Physico-chemical and radiological characterization of cement mortars manufactured by using phosphogypsum as setting regulator

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Introduction

Phosphogypsum (PG) is a waste generated in the production of phosphoric acid by the sulphuric acid route, which phosphate rock ($Ca_{10}(PO_4)_6F_2$) is subjected to a dissolution with sulphuric acid (H_2SO_4). PG is mainly composed by calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$), some metals impurities (e.g., As, Cd, Sr), and natural radionuclides from ^{238}U decay-series. These pollutants are transferred from the phosphate rock to both phosphoric acid and PG during the chemical process. The PG, as a consequence, is considered as a NORM (naturally occurring radioactive material) compound (Gázquez et al., 2014).

In the southwest of Spain, PG has been stored in piles on wetlands of Huelva estuary for more than 45 years. Currently, those piles reach 5 m of height, covering an area of about 1000 ha. It is estimated that there are over 100Mt of PG stored in these stacks, which involve potential radiological and environmental risks (Bolívar et al., 2009; Pérez-López et al., 2010). Therefore, the valorisation and recycle of this stored PG could help in the mitigation of this environmental problem. In addition, the annual worldwide PG production is around 200–280 Mt, doing that nowadays many researches were focused on the search of new uses of PG as, for example, agricultural fertilizers, soils stabilization, gypsum plaster, cements and concretes, etc. However only the15% of the worldwide production is recycled (López et al., 2011).

In this sense, we have studied a new application of PG in civil engineering, consisting in to use this by-product as setting retarders to replace the natural gypsum in cement mortar. This study aims the physico-chemical and radioactive characterization of the different raw materials used, and the new obtained cements in order to evaluate the technological properties as well as their environmental risks.

Materials and Methods

PG was sampled in December 2015 from the phosphogypsum piles of Huelva. PG was used in this study without any prior treatment (PG-NP), and also has been subjected to different pre-treatment: (a) PG-S: PG was sieved through 125 µm of mesh; (b) PG-B: PG was burned at 400 °C during two hours and then cooled at room temperature; (c) PG-W: PG was washed twice with distilled water in relation 1:10 (S/L), in each washed it was stirred during 40 min and allowed settle for 20 min. Finally, the solution was filtrated and the PG was dried at 40 °C during 48h.

In addition, commercial clinker and normalized sand have been employed in the manufacturing of the cement mortars, in which were subjected to 100% humidity and 20 °C as curing conditions. The proportion of materials used in the mortars were done according to regulations of building materials.

Several techniques were used to characterise the raw materials and products obtained in this study, such as XRF, ICP-MS, XRD, SEM–EDS and laser granulometry. Naturally occurring radionuclides were determined by both gamma spectrometry and alpha spectrometry. In order to evaluate the potential environmental impact, leaching tests were also applied.

Results and Discussion

The results show that all samples of PG present the same particles size distribution, even the sieved PG-S sample. Approximately, 90% of their particles have a diameter (%V) less than 100 µm.

The concentrations of major elements are shown in Table 1, observing that no significant differences there are between PG-NP, PG-S and PG-W samples. However, Ca and S concentration is higher in the PG-B than in PG-NP (23 % for both elements), due to a concentration effect because of the loss of water from sulphate calcium dihydrate ($CaSO_4 \cdot 2H_2O$).

According to DRX results the PG-NP, PG-S and PG-W samples contain gypsum as main crystal phases (92%), while for PG-B the main crystal phases are anhydrite (63% $CaSO_4$), and basanite (28%$CaSO_4 \cdot 1/2H_2O$). Clinker sample, as it is expected, is composed of alite (63% Ca_3SiO_5), belite (22% Ca_2SiO_4) and Brownmillerite (10% Ca_2AlFeO_5), which is in agreement with the literature (Hewlett et., 1998).

The SEM-EDS analysis show that PG-NP, PG-S and PG-W samples presents the typical habit of gypsum, such as tabular crystals, elongated frequently mottled in swallow tail or spear head. On the other hand, PG-B sample presents massive aggregates of variable grain size, which are mostly available in groups of parallel or radial fibres, i.e. presents exfoliations, typical of basanite and anhydrite.

Table 1. Concentration of mayor elements (%). D.L. Detection limit

	Al	***Ca***	***F***	***Fe***	***Na***	***O***	***P***	***S***	***Si***	***P.C.***
DL	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**-**
PG-NP	0.08	22.5	1.26	0.03	0.07	34.9	0.22	16.74	0.40	23.66
PG-S	0.08	22.8	1.44	0.04	0.07	35.2	0.22	16.86	0.38	22.83
PG-W	0.09	23.1	1.72	0.03	0.02	35.7	0.20	17.06	0.47	21.57
PG-B	0.10	27.7	1.44	0.04	0.07	43.0	0.28	20.56	0.55	6.18

Due to the relative high levels of natural radionuclides in the PG, a significant radiation exposure could be received from building materials containing this by-product. Different international recommendations propose reference values for the natural radionuclide concentrations in building materials. The European Union regulation defines the external risk index (I=C(^{226}Ra)/300+C(^{228}Ra)/200+ C(^{40}K)/3000), being C the respective activity concentration of the considered radionuclide. This index should not exceed the value of 1 for materials used in bulk amounts, e.g. concrete, or has to be lower than 6 for superficial and other materials with restricted use, e.g. tiles, boards, etc.

The obtained external risk indexes for mortars manufactured (CM) in this study are shown in Table 2. It can be seen that index values are much lower than the established value for materials used in bulk amounts.

Table 2. The activity concentration index I in cement mortars manufactured.

CODE	SAMPLE COMPOSITION	PROPORTIONS	INDEX
CM-1	*PG-NP; CK; SAND*	1:40:120	0.145
CM-2	*PG-S; CK; SAND*	1:40:120	0.143
CM-3	*PG-B; CK; SAND*	1:40:120	0.148
CM-4	*PG-W; CK; SAND*	1:40:120	0.143

Conclusions

This study evaluates the environmental risk of cement mortars manufactured with PG as an additive for setting retardant. The results reveal that the cement mortars do not present any environmental or health risk, whatever the type of pretreatment to which PG samples can be subjected. In this sense, an exhaustive study of mechanical properties of these mortars is being carried out in order to obtain commercial products.

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