



# Influence of phosphorus from phosphogypsum on the initial hydration of Portland cement in the presence of superplasticizers



Fernando do Carmo Holanda<sup>a, \*</sup>, Holger Schmidt<sup>a</sup>, Valdecir Angelo Quarcioni<sup>b</sup>

<sup>a</sup> MC-Bauchemie Brazil, Henry Martin Street, 235, Vargem Grande Paulista, São Paulo 06730-000, Brazil

<sup>b</sup> IPT-Institute for Technological Research, Prof. Almeida Prado Avenue, 532, São Paulo 05508-901, Brazil

## ARTICLE INFO

### Article history:

Received 31 March 2016  
Received in revised form  
18 June 2017  
Accepted 13 July 2017

### Keywords:

Concrete  
Phosphogypsum  
Hydration  
Superplasticizer

## ABSTRACT

Phosphogypsum is widely used for the total or partial substitution of natural gypsum in the production of Portland cement. However, contaminants from the phosphogypsum, such as chemicals that contain phosphorus, may affect the performance of the binder, especially when it is applied to concrete that uses chemical admixture. The goal of this study is to evaluate the impact of successive increments of  $\text{Na}_2\text{HPO}_4$  on the hydration of cements that are produced with low or high phosphorus concentrations in the presence of ether–polycarboxylate–based (PCE) and sulfonated–naphthalene–formaldehyde–based (SNF) superplasticizers. Two binders with the same clinker size were produced in the laboratory with natural (phosphorus–free) gypsum and phosphogypsum (contaminated). The isothermal calorimetry and thermogravimetry (TG/DTG) techniques were used to evaluate the heat flow behavior and the formation of portlandite at the end of the induction period ( $P_i$ ), at the maximum heat flow ( $P_{\text{max}}$ ), and at the final 72-h stage ( $P_{72}$ ). The results indicate that the greatest impact on hydration occurs at phosphorus concentrations between 0.83% and 1.64% in the form of  $\text{P}_2\text{O}_5$  in the phosphogypsum and especially at a concentration of 1.13%. Nonetheless, in all cases, the formation of portlandite after 72 h is very similar.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Cements and chemical admixture that directly interact with the binder particles are fundamental components of concretes in civil construction. However, the cause–and–effect relations of phosphorus contamination from phosphogypsum in mixtures that contain highly–efficient water reducers are still not well known. Phosphogypsum is obtained as an industrial byproduct of the production of phosphoric acid. Approximately 170 million metric tons of residual calcium sulfate are generated worldwide every year, and only 15% of it is reused [1]. In Brazil, 5.6 million metric tons of this material are generated annually [2].

Phosphogypsum is mostly composed of calcium sulfate, but it also contains elements such as phosphorus and fluorides that are derived from its production process. On average, the byproduct contains between 0.1% and 1.5% of  $\text{F}^-$  and from 0.1% to 1.8% of  $\text{P}_2\text{O}_5$

in addition to small amounts of heavy–metal ions. This may cause pollution of the water, soil and air. In general, approximately 4.5 metric tons of residual calcium sulfate are generated per metric ton of phosphoric acid produced [3,4].

Studies on cement hydration phenomena in pure crystalline phases of clinker showed that, similarly to natural gypsum, phosphogypsum reacts with the  $\text{C}_3\text{A}$  phase in the presence of  $\text{Ca}(\text{OH})_2$  to form hydrated sulfoaluminates that regulate chemical reaction rates; however, the by-product contaminants may adversely affect the hydration kinetics [5,6]. The presence of phosphorus, as well as its association with fluoride ions, is associated with a strong delay in cement hardening time [7,8]. However, the addition of high concentrations of soluble phosphorus to cement suspensions accelerates hydration chemical reactions and alterations in rheological properties, shifting the expected continuous delay [9].

