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Research paper

Valorization and inertization of galvanic sludge waste in clay bricks

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ABSTRACT

Galvanic sludge wastes (GSW) are produced by the physico-chemical treatments of wastewater generated by electroplating plants. These materials have a significant potential for the production of clay ceramic bricks. This paper focuses on the viability of the inertization of heavy metals from GSW mixed with clays. The original materials were obtained by mixing three types of raw clay (red, yellow and black) in equal parts with GSW. These mixtures were characterized by XRD, XRF, and chemical elemental analysis CHNS. The dosage of GSW in the clay–GSW bricks was up to 5 wt.%. The bricks were then manufactured using conventional processes. The influence of the amount of GSW was evaluated after firing the clay–GSW composites at 950 °C for 1 h. The engineering properties of the fired samples, such as density, water absorption, open porosity, water suction and compressive strength, with and without the GSW, were determined. The incorporation of GSW into the clay mix clearly decreased the linear shrinkage and bulk density of the bricks in comparison with the fired clay used as a control. These GSW–clay composites also showed lower open porosity. According to the results obtained for the bulk density of the bricks, samples with GSW addition showed slightly lower values of open porosity than clay bodies, indicating that the GSW–clay samples had slightly higher closed porosity values. This was also shown by SEM. The open porosity, SEM and pore size distribution tests indicated that the porosity generated by the addition of GSW was mainly closed and, therefore, GSW bricks had excellent mechanical properties. The environmental risks of the incorporation of GSW, rich in heavy metals (Cr, Zn, Ni and others), to a clay matrix were evaluated by leaching tests of the fired products. The results indicated a successful inertization of the pollutants.

1. Introduction

Galvanization and surface treatments prevent corrosion in metals and alloys. These processes consume a large amount of water in the processes of production, as well as in washing steps (Ribeiro et al., 2004). This results in large amounts of wastewater, which needs a series of treatments to reach the environmental requirements before being discharged out of the plant. In addition, large amount of sludges is produced by the physico-chemical treatment of wastewater generated in electroplating plants. These sludges contain a noticeable amount of heavy metals, colloidal aluminium hydroxide, aluminium sulphate (used as a flocculating agent), sodium and calcium ions (generated in neutralizing solutions) and water, and are considered as potential eco-toxic residues (Dufour et al., 1999). To solve the environmental problems posed by the sludge, it is subjected to exhausted baths. The presence of Cr (III) in this waste can promote the formation of free Cr (VI), which is soluble in water and carcinogenic in nature (Silva et al., 2008). In the European Union 100,000–150,000 t/year of this type of sludge is produced (Magalhaes, 2002; Ribeiro et al, 2002, 2004; Magalhaes et al., 2005a), which is a serious waste management issue.

The production of galvanic sludge wastes (GSW) in the developed and underdeveloped countries is higher than 1,000,000 t/year (Silva et al., 2008). The most common way to dispose of these wastes is landfill deposition. However, the deposition of galvanized sludge in landfill is a not a very environmentally friendly alternative. To solve this problem, hydrometallurgical technologies can be applied to reuse the valuable metals in the effluents (Rossini and Moura-Bernades, 2006). There are important research works on the extraction and reuse of heavy metals (Ni, Zn, Cu and others) extracted from the dry residue and effluents (Silva et al., 2005).

The chemical characteristics of the GSW are important parameters in recycling processes. Ceramic products, such as bricks, stoneware or tiles, have a very heterogeneous composition since they are formed by clay materials which have a wide range of compositions (Couto et al., 2003). According to Reinosa et al. (2010), the building industry is the

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Table 1
Chemical composition of GSW and industrial clay obtained by XRF.

Element oxides	Content (mass %)	
	Galvanic sludge	Clay
SiO_2	3.01	55.82
Al_2O_3	0.11	12.13
Fe_2O_3	3.35	4.83
MnO	0.09	0.03
MgO	3.77	1.49
CaO	7.77	9.21
Na_2O	2.20	0.49
K_2O	0.04	2.78
TiO_2	–	0.83
P_2O_5	0.43	0.12
Cl	0.89	–
Co_3O_4	0.14	–
Cr_2O_3	12.73	–
CuO	1.52	–
NiO	1.58	–
SO_3	1.78	–
SrO	0.16	–
ZnO	23.79	–
Loss on ignition at 950 °C	36.62	10.55
Total	99.98	98.28

Footnote: The slight difference with the loss of ignition results for clay reported in Table 3 can be associated to processing conditions of the green solid bricks.

most suitable technological activity sector to consume solid wastes. The reason for this is the large quantity of raw materials used by the sector as well as the large volume of final products required. Clays usually exhibit high cation exchange capability, due to their surface charge properties (Benjelloun et al., 2001; Bergaya et al., 2006). Clay can also be used to immobilize harmful heavy metals ions (Churchman et al., 2006; Addy et al., 2012). Furthermore, clay minerals are silicate phases that can incorporate considerable amounts of metals in their structures.

