



Synthesis, hydration and durability of rice hull cements doped with chromium

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ABSTRACT

This work describes the synthesis, hydration and durability behavior of β - Ca_2SiO_4 doped with chromium. β - Ca_2SiO_4 is a component of commercial cement. Rice hull is an agricultural residue containing about 10% of silica as inorganic constituent. The controlled burning of rice hull was used to obtain this biogenic silica, used as starting material. In many situations chromium is added during cement preparation in order to promote encapsulation, at temperatures around 1500 °C. The synthesis presented here is completed at 800 °C, causing a substantial reduction in energy consumption. Moreover, chromium is chemically bonded to cement crystal, which is safer than simple physical encapsulation. Results show that chromium can be inserted into the structure of β - Ca_2SiO_4 up to 1% (molar ratio). Hydration degree and durability studies show that insertion of chromium causes no deleterious effects on physical and chemical properties of these doped materials when compared to β -pure Ca_2SiO_4 .

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1. Introduction

Portland cement is produced in almost every region of the world. Cement is an inexpensive material, easily stored and transported; also, it can be prepared from a large variety of raw-materials [1]. It is estimated that world concrete consumption is greater than 5.5 billion tons yearly. Despite those impressive numbers, commercial cement manufacture causes important environmental problems. It accounts for nearly 5–6% of total carbon dioxide emissions [2].

The chemical composition of commercial cement is variable, since cement-based materials must satisfy engineering and technical needs, such as chemical durability and mechanical resistance [3]. Essentially the main components of Portland cement are two calcium silicates: Ca_3SiO_5 ($\approx 50\%$ w/w) and β - Ca_2SiO_4 ($\approx 25\%$ w/w). From the environmental viewpoint, β - Ca_2SiO_4 presents many advantages over Ca_3SiO_5 . It can be prepared using lower amounts of raw-materials (minimizing carbon dioxide release) and it can be synthesized at lower temperature. In this sense, the production of cements containing higher amounts of β - Ca_2SiO_4 is very promising [4,5].

Rice hull is a renewable biomaterial, very abundant in many different countries, such as Brazil, China and India. It contains silica (SiO_2) as the major inorganic component (usually around 10–30% w/w) and organic compounds such as lignin and cellulose [6]. In many underdeveloped countries, the most common procedure is the burning of rice hull at rice fields; this practice may cause many

environmental and health problems, due to production of particulate material. On the other hand, the separation of inorganic and organic components is relatively simple, suggesting that the inorganic material (SiO_2) could be used in productive processes. This biogenic silica shows a high potential in the synthesis of several silicates, due to low cost and availability.

In earlier works Rodrigues [7,8] developed a method for the synthesis of β - Ca_2SiO_4 using silica derived from rice hull as starting material. The method combines sonochemical and solid-state chemical reactions. The synthesis was completed at 800 °C. The utilization of an agricultural residue to produce cementitious materials is a very interesting aspect, since it may contribute to avoid air and soil contamination. Furthermore, the valorization of by-products is an important trend in productive processes [9,10].

Additionally, the utilization of β - Ca_2SiO_4 as cement requires further information regarding physical and chemical properties. A fundamental aspect in cement chemistry is the hydration process, i.e., the chemical reactions between anhydrous calcium silicates and water, rendering a hydrated material. For instance, the development of mechanical resistance is directly dependent on hydration rate and so, it plays an important role in order to understand and assure that these materials can be functional [11]. In the case of β - Ca_2SiO_4 hydration rate is a crucial aspect, since Ca_3SiO_5 hydrates much faster [1,12].

This work presents the synthesis, hydration and durability behavior of β - Ca_2SiO_4 doped with chromium. Chromium was chosen as dopant for several reasons. In the first place, chromium compounds can be mechanically stabilized into concrete and mortar structures. The solidification/stabilization method is used as remediation process, to avoid environmental contamination

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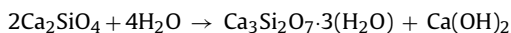
[13,14]. In many situations, physical entrapment is responsible for the stabilization of hazardous components. In the method presented here, physical and chemical stabilization processes may occur, since chromium is chemically bounded to a crystalline structure, enhancing stabilization process. In addition, the effect of chromium on hydration and durability of β - Ca_2SiO_4 is also presented.

