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Low-temperature synthesis of cements from rice hull ash

Flávio A. Rodrigues*

Universidade de Mogi das Cruzes, Prédio I, sala 1S 15 (CIIB), Av. Cândido Xavier A. Souza, 200 C. Cívico, Mogi das Cruzes, SP, 08780-210, Brazil

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Abstract

Rice hull is an agricultural by-product containing about 20% of silica. Usually, this material is burned at the rice fields generating small silica particles, which may cause respiratory and environmental damage. This work describes the use of rice hull ash as a raw material to prepare Ca_2SiO_4-related cements, which is a component of commercial Portland cement. Rice hull was heated at 600 °C rendering silica with a surface area of 21 m^2 g^{-1}. This material was mixed with CaO and $BaCl_2{\cdot}2H_2O$ in several proportions, added stoichiometricaly in order to keep a ratio (Ca + Ba)/Si = 2. The solids were mixed with water 1:20 (w/w) and sonicated for 60 min. The suspensions were dried and heated at several temperatures (from 500 to 1100 °C). The resulting solids were analyzed by FT-IR spectroscopy and X-ray diffraction. Cements with structure similar to that of β-Ca_2SiO_4 were obtained at temperatures as low as 700 °C, according to the composition.

Keywords: Cement; Ca_2SiO_4; Cement manufacture; Chemistry

1. Introduction

Portland cement is one of the most consumed materials; world per capita consume is estimated to be about 200 kg/person/year or the equivalent to 1 ton of concrete/person/year [1]. The traditional method used for the production of cement is based on solid-state reactions, carried out at temperatures around 1450 °C [2]. Portland cement is a complex material, composed basically by calcium silicates, calcium aluminates and calcium aluminoferrites, among others. The calcium silicates, Ca_3SiO_5 and β-Ca_2SiO_4, determine most of the adhesive properties of concrete as well as its strength and durability. These silicates account for nearly 75% of ordinary cement. Both silicates show about the same characteristics after complete hydration, such as physical and mechanical properties, although Ca_3SiO_5 hydrates much faster [3,4].

Cements composed exclusively by β-Ca_2SiO_4 present great economic and environmental interest because they can be prepared at lower temperatures and consume less CaO. An excellent review about the subject was presented by Chaterjee [5,6]. In conventional cement manufacture, $CaCO_3$ is the main source of CaO and during the burning of raw materials, great amounts of CO_2 are released. It is worth to mention that cement industry generates about 8% of total CO_2 emission [7]. Similarly, a decrease in the temperature needed to obtain the cement is very important since it will reduce the energy and fossil fuels consumption. Many attempts have been made in order to synthesize β-Ca_2SiO_4 cement [8–10]. Those works have used hydrothermal treatment as synthetic method, since silica shows higher solubility under these conditions [11,12]. Also, research dealing with β-Ca_2SiO_4 cements from alternative raw materials [13,14], durability [15,16] and synthetic procedure [17] has been reported.

On the other hand, rice hull is an abundant material, produced in many countries around the world containing approximately 20–25% of silica. Rice hull is usually discarded and burned at the fields. This common practice can lead to serious environmental damage, since silica particles remain suspended in the air being a potential cause of respiratory diseases. In Brazil, for example, about 2.5×10^6 ton of rice hull ash is generated each year. It seems a reasonable assumption that this agricultural waste presents a very high potential to be used in large scale, such as in cement industry.

* Tel.: +55-11-4798-7103; fax: +55-11-4978-7225.
E-mail address: flaviorodrigues@yahoo.com (F.A. Rodrigues).

