

1 **Influence of the addition of phosphogypsum on some properties of ceramic tiles**

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16 **Abstract**

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

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26 Keywords: phosphogypsum; NORM; ceramic; leaching; valorisation.

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## 28 **1. Introduction**

29 Any process that requires the use of raw materials and applies physical and/or chemical  
30 transformations to obtain products generates waste and impacts the environment. It is  
31 necessary to develop sustainable industrial processes in which the waste generated will  
32 be used as raw materials for new commercial products and applications. The industrial  
33 production of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) from phosphate rock ore (mainly fluorapatite,  
34  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) by the wet process (using  $\text{H}_2\text{SO}_4$ ) produces a gypsum-rich by-product called  
35 phosphogypsum [1–3]. The industrial process is shown by the following chemical  
36 reaction (Eq. 1):



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

43 The city of Huelva (in south-west Spain) presents the only centre of production of  
44 phosphoric acid in Spain, and the largest centre in Europe. Production began in 1968, and  
45 since then 120 million tonnes of PG has been deposited in a stack occupying a large part  
46 (1200 ha) of the salt-marshes of the Tinto River [3,10]. After looking unsuccessfully for  
47 sustainable solutions to the stockpiling of waste, the plant ceased dumping PG in

48 December 2010. However, the waste piles remain, and without an apparent solution. The  
49 urgent need to perform the current study is related to the great social interest for an action  
50 plan that proposes solutions to the problem of the PG stacks.

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

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

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

## 69 **2. Materials and Methods**

### 70 **2.1. Materials and sample preparation**

71 A representative sample of PG was collected directly from the piles in the city of Huelva.  
72 PG was directly collected from the pile number 2, where a representative sampling of the  
73 area was performed by taking 10 samples at 50 cm in depth trying to avoid the superficial  
74 weathering produced by the rain. In general, the variability (given as standard deviation  
75 of the mean) of the major elements, trace elements and natural radionuclides was smaller  
76 than 20%. The PG was dried at 60 °C for 48 hours until constant weight (to remove  
77 moisture without losing the structural water), then ground and homogenised in a planetary  
78 mill at 400 rpm for 20 min. According to previous studies [2,3], the major components of  
79 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  
80 Paraná river bank near to Presidente Epitácio county, Brazil; as determined by Teixeira  
81 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  
82 used are kaolinitic, with a little mica and iron oxide content, being their composition very  
83 similar to the clays from Sierra de Aracena (Huelva province, Spain)[23]

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

95 example, the sample with a 5 wt.% PG addition fired at 1150 °C would be 5-1150 (Table  
96 1).

## 97 **2.2. Methods**

98 The clay texture (sand, silt, and clay fractions) was characterised using the pipette method  
99 [24] and the PG particle size was analysed by laser granulometry in wet suspension with  
100 water as dispersant, using a Malvern Mastersizer 2000 particle sizer with the Hydro  
101 2000M accessory. The mineral phases were identified by X-ray diffraction (XRD) in a  
102 Shimadzu diffractometer (model XRD 6000), using Cu  $\kappa\alpha$  radiation working at 1.2 kW  
103 (40 kV and 30 mA). Data were recorded in the 5–60°  $2\theta$  range (step size equal to 1°  
104  $\text{min}^{-1}$ ). Major and trace elements were analysed by inductively coupled plasma mass  
105 spectrometry (ICP-MS) using an HP branded computer (model HP4500®) at the  
106 Activation Laboratories Ltd (ACTLABS, Ontario, Canada), which meet the ISO/IEC  
107 17025 Quality System standard. The quality control included the use of a reagent blank,  
108 standard reference materials, and replicates. The average accuracy of the analytical data  
109 was  $\pm 5\%$ .

110 Thermogravimetric analysis (TGA) of the powder samples (particle size 80–100  $\mu\text{m}$ ) was  
111 simultaneously conducted in a TA Instruments thermogravimetric analyser with  
112 differential scanning calorimeter (TGA-DSC, model SDT Q600). Thermogravimetric  
113 scans were performed between 25 °C and 1450 °C at 10 °C  $\text{min}^{-1}$  in flowing air, using  
114 platinum crucibles with calcined  $\text{Al}_2\text{O}_3$  as a reference material. The DSC/TGA curves  
115 were normalised regarding the sample weight.

116 The sintering behaviour of the fired specimens, for each composition and temperature,  
117 was tested according to the bulk density (BD), apparent porosity (AP), and water  
118 absorption (WA) according to standard procedures ISO 10545-3 [25] and ASTM

119 C373-14 [26]. The BD ( $\text{g cm}^{-3}$ ) was measured by dividing the dry mass by the external  
120 volume; the AP (%) was calculated by dividing the internal volume by the external  
121 volume; and the WA (%) was determined by dividing the internal volume by the dry  
122 mass. Moreover, linear shrinkage (LS) was calculated using the standard method ASTM  
123 C326-9 [27]. The LS was obtained by measurements of the samples before and after the  
124 firing stage using a digital calliper (Mitutoyo, precision of  $\pm 0.01$  mm). The technological  
125 properties were evaluated by bending strength (BS), determined in a Contenco testing  
126 machine (model UMC-20T) according to ISO 10545-4 [28] and ASTM C674-13 [29].  
127 Moreover, a triplicate analysis was performed in order to evaluate the repeatability and  
128 reference specimens were used, and for that, all technological properties are expressed  
129 with their standard uncertainties.