2. Materials and methods

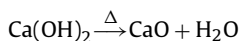
Rice hull was used as the natural source of silica. Silica was obtained by slow heating of rice hull at 600°C . The silica was washed several times with distilled water to remove minor soluble salts. This biogenic silica was characterized by infrared and X-ray diffraction, and is partially amorphous, presenting a surface area of $20\text{ m}^2\text{ g}^{-1}$. Calcium oxide (Nuclear), barium chloride (Vetec), chromium oxide (Nuclear), analytical grade reagents, were used without further purification. Barium chloride was used in small proportion (2%, molar ratio, in relation to calcium oxide) in order to stabilize the β -phase [7,8]. Chromium oxide was used to replace calcium oxide in the following proportions: 1, 2, 4, 5 and 10% (molar ratio). The solids, in stoichiometric proportions, were mixed together and aqueous suspensions were obtained, with ratio water:solids of about 20:1 (w/w). The suspensions were treated in an ultrasonic bath (Thornton, 25 kHz) for 60 min and dried overnight at 100 – 110°C . After this treatment, an intermediate silicate and unreacted material was obtained. These solids were calcined at 800°C for 3 h. According to chemical composition, after this procedure, the synthesis was completed. The solids were characterized by X-ray diffraction (Shimadzu, XRD 6000, Cu $K\alpha$ radiation, 50 kV and 40 mA). AFM images (Shimadzu, SPM 9600) were obtained using dynamic mode. Prior to analysis, the powdered material was pressed into circular discs to facilitate the image acquisition.

Thermogravimetric analysis (TGA) was used to evaluate the hydration rate of β - Ca_2SiO_4 and doped β - Ca_2SiO_4 . Analyses were carried out under nitrogen atmosphere, using a heating rate of 20°C per min. Initially, 1 g of each solid was mixed with 0.5 g of distilled water, freshly boiled. Samples were kept at room temperature and 100% of relative humidity in sealed containers to avoid contamination. Prior to analysis, the samples were treated with acetone to stop hydration [15]. In all cases, at least 3 individual measurements were performed.

Hydration rate can be determined using the following equation:



The amount of calcium hydroxide generated is proportional to hydration rate [16]. In this sense, thermal decomposition of calcium hydroxide is used to estimate hydration degree, as presented below.



Durability plays a fundamental role in the utilization of materials for construction. In order to perform these studies, test specimens were prepared and submitted to situations that simulate environmental and aggressive exposure conditions.

2.1. Test specimen preparation

In all experiments, test specimens were prepared using water/cement ratio of 0.50 (w/w) and a ratio cement to sand of 1:3 (w/w). Cylindrical test specimens were prepared having a diameter of 3 cm and height of 5 cm. Cement, sand and distilled water were mixed together in order to render a fresh paste, molded into

Table 1

Experimental conditions used to prepare specimen tests for durability studies.

Mortars	Commercial cement	Doped β - Ca_2SiO_4 (%)	w/c	Cement/sand ratio
Control	100	0	0.55	1:3
Blended	80	20	0.55	1:3

polyethylene flasks, and cured for 28 days at room temperature and 100% of relative humidity, prior to experiments.

Durability studies were conducted in a comparative way. In all experiments, two kinds of test specimens were prepared: “control samples”, where only commercial cement (Tupi, CP IV) was used and “blended materials” where β - Ca_2SiO_4 doped with chromium was used to replace 20% (w/w) of commercial cement. Table 1 summarizes the experimental conditions used to prepare test specimens for durability studies.

