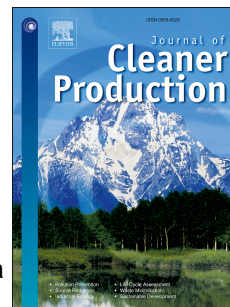


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PII: S0959-6526(19)33622-4

DOI: <https://doi.org/10.1016/j.jclepro.2019.118752>

Reference: JCLP 118752

To appear in: *Journal of Cleaner Production*

Received Date: 4 June 2019

Revised Date: 5 September 2019

Accepted Date: 5 October 2019

Please cite this article as: Rosales J, Pérez SM, Cabrera M, Gázquez MJ, Bolivar JP, de Brito J, Agrela F, Treated phosphogypsum as an alternative set regulator and mineral addition in cement production, *Journal of Cleaner Production* (2019), doi: <https://doi.org/10.1016/j.jclepro.2019.118752>.

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TREATED PHOSPHOGYPSUM AS AN ALTERNATIVE SET REGULATOR AND MINERAL ADDITION IN CEMENT PRODUCTION

J. Rosales¹, S.M. Pérez^{2,3}, M. Cabrera¹, M.J. Gázquez⁴, J.P. Bolívar^{2,3}, J. de Brito^{5*}, F. Agrela¹

¹Construction Engineering Area, University of Córdoba, Córdoba, Spain, jrosales@uco.es, manuel.cabrera@uco.es, irlagsaf@uco.es

²Department of Integrated Sciences, Area of Applied Physics, University of Huelva, Campus de El Carmen, Huelva, Spain, silvia.perez@dcu.uhu.es, bolivar@uhu.es

³Research Centre on Natural Resources, Health and the Environment (RENSMA), University of Huelva, Huelva, Spain

⁴Department of Applied Physics, University of Cádiz, Cádiz, Spain, manuel.gazquez@dfa.uhu.es

⁵ CERIS Research Institute, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal, jb@civil.ist.utl.pt

*Corresponding author

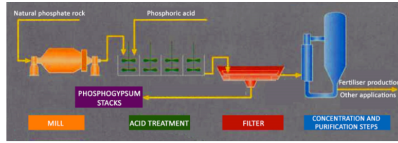
Abstract

Various treatments of phosphogypsum samples extracted in Huelva, Spain, curing conditions and incorporation ratios were studied to evaluate the viability of being used as set regulator or as supplementary cementitious material to improve the mechanical behaviour of cement mortars.

The physical-chemical properties, mechanical behaviour and environmental impact of these phosphogypsum-based cement mortars were determined.

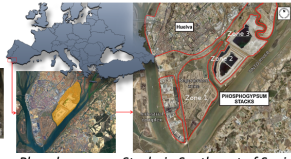
It was concluded that the phosphogypsum treatments and curing conditions influence the mineralogical transformations of mortars and therefore also the mechanical behaviour of the mortars tested. Furthermore, the heavy metal impurities in the phosphogypsum were immobilized in the cement matrix, leading to a clear improvement of the technical properties of cement mortars made with this waste compared to the traditional use of natural gypsum.

Keywords: phosphogypsum treatments, pozzolanic addition, curing conditions, cement mortars, technical properties.



PHOSPHORIC ACID PRODUCTION

**WASTE
PHOSPHOGYPSUM**



Phosphogypsum Stacks in Southwest of Spain

- P-D** Phosghogypsum dried
- P-C** Phosghogypsum crushed and sieved
- P-B** Phosghogypsum burned
- P-W** Phosghogypsum washed

MATERIAL TREATMENTS

**PHYSICAL AND CHEMICAL
PROPERTIES**

EFFECTIVENESS AS SETTING REGULATOR TIME IN CEMENT
INFLUENCE ON MECHANICAL BEHAVIOUR

MORTARS MANUFACTURING

Underwater curing	Dry chamber curing
Series 1	Series 1
2,5% addition	2,5% addition
Series 2	Series 2
5% addition	5% addition

ANALYTICAL METHODS

TECHNOLOGICAL TESTS

**ENVIRONMENTAL AND
HEALTH ANALYSIS**

Journal Pre-proof

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¹Construction Engineering Area, University of Córdoba, Córdoba, Spain, jrosales@uco.es, manuel.cabrera@uco.es, ir1agsaf@uco.es²Department of Integrated Sciences, Area of Applied Physics, University of Huelva, Campus de El Carmen, Huelva, Spain, sillvia.perez@dcu.uhu.es, bolivar@uhu.es