130 Field emission scanning electron microscopy (FESEM) observations on fired samples  
131 were accomplished in a HITACHI S-4800P microscope with an acceleration voltage of  
132 20 kV. For analysis of phase assemblages and morphology, fresh fracture surfaces were  
133 etched for 4 min in 15 % HF solution then washed ultrasonically with distilled water and  
134 ethylic alcohol and dried. Moreover, to analyse the porosity evolution during firing, cross-  
135 sectional samples were grinded with SiC powder and subsequently polished to  $1 \mu\text{m}$  with  
136 diamond pastes. Prior to FESEM observations, the samples were coated with Au-Pd in a  
137 Balzers SCD 050 sputter. The semi-quantitative analysis of different phases was achieved  
138 by energy dispersive X-ray spectroscopy (EDS) with a Link eXL detector provided by a  
139 beryllium (Be) window. The distribution of Si, Al, Ca, and Fe among different crystalline  
140 phases was examined by digital X-ray mapping.

141 According to the regulations of the Environmental Protection Agency (EPA), PG is  
142 considered hazardous. To study the pollutant mobility in both the raw materials and  
143 ceramic bodies, the EPA's toxicity characteristic leaching procedure (TCLP) was carried

144 out [30]. In addition, the leachates were analysed by both alpha spectrometry and ICP-  
145 MS techniques.

146 Natural radionuclides were measured in both raw materials and samples by high-  
147 resolution low-background gamma spectrometry with a hyper-pure germanium detector  
148 (HPGe) with a carbon window, through the following energies:  $^{210}\text{Pb}$  (46.5 keV),  $^{234}\text{Th}$   
149 (63.3 keV),  $^{226}\text{Ra}$  (via 352 keV of  $^{214}\text{Pb}$ ) and  $^{40}\text{K}$  (1460 keV). The activity concentrations  
150 in leachates obtained during the TCLP method were measured by alpha-particle  
151 spectrometry with ion-implanted Si detectors. U-isotopes, Th-isotopes, and  $^{210}\text{Po}$  were  
152 isolated by a tributylphosphate sequential extraction method [31]. Furthermore, the  
153 activity concentration index (I) was determined to evaluate the potential radiological risks  
154 [32]. The effective radium activity is defined as the  $^{222}\text{Rn}$  concentration generated by  
155  $^{226}\text{Ra}$  contained inside the material and transported through its pores. According to  
156 Krisyuk [33], it is calculated by multiplying the  $^{226}\text{Ra}$  concentration ( $\text{Bq kg}^{-1}$ ) by the  
157 effective radium activity, which is determined under specific experimental conditions  
158 from the growth curves of radon inside a closed chamber.

### 159 **3. Results and Discussion**

#### 160 **3.1. Material Characterisation**

161 Fig. 1 shows the results of the particle size analysis of the PG used in this study. It revealed  
162 an asymmetric particle size distribution with a wide range of particle sizes. Two different  
163 populations were observed (see Fig. 1); the main fraction presents the major population  
164 around 50  $\mu\text{m}$ , and the second population is around 4  $\mu\text{m}$ . According to the particle size,  
165 the clay fraction of the total particles (particle size below 2  $\mu\text{m}$ ) is below 20 %, the silt  
166 fraction (particle size between 50 and 2  $\mu\text{m}$ ) is 40 %, and the sand fraction (particle size  
167 above 50  $\mu\text{m}$ ) is 40 %.

168 The textural characterisation (sand, silt, and clay) of the clay sample using the pipette  
169 method showed a great plasticity, according to the high clay minerals fraction (51.6 %).  
170 Consequently, a considerable amount of water (12 wt.%) was required to shape the tiles  
171 easily. The silt and sand fractions of the clay were 23.9 % and 24.5 % respectively.

172 In accordance with the mineralogical analysis (Fig. 2a), the crystalline components of the  
173 clay were quartz ( $\text{SiO}_2$ ), kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), illite ( $\text{KAl}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ ), goethite  
174 ( $\text{FeO}(\text{OH})$ ) and gibbsite ( $\text{Al}(\text{OH})_3$ ). The XRD pattern of the PG (Fig. 2b) confirmed it  
175 was exclusively of the mineral phase gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Fig. 3 shows a sequence of  
176 diffraction patterns of the clayed material, with 0, 5, 7.5, and 10 wt.% PG, sintered at  
177 1150 °C. As shown in Fig. 3, after the firing process, the peaks associated with clay  
178 minerals (kaolinite and illite) disappear because of the destruction of the crystalline  
179 structure at 450–900 °C. Above 900 °C, new mineral phases such as mullite  
180 ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) appear, due to the crystallisation process. As a consequence of mullite  
181 formation, a reduction in the intensities of the XRD peaks of quartz was observed (Fig.  
182 3). Moreover, after the firing process, hematite was identified, and goethite disappeared.  
183 The iron from the goethite decomposition, and the release of iron by illite during the  
184 breakdown of its mineral structure, form the new mineral phase detected; hematite [34].  
185 Furthermore, the XRD patterns show the formation of new mineral phases with the  
186 addition of PG (Fig. 3), such as the calcium silicates wollastonite ( $\text{CaSiO}_3$ ) and anorthite  
187 ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ). The gibbsite decomposition, and the release of aluminium by kaolinite  
188 and illite together with the Ca from the PG form the anorthite. The intensities of the peaks  
189 associated with these calcium silicates (wollastonite and anorthite) increase with the  
190 percentage of gypsum in the specimens. PG has an important content of calcium sulphate,  
191 a nucleating agent that may have influenced the crystallisation of mineral phases like  
192 wollastonite [35].