2.2. Total water absorption, capillary absorption and resistance to acid tack

After the 28-day curing time, test specimens were dried for 48 h at 100 – 110°C , until constant weight, in order to remove the excess of water. Total water absorption was determined by re-immersion of test specimens in water and verified the mass variation. Results are average of at least 5 individual measurements. This experiment gives information about the porosity of each sample. In capillary absorption experiments, test specimens were put in contact with water, only by the inferior surface. Under these circumstances, water absorption was due mainly to capillary rise.

In acidic attack, the test specimens were initially immersed into water, to determine their saturated mass. After this, test specimens tests were immersed in solutions of HCl 0.01 mol L^{-1} , and the mass variation was determined as a function of time.

3. Results and discussion

The synthesis of dicalcium silicates doped with chromium was investigated using X-ray diffraction. Several concentrations of chromium were studied, varying from 1 to 10% (molar ratio). It was found that the maximum amount of chromium that could be inserted into the crystalline structure of β - Ca_2SiO_4 was limited to 1%. Fig. 1 shows the X-ray patterns for the sample containing 1 and

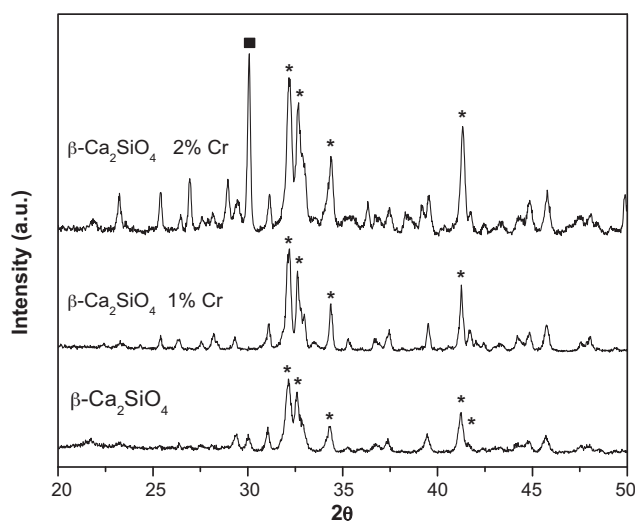


Fig. 1. X-ray diffraction patterns for β - Ca_2SiO_4 and β - Ca_2SiO_4 doped with 1% and 2% of chromium prepared at 800°C (*, β - Ca_2SiO_4 characteristic peaks; ■, unidentified phase).

