

# Chemically-modified Calcium Silicates from Rice Hull Ash: Synthesis and Hydration Behavior

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## 1. Introduction

There is a continuous interest in the utilization of agricultural by-products and residues in productive processes, in order to provide inexpensive, renewable and environmental-friendly technologies and materials [1-2]. Klass [3] has presented many important sources and applications of such materials, broadly named as biomass.

Rice hull is an abundant by-product of agricultural activities around the world. Rice hull is basically composed of organic and inorganic components. The major organic constituents are cellulose, hemicelluloses, lignin, and carbohydrates. It also contains about 20% of silica as inorganic material which is responsible for its rigidity and intrinsic mechanical resistance. Minor components such as potassium, calcium and magnesium salts and oxides may also be present [4].

The controlled heating of rice hull renders silica making it a useful resource for utilization in materials science and other areas. Many studies have addressed the utilization of rice hull ash in different areas such as fillers, adsorbents and construction materials [5-6].

Portland cement is a very complex material, composed of many components such as calcium silicates, calcium aluminates and gypsum among others. On the other hand, it is well-known that two calcium silicates are the most important components. Together,  $\text{Ca}_3\text{SiO}_5$  and  $\beta\text{-Ca}_2\text{SiO}_4$  correspond to about 70% of cement mass, although this composition can be different according to local cement production. They also are responsible for most of properties such as mechanical resistance and durability of mortars and concrete. Typically, commercial cement is produced in rotary kilns at temperatures around 1500°C through solid-state chemical reactions [7]. In some aspects,  $\beta\text{-Ca}_2\text{SiO}_4$  has some advantages over  $\text{Ca}_3\text{SiO}_5$  because its production demands less energy and raw-materials. These are very important issues in cement industry. It is estimated that 6% of all carbon dioxide produced by human activities are derived from cement industry, showing the importance of saving raw-materials and the need of new “clean” processes [8,9]. On the other hand, the major limitation of  $\beta\text{-Ca}_2\text{SiO}_4$  is the reactivity of this material in relation to water.  $\text{Ca}_3\text{SiO}_5$  hydrates much faster than  $\beta\text{-Ca}_2\text{SiO}_4$ .

The purpose of this work is the synthesis of chemically-modified  $\beta\text{-Ca}_2\text{SiO}_4$  cements using silica derived from rice hull as starting material. Several oxides were used as dopants: MnO, CdO, ZnO,  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ . The synthesis and hydration behavior of these doped-dicalcium silicates were studied.

## 2. Methods

Silica was obtained from heating rice hull at 600°C. X-ray diffraction confirms the formation of silica having the cristobalite structure along with amorphous material. Analytical grade reagents, CaO (Nuclear), MnO, (Mallinckrodt), CdO (Acrós Organics), ZnO (Mallinckrodt), Al<sub>2</sub>O<sub>3</sub> (Vetec), Cr<sub>2</sub>O<sub>3</sub> (Acrós Organics) and barium chloride (Mallinckrodt) were used in stoichiometric proportion, in order to render the desired calcium silicates, containing each dopant. It is important to note that dicalcium silicate ( $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>) presents a ratio Ca/Si= 2 while the materials synthesized in this work present a ratio (Ca+Z)/Si = 2.0, where “Z” corresponds to dopant added (Mn, Cd, ZnO, Al or Cr). The dopant level was studied in the range from 1 to 10% (molar ratio). Also in all preparations presented here, a small amount of barium (2%, molar ratio) was added during the process. Previous publications [10-11] have shown that the addition of barium facilitates the formation of the  $\beta$ -phase although the involved mechanism is not yet fully understood [12]. For the sake of simplicity, in the following discussion, barium will be omitted in the chemical formula of prepared samples. Figure 1 presents a representation of synthetic procedure.

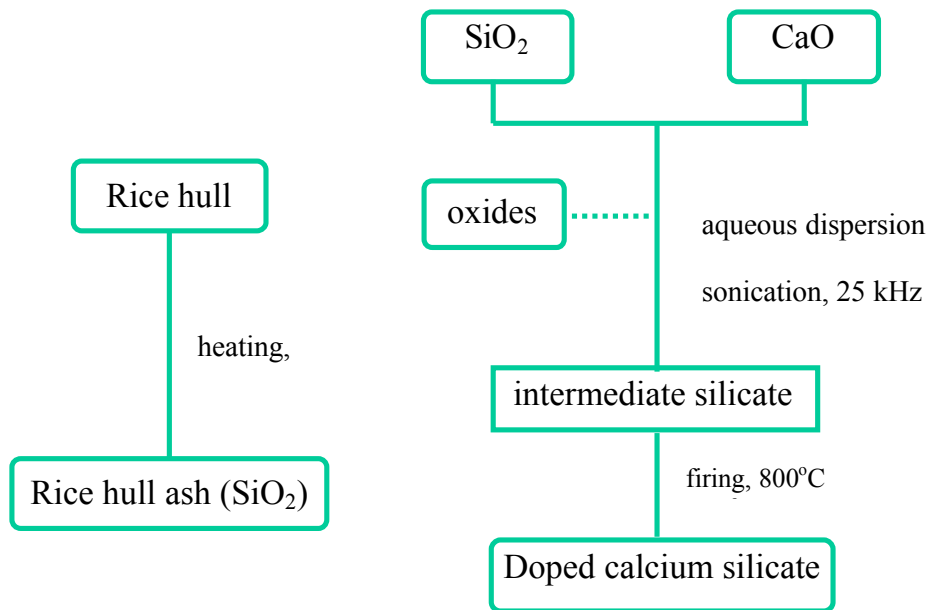


Figure 1: Synthetic method for preparation of doped-dicalcium silicates

The solids were mixed together and water was added in order to render suspensions with a water/solid ratio of about 20. The suspensions were sonicated in an ultrasonic bath (Thornton, 25 KHz) for 60 minutes. Scanning electron microscopy has shown that sonication has the effect of lower the average size of solid particles which facilitates the next step of synthesis. The suspensions were dried overnight at 100-110°C. It was observed in all cases, that intermediate silicates having a ratio Ca/Si  $\cong$  1.6 were obtained, determined by acid-base titration and confirmed by