193 In agreement with the XRD results, the chemical analysis showed that PG is mainly  
194 composed of SO<sub>3</sub> (52.2 wt.%) and CaO (30.6 wt.%); similar results have been reported  
195 in other studies [15,36]. The main trace elements identified in PG are (in order of  
196 abundance), Sr, Cr, Cu, Mn, Zn, Pb, and Zr; all present, however, in concentrations  
197 smaller than in unperturbed soils [37]. The chemical analysis (Table 2) shows that clay is  
198 composed of high amounts of silica (48.82 wt.%), alumina (27.67 wt.%), and iron oxide  
199 (7.09 wt.%) and potassium oxide (2.55 wt.%). These results are in accordance with the  
200 mineral composition obtained previously by XRD analysis. Regarding the trace  
201 impurities, Mn, Cu, Zn, Cr, Ni, Sr, Pb, and Co were detected in clay. Some trace elements  
202 (Cu, Zn, Cr, and Pb) are present in concentrations higher than in uncontaminated soils  
203 [36]. On the other hand, the mean valued obtained in this study for major, trace metals  
204 and radionuclide are in accordance with the obtained for several previous studies carried  
205 out in the same place [3,8,38-40]. The DSC/TGA analysis of PG and clay are represented  
206 in Fig. 4. The losses on ignition (at 1150 °C) were 16.55 wt.% and 12.83 wt.%, for PG  
207 and clay respectively. Fig. 4a shows the DSC/TGA curves for the clay, in which one  
208 exothermic and four endothermic peaks were identified. The first endothermic peak at  
209 ~76 °C is associated with a weight loss of 2 %, which corresponds to the endothermic  
210 evaporation of unbound water. Another endothermic peak at ~262 °C with a weight loss  
211 of 1 % corresponds to the thermal decomposition of non-volatile organic compounds, the  
212 volatilisation of lighter organic fragments, and especially to the decomposition of Al and  
213 Fe hydroxides (gibbsite and goethite, respectively). The largest mass loss (8 %) occurs at  
214 ~492 °C, due to the endothermic dehydroxylation of clay minerals as, the decomposition  
215 of kaolinite, and the loss of structural water of illite. The third peak at ~966 °C is  
216 exothermic and it is characteristic of the crystallisation of mullite. Finally, an endothermic

217 descent at ~1200 °C is related to the formation of a liquid phase derived from the feldspar  
218 component and the silica released [41].

219 The thermal behaviour of PG (Fig. 4b) shows five areas of weight change; one exothermic  
220 and four endothermic peaks. The first endothermic area at ~66 °C is associated with the  
221 partial dehydration of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) to give hemihydrate gypsum  
222 ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ). In the second endothermic peak at ~117 °C, the dehydration of the  
223 hemihydrate gypsum begins. In the third endothermic effect at ~158 °C, the main mass  
224 loss (10 %) occurred due to the complete removal of crystallisation water and the  
225 consequent formation of soluble anhydrite III ( $\text{CaSO}_4$  III). The fourth thermal effect, an  
226 exothermic peak at ~433 °C, is related to the transformation of soluble anhydrite III into  
227 insoluble anhydrite II. Finally, an endothermic peak at ~1217 °C takes place due to the  
228 total decomposition of calcium sulphate into calcium oxide (CaO) and sulphur dioxide  
229 ( $\text{SO}_2$ ). The results are in concordance with the results obtained by XRD and with other  
230 researchers [42,43].

231 Fig. 5 shows the DTA curves of mixtures of clay with 0, 5, 7.5, and 10 wt.% of PG. The  
232 thermal behaviour of the mixtures was similar to that of the clay, although with the  
233 addition of PG, some areas associated with the thermal behaviour of gypsum appeared.  
234 Moreover, the chemical composition of the clay was altered with the addition of PG,  
235 changing the reactions that occurred during the firing process. The endothermic peaks  
236 around 262 °C and 492 °C were reduced in samples with added PG due to the amount of  
237 clay substituted by PG.

238 FESEM observations of polished surfaces of the ceramic samples fired at 1150 °C are  
239 shown in Fig. 6. In 0-1150 sample (Fig 6a), a dense matrix is observed; porosity mainly  
240 consists of fine closed pores (< 5 µm) distributed throughout the clay matrix, with some  
241 open porosity composed by interconnected irregular channels with a size below 5 µm.

