

Valorizing Phosphogypsum as a Set Retarder in Portland Cement: Investigation on its Heavy Metals Release into Buffered Aqueous Media

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Abstract- Phosphogypsum is a by-product in phosphate fertilizers and phosphoric acid industries. It is valorized as a set retarder in Portland cement replacing the gypsum rocks. In this study, influence of phosphogypsum contents on concrete and Portland cement properties was investigated. Phosphogypsum was mixed with Portland cement at different mass contents extended from 1 to 20% wt/wt. Setting time, specific area of Portland cement and response to compression strength were followed. Chemical characteristics and heavy metals release into buffered acidic and alkaline aqueous solutions were also investigated. Obtained results showed that less than 8% of phosphogypsum is the best mass content to enhance cement quality without altering significantly the mechanical properties. The highest compressive strength applied to concrete was recorded after 28 days under saturated humidity conditioning. Conversely, the increase of phosphogypsum content in cement over than 8% resulted in a decrease of mechanical strengths of the corresponding concrete. Metal leaching experiments were conducted on different mixture of concrete mortars immersed in buffered acid solutions. Leaching results have showed that highest concentration of chromium, zinc, copper and lead are transferred to aqueous media during the first three days of impregnation. Zinc had a particular behavior. It was entrapped in concrete mortars before being transferred into aqueous solutions. In addition, metal release was significantly enhanced when phosphogypsum contents increased in the cement.

Key words- valorizing, phosphogypsum, Portland cement, heavy metals, setting time, compression strength

I. INTRODUCTION

Phosphogypsum is one of the most important solid wastes generated by phosphate fertilizer industries. Many aquatic media in the Mediterranean basin were considerably degraded because of direct phosphogypsum release or its storage under atmospheric weathering conditions (Marroc, Tunisia, Spain, Lebanon and Syria) [1-7]. Phosphate fertilizer industries use mainly phosphate ores sedimentary deposits as raw materials [8]. During industrial process, heavy metals, radionuclides and residual fluoride acid are transferred from phosphate rocks to phosphogypsum by-products [5; 9; 10]. Phosphogypsum (PG) is mostly calcium sulfate di-hydrate or hemi hydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$), It contains high levels of impurities, radionuclides (Ra, U, Th, Po) and trace elements such as Cr, Zn, Cu, Pb and Cd [7; 11]. Impurity contents depend on the original phosphate ores, the manufacturing process and the industrial control [1].

The most important two challenges in PG management that confront phosphate fertilizer plants are to reduce pollutants and enhance the PG usefulness. Currently, PG is stored into piles in the vicinity of the factory. Only 15% of worldwide production are recycled [1]. In some countries, it is valued as a fertilizer or a substitute of gypsum in Portland cement and construction concretes [12].

In the last stage of Portland cement manufacturing process, the natural gypsum is commonly supplemented during clinker grinding to delay the rapid reaction between C_3A ($\text{CaO} \cdot \text{Al}_2\text{O}_3$) and water and to regulate cement setting properties. Gypsum is added in an optimal proportion (about 5% wt/wt) to increase setting time as a result of sulfate dehydration properties [13]. Since both phosphogypsum and naturel gypsum have a similar mineralogical phase and the same function as retarders of cement solidification, PG started to be valorized in construction materials and lowered the cement production price [14-16]. However, its valorizing in Portland cement is still a relevant environmental question since entrapped pollutants behaviors are not well known in the literature and whether their release in the medium may occur under natural conditions.

The present study aims to investigate the becoming of heavy metals (Pb, Cr, Zn, and Cu) originally present in PG added as set retarder to Portland cement clinker. As external applications are the main use of concrete, the latter is exposed to a great number of deleterious ions such chloride, sulfate, nitrate and carbonate. Hence, metal release from concrete conditioned in synthetic buffered and acidic aqueous solutions is studied to identify transfer and leaching mechanisms. Optimal PG contents in Portland cement are also determined as function of concrete and cement mechanical properties.