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Table 1
Relative amount of SiO_2, CaO and $Ba_2Cl_2{\cdot}2H_2O$ used in each preparation and the percentage of Ca replacement

% of Ca replacement	Relative amount of substance (mol)		
	SiO_2	CaO	$BaCl_2{\cdot}2H_2O$
0	1	2	0
2	1	1.96	0.04
4	1	1.92	0.08
6	1	1.88	0.12
8	1	1.84	0.16
10	1	1.8	0.20

Recently, a method using rice hull ash as raw material for the synthesis of β-Ca_2SiO_4 was presented [8]. Hydrothermal processing was employed and the synthesis of β-Ca_2SiO_4 at temperatures as low as 700 °C was demonstrated. It was established that the partial replacement of Ca by Ba atoms was necessary in order to stabilize the formation of β-Ca_2SiO_4 [8]. Ca_2SiO_4 has five crystalline phases, and in general, the β-phase is the predominant one, although other phases are usually present.

This work describes a method for the production of β-Ca_2SiO_4 cement from rice hull ash. In contrast to previous works, the hydrothermal treatment was replaced by sonication, which is equally efficient although much less expensive.

2. Methods

Rice hull was obtained from Bariri, São Paulo. This material was slowly heated in an open furnace up to 600 °C, rendering silica, in the form of a white powder. After each preparation, infrared spectroscopy was used to check the presence of SiO_2 and the absence of SiC. After heating rice hull at this temperature, there are only traces of minor components, such as potassium and sodium.

CaO (Mallinckrodt, analytical grade reagent) was heated to 1000 °C prior to use. $BaCl_2{\cdot}2H_2O$ (Synth, analytical grade reagent) was used without further purification.

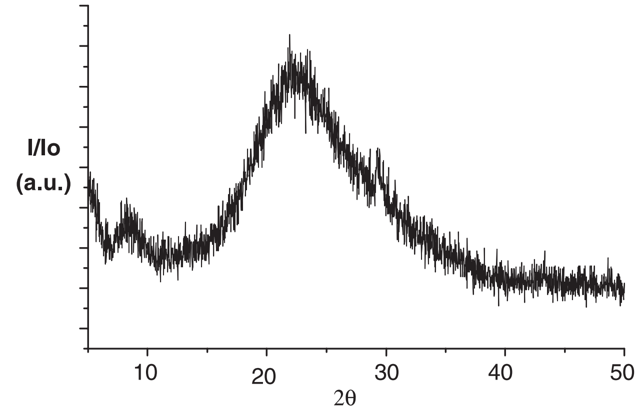

Fig. 2. X-ray diffraction pattern obtained after heating rice hull at 600 °C.

Partial substitution of Ca by Ba to stabilize the desired solid was performed by the stoichiometric addition of silica, CaO and $BaCl_2{\cdot}2H_2O$ keeping a ratio (Ca + Ba)/Si = 2, which is similar to that of β-Ca_2SiO_4. Ba replaced Ca in proportions varying from 2% to 10% (molar basis). Samples without Ba were prepared as control. Table 1 lists the relative amount of materials used for each preparation as well as the amount of Ca replacement.

Distilled water was added to these mixtures of solids and the suspensions were sonicated for 1 h (Thornton GA 240, 25 kHz). The water to solids ratio was kept about 20:1. After this, the suspensions were dried at 60 °C for 1 day. The resulting materials are mixtures of calcium silicates and the respective salts and hydroxides of Ca and Ba. For simplicity, these solid mixtures will be hereafter designated as intermediate silicates. These intermediate silicates were heated from 500 to 1100 °C, rendering in some cases the cement.

The materials obtained after each step were characterized by infrared spectroscopy, (FT-IR Perkin–Elmer 16PC), X-