³Research Centre on Natural Resources, Health and the Environment (RENSMA), University of Huelva, Huelva, Spain

⁴Department of Applied Physics, University of Cádiz, Cádiz, Spain, manuel.gazquez@dfa.uhu.es

⁵ CERIS Research Institute, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal, jb@civil.ist.utl.pt

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Abstract

Various treatments of phosphogypsum samples extracted in Huelva, Spain, curing conditions and incorporation ratios were studied to evaluate the viability of being used as set regulator or as supplementary cementitious material to improve the mechanical behaviour of cement mortars.

The physical-chemical properties, mechanical behaviour and environmental impact of these phosphogypsum-based cement mortars were determined.

It was concluded that the phosphogypsum treatments and curing conditions influence the mineralogical transformations of mortars and therefore also the mechanical behaviour of the mortars tested. Furthermore, the heavy metal impurities in the phosphogypsum were immobilized in the cement matrix, leading to a clear improvement of the technical properties of cement mortars made with this waste compared to the traditional use of natural gypsum.

Keywords: phosphogypsum treatments, pozzolanic addition, curing conditions, cement mortars, technical properties.

34 **1. Introduction**

35 The generation and management of any type of waste is a serious environmental prob-
36 lem in today's society. Thus, the reduction of its generation and its appropriate man-
37 agement are necessary to avoid serious impacts on the environment that can cause pol-
38 lution affecting the ecosystems and human health [1].

39 Phosphogypsum (PG) is an industrial by-product of the fertiliser industry, mainly from
40 the production of phosphoric acid.

41 Approximately 250 Mt of PG are generated around the world as an inorganic by-
42 product in several industrial processes [2, 3]. In Spain, due to the manufacture of a
43 number of fertiliser products during the years 1968–2010, around 100 Mt of this waste
44 accumulated in stacks located 1 km from the city of Huelva [4].

45 One of the main uses of PG investigated so far is the application of this by-product as a
46 fertilizer in agricultural soils [5]. Actually, only 15% of world production is used and
47 recycled [6]. The remaining 85% is accumulated in large areas raising environmental
48 issues [4]. The valorisation of this by-product is highly dependent on the properties of
49 the PG and the country of origin.

50 A very important and appealing use of PG could be in the cement manufacturing pro-
51 cess. PG could be used there as a replacement for natural gypsum (NG), as a setting
52 retarder [7, 8]. Based on previous works, this paper analyses the use of PG as setting
53 retarder replacing NG, evaluating its potential of improving the mechanical behaviour
54 of cement mortars. This leads to a study of the application of the PG accumulated into
55 stacks located in Huelva, Spain and stored without recovery.

56 The application of various PG treatments could improve the properties of construction ma-
57 terials manufactured with it [9]. Treated PG can be used as an ingredient of plaster [10-12].
58 Higher compressive strength values of Portland cement were shown with calcined PG [13].

59 This is due to the structure anhydrite cement generation by heating PG at 1000 °C [14].
60 In addition to the mechanical properties, environmental aspects must be considered, due
61 to the presence of impurities in the stored PG [15-17]. The impurities' origin depend on
62 the phosphate rock used as raw material and the manufacturing processes used [18]. PG
63 contains 5–6% impurities, which can be heavy metals, radionuclides or fluorides [19].
64 The impurities present in PG directly affect the mechanical properties of cement mortars
65 manufactured with this by-product. It has been found that several impurities, such as
66 P_2O_5 , F or organic matter, can be removed by washing with water [11].
67 For this reason, and based on previous comments, the main objective of this study has been
68 to analyse the influence of the untreated PG and of the different treatments, incorporation
69 ratios and curing conditions on the technological properties, mineralogical characteristics
70 and environmental and health aspects of cement mortars manufactured with PG from Spain.

71 **2. Experimental programme**

72 **2.1. Materials**

73 This study evaluated representative samples of the deposits of PG located in Huelva,
74 Spain. The samples were processed through four treatments. First, a control sample was
75 manufactured with clinker and natural dihydrated gypsum (Control-NG); it was then
76 compared with those manufactured with PG prepared by various treatments as a substitute
77 of natural gypsum. Finally, to compare the properties of these mortars with a commercial
78 cement, a sample was manufactured with cement CEM I 42.5R without additions (OPC).

