Review Article

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

Mariella Cortez Caillahua *, Francisco José Moura

Departamento de Engenharia Química e de Materiais, Pontifícia Universidade Católica do Rio de Janeiro, Rua Marquês de São Vicente, 225, Cx. Postal: 38097, Gávea-Rio Janeiro, RJ 22451-900, Brazil

A R T I C L E  I N F O

Article history:
28 September 2017

Keywords:
FGD gypsum
Gas desulfurization
Calcium sulfate hemihydrate
Portland cement

A B S T R A C T

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 (CaSO4·0.6H2O) and hannebachite (CaSO4·0.5H2O) 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.

© 2017 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Mariella C. Caillahua, master degree in materials and chemical and metallurgical processes engineering, Pontifical Catholic University of Rio de Janeiro. She attended the University “Mayor de San Marcos” at Peru and graduated with a B.S. in chemistry engineering, and spent several years working in the field of industrial water treatment. She was a member of highly specialized technical teams for assessed the working and facilities conditions, developing subsequently customized chemicals according to the characteristics of each industrial process and facility. At 2002, she started working in environmental analysis laboratories; her capabilities include air, water and soil analysis. She specialized in accredited analysis for the environmental, participating in rigorous programs of inter-lab comparisons and on-site assessments based on international standards. She has acted as assessor in the implementation and adaptation of analytical methods for accreditation with the international standard ISO/IEC 17025, designed for the accreditation of Testing and Calibration Laboratories. Currently she is pursuing her PhD in Materials and Processes Engineering and working as a university professor in the area of environmental engineering.

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-, titan-, tartar-, and desulphogypsum have chemical composition similar to the natural gypsum, but
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 gypsiums 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.

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 (Analytical) 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 cm³ 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>
<thead>
<tr>
<th>Mortar</th>
<th>Clinker</th>
<th>Limestone</th>
<th>Slag</th>
<th>Natural gypsum</th>
<th>FGD gypsum</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>56.5</td>
<td>10</td>
<td>30</td>
<td>3.5</td>
<td>0</td>
</tr>
<tr>
<td>M2</td>
<td>56.5</td>
<td>10</td>
<td>30</td>
<td>2.5</td>
<td>1.0</td>
</tr>
<tr>
<td>M3</td>
<td>56.5</td>
<td>10</td>
<td>30</td>
<td>1.4</td>
<td>2.1</td>
</tr>
<tr>
<td>M4</td>
<td>56.5</td>
<td>10</td>
<td>30</td>
<td>0</td>
<td>3.5</td>
</tr>
</tbody>
</table>
natural gypsum. The maximum percentage of gypsum in the mortars was 3.5 wt%.

2.4. Specimen test methods

According the Brazilian regulations the Portland cement must achieve the chemical, physical and mechanical requirements established by NBR 11578 [23]. These requirements were dictated by the respective regulations: Ignition loss NBR NM 18 [24], insoluble residue NBR NM 22 [25] and content of sulfur trioxide NBR NM 16 [26]. In accordance with the Brazilian standards NBR NM 43 [27] the mortars were prepared with a ratio water/cement of 0.48 to supply a paste of normal consistency. The surface area was measured according to the procedure described in the standard NBR NM 76 [28]. The mechanical properties of cement samples were tested for setting time and compressive strength. The ratio of mix cement/sand/water was of 1:3:0.48 according to the specifications of the Brazilian Standards NBR NM 65 (setting time) [29] and NBR 7215 (compressive strength) [30].

3. Results and discussion

3.1. Characterization of natural gypsum and FGD gypsum samples

The cumulative curve of the particle size distribution showed fine particles in the FGD gypsum sample, 90% of the total volume smaller diameters of 16.8 µm, 50% of the volume smaller diameters than 7.4 µm and 10% smaller diameter than 1.8 µm (Fig. 1). Particle size distribution indicates symmetry with respect to particle size with a higher frequency, around 8 µm (Fig. 2). Fig. 2 shows a broad distribution extending from a minimum of 0.3 µm to a maximum of 500 µm and peaks for particles around 1 µm and 50 µm and within the range between 200 and 300 µm.

The composition and percentage of FGD gypsum may vary depending on their origin. According to the XRF results, the FGD gypsum had similar chemical compositions compared with other FGD gypsum reported in the literature [6,13,21]. The FGD gypsum consists essentially of calcium sulfate and other components in smaller amounts (Table 3).