thermogravimetric analysis. These intermediate silicates were grounded and heated up to 800°C for 180 minutes.

Samples were analyzed by FTIR spectroscopy (Spectrum One, Perkin-Elmer) using KBr discs and 16 accumulations. Thermal analyses were performed using TGA and DTA (Pyris, Perkin-Elmer). Both analyses were carried out under nitrogen atmosphere and using a heating rate of 40°C/minute. Typically samples between 10 to 40 mg were used. X-ray diffraction data were obtained using Shimadzu equipment (powder method, monochromatic Cu K $\alpha$  radiation, 50kV and 40 mA.).

Hydration of “pure” dicalcium silicate and doped-materials were examined by thermogravimetric analysis. The method is based on the formation of calcium hydroxide as product of hydration.

### 3. Results and Discussion

The synthesis of each material after firing intermediate silicate at 800°C was studied by x-ray diffraction and infrared spectroscopy. Heating effect on the synthesis of dicalcium silicate studied by FTIR is presented in figure 2. The main characteristics of this set of spectra are: the large band located at around 1500  $\text{cm}^{-1}$  is due to Ca-O stretching mode (due to the presence of calcium oxide). This band is clearly observed after heating the intermediate silicate at 600°C (upper line). The same spectrum also shows a sharp peak located at 870  $\text{cm}^{-1}$ , due to the presence of the intermediate silicate. Continuous heating of these samples (at 700 and 800°C) causes a progressive disappearance of the band located at 1500  $\text{cm}^{-1}$ .

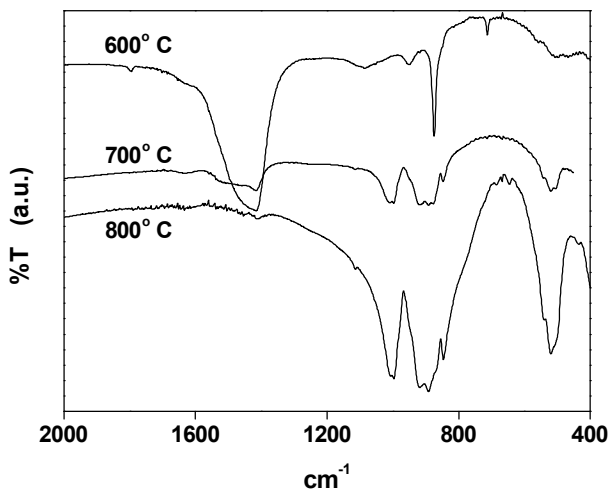


Figure 2: Heating effect on intermediate silicate: FTIR spectra for “pure” dicalcium silicate.

X-ray diffraction analysis was used to confirm the synthesis of each doped-dicalcium silicate. Under the experimental conditions studied here the synthesis is not complete in many situations, according to dopant

level. Also, in many cases,  $\beta$ -phase was not obtained or a mixture of phases was observed. Table I displays the maximum amount of dopant introduced for each silicate, considering only the formation of  $\beta$ -phase.

Table 1: Maximum amount of dopant introduced into  $\beta$ -dicalcium silicate

Dopant	Maximum amount (%)
Mn	5
Cd	10
Zn	10
Al	1
Cr	1

It can be observed that when cadmium and zinc were used as dopant a maximum substitution level of 10% was obtained. When manganese was used only 5% of insertion was attainable. In the case of manganese, it was observed that insertion of 10% of manganese oxide renders a mixture of two phases. On the other hand, the maximum amount of dopant for aluminum and chromium was found to be just 1%. This behavior was attributed to the type (2:3) and size of oxides.

Table 2 shows the hydration degree for “pure”  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> and doped  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> after 28 days, determined by TGA.

Material	Hydration degree % (28 days-curing period)
$\beta$ -Ca <sub>2</sub> SiO <sub>4</sub>	55 ± 5
$\beta$ -Ca <sub>2</sub> SiO <sub>4</sub> (Mn 5%)	50 ± 6
$\beta$ -Ca <sub>2</sub> SiO <sub>4</sub> (Cd 10%)	52 ± 8
$\beta$ -Ca <sub>2</sub> SiO <sub>4</sub> (Zn 10%)	48 ± 7
$\beta$ -Ca <sub>2</sub> SiO <sub>4</sub> (Al 1%)	59 ± 4
$\beta$ -Ca <sub>2</sub> SiO <sub>4</sub> (Cr 5%)	57 ± 5

As it can be observed the insertion of dopants does not cause a significant variation in  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> hydration. These results indicate that many industrial residues could be inserted into dicalcium silicate structure. Further studies are necessary to evaluate long-term performance of these doped-dicalcium silicates, as well as the effects on mechanical properties, durability and economic viability.

#### 4. Acknowledgements

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