79 *2.1.1. Phosphogypsum*

80 Four types of processed PG's were used in this study:

- 81 (1) dried phosphogypsum (PG-D): material dried in an oven for 48 hours at 40 °C;
- 82 (2) crushed phosphogypsum (PG-C): PG crushed using a ball mill and subsequently

83 sieved through a 125 μm mesh;

84 (3) burned phosphogypsum (PG-B): obtained by the calcination of PG in a muffle at

85 800 $^{\circ}\text{C}$ for 18 h;

86 (4) washed phosphogypsum (PG-W): washed in a beaker with distilled water at a liq-

87 uid/solid ratio of 10:1; during this first washing, PG was stirred for 40 min, then left

88 to stand for 20 min and the pH of the material was measured; finally, it was filtered

89 with laboratory paper; a second washing was performed after filtering with the same

90 procedure; finally, the material was dried for 48 h in an oven at 40 $^{\circ}\text{C}$.

91 The particle size distribution was determined using wet laser diffraction (Malvern Mas-

92 tersizer). Figure 1 shows the morphology of the material particles and the variations in

93 particle shape and size.

94 The particle distribution of the material was fundamentally dependent on the type of

95 phosphate rock used as raw material and the conditions of the manufacturing process

96 [20, 21]. Regarding the four types of materials obtained in the laboratory, PG-C showed

97 a finer particle distribution due to the crushing process to which it was subjected.

98 The chemical properties of the different PG samples are summarised in Table 1.

99 Table 1. Chemical composition of the raw materials (wt%)

PROPERTIES		OPC	Ck	NG	PG-D	PG-C	PG-B	PG-W	
	Si	7.78	8.40	2.98	0.40	0.38	0.55	0.47	
	Ca	48.2	49.3	23.3	22.5	22.8	27.7	23.1	
	K	0.28	0.26	0.08	-	-	-	-	
	Mg	0.49	0.42	0.37	-	-	-	-	
	Fe	3.53	3.78	0.07	0.03	0.04	0.04	0.03	
Elemental con-	Al	UNE-EN 196-2:2014	1.32	1.49	0.83	0.08	0.08	0.10	0.09
	content (%)		F	-	-	-	1.26	1.44	1.44
	Na	-	0.10	-	0.07	0.07	0.07	0.02	
	P	0.07	0.07	0.12	0.22	0.22	0.28	0.20	
	S	1.55	0.79	20.41	16.74	16.86	20.56	17.06	
	Ti	0.08	0.07	0.03	0.02	0.02	0.01	0.02	
	Loss on ignition (975 $^{\circ}\text{C}$)	UNE-EN 1744-1:2010	2.03	0.34	21.41	23.66	22.83	1.18	21.57

100
 101 PG-D was mainly composed of Ca and S: 22.5% and 16.74%, respectively. In addition,
 102 the sample contained 1.26% of F; the rest of components were in proportions lower than
 103 1%. The compositions of PG-C and PG-W were similar. However, there were slight vari-
 104 ations in Ca and S contents in the PG-B sample. In this case, the proportions of Ca and S
 105 increased, resulting in 27.7% of Ca and 20.56% of S, although the same Ca/S relation was
 106 sustained. On the other hand, the decrease of Loss on Ignition (LOI) in PG-W was due to
 107 the loss of impurities through the washing treatment.

108 Table 1 shows that the Ca/S ratios of the PG samples were higher than those of NG.
 109 This led to consider that PG does not only act as a setting regulator in the manufacture
 110 of cement mortars; its use also improves the mortar's mechanical properties. High Ca/S
 111 ratio, high free lime content and high anhydrite content present in the mineral additions
 112 improve the pozzolanic activity and cementing properties [22, 23].

113 After the initial evaluation of the materials that showed high content in Ca and S, the
 114 determination of the mineralogical phases of PG and NG was carried out (Table 2).