![Fig. 1 – Cumulative particles volume of FGD gypsum.](image1)

![Fig. 2 – Particle size distribution of FGD gypsum.](image2)

**Table 3 – XRF chemical composition of FGD gypsum.**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>FGD gypsum sample</th>
<th>FGD gypsum reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>45.87</td>
<td>31.84</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.20</td>
<td>1.85</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.10</td>
<td>0.24</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.30</td>
<td>0.12</td>
</tr>
<tr>
<td>MgO</td>
<td>0.13</td>
<td>0.05</td>
</tr>
<tr>
<td>SO₃</td>
<td>47.97</td>
<td>43.79</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.20</td>
<td>NR</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.14</td>
<td>0.06</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.09</td>
<td>NR</td>
</tr>
<tr>
<td>SrO</td>
<td>0.20</td>
<td>NR</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>3.80</td>
<td>20.22</td>
</tr>
</tbody>
</table>

NR, no report.

The value of loss on ignition (LOI) indicates lower concentration of volatile compounds as CO₂ and lower content of total moisture in FGD gypsum sample. Differences in the values of LOI indicate different types of hydrate calcium sulfate

![Fig. 3 – XRD pattern of natural gypsum (Rietveld refinement).](image3)
presents in FGD gypsum; these results were confirmed by DTA/TG and DRX analyses.

XRD diagram of natural gypsum presents dihydrate calcium sulfate as main mineral phase with some traces of anhydrite (Fig. 3). Overlapping diffraction patterns of both samples indicates different phases presents in them (Fig. 4). The peaks intensities at sample of FGD gypsum are much smaller. The quantification of phases using XRD-Rietveld technique was applied to determine the composition of FGD gypsum. Differences between XRD patterns computed from database and obtained from FGD gypsum sample possibly indicate phases unadjusted. Were identified 38.97% of bassanite (CaSO₄·0.6H₂O) and 26.04% of hannebachtite (CaSO₄·0.5H₂O) as predominant minerals of the FGD gypsum sample. Low concentrations of anhydrite (3.86%) and other compost as sulfates, carbonates, phosphates and silicates of calcium, aluminum, magnesium and strontium also were identified (Fig. 5).

SEM images show two types of particles, large tabular particles from natural gypsum (Fig. 6) and rounded particles from FGD gypsum sample (Fig. 7). Its spherical shape is irregular, with variable diameter and smooth surface. Based on elemental analysis by EDS, natural gypsum particles contain high atomic content of sulfur, calcium and oxygen, and low percentages of impurities as silicon, aluminum, magnesium, potassium and iron. As expected, the FGD gypsum particles also contain high atomic content of sulfur, calcium, and oxygen. In addition was identified the presence of aluminum, silicon, magnesium, potassium, strontium, zinc, iron, phosphorus and chloride. This fact is confirmed by the fluorescence analysis and X-rays diffraction performed on the material.

In the natural gypsum, the mass loss was approximately of 19% between 131 and 245 °C, corresponding to the loss of free and structural water (Fig. 8). Three endothermic peaks are observed on the DTA curve as result of the dehydration reactions of gypsum (Fig. 9). Firstly a very low mass loss from ambient temperature to 45 °C, the second peak was found at 165 °C corresponding to the greatest mass loss by the conversion of the dihydrate to hemihydrate. The third peak at 193 °C indicates the dehydration of hemihydrate to anhydrite. Finally, an exothermic peak is observed at 350 °C, which is characteristic of the crystalline transformation of soluble anhydrite to insoluble anhydrite.

The thermogravimetric behavior of dehydration of the FGD gypsum is showed in the TG/DTG (Fig. 10) and DTA (Fig. 11) curves. It was obtained a minimal mass loss between 45 °C and 180 °C (2.13%), the presence of dihydrate phase is not significant in the sample. Above 180 °C begins the exothermic effect associate to the conversion of anhydrite III to anhydrite II, it was found about at 282 °C. The total mass loss in FGD gypsum was approximately 11%. Others processes were observed on the curves and could be the result of the dehydration reactions of some impurities in the FGD gypsum sample.
A sharp endothermic peak is reduced to 352 °C with a mass loss of 5.8% and two exothermic peaks were found around 533 °C and 670 °C. Discrepancies on the FGD gypsum dehydration behavior can be probably due to different crystalline characteristics and contained of impurities such as ash and limestone.