242 The addition of 5 wt.% PG leads to fired samples with a lower amount of fine closed  
243 porosity (Fig. 6b), but a slightly higher number of larger isolated pores ( $> 10 \mu\text{m}$ ) that  
244 form coarse closed porosity due to the release of gaseous  $\text{SiO}_2$  during the thermal  
245 decomposition of PG. The coarse closed porosity increases as the amount of PG in the  
246 initial composition increases (Figs. 6c; 6d), which is likely to be responsible for the  
247 reduction observed in bending strength, given that these pores can act as stress  
248 concentrators and facilitate fracture [44].

249 Fig. 7 shows micrographs taken on etched surfaces of the ceramic 0-1150. Etching with  
250 HF solution leads to the partial removal of the glass phase, and consequently the different  
251 crystalline phases detected by XRD are highlighted. The microstructure is comprised of  
252 a dense matrix in which diverse crystals and regions with distinctive morphology are  
253 included (Fig. 7a). High magnification observation allows the dense matrix to be  
254 recognised, consisting of small prismatic crystals showing a high aspect ratio (3–10:1),  
255 which correspond to Type II secondary mullite derived from a kaolinite/illite mixture  
256 (Fig. 7b). The potassium and iron in the clay composition develop a liquid phase at low  
257 temperatures, which facilitates the growth of these crystals, so they achieve higher aspect  
258 ratios than mullite crystals formed from pure kaolinite relicts [45]. Moreover, quartz  
259 crystals are also observed in the matrix that are clearly identified by EDS analysis (Fig.  
260 7c), as well as crystalline regions consisting of mullite needles with very high aspect ratio  
261 (30–40:1) that correspond to Type III secondary mullite, likely derived from areas where  
262 kaolinite, illite, and quartz are finely mixed. In such areas, mullite crystals are enclosed  
263 in a more fluid liquid, which promotes the growth of longer crystals (Fig. 7d).

264 The elemental mappings of Si, Al, Ca, and Fe related to samples fired at  $1150 \text{ }^\circ\text{C}$  are  
265 shown in Fig. 8. The hematite and Ca-enriched phases are identified by colour  
266 dissimilarities caused by different concentrations of these ions in each of the observed

267 crystalline phases. As expected, the prevalence of these Ca- or Fe-enriched phases is  
268 higher with greater additions of PG. The addition of greater amounts of PG gives rise to  
269 negligible changes in the microstructure after firing in terms of the morphology of the  
270 matrix, quartz, and secondary mullite crystals, as shown in Fig. 8b where the  
271 microstructure of the ceramic 5-1150 is shown. Nevertheless, the greatest effect of adding  
272 PG is the occurrence of neo-formation phases embedded in the ceramic matrix.

273 Figs. 9(a–b) show elemental mapping and a SEM/secondary electron (SE) image  
274 corresponding to a Ca-enriched region in the sample 5-1150. It is likely that these regions  
275 are developed from areas where pure PG was located in the green body. As a result of gas  
276 release during the thermal decomposition of PG, these Ca-enriched regions show higher  
277 porosity than the ceramic matrix. Although the existence of anorthite and wollastonite  
278 has been detected by XRD, it is not possible to identify the crystals corresponding to each  
279 of these phases by SEM as the region shows a homogeneous morphology consisting of  
280 granular aggregates. Regarding the hematite phase, Figs. 9(c–d) show elemental mapping  
281 and a SEM/SE image corresponding to hematite crystals showing globular habit,  
282 observed in the sample 7.5-1150.

### 283 **3.2. Technological properties**

284 The technological properties of fired tiles shown in Table 3 indicate that water absorption  
285 (WA) is a function of firing temperature, due to an increase of amorphous silica with  
286 sintering temperature and thus formation of mullite [46]. The amorphous silica and  
287 alumina are liberated when the kaolinite structure is broken, around 500 °C, and disappear  
288 when mullite is crystallised at 950 °C. The WA was reduced with the addition of PG for  
289 all temperatures, in agreement with the SEM study, but for 10-1150, the WA increased.  
290 The amorphous silica, which forms mullite during the sintering process, serves as a binder  
291 for the fine particles of PG, occupying the spaces between the granules. Hence, greater

292 PG additions reduce the WA in the ceramic bodies by the increasing of interconnected  
293 pores.

294 In the same way, the apparent porosity (AP) decreases with the concentration of PG and  
295 especially with the increase of firing temperature. Both WA and AP are directly related  
296 to the open porosity, and therefore both present the same behaviour [43,47]. WA is an  
297 important property because it is related to the effective realisation of the sintering process  
298 by the liquid phase. In terms of freeze–thaw cycles and stain resistance, low values of  
299 WA and AP are advantageous. Moreover, lower values of WA signify less drying time.

300 The sintering behaviour has indicated that the linear shrinkage (LS) is directly connected  
301 with firing temperature (Table 3). As mentioned previously, higher temperatures mean  
302 better sintering and consequently better properties: lower AP and WA. The results for LS  
303 are consistent with those observed for AP and WA, because LS behaviour is inversely  
304 related to WA and AP. The maximum shrinkage values were obtained at 1150 °C (LS ≈  
305 12); almost four times higher than at 950 °C (LS ≈ 3). These LS results were related to  
306 the greater densification of the ceramic bodies with increased firing temperatures.

