

Technological and Environmental Behaviour of Traditional Ceramic Bodies Obtained by Recycling of Two Types of Residues

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Abstract: In this research we evaluated the feasibility of incorporating MSW fly ashes and copper slag in the manufacture of traditional ceramic materials, in addition to assessing the immobilization of As and Pb in tiles, linear contraction, bending strength and water absorption (WA), were measured. A decrease in the WA was obtained by increasing the addition of both residues. It is feasible to substitute around 40% of standard clay for these by-products, with an improvement in the technical specifications of the specimens compared to the ceramic bodies manufactured without adding by-products. Furthermore, the immobilization of arsenic and lead was tested in the fired bodies. The immobilization of both elements improves as the firing temperature increases, as evidenced by the leaching tests. Regarding the Pb and As content, all the tested samples comply with established limits for non-hazardous landfill waste (Spanish laws).

Keywords: fly ashes; copper slag; ceramic behaviour; leaching tests; recycling wastes



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1. Introduction

The management and minimization of MSW (municipal solid waste) has become a huge problem at the global level, brought on by the increase in large cities in the world and the growth of industrialization and urbanization. The production of MSW in Spain is up to 21 million tons/year. Around 30% of these residues are sent to composting plants and around 6% are intended for incineration [1,2]. Incineration reduces the volume of residue by 90% but generates new wastes: fly ashes and sludge. The fly ash production is around 25 or 30 kg per incinerated ton. The fly ashes contain Al_2O_3 , CaO and SiO_2 together with metalloids, metals and dangerous organic compounds. The most beneficial protocol would be to transform this waste into a useful and inert raw material for the manufacturing of ceramics [3–5]. Furthermore, pyrometallurgical processes produce a high content of slag [6]. Modern primary smelters generate around 2500 kg of copper slag (Cu-slag) for 1000 kg of Cu generated [6]. Recycling of the cited by-products has environmental and economic benefits. For example, in construction, slags can be used as abrasive material, filler material [7] or in the production of mortars and concretes. Slags with high SiO_2 (9–69%) and FeO (0.6–65%) content are more common. The presence of Cu, Zn, Ni and Pb and As in this waste make it an important environmental pollutant [8]. The ceramic industries have great potential to absorb mining, industrial or incineration plant by-products. However, the use of these residues in the manufacture of ceramic bricks is very scarce or non-existent in some European countries.

This work presents the results obtained after replacing a high percentage of clay rich in carbonates and silica with Cu-slag and MSW fly ashes. The aim of this paper is to improve and test some technological properties and to test the immobilization processes of toxic elements (As and Pb) contained in contaminating wastes at different fired cycles.

The highlights of this note are (a) to valorise and give new uses to two types of waste that are very harmful to the health of humans, animals and ecosystems and (b) to improve the technological properties of ceramic test bodies made with these residues to enable formulation of compositions on demand to give constructive solutions in the manufacture of bricks, roofing tiles and ceramic flooring and coatings.

2. Materials and Methods

Selected MSW fly ash and Cu-slag samples were dried in a laboratory stove at 115 °C and subsequently ground using a ball mill. The chemical analysis of Cu-slag, fly ash and clay (Table 1) was accomplished by a PW1606 X-fluorescence (Philips, Eindhoven, The Netherlands) and ICP-MS (PerkinElmer, Glenbrook, CT, USA). The soluble SO_4^{2-} and Cl^- and were analysed by gravimetry and titration, respectively. The CaCO_3 percentage was calculated by calcimetry. Total organic matter was measured by calcination at 500 °C. The loss-on-ignition (LOI) was determined at 1000 °C.

Table 1. Chemical composition of ceramic clay, MSW fly ash and copper sludge used in the formulation of compositions.

Ceramic Clay	
SiO_2	52.59 (%)
Al_2O_3	15.85 (%)
Fe_2O_3	5.95 (%)
CaO	12.29 (%)
MgO	1.95 (%)
Na_2O	0.373 (%)
K_2O	5.20 (%)
P_2O_5	0.225 (%)
Total SO_3	0.650 (%)
O.M. 500 °C	2.00 (%)
LOI (1000 °C)	12.20 (%)
CaCO_3	26.00 (%)
SO_4^{2-} (solubles)	4420 (ppm)
Cl^- (solubles)	139.90 (ppm)
MSW Fly Ash	
O.M. 500 °C	42.50 (%)
LOI (1000 °C)	63.97 (%)
CaCO_3	8.96 (%)
SO_4^{2-} (solubles)	8055 (ppm)
Cl^- (solubles)	739.1 (ppm)
SiO_2	12.55 (%)
Al_2O_3	45.30 (%)
Fe	9281 (mg/kg)
Ca	57 (mg/kg)
Mg	43 (mg/kg)
Na	1231 (mg/kg)
K	2325 (mg/kg)
P	32.36 (mg/kg)
Cu	91 (mg/kg)
Zn	166 (mg/kg)
Pb	49 (mg/kg)
Hg	0.25 (mg/kg)
As	0.22 (mg/kg)
Cd	3.38 (mg/kg)

Table 1. Cont.