115 Table 2. Mineral composition of the raw materials (%)

Mineral phase	NG	PG-D	PG-C	PG-B	PG-W
Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	91.5	92.2	91.7	<0.1	92.7
Bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$)	1.5	<0.1	<0.1	28.1	<0.1
Anhydrite (CaSO_4)	<0.1	<0.1	<0.1	62.7	<0.1
Dolomite ($\text{CaMg}(\text{CO}_3)_2$)	5.6	<0.1	<0.1	<0.1	<0.1
Calcite (CaCO_3)	<0.1	4.8	1.8	4.1	3.0
Quartz (SiO_2)	0.9	1.9	3.9	4.3	1.4
Fluorite (CaF_2)	<0.1	<0.1	1.2	0.9	1.1
Chukhrovite (Ca) ($\text{Ca}_4\text{AlSi}(\text{SO}_4)\text{F}_{13} \cdot 12(\text{H}_2\text{O})$)	<0.1	1.1	1.5	<0.1	1.8

116
 117 The NG and PG with different treatments are composed mostly of gypsum, except for
 118 the calcination treatment (PG-B) that is composed mostly of bassanite and anhydrite,
 119 due to the loss of water in the process.

120 2.1.2. *Cement (OPC), clinker (Ck) and natural gypsum (NG)*

121 Portland cement clinker (Ck), made of limestone and clays heated to 1450 °C, was used
 122 to manufacture PG mortars. NG is added to the clinker in the final cement grinding pro-
 123 cess, as a set retarder; the usual levels of addition are between 3% and 5%. Therefore,
 124 NG was studied to compare its properties with those of PG. As shown in Table 1, NG is
 125 characterised by its high concentrations of Ca (23.3%) and S (20.41%). The remaining
 126 elements (Al, Fe, Mg, S and Ti) are present at less than 1%, except Si (2.98%).
 127 Additionally, the study of cement mortars manufactured with commercial Portland ce-
 128 ment type CEM I 42.5R was carried out. The chemical properties of this cement are
 129 shown in Table 1.

130 **2.2. Mix proportions**

131 The various treated PG's (PG-D, PG-C, PG-B, PG-W) were used at two percentages of
 132 addition to clinker (2.5% and 5%) for the evaluation of the properties of the cement
 133 produced.. Further, a control mortar with NG (Control-NG), a mix with NG and PG-D
 134 (NG-PG-D 50/50) and a reference cement mortar with commercial Portland cement
 135 only (OPC) were manufactured. The nomenclature of each manufactured cement mortar
 136 is shown in Table 3.

137 Table 3. Nomenclature of the cement mortars

MORTAR	DESCRIPTION
OPC	Reference mortar manufactured with Cem I 42.5R
Control-NG	Control mortar manufactured with NG
NG-PG-D-50/50	Mortar with NG and dried PG in the same proportion (50%)
PG-D	Mortar with dried PG
PG-B	Mortar with combusted PG
PG-C	Mortar with crushed and sieved PG
PG-W	Mortar with washed and filtered PG

138 The mix proportions are shown in Table 4. Six pieces of each specimen were manufac-
 139 tured. All samples were mixed in a laboratory drum mixer. Then, the fresh mortar sam-
 140

141 ples were placed in moulds and homogenised using a vibrating table. Finally, to evalu-
 142 ate the influence of curing on the mortars, they were cured in two ways: in a curing
 143 chamber at 50% humidity and 20 °C temperature and immersed in a water tank (hu-
 144 midity of 100% and temperature of 20 °C).

145 Table 4. Mortars mix proportions

		CONTENT (g)					
Reference		SS (Standard Sand)	PG	NG	Cement	Clinker	Water
	OPC	1350	-	-	450	-	225
Series 1 (2.5%)	2.5Control - NG	1350	-	11.25	-	438.75	225
	2.5NG-PG-D-50/50	1350	5.625	5.625	-	438.75	225
	2.5PG-D	1350	11.25	-	-	438.75	225
	2.5PG-C	1350	11.25	-	-	438.75	225
	2.5PG-B	1350	11.25	-	-	438.75	225
	2.5PG-W	1350	11.25	-	-	438.75	225
Series 2 (5%)	5Control - NG	1350	-	22.5	-	427.5	225
	5NG-PG-D-50/50	1350	11.25	11.25	-	427.5	225
	5PG-D	1350	22.5	-	-	427.5	225
	5PG-C	1350	22.5	-	-	427.5	225
	5PG-B	1350	22.5	-	-	427.5	225
	5PG-W	1350	22.5	-	-	427.5	225