307 Interestingly, different trends were seen with the addition of PG in the ceramic bodies  
308 fired at different temperatures. At 950 °C, the LS remained constant with increasing PG;  
309 at 1050 °C, the LS increased slightly with increasing PG; and at 1150 °C, the LS  
310 decreased slightly with increasing PG. As expected, the LS of ceramic bodies is a function  
311 of the firing temperature and, to a lesser degree, the PG content. In terms of the resistance  
312 of ceramic bodies, lower LS values are better to avoid internal defects such as cracking  
313 or other similar faults during firing. LS is associated with the liquid phase formation  
314 during sintering; this is good for all properties. A lower LS signifies greater preservation  
315 of the size of the ceramic piece after the firing process. According to the LS results, the  
316 addition of PG reduced the shrinkage and deformation of the material during the firing

317 process due to two factors; the occupation of pores by PG particles, and the non-plastic  
318 behaviour of the PG compared to the clay. Both factors reduced the great plasticity in the  
319 clay and thus improved the stability of the material.

320 The results for bulk density (BD) were in accordance with the LS behaviour, as both  
321 properties are directly related. At 950 °C, the BD values remained practically constant  
322 with different percentages of PG; at 1050 °C, the BD increased slightly with increasing  
323 PG (Table 3); and at 1150 °C, the BD decreased with increasing PG.

324 Table 3 shows that bending strength (BS) values were similar or even higher in ceramic  
325 bodies fired at 1050 and 1150 °C with additions of up to 7.5 wt.% PG than in the reference  
326 materials (0-1150). This occurred due to the denser, lower-porosity material obtained at  
327 these temperatures. The incorporation of PG produces two effects, on the one hand, it  
328 favors the formation of wollastonite and the reduction of plasticity in the clay that  
329 improves the microstructure and increases the resistance, and on the other hand, the PG  
330 decomposition releases gases causing closed porosity (>10µm) that weakens the  
331 structure.

332 The best resistance results were obtained from the samples 5-1050 and 5-1150; the  
333 decrease in the AP caused by the low addition of PG, in particular the reduction of  
334 plasticity in the clay and fine closed pores in the fired material, improved the sintering  
335 behaviour of the ceramic bodies during the firing process and their resistance to rupture.  
336 On the other hand, a 10 wt.% addition of PG reduced the resistance of the bodies; the  
337 rupture tension values were lower because the AP increases because coarse closed and  
338 interconnected open porosity increased (Table 3). In general, the addition of PG decreases  
339 the bending strength due to the coarse closed porosity increased. On the other hand, low  
340 percentages of PG and high sintering temperatures increased the resistance probably

341 because in those cases the beneficial effect of the formation of wollastonite prevails over  
342 the resistance reduction due to the development of closed pores

343 On the other hand, the BS in samples fired at 950 °C decreased with increasing PG  
344 concentrations. All of them presented lower values than the reference material (0-950).  
345 This diminution of BS was produced by the increasing of interconnected pores and  
346 consequently by the increasing of fracture points. Moreover, the decrease in BS values in  
347 samples fired at 950 °C with added PG can be attributed to the fact that quartz does not  
348 participate in the formation of new phases at sintering temperatures lower than 1000 °C,  
349 instead acting as fracture points.

350 Ceramic tiles are classified in the standards EN 14411 [48] and ANSI A137.1 [49]  
351 according to the WA coefficient and the BS. The European Norm EN 14411 [48]  
352 establishes the following classifications: BIb requires 0.5–3 % WA and 30 MPa BS; BIIa  
353 requires 3–6 % WA and 22 MPa BS; BIIb requires 18 MPa BS and 6–10 % WA; and  
354 finally, BIII requires  $\geq 10$  % WA and 15 MPa BS. All samples fired at 950 °C had WA  
355 values above 10 %, belonging to the BIII group, but the minimum resistance value was  
356 not reached. The specimens fired at 1050 °C are classified in the BIIb group, with BS  
357 values above 18 MPa (between 21.1 and 25.3 MPa) and WA results between 8–10 %.  
358 Samples 5-1150 and 7.5-1150 belong to the BIb group, with WA below 3 % ( $WA \approx 2.9$   
359 %) and BS above 30 MPa (32.6–34.5 MPa). Finally, sample 10-1150 is classified in the  
360 BIIa group, with a WA value of 4.7 % and a BS above 22 MPa (25.4 MPa).

361 Furthermore, the American National Standard ANSI A137.1 [49] establishes a  
362 classification based on the WA and the forming method, in our case by pressing. The  
363 specimens 5-1150 and 7.5-1150 are classified as vitreous (0.5–3 % WA) with a BS above  
364 the 32 MPa requirement, and belong to the P2 group. The sample 10-1150 is classified in  
365 the P3 group, a semi-vitreous ceramic (3–7 % WA) with a BS above the 22 MPa

366 requirement for floor tiles. Finally, the samples fired at 950 and 1050 °C are classified as  
367 non-vitreous (7–20 % WA) and belong to the P4 group, however the samples fired at 950  
368 °C did not meet the minimum value for wall tiles (BS > 15 MPa).