Cu-Slag	
SiO ₂	51.07 (%)
Fe ₂ O ₃	17.19 (%)
CaO	18.33 (%)
MgO	1.10 (%)
K ₂ O	2.19 (%)
CuO	0.92 (%)
SO ₃	0.15 (%)
Al ₂ O ₃	8.95 (%)
Zn	0.20 (%)
Co ₃ O ₄	0.08 (%)
PbO	0.31 (%)
As ₂ O ₃	0.49 (%)
LOI	−1.17 (%)

The mineralogical characterization of the selected clay was determined by X-ray diffraction (Cu-K α radiation 50 kV, 30 mA) using a Siemens device (Siemens D5000D, Berlin, Germany). Different treatments were prepared for clay minerals analysis. Mixtures and firing cycles were design based on previous own experiences and revised literature [3,4]. Experimental tests were performed on several mixtures of clay + MSW fly ash + Cu-slag. The formulations for ceramic tests consisted of the following compositions with Cu-slag: 0 (control), 15, 20, 25, 30 and 35% (wt.%), and MSW fly ash waste: 0 (control), 1, 2, 3, 4, 5 and 10 (wt.%). The first step was drying for 24 h at room temperature and the second stage was oven drying to 105 °C (heating speed: 8 °C/h). This two-stage process is commonly used in the brick and ceramic tile industry. In stage 1 the drying rate is rapid and constant as water evaporates from the surface into the surrounding air and water from the interior migrates by capillary action to the surface to replace it. In stage 2 the moisture content is reduced to where the ceramic grains are in contact. The green test bodies (unfired) were pressed using a uniaxial press. A firing cycle was designed (Troom–500 °C: 2 h; 500–650 °C: 2 h; 650–Tmax: 2 h; Tmax: 900, 950, 1000 and 1050 °C over 4 h following normal European industrial practice. Figure 1 shows the aspect of test bodied fired at different temperatures (900, 950, 1000 and 1050 °C).

The linear contraction was tested following the methodology described in [4,9] for dried (D.L.C.) and heated (H.L.C.) tiles. The WA (%) has measured following UNE-EN ISO 10545-3:2018 [10]. Bending or Flexural strength (σ_f) was tested using an INSTRON 1011. All determinations were carried out in triplicate. Studied residues contain significant amounts of pollutants, mainly Pb and As. The mobility of a toxic element defines its dangerousness. Therefore, a test of pH dependence was carried out. For the powder mixtures tested, the initial pH value was up to 9. HNO₃ (5 mol/L) was added to reduce pH. The significant content of CaCO₃ present in both fly ash (7%) and clay (>22%) neutralizes this chemical reaction, and Ca(NO₃)₂ is formed. Dangerous and toxic elements leaching were evaluated using the equilibrium leaching tests following the UNE-ENVI 12506: 2001 [11]. Samples were sieved (particle size of at least 95% (mass) < 10 mm) and dried at a temperature < 40 °C. These samples were placed in polyethylene bottles together with water (liquid/solid ratio = 10 L/kg). A shaking device was used to shake the bottles for 24 h. Finally, solid particles were allowed to settle for 15 min and the eluate was filtered through 0.45 μ m membrane filters in a vacuum device. ICP-MS determinations were carried out with matrix-matched standards. The recovery values of the elements were quantified, and the relative standard deviations were calculated.