146

147 2.3. Test methods

148 This study evaluated the cement mortars manufactured with PG as a substitute of NG
 149 according to three essential characteristics:

- 150 (1) Technological tests to evaluate the mechanical behaviour and durability properties
 151 of the cement mortars: consistency, density and setting time of fresh mortars, and
 152 flexural strength, compressive strength and shrinkage of hardened mortars;
- 153 (2) A mineralogical study of the manufactured mixtures by X-ray diffraction (XRD)
 154 to understand the behaviour of hardened mortars manufactured with PG. The
 155 mineralogical analysis was carried out by powder XRD analysis on a Bruker
 156 (model D8 Advance A25) with Cu anti coat. The measurement conditions were:
 157 2 θ of 10–120°; step = 0.015°; t = 0.5 s; tube conditions: 40 KV and 30 mA; fixed
 158 divergence gap of 0.1°; 30 rpm spin and Ni filter. For the quantitative analysis

159 by XRD, the Rietveld method was used (TOPAZ v. 4.2 software);

160 (3) A potential environmental impact of the manufactured mortars: leaching tests car-

161 ried out on materials as in EN 12457-2 procedure. To evaluate the effect of PG

162 within the cement matrix, cement mortars manufactured with 5% PG were studied

163 as per the NF X31-211 monolithic leaching test. Before leaching, the mortars were

164 cured for 28 days at room temperature. This test was carried out at the natural pH

165 of the sample and the concentration of heavy metals was determined in lab by in-

166 ductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer NexionX):

167 equipped with sample introduction system, Argon plasma ionization and quadru-

168 pole ion detection. The Simple Quadrupole is a low resolution mass spectrometer

169 with which it has been performed and a semi-quantitative analysis).

170 Table 5 shows the test standards used.

171 Table 5. Mortars' characterization tests

		Test method	Curing time	
Technological tests	Properties of fresh mortar			
		Consistence	UNE-EN 1015-3	0 days
		Bulk density	UNE-EN 1015-6	0 days
		Setting times	UNE-EN 196-3	0 days
	Properties of hardened mortar			
		Compressive strength	UNE-EN 196-1	1, 7, 28 days
	Flexural strength	UNE-EN 196-1	1, 7, 28 days	
	Shrinkage	UNE 83831	1, 7, 14, 28, 56 days	
Mineralogical study	Powder X-ray diffraction (XRD)		28 days	
Environmental feasibility	Leaching test raw material	EN 12457-2	0 days	
	Monolithic leaching tank test	NF X31-211	28 days	

172 In order to evaluate and characterise as a whole the mechanical behaviour resulting

173 from of the use of PG in cement mortars, multivariate approaches were applied. In this

174 context, the following parameters were used: flexural strength (FS) and compressive

175 strength (CS). Both mechanical properties are considered quality indicators to evaluate

176 the potential use of different waste types in new cements [24].

177

178 Statistical data analysis was carried out using multivariate principal component analysis
179 (PCA). The R v.3.3.0 freeware was used to perform the statistical analysis [25]. Prior to
180 the statistical analysis, a detailed data exploration was carried out for each PG treatment
181 and the mechanical parameters were analysed for normality (Shapiro–Wilk test) and
182 homogeneity of variance (Fligner test) using the package ‘mvnormtest’ [26]. Log trans-
183 formation was used for both CS and FS variables in order to archive normality.

184 The study evaluated the patterns of variability in the influence of both PG treatment and
185 incorporation ratio under different curing conditions. To test them, models were analysed
186 according to univariate analysis of variance (ANOVA) and were compared using the Chi-
187 square test for $p \leq 0.05$. Firstly, it was necessary to choose the best-fit model, which was
188 carried out by statistical indicators (e.g. adjusted R^2 and Akaike information criterion
189 (AIC)). In addition, the error measures of the root mean square error (RMSE) were calcu-
190 lated for each model developing an objective comparison of the performance of each.

191 Then, principal components analysis (PCA) was carried out to evaluate the mortars’ me-
192 chanical behaviour at 28 days and establish the degree of discrimination and/or association
193 between them. Two PCAs in particular were carried out: 1) whole-experiment design (e.g.
194 curing treatment conditions, incorporation ratios of PG, and PG treatments), and 2) for each
195 curing condition separately (e.g. dry-chamber and underwater-curing treatment conditions).