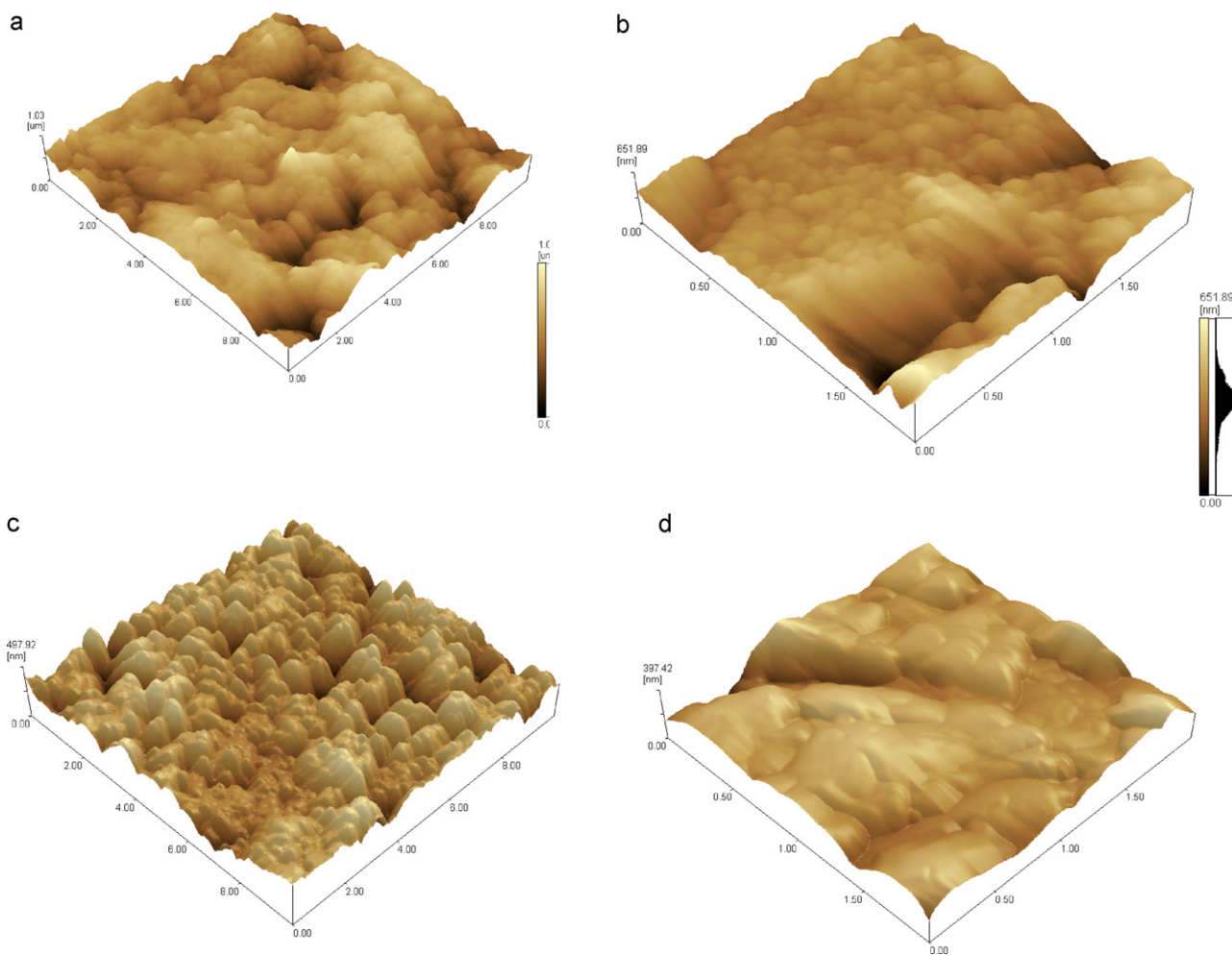


Fig. 2. AFM images of β - Ca_2SiO_4 and β - Ca_2SiO_4 doped with 1% of chromium: (a) and (c) areas correspondent to $10\ \mu\text{m} \times 10\ \mu\text{m}$ and (b) and (d) detailed view: $2\ \mu\text{m} \times 2\ \mu\text{m}$.

2% of chromium along with the “pure” β - Ca_2SiO_4 . It can be seen that the addition of Cr (2%) renders a mixture of phases.

When higher concentrations of chromium (from 2 to 10%) were used the crystalline structure (β -phase) could not be preserved, rendering complex mixtures of calcium silicates and unreacted calcium and chromium oxides. Preliminary studies showed that these solids do not present hydraulic activity and could not be used as cement.

The level of insertion of substituent species into the crystalline structure of β - Ca_2SiO_4 seems to be dependent on the nature of the oxide used during the process [17,18]. Also, it should be pointed out that literature reports some works dealing with the insertion of metals into the crystalline structure of β - Ca_2SiO_4 [19–21]. However, since the syntheses of these materials were performed in different ways, a direct comparison between results is not a simple task. It seems that there is a maximum limit to insert different atoms into the crystalline structure of β - Ca_2SiO_4 . Considering the initial results, all the remaining experiments were carried out using only β - Ca_2SiO_4 and β - Ca_2SiO_4 doped with 1% of chromium.

Atomic force microscopy (AFM) images were used to characterize the particles of pure dicalcium silicate and dicalcium silicate doped with 1% of chromium. Fig. 2 displays AFM images of selected areas, Fig. 2a and c presents a larger view ($10\ \mu\text{m} \times 10\ \mu\text{m}$) while Fig. 2b and d shows smaller regions ($2\ \mu\text{m} \times 2\ \mu\text{m}$). The examination of Fig. 2 shows that the surface of these materials presents many irregularities and high rugosity. Regarding physical properties [22], the presence of significant roughness improves the

contact between the solid and water (wetting behavior) which may facilitate hydration process, an important parameter in terms of technological application. When detailed regions (Fig. 2b and d) are analyzed, similar trends can be better observed: the surface profile is quite variable, showing many small agglomerates with dissimilar diameters. It should be pointed out that several images were acquired and those presented here, were selected since they represent the entire sample.

