Valorization of phosphogypsum in Supersulfated Cement (SSC): a contribution for binders free of CO\textsubscript{2} emissions

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Abstract. Phosphogypsum is a by-product from the production of phosphoric acid. In this process, the raw phosphate is treated by sulfuric acid and, besides the main product which is phosphoric acid (H\textsubscript{3}PO\textsubscript{4}), gypsum and a small quantity of hydrofluoric acid are obtained. For every tonne of phosphoric acid made, about three tonnes of phosphogypsum (calcium sulfate dehydrate) are yielded. Despite its use in Portland cement replacing natural gypsum (around 5%), the consumption of phosphogypsum represents less than a few percent. On the other hand, supersulfated cements (SSC) is a binder comprised for calcium sulfate (10-20%). The fact of SSC comprises more calcium sulfate in its composition allows a higher consumption of phosphogypsum. In addition, SSC are composed the most part of blast-furnace slag (up to 90%) and only a small dosage of hydroxide as activator. This contribution highlights research conducted to compose a binder free of CO\textsubscript{2} emission, made only for phosphogypsum (as an alternative calcium sulfate source) and blast furnace slag. Natural source of calcium sulfate (gypsum) was also used as a comparison study. The analysis of results showed that SSC made with phosphogypsum met the minimum compressive strength requirement by the European standard for supersulfated cement (EN 15743/2010), showing promise as alternative binders to Portland cement.

Introduction

Phosphogypsum (PG) is a byproduct of the fertilizer industry, formed during the production process phosphoric acid from a phosphate rock (Ca\textsubscript{5}(PO\textsubscript{4})\textsubscript{3}F) and sulfuric acid (H\textsubscript{2}SO\textsubscript{4}). In this process the resulting rock is dissolved in acid phosphoric acid (H\textsubscript{3}PO\textsubscript{4}), gypsum (CaSO\textsubscript{4}.2H\textsubscript{2}O) and hydrofluoric acid (HF) \cite{1,2,3}:

\[
\text{Ca}_5(\text{PO}_4)_3\text{F} + 5\text{H}_2\text{SO}_4 + 10\text{H}_2\text{O} \rightarrow 3\text{H}_3\text{PO}_4 + 5\text{CaSO}_4.2\text{H}_2\text{O} + \text{HF}
\] (1)

The phosphogypsum consists mainly of calcium sulfate dihydrate (CaSO\textsubscript{4}.2H\textsubscript{2}O) with small amounts of silica and some impurities due to the nature of the phosphate rock used in process \cite{4}. For each kg of phosphoric acid produced are generated approximately 5 kg of PG \cite{2,5,6}.

World production of phosphogypsum is around 280 million tons per year and in Brazil its is about 4.5 million tons per year \cite{7}. In general the PG is used in agriculture (for soil stabilization) and construction (preparation of materials for construction / road construction), but in insufficient quantities to absorb all PG generated. The reuse of PG, especially in construction, is based on technical, economic and ecological \cite{1,2,5,6}. In the world, up to 15% of PG produced is used in construction, in general, used in the production of Portland cement \cite{7}.

The use of the PG in the production of cement is due to its chemical similarity with the gypsum which is a raw material used in the production of cement \cite{8}. However the use gypsum in
Portland cement (which is the most used worldwide), is less than 5%. However, in supersulfated cement (SSC), the amount of calcium sulfate is 10-20%. Addition of gypsum, SSC is comprised of up to 90% blast furnace slag and a minor amount of an alkali activator [9,10,11,12].

The alkali activator promotes the increase of pH needed for the dissolution of the slag. The aluminum ions, calcium and silica react with the calcium sulphate (CS) to form ettringite (CSAG) and calcium silicate hydrate (CSH) as shown in equation 2 [13].

\[
C_5S_3A + CH + 3CS + 34H \rightarrow C_6A_3S_3H_{32} + 3CSH
\]  

Depending on the reactivity of the slag, gypsum as a secondary phase (formed from the hydration of the anhydrous calcium sulfate) and hydrotalcite can also be formed [12]. Although the solubility of calcium sulfate in water is not significantly affected by pH variations, ions present in a solution may involve an increase in its solubility [14].

The source of calcium sulfate can be present as gypsum (CaSO4.2H2O), bassanita (CaSO4.0.5H2O) and anhydrite (CaSO4) [15,16]. Recent studies show that the use of a source of anhydrous calcium sulfate (CaSO4) has better compressive strength and setting time results [6]. As a result, it is necessary the calcination of source of calcium sulfate to eliminate the H2O molecules present in the composition to the anhydrous phase [6,17].

The aim of this study is to use phosphogypsum to replace conventional raw material (gypsum rock) in supersulfated cements.

Materials and Methods

The SSC was made with blast furnace slag, PG as a source of calcium sulfate, and a small amount of potassium hydroxide (KOH) used as alkaline activator. The conventional source of calcium sulfate (gypsum rock) was also used as comparison.