196 A Q-mode analysis was used by the PCA through the principal functions in the psych pack-
197 age for carry out the breakdown of the data matrix between populations [27]. Through this
198 analysis, a set of variables (dimensions) are created, which are the result of linear combina-
199 tions of the variables of origin. The new dimensions are independent between themselves
200 and their classification is done according to the variation shown. An orthogonal varimax
201 gross rotation was used for the estimation of the factor loads after the initial extraction by
202 the main method. Only factors with SS (sum of squares) loadings > 1 were extracted.

203 3. Results and discussion

204 3.1. Technological tests

205 3.1.1. Consistency, density and setting time

206 The consistency and density of the cement paste were estimated before the setting time.
 207 The use of PG in mortars resulted in consistency values lower than that of the OPC
 208 mortar. As the PG incorporation ratio increased, the consistency values decreased (Ta-
 209 ble 6). It was observed that PG made the paste stiffer, and therefore more water was
 210 required to obtain a consistency similar to that of the control mortar [28]. Bhadauria and
 211 Thakare [28] showed that at 5% incorporation of PG the consistency was very close to
 212 control values, and similar to the results obtained in our work (Table 6).

213 Table 6. Physical properties of the fresh mortars

		<i>Consistency (mm)</i>		<i>Density (g/cm³)</i>		<i>Setting time (minutes)</i>	
		<i>UNE-EN 1015-3</i>		<i>UNE-EN 1015-6</i>		<i>UNE-EN 196-3</i>	
						<i>Initial</i>	<i>Final</i>
	OPC	166		1937		169	216
Series 1 (2.5%)	2.5Control - NG	157		2031		149	193
	2.5NG-PG-D-50/50	156		1997		163	211
	2.5PG-D	153		1974		153	209
	2.5PG-C	156		1991		132	197
	2.5PG-B	154		1982		158	213
	2.5PG-W	159		1987		146	203
	Series 2 (5%)	5Control - NG	135		2028		141
5NG-PG-D-50/50		152		2063		150	198
5PG-D		146		1996		181	246
5PG-C		149		2023		166	224
5PG-B		148		2003		186	221
5PG-W		153		2016		193	264

214 Table 6 shows that the PG treatment did not significantly influence the consistency val-
 215 ues obtained. The lowest consistency values were obtained for PG-D in both series:
 216 153 mm and 146 mm, respectively.
 217

218 Unlike the consistency values, as the PG incorporation increased, the density values
 219 also increased (Table 6). This property was significantly influenced by the PG type.

220 Table 6 shows that mortars manufactured with crushed, burned and washed PG resulted

221 in an increase in density with respect to mortars manufactured with PG-D. This can be
222 attributed to the removal of impurities [29], due to the formation and hardening of the
223 hydration products, the open pores are filled and the density increases [30].

224 The setting times (initial and final) showed significant increases as the incorporation
225 ratio of PG increased. Similar values were obtained in a previous work [31]. The setting
226 time was always shorter for PG mortars than for the OPC mortar for 2.5% incorpora-
227 tion. Using more than 2.5% PG, the setting time increased gradually; however, this was
228 different for Control-NG and NG-PG-D 50/50, possibly because NG has low phospho-
229 rus content in relation to the PG, as shown in Table 1. The presence of phosphorus in-
230 creases the setting time and, for this reason, the use of NG in the cement paste led to a
231 faster setting time [31, 32].

232 The processed sample PG-C with 5% incorporation showed optimum results for both
233 initial and final setting times (relative to OPC). The latest setting time was obtained for
234 5% PG specimens. Previous studies have shown that an increase in the amount of impu-
235 rities such as fluorides [11] leads to an increase in setting time [33-36]. Table 6 shows
236 that PG-W resulted in the highest setting times, because this procedure can lead to an
237 increase in the proportion of non-soluble impurities present in the sample.

238 *3.1.2. Compressive and flexural strength*

239 Figures 2 and 3 show the results of CS and FS of the manufactured mortars. This study
240 demonstrated that mortars cured at similar temperature and different humidity presented
241 different technical properties. It was observed that mortars cured in underwater condi-
242 tions obtained higher CS values than those cured in dry-chamber conditions for all
243 treatments and incorporation ratios.

244 All cement mortars manufactured with PG showed higher values of CS than those man-
245 ufactured with NG (Control-NG).