### 369 **3.3. Environmental study**

370 The radioactive characterisation of the ceramic bodies and raw materials should be the  
371 first step to evaluating the radiological impact associated with the use of PG. According  
372 to Table 4, PG shows a <sup>226</sup>Ra concentration higher than the safety threshold (1000 Bq  
373 kg<sup>-1</sup>) for NORMs, established by UNSCEAR in 1988 [50]. The main radionuclides are  
374 <sup>226</sup>Ra and <sup>210</sup>Pb, with activity values of 1080 and 720 Bq kg<sup>-1</sup> respectively. The  
375 radionuclides in clay are in secular equilibrium with their daughters and show similar  
376 concentrations to the average worldwide values for soils. The average activity  
377 concentrations in soil – reported by UNSCEAR in 2008 [51] – of <sup>226</sup>Ra, <sup>228</sup>Ra, and <sup>40</sup>K  
378 are 32, 25, and 412 Bq kg<sup>-1</sup> respectively, and Radiation Protection 112 [32] established a  
379 control threshold of 40 Bq kg<sup>-1</sup> of <sup>226</sup>Ra and <sup>228</sup>Ra and 400 Bq kg<sup>-1</sup> of <sup>40</sup>K. Moreover, the  
380 activity concentration of the ceramic bodies shows that the radionuclides <sup>226</sup>Ra and <sup>210</sup>Pb  
381 increased with increasing PG (Table 4). The concentrations of <sup>228</sup>Ra, <sup>228</sup>Th, and <sup>234</sup>Th  
382 were constant for all mixtures and firing temperatures. On the other hand, the activity  
383 concentration of <sup>40</sup>K decreased with the increase of PG, since the concentration in PG is  
384 10 times lower than in clay.

385 In order to evaluate the environmental impact of adding PG to building materials, the  
386 activity concentration index (I) was calculated according to Eq. 2:

$$I = \frac{C_{226Ra}}{300} + \frac{C_{232Th}}{200} + \frac{C_{40K}}{3000} \quad [\text{Eq. 2}]$$

387 where  $C(^{226}\text{Ra})$ ,  $C(^{232}\text{Th})$ , and  $C(^{40}\text{K})$  are the respective activities for  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ , and  
388  $^{40}\text{K}$  in the ceramic bodies, expressed in  $\text{Bq kg}^{-1}$ . International regulations establish that  
389 this index should not exceed a value of 6 for superficial materials [32]. Values under this  
390 limit prevent the external dose received by occupants in buildings using this material from  
391 exceeding the established limit of  $1 \text{ mSv year}^{-1}$  [52]. The index I (Table 4) shows that PG  
392 could be used as additive in the manufacture of ceramic bodies, since the values obtained  
393 are clearly lower than the limit for superficial materials ( $I < 6$ ). Furthermore, the results  
394 of this index were significantly lowered in comparison with the results achieved in other  
395 studies using other additives in ceramics [43,48,53]. Moreover, sample analysis  
396 confirmed that, for all firing temperatures studied, samples containing up to 5 wt.% PG  
397 could be used even as bulk material, as the index I does not exceed the limit of 1  
398 established for bulk materials [32]. Hence, in accordance with the limits established in  
399 the standards, tiles manufactured exclusively with PG are permitted for use as superficial  
400 materials.

401 The radon characteristics of the ceramic bodies were analysed since raw materials with  
402 high  $^{226}\text{Ra}$  activity concentrations have been used. The effective radium activity is the  
403 main characteristic to be studied, and it is defined as the fraction of  $^{222}\text{Rn}$  produced by  
404 the  $^{226}\text{Ra}$  contained inside the grains that is able to escape into the pores within the  
405 material. The measurement of the effective radium concentration from the ceramic bodies  
406 was calculated according to the method developed by López-Coto et al. [33]; i.e. the  
407 product of the  $^{226}\text{Ra}$  concentration ( $\text{Bq kg}^{-1}$ ) and the emanation factor, determined under  
408 specific experimental conditions. The radium effective concentrations were below the  
409 detection limit of  $5 \text{ Bq kg}^{-1}$ ; lower than ordinary construction materials such as cement  
410 ( $10 \text{ Bq kg}^{-1}$ ) [32]. To assess the contribution of building materials to indoor radon  
411 concentrations, a specific scenario was considered; in this case a standard room ( $5 \times 5 \times$

412 2.5 m) with an air exchange rate of  $0.5 \text{ h}^{-1}$  was assumed. The contribution to indoor radon  
413 concentration in the room due to emissions – using worst-case conditions – was below 4  
414  $\text{Bq m}^{-3}$ . This value is in accordance with the limit of  $100 \text{ Bq m}^{-3}$  established by the  
415 Commission Recommendation 90/143/Euratom [54] for new construction materials.