In the present study, the slag came from a Brazilian steel company and its composition is presented in Table 1. The amount of Al2O3 is relatively low, however, it meets the current EN 15743 limits. X-ray diffraction (XRD) showed that the slag presented glass structure and a particle size smaller than 60 µm with a d50 of 8 µm (Fig. 1).

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Slag (%)</th>
<th>EN 15743</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>32.2</td>
<td>-</td>
</tr>
<tr>
<td>Al2O3</td>
<td>8.2</td>
<td>-</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>CaO</td>
<td>49.5</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>SO3</td>
<td>1.4</td>
<td>-</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>K2O</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>MnO</td>
<td>1.3</td>
<td>-</td>
</tr>
<tr>
<td>CaO+MgO+SiO2</td>
<td>86.7</td>
<td>≥66.7</td>
</tr>
<tr>
<td>(CaO+MgO)/SiO2</td>
<td>1.7</td>
<td>≥1.0</td>
</tr>
</tbody>
</table>
Fig. 1. X-Ray diffractogram and particle size distribution of slag used.

The sources of calcium sulfate (PG and gypsum rock) also came from Brazil (Fig. 2). Table 2 presented the chemical composition of gypsum rock and PG, respectively, where it is possible to observe the similarity between them mostly represented by sulfate (SO₃) and calcium oxide (CaO).

To obtain anhydrite (CaSO₄) for SSC, both PG and gypsum rock were burned for 1 h at 650°C and their mineralogical composition was confirmed by XRD (Figs. 3 and 4).

Table 3 shows that the hydrogenic potential (pH) of gypsum rock and PG di-hydrated and calcined (anhydrite). It is possible to observe that the pH of PG is slightly lower than that observed for the conventional source but significantly less than when calcined.

![Fig. 2. PG: a)di-hydrated and b) calcined (anhydrite)](image)

**Table 2.** Chemical composition (%) of calcium sulfate PG and gypsum rock.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>PG</th>
<th>Gypsum rock</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃</td>
<td>46,8</td>
<td>43,5</td>
</tr>
<tr>
<td>CaO</td>
<td>38,5</td>
<td>35,2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1</td>
<td>0,5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0,3</td>
<td>0,1</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0,2</td>
<td>0,7</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>--</td>
<td>0,6</td>
</tr>
<tr>
<td>MgO</td>
<td>0,2</td>
<td>--</td>
</tr>
<tr>
<td>SrO</td>
<td>0,1</td>
<td>0,7</td>
</tr>
<tr>
<td>TiO₂</td>
<td>--</td>
<td>0,4</td>
</tr>
<tr>
<td>K₂O</td>
<td>0,1</td>
<td>--</td>
</tr>
<tr>
<td>MnO</td>
<td>&lt;0,1</td>
<td>--</td>
</tr>
<tr>
<td>BaO</td>
<td>--</td>
<td>0,3</td>
</tr>
<tr>
<td>CeO₂</td>
<td>--</td>
<td>0,2</td>
</tr>
<tr>
<td>F</td>
<td>--</td>
<td>0,2</td>
</tr>
<tr>
<td>Loss ignition</td>
<td>12,82</td>
<td>17,7</td>
</tr>
</tbody>
</table>
Table 3. pH of calcium sulfate di-hydrated and calcined (anhydrite).

<table>
<thead>
<tr>
<th>pH</th>
<th>PG</th>
<th>Gypsum rock</th>
</tr>
</thead>
<tbody>
<tr>
<td>di-hydrated</td>
<td>5.7</td>
<td>7.6</td>
</tr>
<tr>
<td>calcined</td>
<td>7.1</td>
<td>11.3</td>
</tr>
</tbody>
</table>

Fig. 3. X-Ray diffractograms of gypsum rock di-hydrated and calcined (anhydrite).

Fig. 4. X-Ray diffractograms of PG di-hydrated and calcined (anhydrite).

Preparation of mortars and pastes

The SSC ratios were prepared with 10 and 20% and PG percentage variation of alkali activator (KOH) between 0.2 and 0.5% according to Table 2. In order to compare the performance of the PG, the same proportions of SSC were also studied using gypsum rock.

The mortars were prepared in the proportion 1: 2.75: 0.485 (SSC: sand: water) and were prepared in prismatic molds (4cmx4cmx16cm). After 24 h, the mortars were demoulded, immersed in lime water at a concentration of 3g / l up to 7 and 28 days for compressive strength tests.

Pastes with a w/c ratio of 0.4 were prepared. Using a TamAir isothermal calorimeter, heat evolution measurements were determined on 20g of SSC over a hydration period of 7 days at 23°C. For XRD analysis, these pastes were cured in saturated lime water solution and at 7 days were crushed into particles smaller than 9.5 mm, immersed in acetone for 2 h and dried by filtration to
remove the pore fluid. These dried samples were crushed again to obtain particles smaller than 150 µm. These powders were then submitted to X-ray diffraction analysis using CuKα radiation, over a 2θ range of 3°–70°, using steps of 0.02° and 10 s counting time.