The constituents of environmental concern presents in the leachates [31] and solubilized [32] extract are showed in Table 4. All the leachable contents remained below the required limited values by the Brazilian Standards (As, Ba, Cd, Pb, Cr, Hg, Ag, and Se). Therefore the FGD waste may be classified as class II – non-hazardous. Solubilized extract concentrations for metals as Cd and Se were slightly higher than standard limit. As and Pb contents was lower of both standard and method detection limit. Method detection limit

Fig. 7 – SEM images of FGD gypsum: (a) agglomerated particles, (b) particles dispersed in 1% alcohol.

Fig. 8 – Mass loss curve for the dehydration of natural gypsum.

Fig. 9 – DTA curve of natural gypsum.

Fig. 10 – DTG/TG curves of FGD gypsum.

Fig. 11 – DTA curve of FGD gypsum.
by Hg was greatest standard limit. According the results and correspond standard FGD waste is classified as class II A – not inert [33].

3.2. Specimens’ preparation

Results of chemical composition and thermogravimetric analyses confirmed the existence of higher amount of hemihydrated compounds (bassanite and hannebachite) in the FGD gypsum. Because the influence these compost in the hydration of cement there was no need to thermally treat the FGD gypsum before utilizing it in the preparation of the mortars. Considering the low content of environmental concern elements present in FGD gypsum sample and due small amounts of gypsum added to the cement was not necessary to remove these impurities.

3.3. Specimens test

The prepared mortars meet the requirements set by the standard NBR 11578 for Portland cement type PC II-E32 (Table 5). As expected the ignition loss content decreases with increasing FGD gypsum percentage in mortars. The specific surface and sulfur trioxide content also decreased with the increase of FGD gypsum in mortars but the values were still within the limits established by the standard. The insoluble residue content varies slightly for all mortars. The water/cement ratio was 0.48 for all mortars therefore, the paste of normal consistency remain almost constant.

Fig. 12 shows the difference of the initial and final setting time among mortars tested. Both initial and final setting times incremented with increasing FGD gypsum ratio. The maximum value of setting time was reached by the mortar containing only FGD gypsum, mortar M4. The setting time was an hour delay when compared to the result of natural gypsum. Similar results were reported by researchers in Greece [21] for natural gypsum and FGD gypsum blends with percentages around the 3.5% SO3. Also, the same tendency

### Table 4 – Results of leachates and solubilized extract and the maximum concentration established by the NBR 10004.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Run 1</th>
<th>Run 2</th>
<th>ABNT NBR 10004:2004</th>
<th>Run 1</th>
<th>Run 2</th>
<th>ABNT NBR 10004:2004</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.04</td>
<td>0.04</td>
<td>0.2</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.13</td>
<td>0.10</td>
<td>1.0</td>
<td>&lt;0.008a</td>
<td>&lt;0.008a</td>
<td>0.01</td>
</tr>
<tr>
<td>Barium</td>
<td>0.33</td>
<td>0.38</td>
<td>70</td>
<td>0.31</td>
<td>0.35</td>
<td>0.7</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.02</td>
<td>0.02</td>
<td>0.5</td>
<td>0.009</td>
<td>0.008</td>
<td>0.005</td>
</tr>
<tr>
<td>Lead</td>
<td>0.01</td>
<td>0.02</td>
<td>1.0</td>
<td>&lt;0.004a</td>
<td>&lt;0.004a</td>
<td>0.01</td>
</tr>
<tr>
<td>Cooper</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.008</td>
<td>0.008</td>
<td>2.0</td>
</tr>
<tr>
<td>Chromium</td>
<td>&lt;0.001a</td>
<td>&lt;0.001a</td>
<td>5.0</td>
<td>0.004</td>
<td>0.005</td>
<td>0.05</td>
</tr>
<tr>
<td>Manganese</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.059</td>
<td>0.054</td>
<td>0.1</td>
</tr>
<tr>
<td>Mercury</td>
<td>&lt;0.006a</td>
<td>&lt;0.006a</td>
<td>0.1</td>
<td>&lt;0.006a</td>
<td>&lt;0.006a</td>
<td>0.001</td>
</tr>
<tr>
<td>Silver</td>
<td>&lt;0.001a</td>
<td>&lt;0.001a</td>
<td>5.0</td>
<td>&lt;0.001a</td>
<td>&lt;0.001a</td>
<td>0.05</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.31</td>
<td>0.26</td>
<td>1.0</td>
<td>0.06</td>
<td>0.09</td>
<td>0.01</td>
</tr>
<tr>
<td>Sodium</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>174</td>
<td>175</td>
<td>200</td>
</tr>
<tr>
<td>Zinc</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.067</td>
<td>0.047</td>
<td>5.0</td>
</tr>
</tbody>
</table>

*a Method detection limit.