An important issue associated to β - Ca_2SiO_4 and related-cements is the hydration rate. For instance, Ca_3SiO_5 , the major component of Portland cement hydrates faster than β - Ca_2SiO_4 . In this work we followed hydration process using thermogravimetric analysis (TGA). Hydration degrees for β - Ca_2SiO_4 and β - Ca_2SiO_4 doped with 1% of chromium are presented in Fig. 3. It can be seen that both calcium silicates present about the same hydration behavior. Furthermore, hydration rate for β - Ca_2SiO_4 , after 60 days, is comparable to those found in literature [23].

It is important to note that the insertion of chromium does not delay the hydration process. Most of the works in this area have dealt with the addition of dissolved metals in water, to promote the hydration of calcium silicates. Here in contrast, chromium is part of the chemical structure of the silicate. For instance, the addition of calcium salts tends to accelerate the hydration of β - Ca_2SiO_4 [24]. Similar behavior was observed when solutions of chromium nitrate were added to β - Ca_2SiO_4 [25]. However, the effect of other metals can be far complex. Cadmium and lead salts tend to retard the process [26].

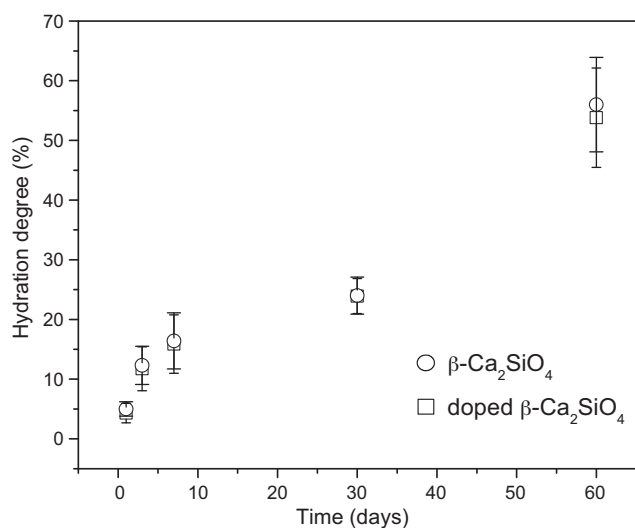


Fig. 3. Hydration degree for β - Ca_2SiO_4 and β - Ca_2SiO_4 doped with 1% of chromium.

Table 2

Total water absorption for test specimen prepared with commercial cement (control) and specimen test prepared with β - Ca_2SiO_4 doped with 1% of chromium.

Material	Water absorption
Control	7.02 ± 0.63
Blended material	7.08 ± 0.71

Durability studies are also of fundamental importance to evaluate possible use of these cement-based materials. All experiments were conducted using two sets of test specimens: “control” (commercial cement) and “blended” material (material composed of 80% of commercial cement and 20% of β - Ca_2SiO_4 doped with 1% of chromium). Hereafter, for the sake of simplicity, these materials will be named “control” and “blended material”.

Initial assessment of porosity was performed by measuring total water absorption (Table 2) and capillary absorption (Fig. 4).