246 With respect to incorporation ratio, it was generally observed that for Series 1 (2.5%
247 incorporation), the processed materials showed higher CS values under both curing
248 conditions and for all ages than the 2.5 PG-D, 2.5 Control-NG and 2.5 NG-PG-D 50/50
249 mortars. The PG treatments influenced more significantly the CS values of mortars
250 cured in the dry chamber (Figure 2.B).

251 In Series 1 (2.5% incorporation), the highest values of CS were obtained for PG-W.
252 Similar results were shown in previous studies, in which different treatments eliminated
253 the impurities present in PG, showing that the use of these materials at small percent-
254 ages increased the CS relative to mortars manufactured with unprocessed PG [37].

255 As the incorporation ratio of PG increased, CS also increased in underwater-cured ce-
256 ment mortars, due to the additional hydration of mortars, which leads to a faster poz-
257 zolanic reaction. Mortars manufactured with 5% PG obtained higher CS values than
258 OPC and 5Control-NG mortars cured in underwater conditions (Figure 2.A). Similar
259 results were obtained by several authors, who found that the incorporation of up to 10%
260 of PG in mortars and concrete led to an increase in the CS values [31, 38].

261 The increase in CS was related to the setting time. For 5% PG incorporation and under-
262 water-curing conditions, the final setting time and CS increased, i.e. the delay in setting
263 time is likely to be due to the slow hydration reaction [39] and this in turn to an increase
264 in compressive strength.

265 This showed that a greater incorporation of PG, due to its chemical composition, acted
266 not only as a regulator of setting time. It also provided a cementitious capacity to ce-
267 ment mortars similar to that provided by mineral additions, thus increasing CS. The
268 highest values were obtained for the 5PG-D mortar (58.44 MPa), although the results of
269 CS of mortars manufactured with the various PG treatments can be considered similar.
270 This fact is very important since it reinforces the benefits of adding PG when making

271 cement, by reducing the amount of NG used.

272 Regarding FS, as the PG incorporation ratio increased, the strength also increased for the
273 two curing conditions. This effect was more significant in cement mortars cured in a dry
274 chamber (Figure 3.B) and is in contrast with CS, where the increase in PG incorporation
275 significantly increased the strength of underwater-cured mortars at 28 days (Figure 2.A).

276 All mortars manufactured with 5% PG (with and without treatment) showed higher FS
277 values than those manufactured with commercial cement OPC (OPC) for both curing
278 conditions (Figures 3.A and 3.B).

279 As with the incorporation ratios, the influence of PG treatment was more significant in
280 dry-chamber-cured mortars (Figure 3.B), as the values of CS show (Figure 2.B).

281 Under dry-chamber curing conditions, lower FS values were obtained than in sub-
282 merged curing for all mortars. Even so, the use of PG in the manufacture of mortars led
283 to an improvement in this property with respect to the OPC at 28 days in dry-chamber
284 cured (Figure 3.B). The use of PG was not as clearly an improvement for FS relative to
285 OPC in mortars in underwater curing conditions (Figure 3.A). Therefore, CS and FS
286 values increased as the PG incorporation ratio increased, obtaining higher strength val-
287 ues in underwater-cured mortars.

288 Once the mechanical behaviour of each of the cement mortars has been analysed, a syn-
289 thesis of the optimum treatment parameters, content and curing conditions is shown in
290 Figure 4.

291 3.1.3. Shrinkage

292 The dimensional instability over time of the cement mortars was studied to evaluate the
293 influence of PG incorporation ratio and PG treatment on the performance of mortars. Figure
294 5 shows that the shrinkage values of cement mortars with 2.5% incorporation of PG are

295 very close, independent of the treatment applied to PG, and similar to those of OPC mor-
296 tars. The mortars made with NG presented greater dimensional instability than those made
297 with PG. This concurs with previous studies [40], in which it was demonstrated that a high-
298 er incorporation ratio of NG resulted in an increase in shrinkage for cement mortars; shrink-
299 age increased with increasing amount of gypsum. All mortars made with PG showed a de-
300 crease in shrinkage relative to mortars made with NG, both for series 1 and 2. According to
301 the few available studies, incrementing the incorporation of PG in the mortars increased
302 shrinkage [29, 41]. In cement mortars made with 5% PG, shrinkage values increased signif-
303 icantly relative to mortars made with 2.5% PG and OPC mortars, as shown in Figure 5.