II. MATERIALS and METHODS

A. Sample Preparation

Phosphogypsum was collected from a Lebanese Chemical Fertilizer company located at the north of the country (lat. 34°16'23.38" N, long. 35°39'15.15"E). This factory produces phosphate fertilizers and releases about 96 tons of PG per day into the Mediterranean Sea [17]. This fact has a major impact on the marine environment. A devastated bottom sea near the industry was found where a large area is covered with PG and became completely inert [17]. Four equivalent samples of PG were collected during different production days, grinded and homogenized together in an agate mortar under 400rpm velocity (TTS 50 Drum Mill) then sieved at 200 μ m mesh and stored in the oven under 50°C before being used. A fresh clinker sample was collected at the furnace outlet of a Lebanese Portland cement industry. Clinker was grinded and sieved under 200 μ m sieves to reach a specific area in the range of 3500 and 3600 cm²/g following the ASTM-C305 procedure. Grinded clinker was mixed with sand and water following the ASTM-C109 standard within a weight ratio of clinker to sand of 2.75 and clinker to water of 0.485. Sand quality is used according to ASTM-C778 (99.7% quartz, spherical grain size between 1.18mm and 0.15mm, hardness 7Mohs, melting point 3100°F).

Eight types of concrete cubic mortars (5cm x5cm x5cm) were prepared according to the ASTM-C305, containing different percentages of PG extended from 0 to 20% *wt/wt* (0, 1, 2, 3, 4, 8, 12 and 20% of PG).

Concrete cubes were conditioned under saturated relative humidity (100%) by submersing them in a buffered acidic medium at 23 \pm 2 °C. The buffered media contained equivalent concentrations of 0.0276 mol/L of the most common ions found in aquatic media Na₂SO₄, NaHCO₃ and NaNO₃. Used salt are of 99% purity and provided by Merck. pH was adjusted to 5 by using 0.5N solution of hydrochloric acid (HCl, Merk 36%). Mechanical and physico-chemical tests were performed on all samples after 3, 7 and 28 days; according to ASTM standards the maturity period of concrete is 28 days.

B. Sample Testing

a. Chemical Composition of Used Raw Materials

Pellets of clinker and phosphogypsum were prepared and relative chemical composition was determined by using X-Ray Fluorescence (XRF Thermo Scientific ARL 9900Total Cement Analyzer) (Table 1). Phosphogypsum used in this study contained 2.4% of P₂O₅.

TABLE I CHEMICAL PHASE COMPOSITION OF CLINKER AND PHOSPHOGYPSUM

Component	Clinker	Phosphogypsum
CaO	65.2	44.77
SiO ₂	21.84	0.65
Al ₂ O ₃	5.81	0.10
Fe ₂ O ₃	3.92	0.21
MgO	1.4	1
SO ₃	0.54	48.21
Na ₂ O	0.11	0.1
K ₂ O	0.57	0.1
P ₂ O ₅	0.28	2.4
TiO ₂	0.24	-
Mn ₂ O ₃	-	-

To determine the total content of trace metals, 2 g of PG were ashed at 500°C during 6 hours. The protocol of wet mineralization was followed by stirring the sample in 25 mL of nitric acid 14 M (Merck 67%) under 85°C for 24 hours. A few drops of hydrochloric acid (Merk 37%) were occasionally added. After acid digestion, solution is transferred into a polyethylene tube and the final volume is adjusted with deionized water till 50 mL. Samples were stored at 4°C to be ready for elemental analysis by using a Zeenit-700 Atomic Absorption Spectroscopy.

Contents of Mn, Pb, Cr, Cu and Zn in PG in this study were respectively 5.3 \pm 0.3; 24 \pm 2; 34 \pm 5, 12 \pm 1%; and 74 \pm 8 mg/Kg. Results showed a relatively high concentration of lead in used PG. Moreover, a high concentration of zinc was observed in comparison with Florida PG, but it is still lower than that of Idaho PG (table 2) [18; 19].

TABLE 2 HEAVY METAL CONCENTRATIONS IN THE STUDIED PG COMPARED TO FLORIDA AND IDAHO PG

		Mn	Pb	Cr	Cu	Zn
Concentrations (mg/kg)	Studied PG	5.3±0.3	24±2	34±5	12±1	74 ±8
	Florida PG	15	1	-	8	9
	Idaho PG	2 - 10	3 - 7	10 - 70	10 - 42	18 - 112

b. Physical Properties of cement and concrete

The specific surface area (cm^2/g) of grinded mixtures of cement and phosphogypsum was measured using Blaine test (relation of Argy-Kozeny). The setting regulator parameter was determined for cement-phosphogypsum mixtures. An amount of 650 g of cement or cement-PG mixture was mixed with 156 mL of distilled water according to ASTM - C305 standard to make ball form. The used water was conform to ASTM - D1193. Each ball is placed in the ring of Vicat apparatus. Every 15 minutes, the distance of needle penetration is measured until a penetration depth of 25 mm. Then the initial setting time is recorded. The final setting time is determined when the needle stop to penetrate into the cement ball.