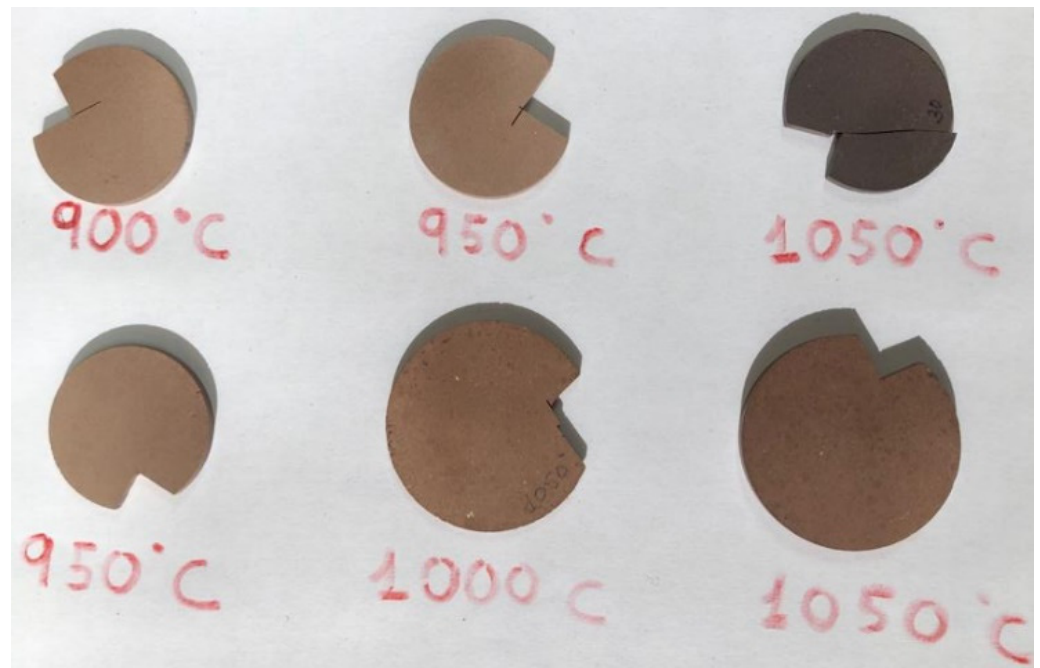


Figure 1. Test bodies fired at different temperatures.

3. Results and Discussion

The selected clay, which is rich in SiO_2 and CaCO_3 with an appreciable Fe_2O_3 content gives rise, after firing, to red pastes. The main mineral phases present were quartz, hematite, clay minerals (illite, chlorite and kaolinite) and low quantities of dolomite, feldspar and calcite. Fly ash comes from MSWI having mixture of crystalline and amorphous phases; mostly amorphousness is higher than 50%, composed of aluminous silicate with silicate material and sulphates. The selected MSW fly ashes have low values of Pb, Cu, Zn, and Hg compared to the contents reported in the literature [1,2]. The mineralogy of the selected fly ash was: quartz (SiO_2), silvine (KCl), anhydrite (CaSO_4), fluorite ($\text{Ca}(\text{OH})_2$), CaClOH and halite (NaCl). XRD patterns of clay, MSW fly ash and Cu-slag can be found in an article published previously [12]. Copper slag is predominantly composed of SiO_2 (>50%), Fe_2O_3 (>17%), CaO (>15%), Al_2O_3 (>8), K_2O (>2%) and MgO (1%). ZnO and CuO are present in percentages less than 1%. However, Pb and As are considered environmental pollutants. The chemical composition of the analysed Cu-slag is different to other standard slags. The standard massive Cu-slag has a chemical composition dominated by FeO (>52 wt.%), SiO_2 (>45 wt.%) and Al_2O_3 (>12 wt.%). It comprises two types of silicate glass, olivine, ferrosilite, fayalite, cristobalite and quartz. The mineralogy of the selected Cu-slag is defined by the presence of cristobalite (SiO_2), clinoferrosilite (FeSiO_3), magnetite (Fe_2O_4) and fayalite (Fe_2SiO_4). Traces of wollastonite (CaSiO_3) and feldspar as microcline (KAlSi_3O_8) were also found.

Figure 2a shows the evolution of values of linear contraction for the control and for the rest of the mixtures tested, which were in the normal range (<10%). Figure 2b shows a clear tendency to a reduction in open porosity when the content of added by-products increases. Consulting the UNE 136020: 2004. CTN 136- Clay products for construction [13], technicians can find specifications that must be met by construction materials, which opens a great versatility of choice of raw materials and by-products to reach the required standards.