304 This study found that the PG's particle influenced the dimensional changes of the mortars,
305 because mortars made with PG-C and PG-B, which have a particle size smaller than PG-D
306 and PG-W, resulted in larger dimensional changes for both series (2.5% and 5% incorpora-
307 tion). For this reason, the shrinkage of 5PG cement mortars could be due to the chemical
308 composition of PG that undergoes slight changes because of the treatments.

309 **3.2. Mineralogical study**

310 Table 7 shows the results of the XRD analysis of the reference, control and mortars
311 made with 5% of PG, processed and unprocessed, under different curing conditions.

312 Curing conditions showed variations in the mineralogical phases of cement mortars. Mor-
313 tars with 5% PG cured underwater showed higher contents of alite, belite, portlandite and
314 ettringite, which means that the internal reactions produced by water in the mortar paste
315 took place slower, achieving greater pozzolanicity in the mixes and an improvement in me-
316 chanical behaviour. The increase in alite values is related to better mechanical behaviour,
317 since alite is the primary strength-contributing phase during Portland cement hydration.

318 Table 7. Structural details for phases that may be present in Series 2 of cement mortars
 319 in relation to curing conditions

Mineralogical phase (%)	Dry chamber curing					
	OPC	5Control - NG	5PG-D	5PG-C	5PG-B	5PG-W
Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	4.8	9.3	1.5	4.4	1.6	1.4
Calcite (CaCO_3)	7.4	11.4	11.5	10.4	10.4	13.9
Anhydrite (CaSO_4)	<0.1	3.1	<0.1	<0.1	<0.1	<0.1
Quartz (SiO_2)	39.5	39.8	42.5	46.5	48.7	52.6
Alite (Ca_3SiO_5)	10.4	9.2	17.7	14.3	18.9	7.2
Larnite (Belite) (Ca_2SiO_4)	13.6	11.5	3.9	7.6	1.2	10.1
Brownmillerite ($\text{Ca}_2\text{AlFeO}_5$)	4.1	4.2	8.2	3.7	2.6	2.4
Portlandite (CaOH_2)	16.6	8.5	11.1	8.6	10.8	8.3
Ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$)	2.9	1.2	3.7	2.8	4.8	3.3
Thaumasite ($\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$)	<0.1	1.3	0.2	1.2	0.6	0.1

Mineralogical phase (%)	Underwater curing					
	OPC	5Control - NG	5PG-D	5PG-C	5PG-B	5PG-W
Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	2.3	2.9	1.2	1.9	2.5	1.8
Calcite (CaCO_3)	8.9	4.6	4.6	4.7	4.3	4.2
Anhydrite (CaSO_4)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Quartz (SiO_2)	46.2	68.1	31.0	45.9	39.8	53.0
Alite (Ca_3SiO_5)	12.6	8.6	20.6	16.8	19.5	8.9
Larnite (Belite) (Ca_2SiO_4)	12.6	5.8	12.0	10.4	10.9	8.9
Brownmillerite ($\text{Ca}_2\text{AlFeO}_5$)	2.9	2.9	3.2	3.5	2.9	4.4
Portlandite (CaOH_2)	10.8	4.7	17.2	13.2	17.2	14.1
Ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$)	2.5	1.1	5.0	2.3	1.7	3.5
Thaumasite ($\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$)	<0.1	1.1	0.7	0.9	0.9	0.6

320
 321 In mortars manufactured with PG, ettringite values increased and gypsum values de-
 322 creased with respect to Control-NG (Table 7). The ettringite crystals formed at an early
 323 stage were connected to each other and built up a framework that was beneficial to early
 324 strength development [42].

325 The increase in ettringite formation was conditioned by a slower final setting time. For
 326 that reason, it was observed that mortars of Series 2 manufactured with PG, in which the
 327 setting time was later than in the Control-NG mortar (Table 6), the amount of ettringite
 328 increased (Table 7). The early ettringite formation acts as a layer that covers the cement
 329 grains and causes a slower setting of mortars [43]. The results showed how the presence
 330 of PG in a reacting cementitious system can influence its setting time and the crystal-
 331 linity of the ettringite formed [44].

332 As seen in Table 7 in the mineralogical phase of the mortars, the curing conditions are

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