416 The potential environmental impact of the ceramic bodies was also evaluated by TCLP  
417 tests [30]. This method classifies waste as hazardous or non-hazardous based on toxicity.  
418 If the extract from a representative sample contains any of the contaminants listed in U.S.  
419 EPA 40 CFR 261.24 [55] at a concentration equal to or greater than the respective value  
420 given, it is classified as hazardous. The results of the TCLP tests are shown in Table 5,  
421 which permit the ceramic bodies to be considered as non-hazardous waste; all of the  
422 leachates were present in values lower than the regulatory levels listed in the U.S. EPA  
423 [55]. The leached concentrations of Cr, Zn, As, Cd, Pb, and Ba exhibited a direct relation  
424 to the initial concentrations in the raw materials (PG and clay) and the percentage of each  
425 in the mix. After 18 h of leaching, the amounts of leachates detected from the new ceramic  
426 bodies were below the allowed U.S. EPA values of  $5 \text{ mg L}^{-1}$  for Cr, As, and Pb;  $25 \text{ mg}$   
427  $\text{L}^{-1}$  for Zn; and  $1 \text{ mg L}^{-1}$  for Cd and Ba.

428 These results indicate that the incorporation of PG into ceramics meets the requirements  
429 for recycling this hazardous waste; the levels are below the ecotoxicity limits, ensuring  
430 that the use of this material will not impact the environment. Moreover, the mobility of  
431 metals (Table 5) studied by the transfer factor (%) show that the sintering process  
432 contributes to the encapsulation and stabilisation of metals in the ceramic matrix,  
433 avoiding the biodisponibility in the leachates. This fact can be observed due to the drastic  
434 reduction of transfer factor values after the firing process. Most of the transfer factor  
435 values in fired samples were below 1 %, showing that the metals largely do not leach out.

436 Furthermore, the radiological environmental impact of the leachates obtained by TCLP  
437 tests were analysed according to the activity concentration and the radionuclide mobility  
438 (Table 6). The results shown the low activity concentration in the leachates obtained. The  
439 highest activity concentration, of  $^{238}\text{U}$ , was obtained from the sample 10-950 ( $0.10 \text{ Bq}$   
440  $\text{L}^{-1}$ ); below the provisional guideline value of  $10 \text{ Bq L}^{-1}$  introduced by the World Health  
441 Organisation (WHO) for total activity content of uranium in drinking water [56], and  
442 clearly lower than values recorded for continental waters (which typically range between  
443  $0.005$  and  $0.5 \text{ Bq L}^{-1}$ ) [57]. The leachates show a  $^{234}\text{U}$  activity concentration between  
444  $0.01$ – $0.06 \text{ Bq L}^{-1}$ , rising to the maximum value in 10-950. This value is two orders of  
445 magnitude lower than the reference level established by the WHO ( $1 \text{ Bq L}^{-1}$ ). The U-  
446 isotopes concentration in leachates is quite low and would therefore have negligible  
447 environmental impact.

448 According to thorium radionuclides, the concentrations of Th-isotopes show the lowest  
449 value in leachates from 0-950 ( $0.05 \text{ Bq L}^{-1}$  of  $^{232}\text{Th}$ ), and the maximum value in leachates  
450 from 10-1150 ( $0.62 \text{ Bq L}^{-1}$  of  $^{228}\text{Th}$ ). The activity concentration of  $^{230}\text{Th}$  presented values  
451 between these. These results were of same order of magnitude as those typical of  
452 continental waters [57], and lower than the guidance levels for thorium radionuclides in  
453 drinking water ( $1 \text{ Bq L}^{-1}$ ) [56], thus their potential radiological impact is negligible.

454 Furthermore, the highest  $^{210}\text{Po}$  activity concentration was  $27.3 \text{ mBq L}^{-1}$  for 10-950 and  
455 the lowest was  $7.0 \text{ mBq L}^{-1}$  for 0-1150. The results were lower than the average values  
456 obtained for  $^{210}\text{Po}$  in continental water ( $0.050$ – $1 \text{ Bq L}^{-1}$ ) [56,58] and below the WHO  
457 threshold for this radionuclide in drinking water of  $0.1 \text{ Bq L}^{-1}$ .

458 Finally, the leachates all showed a similar  $^{226}\text{Ra}$  concentration of  $0.04$ – $0.1 \text{ Bq L}^{-1}$ ; this  
459 range is one order of magnitude lower than the guidance level of  $1 \text{ Bq L}^{-1}$  in drinking  
460 water [56].

461 According to these results, the effective dose equivalent received by the public due to  
462 leachates was not significant, since the natural radioactivity levels measured were lower  
463 than the representative worldwide averages and guidance levels. The radionuclide  
464 mobility was studied based on the transfer factors. Table 6 shows the transfer factors (%)  
465 of the natural radionuclides measured. The results show that radioisotopes will not leach  
466 out after the sintering process, which immobilises the radionuclides in the ceramic matrix.

#### 467 **4. Conclusions**

468 The present work has demonstrated that phosphogypsum can be successfully used as  
469 additive in ceramics. It should be pointed out that developing applications that use PG in  
470 high percentage is not technologically suitable. In the majority of the uses of PG this is  
471 incorporated in small proportions (around 10%) as our methodology proposes for the  
472 ceramics. This method is one more option to help in the storing elimination of this waste  
473 The addition of PG has a beneficial role in the sintering behaviour, decreasing both the  
474 apparent porosity and water absorption. All technological properties are associated with  
475 the formation of mullite, above 950 °C. As shown in the results, higher temperatures mean  
476 better sintering and consequently better properties: lower porosity and water absorption,  
477 and as consequence higher mechanical resistance.