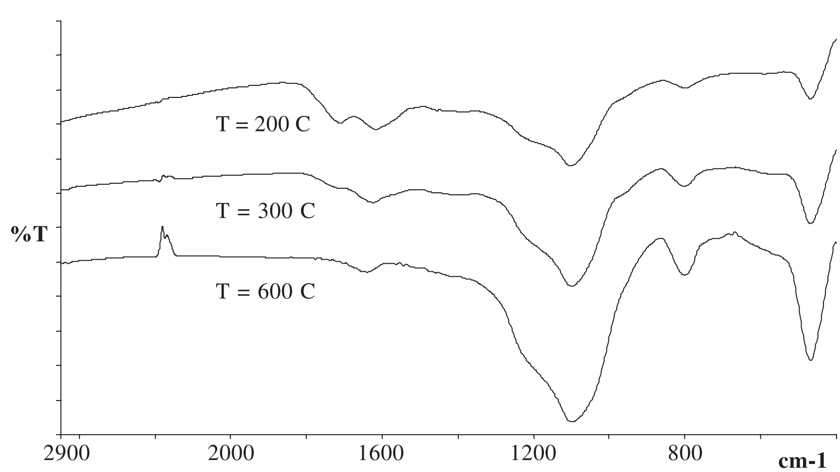

Fig. 1. FT-IR spectra obtained after heating rice hull at 200, 300 and 600 °C.

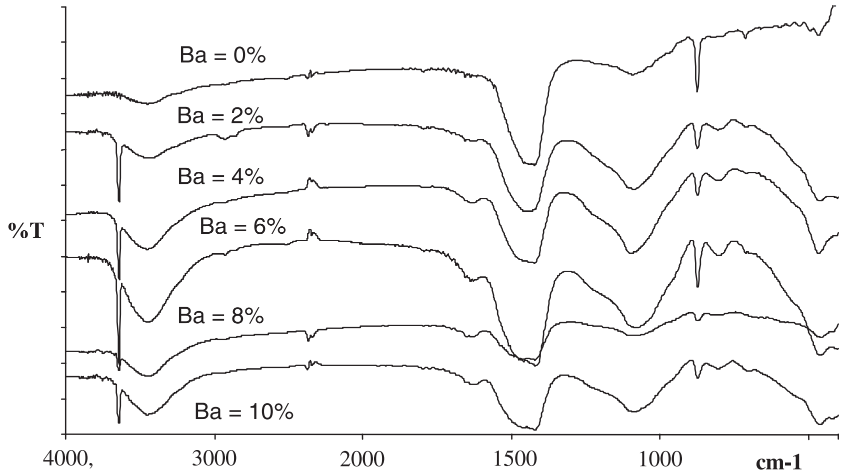

Fig. 3. FT-IR spectra for the intermediate silicates, with different amounts of Ba, after sonication for 1 h.

ray diffraction (Shimadzu) and surface area measurements (liquid nitrogen BET, 3 points).

3. Results and discussion

3.1. Thermal decomposition of rice hull

Fig. 1 displays the FT-IR spectra of rice hull after heating in an open furnace up to 600 °C. It can be seen that even after heating at 600 °C, an organic fraction still remains in the sample (characterized by the C-O-C bending absorption band in the region of 1640 cm^{-1}). Some authors [18,19] have used lower temperatures where the residual organic content is probably higher to obtain silica for applications other than cement preparation.

The broad bands in the region around 1000 and 800 cm^{-1} are characteristic of Si-O-Si stretching modes. The band at 480 cm^{-1} is associated to Si-O bending mode [12].

Fig. 2 shows the X-ray diffraction pattern of rice hull after heating at 600 °C. According to Proctor [20], the peak at approximately $2\theta = 22°$ is characteristic of α-cristobalite. On the other hand, the pattern presented here indicates that this rice hull ash contains an amorphous fraction along with crystalline material.

3.2. Mixture of solids and sonication

The calcium oxide, the silica obtained from rice hull ash and $BaCl_2 \cdot 2H_2O$ were mixed together in several proportions as indicated in Table 1.

After mixing the solids, water was added and the suspensions were sonicated for 1 h, rendering intermediate silicates along with the respective hydroxides in excess. Intermediate silicates have a ratio $(Ca + Ba)/Si \cong 1.6$, which was determined by simple titration of the supernatant against HCl. FT-IR spectra for each of the intermediate silicates with different Ba concentrations are displayed in Fig. 3.