In both experiments, it was not observed any significant change between control and blended material. These preliminary results indicate that the utilization of cements doped with chromium does not influence porosity of test specimens. Total and capillary porosity are important parameters that control the permeation properties of solids and mechanical resistance [27]. For instance, most of degradation processes occurring in concrete structures are

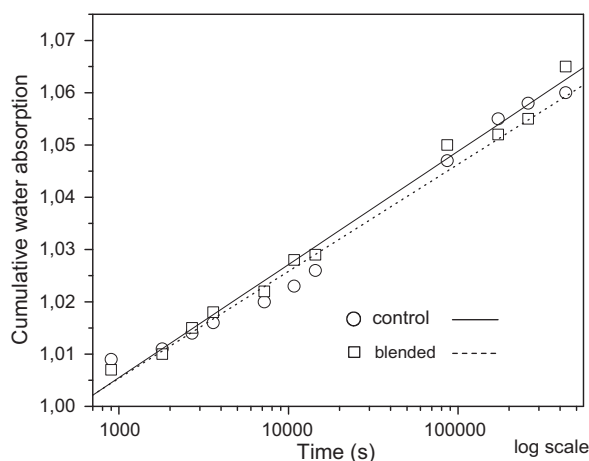


Fig. 4. Cumulative water absorption for control and blended material determined by capillary ascension.

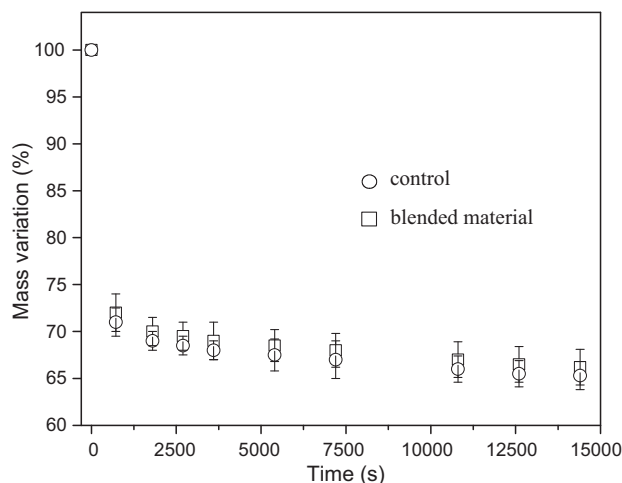


Fig. 5. Acidic attack: mass variation for test specimens: control and blended material.

due to the percolation of dissolved ions and/or gases and are closed related to porosity and pore size distribution [3].

Acidic attack experiments were carried out to evaluate the performance of these materials under aggressive environments. For example, acid rain and the presence of carbon dioxide are increasingly important deleterious processes occurring in civil construction [28,29]. Once again, as displayed in Fig. 5, the performance of test specimens containing β - Ca_2SiO_4 doped with 1% of chromium is similar to commercial cements. Comparable results were obtained for systems containing titanium oxide [30].

These results are very important in terms of solidification and stabilization processes. The method is very useful to permanently immobilize hazardous wastes derived from human activity. In order to accomplish it, concrete or mortars must present low permeability and resistance to aggressive environments. The examination of porosity and resistance to acidic attack shows that partial replacement (20% w/w) of commercial cement by β - Ca_2SiO_4 doped with 1% of chromium causes no damaging effect on the properties associated to durability.

It is important to mention that cement industry experiences many difficulties in terms of sustainability, such as the intensive use of energy and raw-materials. In addition, the production of cement is a heavy-polluter process, generating great amounts of carbon dioxide and organic pollutants [31,32]. In this sense, new processes and technologies, as presented in this work, can be useful to minimize these problems.

4. Conclusions

The synthesis of β - Ca_2SiO_4 doped with 1% of chromium can be accomplished at 800°C , using rice hull as the source of silica. Comparatively, commercial Portland cement is prepared at temperatures around 1500°C . On the other hand, if the concentration of chromium is higher (from 2 up to 10%) the synthesis was not completed, rendering a mixture of solids.

AFM images were used to characterize the morphology of β - Ca_2SiO_4 doped with 1% of chromium. It was observed that this material presents a highly irregular surface.

The hydration degree of β - Ca_2SiO_4 and β - Ca_2SiO_4 doped with 1% of chromium are very similar, showing that insertion of chromium does not slow down the process.

Durability testes show that the partial replacement of commercial cement by β - Ca_2SiO_4 doped with 1% of chromium does not interfere with the performance of test specimens.

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