Compression tests were conducted on immersed concrete cubes after 1, 3, 7, and 28 days of immersion according to ASTM time conditioning and permitted time tolerance extending from ± 30 minutes to ± 12 hours. Once cubes are removed from water, and subjected to compressive strength, applied pressure per unit time is between 900 and 1800 N by using the following calculation: $f_m = P/A$

f_m = Compression strength (MPa)

P = total pressure (N)

A = Surface of the cube (mm^2) (in our case 2500mm^2)

Maximal Accepted Compression Strength variation for the same set of conditioned cubes must not exceed $\pm 8.7\%$.

C. Setting Regulator

a. Aqueous Media Analysis

Several sample collection of aqueous media were taken during the water immersing conditioning of the concrete cubes. Electrical conductivity, residual turbidity and pH were measured respectively by pre-calibrated apparatus (conductimeter, Thermo Orion 3 Star, turbidimeter 2100Q Hach and pH-meter Orion 230 A⁺). Sulfate concentrations were measured using ion chromatograph (Dionex Ion Pac AS 14), and heavy metal release into aqueous media was determined using AAS (Zeenit-700).

Correlation analyses (Pearson R) were carried out between the following parameters: Zn, Cr, Cu and Pb concentrations pH, electrical conductivity, residual turbidity in conditioning aqueous media, and cement Blaine at the 28th day of treatment. Statistical analyses were performed using SPSS 17.

III. RESULTS and DISCUSSION

A. PG Influence on mechanical and physical properties of cement and concrete

The fineness (specific area) or Blaine was determined for all cement treatments containing 0 to 20% wt/wt of phosphogypsum (Fig. 1 A). The specific area decreases as PG amount increases in the cement. It varies between $3615 \text{ cm}^2/\text{g}$ and $2737 \text{ cm}^2/\text{g}$ respectively in cement without PG and in cement with 20% of PG. Such decreasing represents about 25% of the initial fineness. However, it is after the addition of over than 3% of PG that a significant decrease was recorded.

Compressive strength was tested for concrete mortars containing different amounts of phosphogypsum and immersed into the aqueous media for 1, 3, 7, and 28 days. The results are shown in fig. 1 B. All mortars have the same behavior of the compressive strength. Beyond 8% of phosphogypsum in the concrete cubes, the compressive strength decreases significantly and loose about 40% of its initial value when concrete contained 20% of PG. Moreover, obtained results revealed a highest compressive strength of all mortars treatments at the 28th day than that at the 7th and 3rd days of treatment (Fig. 1 B). All concretes doubled their compressive strength performance from the third day to the 28th day of conditioning and thus for all concretes having less than 20% of PG. Compressive strength behavior is in agreement with previous works that used natural gypsum and phosphogypsum as set retarders in Portland cement [16; 20]. It is reported that the compressive strength decrease is mainly related to the increase of the internal pore size [21]. Hence, fineness behavior is in concordance with compressive strength. As the fineness decreases with PG increase, it is expected that the internal pore size increases and as a consequence concrete achieves a less efficient compressive strength.

The compressive strength of cement containing high phosphorous slag at different fineness has been studied by Allahverdi and Mahinroosta [22]. The highest compressive strength was recorded for cement of highest fineness resulting significant reduction of water absorption and total open pore volume of mortar specimens.

A similar study revealed that strength of neat cement cubes are less than that obtained with cement cubes containing 5% PG in 3rd, 7th and 28th days [23]. In addition, a decrease of compressive strength was observed when PG percentage in cement becomes greater than 5%.