The FT-IR spectra in Fig. 3 do not show any significant difference between the intermediate silicates. Sonication appears to affect the overall size of the intermediate silicates and/or the rate of silica dissolution.

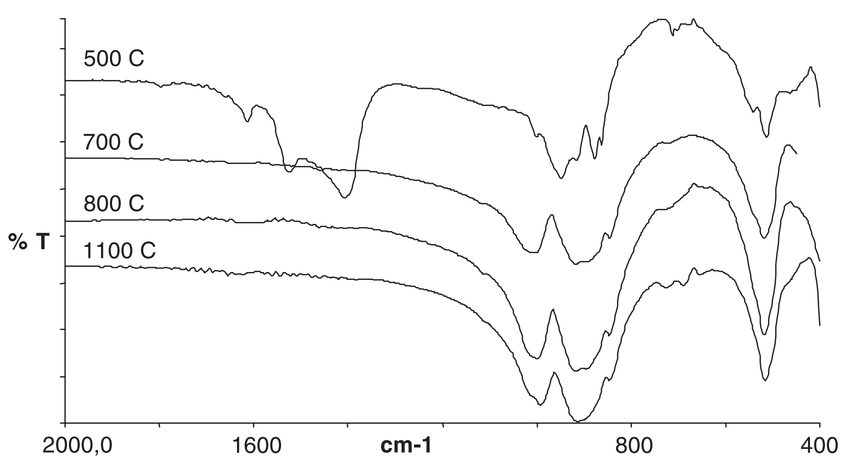

Fig. 4. Effect of heating on the intermediate silicates: percentage of $Ba^{+2} = 2\%$.

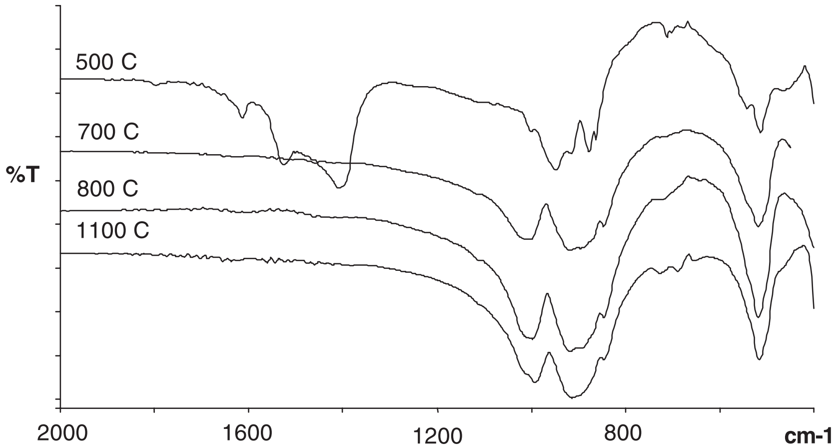

Fig. 5. Effect of heating on the intermediate silicates: percentage of $Ba^{+2} = 10\%$.

In previous works [8], hydrothermal synthesis was used to obtain the intermediate silicate. Sonication, which involves the passage of mechanical waves through a liquid medium, was used to replace the hydrothermal treatment [21,22]. The ultrasound frequency is very large, from 20 kHz up to 100 MHz. Commercial ultrasound equipment usually works within the range 20–40 kHz. In this case when the ultrasound wave collides with the solid sample, it is able to generate very high temperature and pressure. This process can lead to dissolution or even to modify chemical reactions; this area is usually referred as sonochemistry [21,22].

3.3. *Effect of heating*

The intermediate silicates were heated from 500 to 1100 °C. Selected FT-IR spectra are shown in Figs. 4 and 5.