Superplasticizers are commonly used to improve the material properties of concretes and mortars, both while fresh and during hardening. Thus, this study presents state of the art knowledge of the acceptable levels of phosphorus contamination in phosphogypsum. It also discusses the critical concentrations and the advantages and disadvantages of its use in cement production when it

\* Corresponding author.

E-mail addresses: [fernando.holanda@mc-bauchemie.com.br](mailto:fernando.holanda@mc-bauchemie.com.br) (F.C. Holanda), [holger.schmidt@mc-bauchemie.com.br](mailto:holger.schmidt@mc-bauchemie.com.br) (H. Schmidt), [quarciva@ipt.br](mailto:quarciva@ipt.br) (V.A. Quarcioni).

is applied to mixtures that contain superplasticizers. Two binders were prepared, named CEM I-g, which was produced with natural gypsum, and CEM I-f, which was produced with phosphogypsum. The binders were subjected to increases in the  $\text{Na}_2\text{HPO}_4$  content in the mixture water as a phosphorus donor to evaluate the evolution of the hydration in contaminated media with low and high phosphorus concentrations. Complete information about this study can be found in Ref. [10].

## 2. Materials

The clinker that was used in preparing the cements was obtained from a Brazilian cement plant, produced without co-processing. Two calcium sulfates were chosen as setting controllers: natural gypsum (with a low phosphorus concentration) from northeastern Brazil and phosphogypsum (contaminated with phosphorus) that was obtained as a byproduct of the production of phosphoric acid, which was donated by *Vale Fertilizantes* of Cajati, São Paulo, Brazil.

The admixtures used in this study are produced and marketed in Brazil by MC-Bauchemie: a sulfonated–naphthalene–formaldehyde (SNF)-based superplasticizer with normal setting characteristics; and two ether-polycarboxylate-based superplasticizers, designated PCE 1, which promotes greater concrete workability, and PCE 2, which has greater cement particle dispersion power. Disodium phosphate ( $\text{Na}_2\text{HPO}_4$ ) p.a. Merck, 99.0% purity, designated in this study by NP, was used as a contaminant.

## 3. Experimental methods

### 3.1. Characterization of the raw materials

#### 3.1.1. X-ray fluorescence (XRF)

X-ray fluorescence was performed in a Panalytical model Minipal Cement spectrometer on beads that were fused in a Claisse M4 fusion instrument using commercial lithium tetraborate/lithium metaborate by MAXXIFLUX (66.67%  $\text{Li}_2\text{B}_4\text{O}_7$ , 32.83%  $\text{LiBO}_2$  and 0.50%  $\text{LiBr}$ ) as a flux at a ratio of 1 g of sample per 6.75 g of flux.

#### 3.1.2. X-ray diffraction (XRD)

A Rigaku model Windmax 2000 diffractometer was utilized for the X-ray diffraction tests; it operated on copper  $K\alpha$  radiation at 40 kV–30 mA with a sweep of  $3^\circ$ – $65^\circ$  and a sweep rate of  $2^\circ/\text{min}$ . The samples were ground until they could pass completely through a sieve with a mesh size of 0.045 mm. During the preparation of the clinker, 10% zinc oxide (ZnO) that was previously dried at  $600^\circ\text{C}$  was added as an internal standard for Rietveld quantification. The analyses of the natural gypsum and phosphogypsum were carried out directly on the material by the qualitative method without the use of an internal standard. The compounds were identified using the HighScore Plus (version 4.1) software package.

#### 3.1.3. Thermogravimetry (TG/DTG)

The thermogravimetric analysis was performed using a Mettler Toledo thermobalance with a CG 10 Star System Mettler gas purge controller with approximately 30 mg samples that were dried at  $40^\circ\text{C}$  and were fine enough to pass through a sieve with a mesh size of 0.075 mm in an uncovered 70  $\mu\text{L}$  alumina crucible. A gas flowrate of 50 mL/min of ultra-pure nitrogen ( $\text{N}_2$ ) was used with a constant heating rate of  $10^\circ\text{C}/\text{min}$  up to  $1000^\circ\text{C}$ .