For all prepared cement containing different % of PG, the initial and final setting times were much longer in comparison to the ordinary Portland cement having no PG (Fig. 1 C). The longer initial and final setting time was observed for cement containing 20% PG. These extended setting times shown for cements of high PG contents are expected since PG is used for this aim. However, a PG % over than 4 % conducts to an exponential increase of setting time which is not recommended during traditional concrete preparation. It was found that larger is the quantity of fluorides and P₂O₅ coming from PG in cement, higher are the setting times [24 - 27].

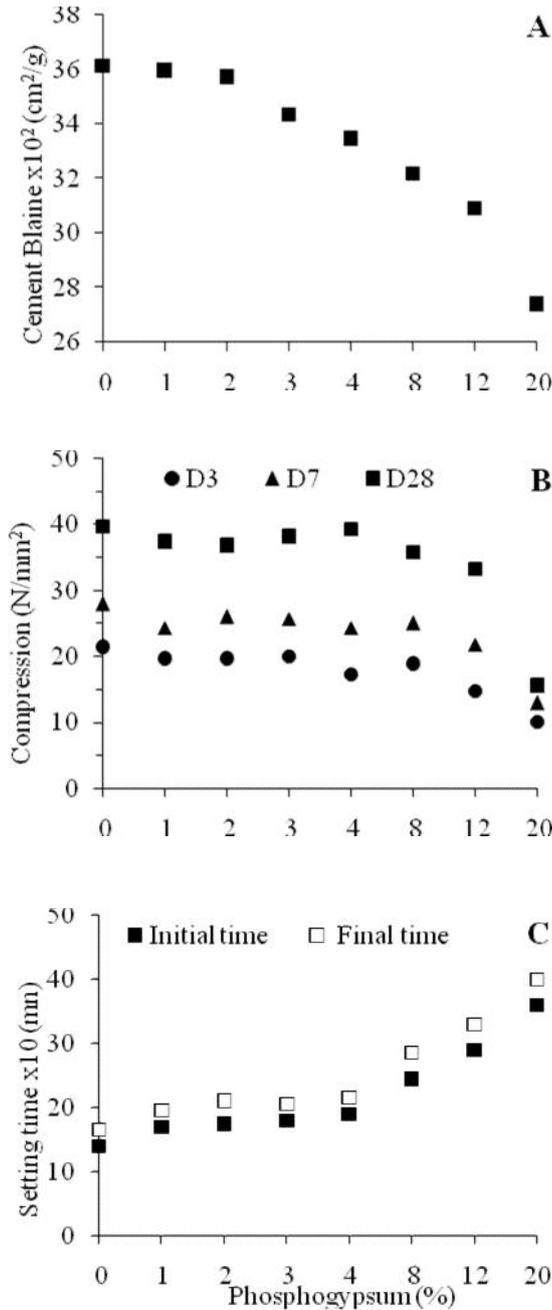


Figure 1 (A) Cement Blaine (specific area), (B) compression strength and (C) setting time as a function of different percentage of phosphogypsum in Portland cement

Cement compressive strength is illustrated in fig. 2 as a function of time for all blaine obtained in cement having PG extended from 0 to 20%. Noting that the lower blaine in the fig. 2 corresponds to the higher content of

PG. Improvement of blaine values is accompanied with compressive strength increase as a function of immersing time (Fig. 2). When the specific surface area is raised from 2737 to 3615 cm²/g, the compressive strength is increased 2.1, 2.15 and 2.56 folds at 3, 7 and 28 days respectively. In fact, the size and the shape of cement grains significantly influence cement hydration. The high specific surface area accelerates the hydration reactions of cements and then cause higher compressive strengths. Similar results were found in another study, where the strength properties of chemically activated high phosphorous slag content cement have been improved with enhanced fineness [22].

