0092	0.0086	0.0101	0.036	0.054	0.049	<DL	<DL	0.012	<DL	<DL	<DL	0.3	0.5
Zn	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.060	<DL	<DL	2.20	25	50
Cl^-	342.6	380.5	327.9	1601.0	1888.0	1608.0	29.07	22.81	21.68	136.5	103.1	103.9	10,000	15,000
F^-	11.20	10.5	10.3	<DL	<DL	48.00	5.13	4.70	3.35	13.80	11.55	9.65	60	150
$SO_4^=$	574.2	1509.8	2315.6	935.0	6173.5	6517.0	1115	2526	2987	1369	3144	4469	10,000	20,000

(<DL) below the detection limits; * Non-hazardous threshold for closed and open landfills