Since the cement stoichiometric ratio (Ca + Ba)/Si = 2 was kept constant, the disappearance of the band at 1440 cm^{-1}, which is due to the presence of "free" CaO in the mixture, indicates the formation of the cement as the temperature is raised [23]. Considering the intermediate silicate has an initial ratio Ca/Si ≈ 1.6, it may be assumed that CaO enters into the structure of the silicate, as a result of heating, rendering, in many cases, a silicate with ratio (Ca + Ba)/Si = 2. This is a simple and convenient way to observe the effect of temperature on the cement synthesis.

The major peaks attributed to β-Ca_2SiO_4 are observed around 900 and 1000 cm^{-1} (Si-O asymmetric stretching) and 520 cm^{-1} (Si-O out of plane bending vibration) which is in reasonable agreement to Mollah et al. [24,25] who studied commercial Portland cement where the peaks of β-Ca_2SiO_4 and Ca_3SiO_5 are very close.

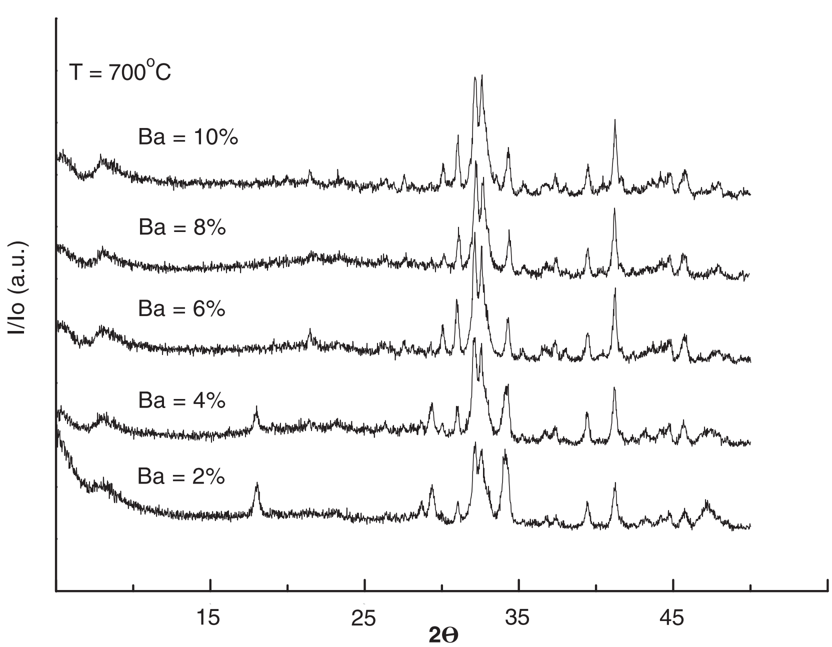

Fig. 6. X-ray diffraction patterns for samples with different Ba amounts after heating at 700 °C.

Also, in order to confirm the presence of the β-Ca_2SiO_4, X-ray diffraction patterns of selected samples were obtained and are displayed in Fig. 6.

These X-ray diffraction patterns correspond to materials after heating at 700 °C and containing variable amounts of Ba. It can be seen that only samples containing at least 6% of Ba render the desired product (β-Ca_2SiO_4, in agreement to file 9-351, I-33-B3 from JCPDS card) at this temperature, without the presence of calcium oxide whose excess is undesirable. On the other hand, if higher temperatures are used, the cement may be obtained with lower amounts of Ba. At 800 °C, the cements with 2% and 4% of Ba were synthesized. In all cases, the absence of Ba does not render the cement. In the range of temperatures studied, the addition of $BaCl_2 \cdot 2H_2O$ to the initial solid mixture was fundamental in order to obtain the cement.

4. Conclusions

This work describes the synthesis of several cements, with variable chemical composition, obtained from rice hull ash. Sonication was shown to be very effective to facilitate the synthetic procedure. The intermediate silicates present a ratio $Ca/Si \approx 1.6$; after heating the desired cements are formed at temperature as low as 700 °C, although accordingly to the chemical composition, higher temperatures are needed. All cements reported are structurally similar to β-Ca_2SiO_4.

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