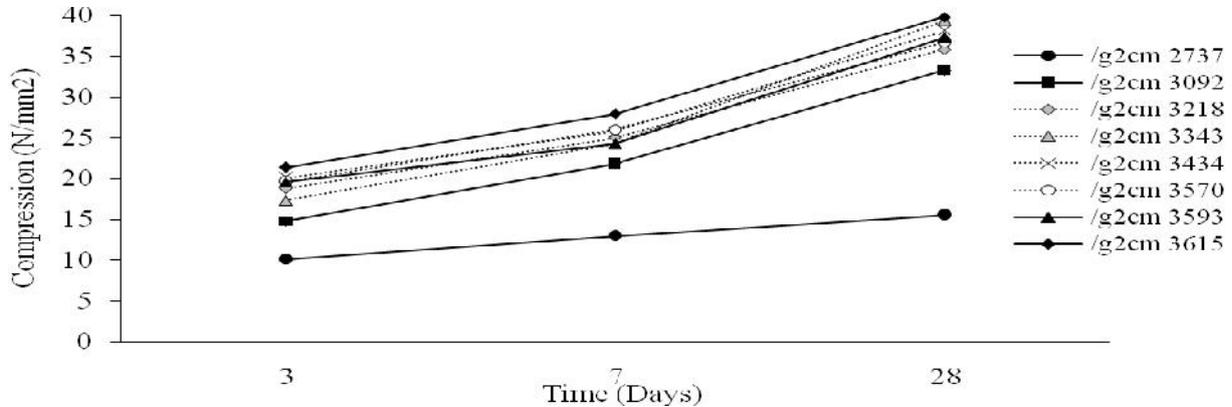


Figure 2 Variation of compressive strength versus time for all cement Blaine

Additionally, Fig. 3 shows that the final and initial setting time decreases with increasing cement specific area. The setting time decline is caused by the acceleration of hydration reactions when the specific area increased. It is also due to the higher cement particle abundance in the same volume, which leads to increased frequency of connecting points. When the level of connection points increases as a consequence of smaller particle size, the setting time decreases [22].

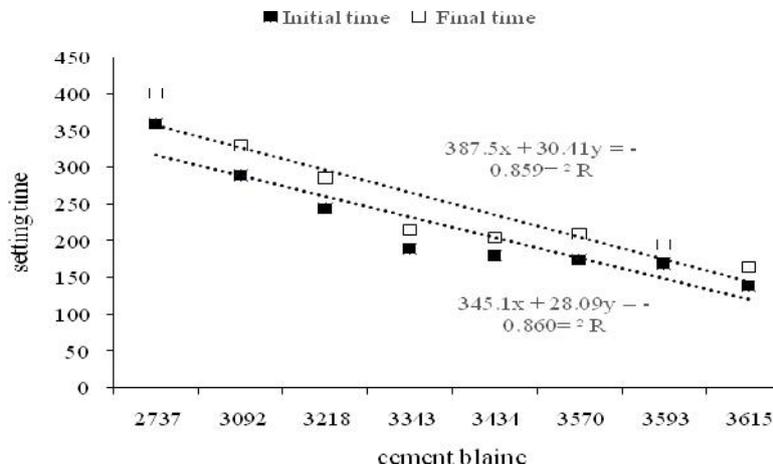


Figure 3 Variations of initial and final setting times as a function of cement Blaine

B. PG influence on chemical and physical properties of the concrete immersing medium

A strong increase in electrical conductivity is observed with increasing aging time and increasing the amount of PG in cement (Fig.4 A). This increase is a clear indication of cement mortar component dissociation that is also proportional to PG content in the concrete. Moreover, an augmentation of medium turbidity was also seen, due to increasing particles in the medium (Fig.4 B). This particle increase begins beyond the 7th day of immersing and is also dependent on the amount of PG, where high residual turbidity becomes more evident for the cement containing 12% PG.

On the other hand, the pH of aqueous medium reveals an important increase from 5 (pH fixed initially by adding HCl) to 12. After the 7th day, pH of different treatments becomes higher than 10 (Fig.4 C). This is mainly due to the substitution reaction of metals and hydroxide-metal complexes by the protons present in the medium. Moreover, sulfate concentrations decreased along the five first days of immersing before increasing in solution as represented in Fig.4 D. Sulfate behavior in the solution can be resumed in two steps. The first stage corresponds to

sulfate absorption from the immersing medium to the concrete cubes where ettringite formation can take place. The second stage that coincides with pH increasing to 12, corresponds to gypsum formation and its release to the immersing medium. This step is the result of lime and sulfate interaction under pH 12 [28]. However, PG addition in the cement is still also a principal source of sulfate increase in the immersing medium. Ettringite and gypsum release into the immersing solution under pH 12 are considered as the main factors for residual turbidity increase.