478 The linear shrinkage increases with temperature and with the amount of PG added, of  
479 samples fired at 950 and 1050 °C; and at 1150 °C, the LS decreased slightly with  
480 increasing PG, reducing the shrinkage and deformation of the material during the firing  
481 process. This is due to the small particles of PG that occupy the pores; the PG has a non-  
482 plastic behaviour compared to the clay used. Both factors reduced the great plasticity of  
483 the clay and improved the stability of the material.

484 The results of the mechanical properties study show that the incorporation of PG does not  
485 cause any significant variation in bending strength values; the results are similar, and in  
486 some cases improved, compared to the reference samples. The addition up to 5 wt.% PG  
487 increases the rupture resistance; samples with 7.5 wt.% PG showed similar results, and  
488 the incorporation of 10 wt.% PG reduced the bending strength.

489 The obtained results are in line with other studies performed on the incorporation of  
490 wastes to ceramic matrix, which conclude that wastes can be included as additives in the  
491 composition ceramic building materials without lead to high variations and even  
492 increasing the technological properties of the fired materials

493 Based on the environmental risk study, the environmental impact is negligible. The metals  
494 and radionuclides are immobilised in the ceramic matrix, avoiding biodisponibility in the  
495 leachates. The radon level and the external dose received by occupants in buildings using  
496 this material do not exceed the established limits.

497 Considering all the results it can be concluded that the ideal conditions for the  
498 combination of this clay with the largest volume of immobilised PG are: the addition of  
499 7.5 % by weight of PG at the sintering temperature of 1050 °C.

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665

666 **Figure Captions:**

667 **Fig. 1.** Granulometric analysis of phosphogypsum.

668 **Fig. 2.** XRD analysis of the raw materials: (a) clay pattern: I—illite, K—kaolinite, Q—  
669 quartz, Go—goethite, Gi—gibbsite; (b) phosphogypsum pattern: G—gypsum, C—  
670 calcium sulphate.

671 **Fig. 3.** XRD patterns superimposed on the fired materials at 1150 °C: M—mullite, Q—  
672 quartz, C—calcium sulphate, W—wollastonite, H—hematite, A—anorthite.

673 **Fig. 4.** DSC/TGA curves (25–1350 °C, 10 °C min<sup>-1</sup>) of the raw materials: (a) clay and  
674 (b) phosphogypsum.

675 **Fig. 5.** DTA curves (25–1350 °C, 10 °C min<sup>-1</sup>) of the different mixtures of clay with  
676 phosphogypsum added (wt.%): (a) 0, (b) 5, (c) 7.5, (d) 10, and (e) 100.

677 **Fig. 6.** FESEM observations on polished surfaces of the ceramics fired at 1150 °C: a) clay  
678 without PG addition (0-1150); b) clay + 5 wt.% PG (5-1150); c) clay + 7.5 wt.% PG (7.5-  
679 1150); d) clay + 10 wt.% PG (10-1150).

680 **Fig. 7.** FESEM/SE images of fresh fractured, etched ceramic prepared from clay without  
681 PG addition and fired at 1150 °C (0-115): a) general microstructure; b) Type II secondary  
682 mullite matrix; c) EDS analysis of quartz particles; and d) Type III secondary mullite  
683 crystals.

684 **Fig. 8.** FESEM/SE images and elemental mappings of Si, Al, Ca, and Fe in ceramics fired  
685 at 1150 °C: a) clay without PG addition (0-1150); b) clay + 5 wt.% PG (5-1150); c) clay  
686 + 7.5 wt.% PG (7.5-1150); d) clay + 10 wt.% PG (10-1150).

687 **Fig. 9.** FESEM/SE images and elemental mappings of Si, Al, Ca, and Fe in ceramics fired  
688 at 1150 °C, prepared from clay with different percentages of PG: a) and b) clay + 5 wt.%  
689 PG (5-1150); c) and d) clay + 7.5 wt.% PG (7.5-1150).

### **Table Captions:**

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

**Table 2.** Chemical concentration analysis of major elements (wt.%) and trace elements ( $\text{mg kg}^{-1}$ ) of the raw materials (clay and PG) and the different mixtures measured by ICP-MS.

**Table 3.** Sintering properties (water absorption, WA; apparent porosity, AP; and bulk density, BD), linear shrinkage (LS), and bending strength (BS) results of tiles fired at different temperatures. Results show average values of 3 measurements.

**Table 4.** Activity concentrations ( $\text{Bq kg}^{-1}$ ) of raw materials (PG and clay), the mixtures (5, 7.5, and 10 wt.% PG), and ceramic bodies. The activity concentration index 'I' was calculated.

**Table 5.** Leachability concentrations of metals obtained by TCLP tests and analysed by ICP-OES. Transfer factor (%) of metal into TCLP extractant.

**Table 6.** Average activity concentrations ( $\text{mBq L}^{-1}$ ) of leachates obtained by TCLP tests and analysed by alpha spectrometry. Transfer factor (%) of radionuclides into TCLP extractant.