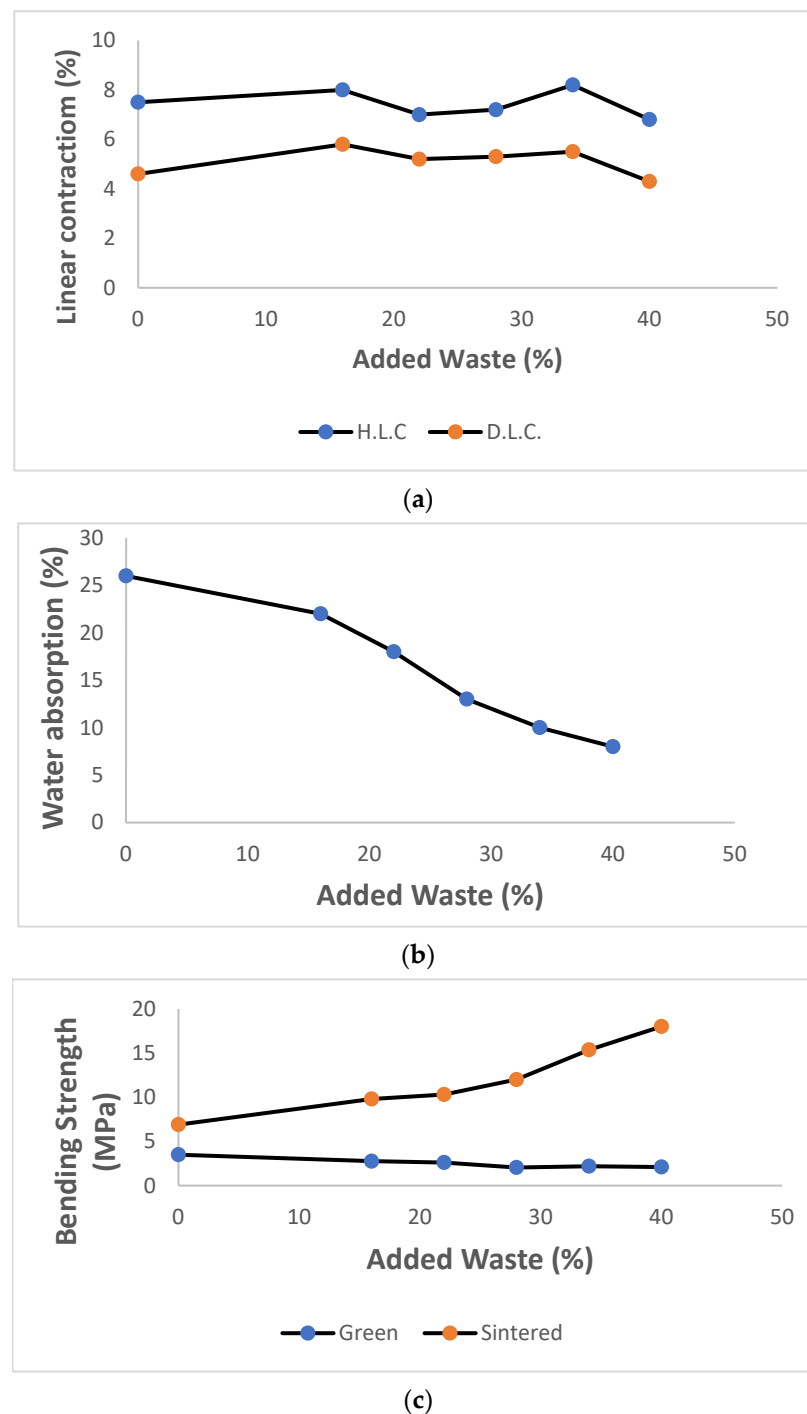


Figure 2. Technological properties for (a) LC at 1050 °C (%), (b) WA (%) at 1050 °C and (c) bending/flexural strength at 1050 °C. Legend: Green—unfired tiles; Sintered—fired tiles.

With the introduction of 3% MSW fly ash + 25% of Cu-slag (28% wastes + 12% clay), the WA value was around 13.2%. This is a good value for structural ceramic materials used in building [13,14]. The addition of these residues makes it possible to obtain structural ceramic materials, which was impossible using only clayey raw materials with a moderate or high content of carbonates [13].

The incorporation of these residues makes it possible to achieve much lower WA values at a similar firing temperature, contributing considerably to the reduction in energy costs and greenhouse gas emissions [5]. The addition of wastes improves flexural strength (Figure 2c). With a proper management in the incorporation of selected wastes, following

the specific materials' international regulations, it is possible to manufacture different types of building materials [5].

Currently with the selected clay it is possible to manufacture non-structural ceramics (e.g., ceramic tiles, pavements and ceramic coatings). With the addition of selected mixture of wastes, the water absorption capacity (WA) and mechanical resistance (bending strength) were significantly improved. However, the additional advantage is that with the addition of 28% of by-products it is feasible to obtain structural ceramics (e.g., solid brick blocks) complying with the technical specifications regulated in the technical code for building materials.