Results and discussion

Fig. 5 presents the compressive strength tests of SSC made with phosphogypsum (PG) and conventional source (rock gypsum) at 7 and 28 days.

All proportions made with 20% of calcium sulfate (80_20) SSC made with PG showed very similar behavior to that made with gypsum, using different proportions of alkali activator, in both the ages. At 7 days, the value decreases with increasing of alkali activator content, but at 28 days, the SSC with 0.5% content provided the highest value and very similar for both sources. Also for both sources, at 28 days, the 0.8% level was found to be excessive, however, much more significantly to the SSC made with gypsum (23 MPa) than with PG (32 MPa).

For all proportions made with 10% calcium sulfate (90_10), the influence of the alkali activator was opposite to SSC made with gypsum and PG, at 7 and 28 days. For the first, the compressive strength decreases with increasing of activator content, while for the PG, the values increase. Also, at 28 days, SSC made with 0.8% of alkali activator and PG reached value significantly higher (39 MPa) than SSC made with conventional source (19 MPa).

The results seem to indicate that the solubility of SSC made with PG is less influenced by the content of alkali activator.

Considering the values required by EN 15743/2010 of 12 and 32.5 MPa at 7 and 28 days, respectively, for the 32,5N class, all formulations made with PG reached the minimum, except for 90_10, with 0.2% of alkaline activator, which reached 30 MPa at 28 days.

![Compressive strength of mortar cubes of SSC containing gypsum rock and phosphogypsum (PG).](image)

Calorimetry

Calorimetry tests presented the curves of heat of hydration rate (Fig. 6) and also the accumulated heat generated from the hydration reactions (Fig. 7).

The curves of heat of hydration rate of SSC containing conventional gypsum (Fig. 6) showed that the samples with higher content of alkali activator (0.8 and 0.5%) presented higher and
earlier peaks, showing reactions of hydration more intense. For samples containing PG (Fig. 7), the behavior of SSC was similar.

Comparing the two sources of calcium sulfate, it is possible to observe that the SSC proportions made with PG showed smaller and later peak, showing a slower process of hydration.

![Fig. 6. Heat flow rate of pastes of SSC containing PG.](image)

![Fig. 7. Heat flow rate of pastes of SSC containing gypsum rock.](image)

Figs. 7 and 8 show the heat accumulated during the hydration of the samples. It can be seen that for both calcium sulfate sources (conventional and PG) and for both proportions (80_20 and 90_10), the heat released is significantly lower when the alkali activator content is 0.2%. Also, for both sources and proportions, the curves obtained with 0.5 and 0.8% tend to be quite close, especially for conventional source, but at the end of the 7 days, heat accumulated values tend 0.5% to be larger or at least remain close.

Even for both sources, the values obtained with the formulation 90_10 were higher than those with 80_20, for the same level of alkaline activator. In general, the values obtained with PG were less than with the conventional source.
Mineralogical analysis

Fig. 10 presents the diffractogram of the sample made with 90% of slag, 10% of calcium sulfate (conventional and PG), and 0.5% of activator, at 7 days. It can be seen that PG showed the same peaks than conventional source, represented by ettringite phase (CCASC) which is resulting from the reaction between the slag and calcium sulphate and by anhydrite phase. However it is noted that in the case of PG, the consumption of the anhydrous phase and (consequently) the ettringite formation was less intense. The presence of crystalline calcium silicate hydrate (CSH) seems to be present only in SSC made with PG and would explain its similar or better results.
Conclusion

In this article, the phosphogypsum (PG) was used as calcium sulfate source to replace the gypsum rock (conventional source) in supersulfated cements (SSC), using two formulations (10 and 20%) and three alkaline activator contents. From the tests, it found:

- The compressive strength values of the SSC samples made with PG showed similar and / or superior than SSC made with gypsum. At 28 days, only the SSC containing 10% of calcium sulphate and 0.2% alkaline activator presented lower results than SSC made with conventional source and did not reach the minimum strength of 32.5 MPa of EN 15743;
- The calorimetry tests showed that the curves of release rate of SSC made with PG showed less intense peak at longer times, indicating a slower hydration kinetics;
- Analysis of X-ray diffraction showed that the SSC made with PG presented a less consumption of anhydrite and formation of ettringite but seems to provide the formation of crystalline CSH;
- The lower pH value for anhydrite from PG (7.1) in relation to the conventional source (11.3) seems to justify a lower kinetics of reaction and the need for a higher content of alkali activator in relation to the conventional source;
- A slower hydration rate provided by SSC made with PG, seems to favor increased mechanical strength and the formation of crystalline CSH, however, addition tests are needed to confirm this hypothesis.

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References