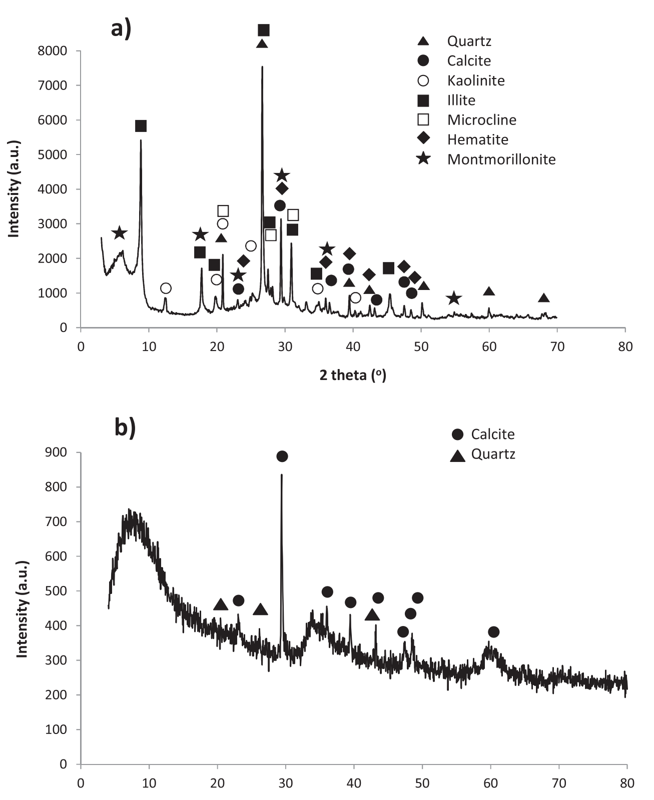

Fig. 1. XRD patterns of (a) clay and (b) galvanic sludge waste used as raw materials in the preparation of bricks.

Table 2
Elemental chemical analysis (CHNS) of raw materials.

Element	Content (mass %)	
	Galvanic sludge	Clay
C	8.758	2.406
H	2.253	0.442
N	0.111	0.051
S	0.133	0.057

Therefore, the ceramic industry is one of the best candidates to consume large amounts of industrial wastes, such as combustion ashes, granite cutting sludge and wastewater sludges (Torres et al., 2004; Reijnders, 2007; Martínez-García et al., 2012). The incorporation of residues such as GSW containing heavy metal ions into a ceramic matrix can be a promising solution to reduce the environmental risks.

There are some studies on the characterization of GSW (Magalhaes et al., 2005a, 2005b), for manufacturing vitrified ceramics (Ferreira et al., 1999; Silva and Mello-Castanho, 2004; Mello-Castanho et al., 2006; García-Vallés et al., 2007) and to obtain vitrified tiles (Reinosa et al., 2010). There are also studies on the encapsulation of GSW in a mixture of calcium sulfoaluminate cement and coal bottom ash (Luz et al., 2006). Recent research works showed the results of in-depth studies on the immobilization, inertization and release kinetics of GSW in ceramic matrix (Magalhaes et al., 2004a, 2004b, 2005a). However, there are few available studies on the use of GSW as raw material for the production of clay bricks (Ferreira et al., 1999; Mymrine et al., 2013). According to the existing literature, the use of GSW as a raw material in the cement industry has been reported (Riganti et al., 1986; Espinosa and Tenorio, 2001; Cioffi et al., 2002; Luz et al., 2009). Espinosa and Tenorio (2001) studied the influence of the addition of different amounts of waste in the clinkerization process analyzing the inertization of sludge in the cement matrix. They concluded that up to 2 wt.% of galvanic sludge did not affect that process. Luz et al. (2009) used the galvanic sludge to design calcium sulfoaluminate cement

Table 3
Technological properties of fired bricks made from clay and GSW mixtures.

Sample	Waste content (mass %)	Linear shrinkage (%)	Mass loss on ignition (%)	Bulk density (g cm^{-3})
C	0	-0.265 ± 0.102	13.84 ± 0.21	1.760 ± 0.051
C-1GS	1	-0.455 ± 0.154	10.32 ± 0.38	1.455 ± 0.040
C-2GS	2	-0.413 ± 0.101	11.18 ± 0.46	1.456 ± 0.039
C-3GS	3	-0.444 ± 0.087	11.38 ± 0.27	1.456 ± 0.037
C-4GS	4	-0.455 ± 0.098	11.65 ± 0.30	1.454 ± 0.046
C-5GS	5	-0.458 ± 0.055	13.87 ± 0.33	1.450 ± 0.048

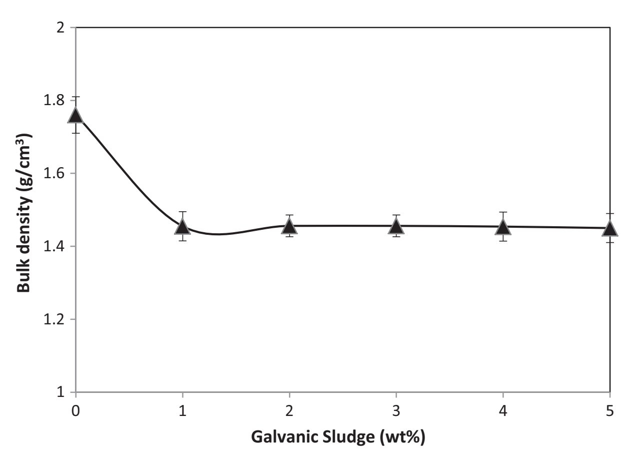

Fig. 2. Bulk density of the fired bricks as a function of GSW addition (1–5 wt.%) to the clay.