



## Influence of the addition of phosphogypsum on some properties of ceramic tiles



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### HIGHLIGHTS

- The addition of phosphogypsum waste in ceramic bodies was evaluated.
- The new ceramic tiles shown even better technological properties than standards.
- No significant environmental impact and human risk on use this building material.
- The use of this waste can reduce the raw materials demands and phosphogypsum piles.

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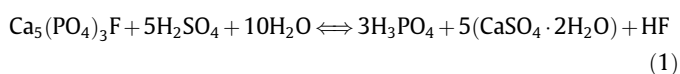
### ABSTRACT

Phosphogypsum (PG) is a waste from phosphoric acid production, and this work evaluates the use of PG as an additive in ceramic manufacturing. Ceramic samples were produced by adding different concentrations of PG (5, 7.5, and 10 wt%) to natural clay, and sintering at 950, 1050, and 1150 °C. Technological and mechanical properties of the obtained ceramics were evaluated. Moreover, the U.S. EPA's toxicity characteristic leaching procedure, Index "I", and the effective radium activity were calculated to evaluate the environmental risks. The use of PG improves the sintering behaviour and the bending strength, while also the environmental impact is negligible.

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## 1. Introduction

Any process that requires the use of raw materials and applies physical and/or chemical transformations to obtain products generates waste and impacts the environment. It is necessary to develop sustainable industrial processes in which the waste generated will be used as raw materials for new commercial products and applications. The industrial production of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) from phosphate rock ore (mainly fluorapatite, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F) by the wet process (using H<sub>2</sub>SO<sub>4</sub>) produces a gypsum-rich by-product called phosphogypsum [1–3]. The industrial process is shown by the following chemical reaction (Eq. (1)):



Nowadays, worldwide PG production is estimated at approximately 100–280 millions of tonnes per year [4,5]; 4.9 tonnes of PG are generated per tonne of phosphoric acid produced. Nevertheless, only 15% of the world's waste PG is recycled [6,7], because it often contains hazardous metals and other potentially toxic elements – even natural U-series radionuclides and organic substances [8,9].

The city of Huelva (in south-west Spain) presents the only centre of production of phosphoric acid in Spain, and the largest centre in Europe. Production began in 1968, and since then 120 million tonnes of PG has been deposited in a stack occupying a large part (1200 ha) of the salt-marshes of the Tinto River [3,10]. After looking unsuccessfully for sustainable solutions to the stockpiling of waste, the plant ceased dumping PG in December 2010. However, the waste piles remain, and without an apparent solution. The urgent need to perform the current study is related to the great social interest for an action plan that proposes solutions to the problem of the PG stacks.

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A review of the literature on the use of PG indicates that the main applications remain in agriculture, cement production, and in the construction and building industry (the object of this study). The 15% of waste PG that is successfully recycled is implemented in the creation of building materials [11–13], as a soil amendment [2], to produce Portland cement [14], in mineral CO<sub>2</sub> sequestration [15,16], and other applications [17].

However, it is essential that the other 85% of waste PG is reused. In other words, there is a strong need to diversify the industrial applications of this waste. Some authors have focused on recycling gypsum for traditional ceramic building materials [18], such as synthetic polymer cement [19], ceramic block [20], and non-fired ceramic [21]. The increasing amount of PG being produced, and thus the need for increasingly large storage areas such as that in the city of Huelva, have led to a considerable need for the development of new economically and environmentally attractive methods to recycle this industrial waste.

Therefore, the objective of this work is to analyse the option of producing ceramic bodies that utilise PG. Ceramics were produced with different firing temperatures and PG proportions, which were analysed in comparison to a standard red ceramic. Several studies in relation to technological properties and environmental implications were carried out.

## 2. Materials and methods

### 2.1. Materials and sample preparation

A representative sample of PG was collected directly from the piles in the city of Huelva. PG was directly collected from the pile number 2, where a representative sampling of the area was performed by taking 10 samples at 50 cm in depth trying to avoid the superficial weathering produced by the rain. In general, the variability (given as standard deviation of the mean) of the major elements, trace elements and natural radionuclides was smaller than 20%. The PG was dried at 60 °C for 48 h until constant weight (to remove moisture without losing the structural water), then ground and homogenised in a planetary mill at 400 rpm for 20 min. According to previous studies [2,3], the major components of waste PG are SO<sub>3</sub>, CaO, F, SiO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub>. The clay used in this study came from the Paraná river bank near to Presidente Epitácio county, Brazil; as determined by Teixeira et al. [22], clay is mainly composed by Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. In our case, the Brazilian clays used are kaolinitic, with a little mica and iron oxide content, being their composition very similar to the clays from Sierra de Aracena (Huelva province, Spain) [23].