Table 2 shows the test bodies and discharge limit regulations for As and Pb together with Co, Cd and Zn leachate amounts for all firing cycles and formulations tested. All regulations for building-residue landfills have been consulted, taking into consideration the future destination of eco-materials produced using toxic residues at the end of their life cycle. All materials tested comply with the current regulations for disposal in landfills (non-hazardous waste) regarding the Pb and As contents. Arsenic and lead have been immobilized in ceramic bodies fired at temperatures of 1000 and 1050 °C. The behaviour of the fired bodies fits well within regulations for their disposal in inert-residue landfills. No clear results were observed in other metals (* Co, * Cd, ** Cu and * Zn, * Leachates conc. of Cd, Zn and Co: <0.02 mg/L, ** Leachates conc. of Cu: <0.10 mg/L.), due to their low concentrations in solution. Different studies have demonstrated that leachate pH is a determinant of the solubility of some elements [8]. Probably, in the As and Pb immobilization process the role played by CaO present in clay and ashes is a determinant of their inertisation [8].

Table 2. Arsenic (As) and lead (Pb) levels (mg/kg) in tests and discharge limits regulated in Spain (BOE, number 97, 23 April 2013, Ministerial Order AAA/661/2013). Legend: W (control, 0%); A (16%), B (22%), C (28%), D (34%) and E (40%).

Tmax: 900 °C Added By-Products (%)	As	Pb	pH Values
W	0.1 ± 0.05	0.08 ± 0.02	7.8 ± 0.2
A	0.59 ± 0.02	0.09 ± 0.02	7.7 ± 0.2
B	0.73 ± 0.03	0.46 ± 0.01	7.9 ± 0.1
C	0.79 ± 0.01	0.65 ± 0.03	8.1 ± 0.2
D	1.2 ± 0.02	0.73 ± 0.01	8.5 ± 0.3
E	1.3 ± 0.05	0.81 ± 0.04	8.7 ± 0.2
Tmax: 950 °C			
W	0.21 ± 0.06	0.06 ± 0.02	7.5 ± 0.3
A	0.35 ± 0.05	0.09 ± 0.01	7.6 ± 0.4
B	0.51 ± 0.03	0.33 ± 0.03	7.8 ± 0.1
C	0.62 ± 0.02	0.52 ± 0.02	8.1 ± 0.3
D	0.82 ± 0.03	0.63 ± 0.01	8.2 ± 0.1
E	0.93 ± 0.06	0.72 ± 0.04	8.3 ± 0.2
Tmax: 1000 °C			
W	0.11 ± 0.02	<0.05	7.4 ± 0.2
A	0.14 ± 0.04	<0.05	7.5 ± 0.1
B	0.23 ± 0.02	<0.05	7.7 ± 0.1
C	0.34 ± 0.04	<0.05	7.8 ± 0.2
D	0.43 ± 0.01	<0.05	8.1 ± 0.1
E	0.49 ± 0.05	<0.05	8.2 ± 0.3
Tmax: 1050 °C			
W	0.04 ± 0.01	<0.05	7.2 ± 0.1
A	0.12 ± 0.02	<0.05	7.4 ± 0.2
B	0.13 ± 0.02	<0.05	7.6 ± 0.3
C	0.19 ± 0.01	<0.05	7.8 ± 0.2
D	0.23 ± 0.03	<0.05	7.9 ± 0.1
E	0.39 ± 0.04	<0.05	7.8 ± 0.2

Table 2. Cont.

Tmax: 900 °C Added By-Products (%)	As	Pb	pH Values
Inert wastes landfill	0.5	0.5	Limits regulated
Non-hazardous wastes landfill	0.2	10	

4. Conclusions

The addition of Cu-slag and MSW fly ashes makes it possible to obtain improved performance in the manufacture of structural ceramics. Pb and As were immobilized during the firing process in bodies fired at 1000 and 1050 °C (A, B, C, and E mixtures). The ceramic industry has great potential to absorb by-products. However, the use of these residues in the manufacture of ceramic bricks, roofing tiles and ceramic flooring and coatings is very scarce or non-existent in some European and other countries. The addition of this kind of residue improves the technological properties giving rise to a wide range of available building materials with higher added value using the same industrial firing cycles [13,14]. Another advantage is that with the addition of selected by-product mixtures, it is feasible to obtain solid brick blocks. The last step of this research is working with industrial-sized ceramic bodies. It will be necessary to carry out a proof of concept together with the ceramic industry in a pilot plan. This would be the last step in bringing this experimental product to market. It is necessary to create a culture of waste recycling in the industry as well as to promote the commitment to the circular economy and responsible consumption.

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