### Table 5 – Physical and chemical properties of mortars.

<table>
<thead>
<tr>
<th>Mortar</th>
<th>Loss on ignition (%)</th>
<th>Insoluble residue (%)</th>
<th>SO3 content (%)</th>
<th>Blaine method4 (cm²/kg)</th>
<th>Paste of normal consistency</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>5.33</td>
<td>1.48</td>
<td>2.16</td>
<td>3980</td>
<td>23.6</td>
</tr>
<tr>
<td>M2</td>
<td>5.31</td>
<td>1.44</td>
<td>1.90</td>
<td>3915</td>
<td>23.2</td>
</tr>
<tr>
<td>M3</td>
<td>5.19</td>
<td>1.39</td>
<td>1.82</td>
<td>3950</td>
<td>23.0</td>
</tr>
<tr>
<td>M4</td>
<td>4.97</td>
<td>1.45</td>
<td>1.56</td>
<td>3880</td>
<td>23.0</td>
</tr>
<tr>
<td>NBR 11578</td>
<td>≤6.5</td>
<td>≤2.5</td>
<td>≤4.0</td>
<td>≥2600</td>
<td>–</td>
</tr>
</tbody>
</table>

*a Specific surface Blaine method.
was obtained in Turkey [6] for mortars prepared with 4% FGD gypsum. The effect of replacing the natural gypsum by FGD gypsum on the compressive strength is showed in Fig. 13 at the ages of 1, 3, 7, and 28 days. The results obtained for all tested mortars were higher than the minimum strength values required by the standard. The compressive strength reaches its maximum values with the mortar M3 (2.1% of FGD gypsum and 1.4% of natural gypsum). When only FGD gypsum is used in the mortar (M4), the resistance is lower than that when used mixtures of natural gypsum/FGD gypsum, but it is still higher compared to the mortar with only natural gypsum (M1). Researches in Turkey also showed optimum strength results for mortars prepared with 4% of FGD gypsum that those prepared with 4% natural gypsum.

4. Conclusions

The FGD gypsum was composed mainly of bassanite (CaSO$_4 \cdot$0.6H$_2$O) and hannebachtite (CaSO$_3$·0.5H$_2$O). It presented a smaller mass loss due to removal of water and volatiles (11%) than did natural gypsum (19%). The natural gypsum almost only consisted of dihydrate (CaSO$_4$·2H$_2$O) with very small impurities of anhydrite.

Concentrations in the leachate and solubilized extract permits classifies the FGD gypsum as class II – not dangerous and class II A – not inert according to the Brazilian normative. The release of inorganic constituents from FGD gypsum were estimated, leachate concentrations for the elements As, Ba, Cd, Pb, Cr, Hg, Ag and Se were lower of the standard limits and concentrations of Cd and Se in the solubilized extract were slightly higher than standard limits.

The setting time was influenced by the percentages of FGD gypsum content in the mortars tested. The initial and final setting time increased with increasing FGD gypsum ratio. A retarding effect of about 1 h was reached with mortars produced only with FGD gypsum than those prepared only natural gypsum.

The compressive strength also was affected by increase of FGD gypsum in the mortars. At all ages the compressive strength of the mortar with 2.1% FGD gypsum/1.4% natural gypsum was higher that to other mixtures. The performances of cements prepared with mixtures FGD gypsum/natural gypsum were better compared with that prepared only with natural gypsum.

Based on information of the literature review and the results obtained in the characterization and evaluations of FGD gypsum it can be conclude that the presence of hemihydrates influences satisfactory in the hydration of cement and it can be used as a retarder additive in the preparation of Portland cement CP-II F 32.

Acknowledgements

The authors appreciate the financial support provided by the CAPES and FAPERJ, the help of Holcim Company (Brazil) by the feasibility of testing in the development theses research, and Professor Rogério Navarro Correia de Siqueira for his important contribution in this research.

References


