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Review Article

Technical feasibility for use of FGD gypsum as an additive setting time retarder for Portland cement

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ABSTRACT

Flue gas desulfurization (FGD) gypsum was evaluated as a setting time retarder to replace the natural gypsum in the production of Portland cement (CP II E-32). The results of physical-chemistry and morphological characterization of both products showed a material of high purity, calcium sulfate dehydrate for natural gypsum, and higher percentages of bassanite ($CaSO_4{\cdot}0.6H_2O$) and hannebachite ($CaSO_3{\cdot}0.5H_2O$) with low concentrations of impurities for FGD gypsum. Based on the results, the FGD gypsum is a suitable alternative to replace natural gypsum. The setting time with FGD gypsum showed about 1 h delay compared with natural gypsum and its effect on compressive strength depend on composition of the mixtures, reaching a maximum value for the mixture of 1.4 wt% natural gypsum and 2.1 wt% FGD gypsum. According to the results of leaching and solubilization tests FGD gypsum residue was classified as a non-hazardous and non-inert.

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1. Introduction

The cement manufacturing industry is the major consumer of gypsum, which is added to the clinker in a percentage of 3–5 wt% [1–3].

Various by-product gypsum such as phosphor-, fluoro-, citro-, boro-, titano-, tartare-, and desulphogypsum have chemical composition similar to the natural gypsum, but

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its use in replacing natural gypsum as cement retarder is limited, mainly due to the variation of moisture and impurities content that can affect the cement workability [4–7]. In Turkey, mechanical properties were tested and compared when the borogypsum was added to the clinker instead of natural gypsum [8]. Portland cements mixtures containing boro-, citro-, and desulphogypsum were hydrated and compared with cement containing natural gypsum. It was found that cements containing by-product gypsums produced more ettringite than these with natural gypsum [9]. The influence of hydration on the mechanic properties of cements prepared with different gypsum types also were studied [10–12]. The properties of gypsum are influenced by its hydration and the properties of the hemihydrates [13,14]. According to Carvalho [15] the hydration of Portland cement can be analyzed as the sum of all the reactions of the individual cement compounds and it is directly related to changes in the material properties such as elastic modulus, strength, creep, shrinkage, etc.

Large amount of FGD gypsum residue are generated in the desulfurization of flue gas process and its direct disposal in landfills for long periods is not the best solution [16–18]. Because the high costs involved for its disposal and the severe restrictions imposed by environmental agencies the use of the FGD gypsum in place of natural gypsum in cement composition is presented as an advantageous alternative [19–22].

The aim of this research is to study the technical feasibility for the use of FGD gypsum in partial or total substitution of natural gypsum as retarder additive of the Portland cement. Three stages were considered to achieve this goal. Firstly, it was carried out the characterization and comparison of FGD gypsum with natural gypsum. Secondly, based on analysis of results of the first stage, four mortars were prepared mixing clinker-FGD/natural gypsum-additives looking for the proper mixture that reaches the technical requirements of the Brazilian standards. Finally, were evaluated some chemical, physical and mechanical properties of the mixtures.

2. Experimental

2.1. *Material and methods*

Natural gypsum and clinker samples were obtained from Holcim SA, Cantagalo unit (RJ-Brazil). Their chemical compositions are shown in Table 1. The sample was ground and sifted with 325 meshes (45 μm diameter). The FGD gypsum used in the study was provided by the steel company generating the waste.

Table 1 – Chemical composition of natural gypsum and clinker.

Constituent	Natural gypsum (wt%)	Clinker (wt%)
CaO	32.53	64.95
SiO_2	1.29	21.08
Al_2O_3	1.02	5.32
Fe_2O_3	0.54	3.15
MgO	0.31	2.61
SO_3	42.01	0.95
K_2O	0.08	0.39
Na_2O	0.04	0.30
Loss on ignition	19.16	–
Insoluble residue	1.30	–
CO_2	1.72	–
Free CaO	–	1.25

2.2. *Characterization of natural and FGD gypsum*

The particle size of the FGD gypsum sample was analyzed by laser particle-size (Malvern, Mastersizer 2000) in liquid solution and stirred at 1700 rpm for 40 min. The reading range was between 0.1 and 1000 μm.

The chemical composition of FGD gypsum was determined by semi-quantitative analysis of XRF on a Philips PW1480 wavelength-dispersive spectrometer.

The mineralogical compositions of samples were determined by X-ray diffraction using a diffractometer X-Pert Pro (Panalytical) with graphite monochromator. Data were collected in 2θ ranging from 10° to 90° with 0.05° 2θ step interval and 1 s per step counting time. Utilizing the ICSD database was applied Rietveld method to quantify the phases.

SEM technique was performed to identify the morphology of FGD gypsum and natural gypsum, the elemental composition of individual particles was determined with energy dispersive spectroscopy (EDS). Both particles FGD and natural gypsum were dispersed in 1% alcohol solution in order to highlight its morphology. A Hitachi TM-3000 operating in high vacuum, tungsten filament of 15 kV and nominal resolution of 50 nm was used.

A simultaneous thermal analyzer (STA-6000) Perkin-Elmer was used to collect thermogravimetric (TG) and calorimetric (DTA) data. The thermal analyzes were performed in dynamic atmosphere of nitrogen at a flow rate of 25 $cm^3 min^{-1}$ and a heating rate of 10 °C min^{-1} to a temperature of 800 °C.

The leaching and solubilization tests can determine the ability of the FGD gypsum to liberate hazardous elements to the environment. These tests were carried out according to Brazilian Association of Technical Standards (ABNT).

No-volatile elements were analyzed based in the technique of optical emission spectrometry with inductively coupled plasma (ICP OES) using an equipment model Optima 7300 DV axial configuration.

2.3. *Specimens' preparation*

The mortars were prepared, mixed and tested according Brazilian norm NBR 11578 for Portland cement CP-II E32 with addition of blast furnace slag. The proportions of the materials to prepare the mortars are given in Table 2. Four specimens were prepared controlling the percent of FGD gypsum and

Table 2 – Composition of mortars evaluated (wt%).

Mortar	Clinker	Limestone	Slag	Natural gypsum	FGD gypsum
M1	56.5	10	30	3.5	0
M2	56.5	10	30	2.5	1.0
M3	56.5	10	30	1.4	2.1
M4	56.5	10	30	0	3.5