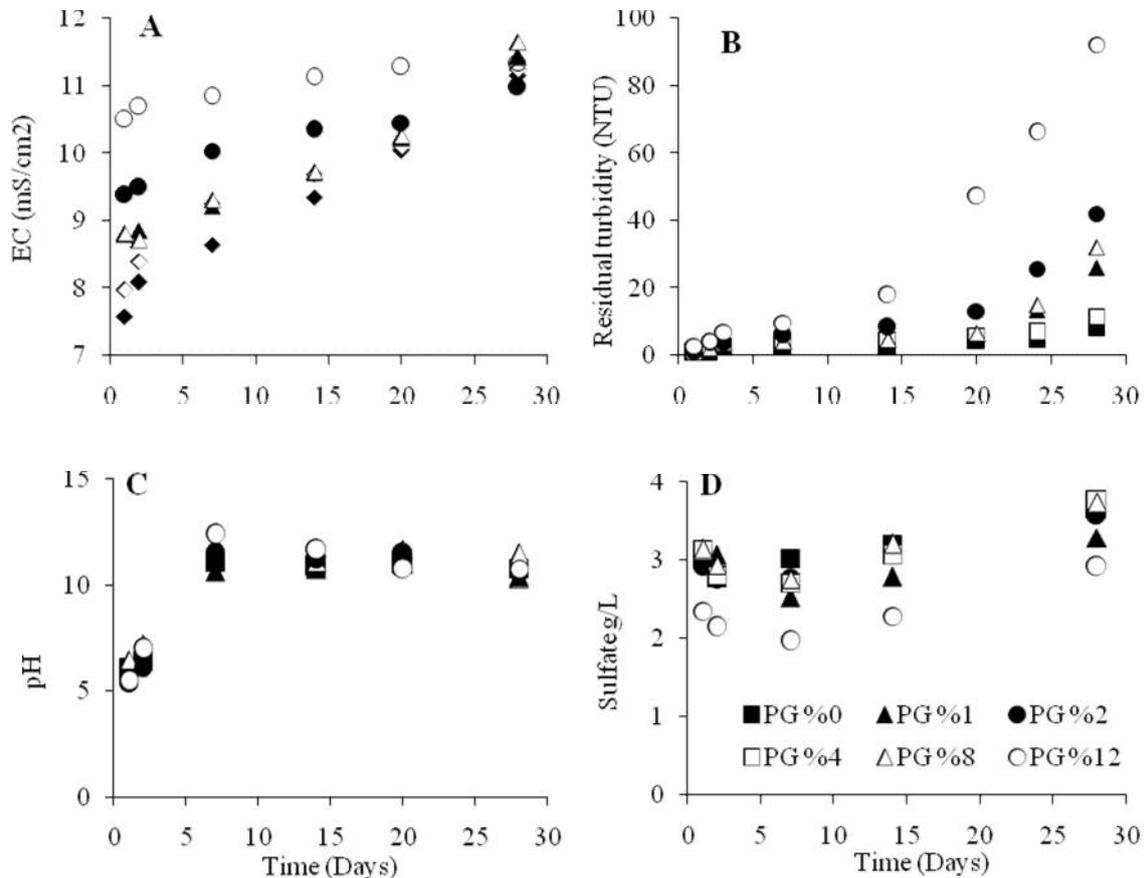


Figure 4 Evolution of EC, turbidity, pH and sulfate concentration in aqueous media as a function of immersing time

Copper, Lead, Chromium and Zinc were monitored in the immersing medium in order to identify the metal release into solution as PG increases in the immersed concrete cubes (fig. 5). Analysis of the aqueous medium exhibits a proportional increase in the concentration of Cu with increasing PG amount in concrete (Fig. 5 A). An increase in copper concentration L^{-1} is observed for the mortars of 0% to 20 % PG throughout the experimental period, where no significant change in concentration was recorded after the third day of immersing. Cu concentration becomes approximately constant. The same behavior can be seen for Pb and Cr (fig. 5 B and 5C). In the first 3 days of conditioning of mortars with increased PG percentage from 0 to 12%, the concentrations in immersing solution are extended from 0.25 to 3.33 $mg L^{-1}$ for Pb and from 0.03 to 1.67 $mg L^{-1}$ for Cr.