### 3.2. Cement preparation

To obtain binders with similar physical and chemical characteristics, the materials were previously homogenized in the

laboratory, and the calcium sulfates were dried at  $40^\circ\text{C}$  for 24 h in a ventilated oven. The raw materials for the cement preparation were ground using a Herzog ball mill with a capacity of 10 kg. A specific area of  $4450\text{ g}/\text{cm}^2$  was defined as ideal in this process, and the material dosage was performed according to the chemical characterization and the limits that were established in the ASTM C150-07 [11] and NBR 5732 [12] norms for  $\text{SO}_3$  concentrations in Portland cement I ( $\leq 4.0\%$ ) to guarantee the development of the final product. The Blaine method was used to control the grinding time using the specific area measurements; to do this, readings were taken every 15 min after 2 h of grinding using the Blaine-Star equipment and a sample mass of 115 g.

### 3.3. Cement characterization

The chemical analysis of the cements was performed by XRF following the methods that were described in Section 3.1.1 and with complementary titrimetry, gasometry, gravimetry and potentiometry methods. For the physical tests, the BET method by Braunauer, Emmet and Teller was applied to determine the specific area from the physical gas adsorption and desorption at the surface of the solid sample. This method is considered to be more precise in terms of the permeability to air (Blaine) due to its greater area sensitivity and range in the measurement. The BET tests were performed with Belsorp Max equipment using nitrogen gas with a sample pre-treatment at a temperature of  $60^\circ\text{C}$  and a pressure of 10–2 psi of  $\text{N}_2$  for 24 h in a Belprep vac-II instrument. The specific mass was determined using a Le Chatelier flask, and the particle size distribution was determined using CILAS equipment that could operate with particles of diameters between  $0.04\text{ }\mu\text{m}$  and  $500\text{ }\mu\text{m}$ . The setting times were determined using the Vicat method based on data from consecutive penetration measurements with a standard 1-mm-diameter needle in the cement paste.

### 3.4. Phosphorus determination

To determine the total phosphorus, a 0.5 g sample was digested with 2.5 mL of nitric acid ( $\text{HNO}_3$ ) in a CEM Mars microwave digestion oven with closed polypropylene containers at a temperature of  $175^\circ\text{C}$  for 4 min and 30 s. This temperature was reached after a heating ramp of 10 min. The concentration of soluble phosphorus was determined after mixing 10 g of the cement samples and of the calcium sulfates in water. The analyses were carried out in an ICP-OES iCAP 6000 Thermo plasma spectrometer with a wavelength of 213.618 nm in axial view, a power of 1300 W, and auxiliary gas and nebulizer (argon) flowrates of 0.5 L/min.

### 3.5. Phosphorus availability

Exploratory tests to determine the soluble phosphorus availability were performed in different suspensions that contained natural gypsum (phosphorus-free reference), phosphogypsum, and the CEM I-g and CEM I-f cements to understand the soluble phosphorus recovery potential as a function of the increasing amount of NP. The delay in hydration kinetics that was promoted by the presence of soluble phosphorus is a result of the adsorption and precipitation phenomena due to the reaction of insoluble phosphorus compounds on the cement particles [8,13,14]. Therefore, this stage of the study was important to evaluate the phosphorus availability in the medium during hydration.

To work with the same calcium sulfate mass ratios that were used in the cements (i.e., 6% for natural gypsum or phosphogypsum), a mass of 12 g was adopted for the calcium sulfates, and 200 g was used for the cements. Based on 67 total phosphorous measurements in phosphogypsum for Portland cement production in

Download English Version:

<https://daneshyari.com/en/article/5436827>

Download Persian Version:

<https://daneshyari.com/article/5436827>

[Daneshyari.com](https://daneshyari.com)