Clay ceramic bodies with additions of 0, 5, 7.5, or 10 wt% of PG were moistened by spraying with distilled water (12 wt%), homogenised the samples manually (12 h), and then pressed in triplicate, utilising a uniaxial manual hydraulic press (Schuz) with a load of 19 MPa in a steel mould, to form specimens of 60 × 20 × 5 mm. The elaborated compositions are shown in Table 1. All specimens were dried at room temperature for 48 h and then at 110 °C in a laboratory oven until constant weight was achieved. The firing of the specimens was performed at different temperatures (950, 1050, and 1150 °C) in a laboratory electric furnace (EDG model 3000) at a heating rate of 10 °C min<sup>-1</sup>. The temperature was held at 100 °C for 30 min to evaporate the remaining structural water, and at the maximum temperature for 1 h to ensure complete sintering. The samples are numbered C-T, where C is the wt% of PG and T is the firing temperature. For example, the sample with a 5 wt% PG addition fired at 1150 °C would be 5-1150 (Table 1).

**Table 1**  
Composition of the different mixtures studied.

	Raw materials (wt%)	
	Clay	Phosphogypsum
Fired at 950 °C		
0-950	100	0
5-950	95	5
7.5-950	92.5	7.5
10-950	90	10
Fired at 1050 °C		
0-1050	100	0
5-1050	95	5
7.5-1050	92.5	7.5
10-1050	90	10
Fired at 1150 °C		
0-1150	100	0
5-1150	95	5
7.5-1150	92.5	7.5
10-1150	90	10

### 2.2. Methods

The clay texture (sand, silt, and clay fractions) was characterised using the pipette method [24] and the PG particle size was analysed by laser granulometry in wet suspension with water as dispersant, using a Malvern Mastersizer 2000 particle sizer with the Hydro 2000M accessory. The mineral phases were identified by X-ray diffraction (XRD) in a Shimadzu diffractometer (model XRD 6000), using Cu K $\alpha$  radiation working at 1.2 kW (40 kV and 30 mA). Data were recorded in the 5–60° 2 $\theta$  range (step size equal to 1° min<sup>-1</sup>). Major and trace elements were analysed by inductively coupled plasma mass spectrometry (ICP-MS) using an HP branded computer (model HP4500®) at the Activation Laboratories Ltd (ACTLABS, Ontario, Canada), which meet the ISO/IEC 17025 Quality System standard. The quality control included the use of a reagent blank, standard reference materials, and replicates. The average accuracy of the analytical data was  $\pm 5\%$ .

Thermogravimetric analysis (TGA) of the powder samples (particle size 80–100  $\mu\text{m}$ ) was simultaneously conducted in a TA Instruments thermogravimetric analyser with differential scanning calorimeter (TGA-DSC, model SDT Q600). Thermogravimetric scans were performed between 25 °C and 1450 °C at 10 °C min<sup>-1</sup> in flowing air, using platinum crucibles with calcined Al<sub>2</sub>O<sub>3</sub> as a reference material. The DSC/TGA curves were normalised regarding the sample weight.

The sintering behaviour of the fired specimens, for each composition and temperature, was tested according to the bulk density (BD), apparent porosity (AP), and water absorption (WA) according to standard procedures ISO 10545-3 [25] and ASTM C373-14 [26]. The BD (g cm<sup>-3</sup>) was measured by dividing the dry mass by the external volume; the AP (%) was calculated by dividing the internal volume by the external volume; and the WA (%) was determined by dividing the internal volume by the dry mass. Moreover, linear shrinkage (LS) was calculated using the standard method ASTM C326-9 [27]. The LS was obtained by measurements of the samples before and after the firing stage using a digital calliper (Mitutoyo, precision of  $\pm 0.01$  mm). The technological properties were evaluated by bending strength (BS), determined in a Contenco testing machine (model UMC-20T) according to ISO 10545-4 [28] and ASTM C674-13 [29]. Moreover, a triplicate analysis was performed in order to evaluate the repeatability and reference specimens were used, and for that, all technological properties are expressed with their standard uncertainties.

Field emission scanning electron microscopy (FESEM) observations on fired samples were accomplished in a HITACHI S-4800P

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