Subsequently, after 28 days of immersing, Pb concentrations rise linearly to reach 0.64 $mg.L^{-1}$ for mortars without PG and 5.21 $mg L^{-1}$ for mortars with 12% PG. At the same conditions, Cr increases from 0.38 to 2.57 $mg L^{-1}$ for mortars with 0 and 12 % of PG, respectively. These results reveal that Cu, Pb and Cr diffuse from mortars to the surroundings medium, thus release takes place mainly during the three first days of immersing then it becomes less important during the remaining period of conditioning. It is reported that metals such as Cu and Pb acts as retarders of setting time for Portland cement. This retardation effect is enhanced by the mechanism of hydration inhibition, due to formation of insoluble compounds around the silicates phase [29; 30].

The concentration of Zn decreases progressively during the first three days of incubation mortar, and then increases again to reach 0.57 $mg L^{-1}$ and 0.78 $mg L^{-1}$ at 28th days for treatment with 1% and 12% of PG respectively (Fig. 5 D). It is clear that the behavior of Zn is different from that of Cu, Pb and Cr. This is probably due to competitive reactions of absorption, adsorption and precipitation. Another laboratory leaching experiments of PG by diluted sulfuric acid solutions has indicated an increase of Zn and Cu solubility and their transfer to the aqueous phase. Moreover, treatments by concentrated acids induced that about 10% of Zn and 10% of Cu were leached from PG [2]. Whatever are the mechanisms of metal leaching previously carried by PG into the concrete mortars, releases of Cu, Pb, Cr, and Zn are evident after three days of conditioning. Such release took place in the beginning under acid pH. Even when pH became highly alkaline, metals remained in solution. Moreover, under

such conditions, it is expected also that metals are mobilized in considerable amounts as solid phase during ettringite and gypsum formation and their release into immersing solution.

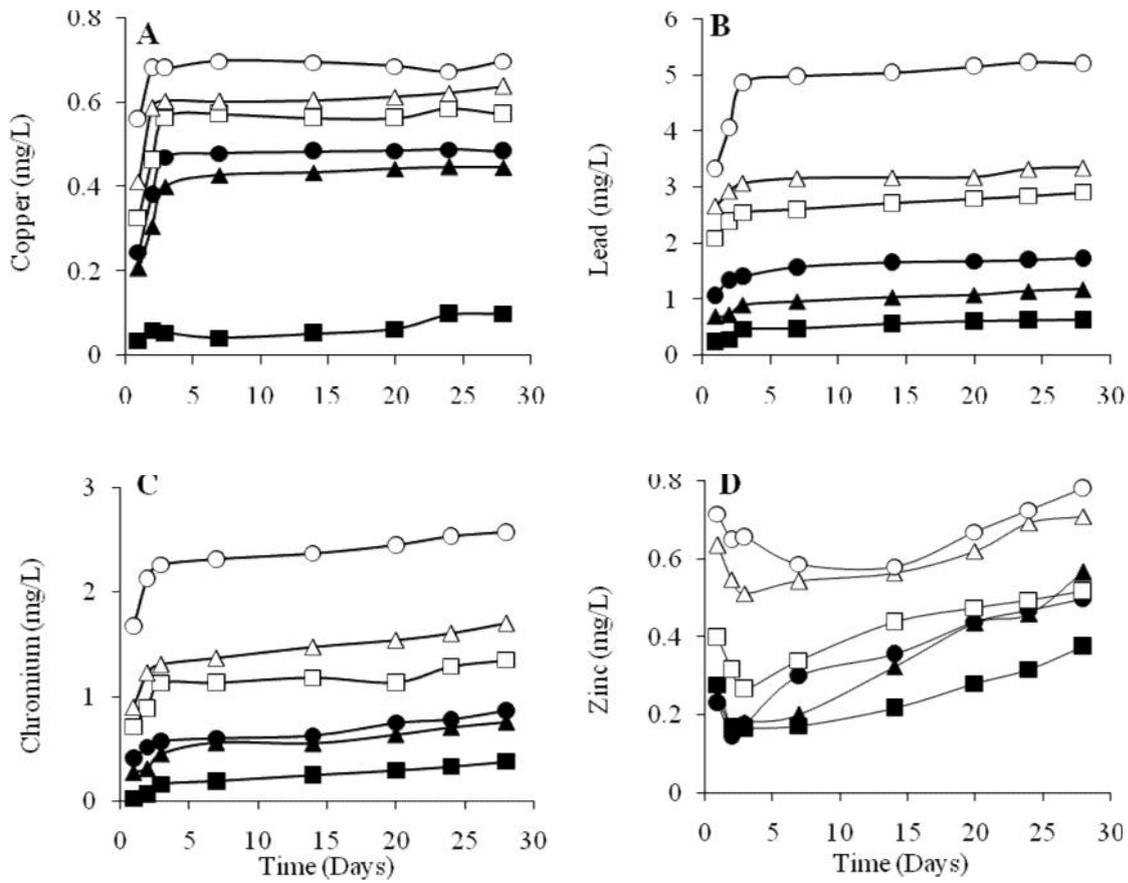


Figure 5 Heavy metal concentrations in aqueous media as a function of immersing time

Pearson correlations between trace metal concentrations (Zn, Pb, Cu and Cr), pH, EC and residual turbidity of immersing medium as well as between cement Blaine are presented in Table 3. Zn, Cr and Pb concentration were found to be negatively correlated to cement Blaine ($R = -0.87$, $P < 0.05$ for Zn; $R = -0.97$, $P < 0.01$ for Cr and $R = -0.9$, $P < 0.05$ for Pb). Noting that cement Blaine was negatively correlated with residual turbidity ($R = -0.9$, $P < 0.05$). Negatively correlated metals and turbidity with blain reveals that the specific area of used cement is the result of particles agglomeration as PG % increase in the cement. When PG is transferred to aquatic medium, disaggregation of agglomerates and dissolution of PG take place conducting to metal release and residual turbidity increase in the aquatic medium. These metals showed positive correlations with medium turbidity ($R = 0.84$, $P < 0.05$; $R = 0.96$, $P < 0.01$ and $R = 0.96$, $P < 0.01$, respectively). Zn content was positively correlated with Pb, Cr and Cu concentrations ($R = 0.87$, $P < 0.05$ for Pb; $R = 0.91$, $P < 0.05$ for Cr and $R = 0.86$, $P < 0.05$ for Cu). Moreover, Cr and Cu concentrations were positively correlated with Pb ($R = 0.99$, $P < 0.01$ and $R = 0.84$, $P < 0.05$, respectively). Positive correlations were found between Cr and Cu ($R = 0.85$, $P < 0.05$).

TABLE 1 PEARSON CORRELATION IN LEACHATES (Zn, Pb, Cr, Cu, pH, TURBIDITY AND CONDUCTIVITY) AND SPECIFIC AREA OF CEMENT

	Zn	Pb	Cr	Cu	pH	Blaine	Conductivity	Turbidity
Zn	1							
Pb	.879*	1						
Cr	.916*	.995**	1					
Cu	.867*	.849*	.852*	1				
pH	-.102	.303	.230	.116	1			
Blain	-.871*	-.973**	-.970**	-.806	-.352	1		
Conductivity	-.203	.127	.063	.197	.582	.013	1	
Turbidity	.844*	.966**	.969**	.746	.183	-.905*	.101	1

* $P < 0.05$, significant correlation at the 0.05 level

** $P < 0.01$, significant correlation at the 0.01 level

IV. CONCLUSION

The present study revealed a good efficiency of PG as a set retarder in Portland cement. It can be valorized without altering concrete mechanical properties when used in optimal amount less than 8%. Hence, valorizing of phosphogypsum in such amount minimizes its release in natural and aquatic media and is considered as an economic added value for Portland cement industry.

However, more attention must be taken into consideration regarding its metal release into aqueous media. Under realistic natural conditions such as acid pH and highly buffered media, Pb, Cu, Zn and Cr can be rapidly released without being entrapped and/or precipitated later under highly alkaline conditions. Metals being correlated together and correlated with residual turbidity enhance that ettringite and gypsum formation contribute in metal persistence in aqueous media under extreme alkaline conditions.

We still think that the external crust is the most attempted and leached part of the mortar cubes as metals remained approximately constant after the third day of immersing solution. Finally, washing generously concretes two or three days after use, can mobilize most of the entrapped metals in the external layer of the product. Such findings are of good interest to valorize such solid waste. It is of great interest to examine the behavior of radioelements when using phosphogypsum as set retarder since their persistence may conduct to continuous radiation emission and to considerable impact on health in internal environment.

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