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Calcium silicate cements obtained from rice hull ash: A comparative study

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This work describes the utilization of rice hull as raw-material for the preparation of two calcium silicates namely, β-$Ca_{1.91}Ba_{0.04}SiO_4$ and β-$Ca_{1.96}Ba_{0.04}SiO_4$. The synthesis was completed at 800°C. Hydration rate and compressive strength of mortars prepared with the two calcium silicates were studied and compared to mortars prepared with commercial Portland cement. Hydration rates for both silicates, studied by thermogravimetric and FTIR analysis are very similar; after 60 days the hydration rates are around 42–43% and reaches 75% after 270 days. Compressive strength experiments were performed using test specimen prepared with commercial Portland cement as reference, and blends of Portland cement and the two calcium silicates, at replacement levels of 10 and 20%. Results have shown that after a 90 days curing period, the compressive strength of the reference and the blends containing 10% of each of the calcium silicates show the same behavior. Using a replacement level of 20% there is a small decrease in compressive strength. This behavior is attributed to the lower hydration rate of these calcium silicates. *© 2006 Springer Science + Business Media, Inc.*

1. Introduction

Dicalcium silicate, β-Ca_2SiO_4 is the second major component of Portland cement, accounting for approximately 25% of its total mass. "Belite-rich" cements, which contain higher amounts of β-Ca_2SiO_4, show great potential to be used in large-scale applications since it has many comparative advantages over conventional Portland cement, such as energy and raw-material savings [1, 2]. β-Ca_2SiO_4 or blended cements may also present higher durability and superior mechanical performance since the hydration of this silicate generates less calcium hydroxide than Ca_3SiO_5, the major component of Portland cement. Under "ideal" conditions, Ca_2SiO_4 releases one third of calcium hydroxide molecules when compared to Ca_3SiO_5, after complete hydration. Calcium hydroxide is a fragile material and does not contribute to mechanical resistance of cement-based materials. It is also easily leached under mild acid conditions, leaving pores and voids inside the structure, contributing to further penetration of aggressive agents. Also it is important to note the deleterious effect of high alkalinity on alkali-silica reaction, sulfate and acidic attack. [3, 4]

Dicalcium silicate, Ca_2SiO_4, has 5 distinct polymorphic phases, namely α, $\alpha'_H\alpha'_L$, β and γ. The identification of each individual phase may be a complex matter. Many studies have been carried out about this subject [5, 6]; the β phase is usually found, although it is possible the formation of solid solutions. It is known however that the γ phase does not show hydraulic activity and that the $\beta \rightarrow \gamma$ transition involves a 12% volume expansion. This process is undesirable in cement industry.

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An important issue related to β-Ca_2SiO_4 is the hydration kinetics. Ca_3SiO_5, the major component of Portland cement, hydrates faster than β-Ca_2SiO_4. According to Young and Mindess [7] the hydration degree of β-Ca_2SiO_4 and Ca_3SiO_5 after 30 days is about 45 and 85%, respectively, although this difference diminishes as time proceeds. Therefore in the initial stages of Portland cement hydration, Ca_3SiO_5 plays the prominent role while β-Ca_2SiO_4 becomes important to development of mechanical resistance only in latter stages.

There are many papers [8–12] addressing the synthesis of β-Ca_2SiO_4 either by hydrothermal [8, 9] and sol-gel [10] processing and solid-state chemical reactions [11, 12]. Each method has its own characteristics and advantages. However, under controlled conditions it is possible the preparation of stoichiometric materials, in contrast to Portland cement, where its individual components incorporate many impurities and foreign ions [13]. At least, from scientific viewpoint, synthesis performed in laboratory conditions would facilitate, for instance, the understanding of the relationship between chemical composition and observed physical-chemical properties, such as hydration rate, durability and mechanical properties, for example.

It is also worth to mention the growing use of alternative materials to prepare cement and specially β-Ca_2SiO_4 [14, 15]. In recent papers, Rodrigues has presented the synthesis of two related calcium silicates whose simplified formula may be described by β-$Ca_{1.96}Ba_{0.04}SiO_4$ and β-$Ca_{1.91}Ba_{0.04}SiO_4$ [16, 17]. Both calcium silicates were stabilized by addition of barium. The utilization of barium during the preparation of dicalcium silicates is a common procedure, although there is not a definitive explanation about the stabilization phenomena induced by this other atoms [18, 19]. Furthermore, the calcium silicate having ratio (Ca+Ba)/Si = 1.95 can proportionate further savings in raw-materials if it behaves in a similar way to the conventional Ca_2SiO_4.

Here we present the synthesis of these two calcium silicates (β-$Ca_{1.96}Ba_{0.04}SiO_4$ and β-$Ca_{1.91}Ba_{0.04}SiO_4$) obtained using silica derived from the heating of rice hull as raw-material and compare their hydration degrees and compressive strength when used in partial replacement of commercial Portland cement.

2. Experimental

Two calcium silicates were prepared, namely β-$(Ca_{1.96}Ba_{0.04})SiO_4$ and β-$(Ca_{1.91}Ba_{0.04})SiO_4$. The basic difference between these silicates is the ratio (Ca+Ba)/Si. In the first silicate this ratio is 2, the same for conventional material. In the second one, this ratio is 1.95. The use of a cement having (Ca+Ba)/Si ratio = 1.95 would save raw-materials and it may also influence the hydration rate since this silicate presents vacancies in the structure. Rice hull, an agricultural residue contains about 20–25% of silica as inorganic component. Silica (cristobalite) was obtained by burning rice hull at 600°C in an open furnace. The resulting material was a white powder and after grounding it presented surface area of 21 $m^2 \cdot g^{-1}$. FTIR spectra showed that SiC was not formed under these conditions. Calcium oxide (Nuclear) and barium chloride (Mallinckrodt), analytical grade reagent were used. The solids were mixed in stoichiometric proportions in order to render the expected calcium silicates. Suspensions of each material were prepared by addition of water in the proportion of about 20:1 (water/solids). The suspensions were sonicated for 60 min (Thornton, 25 kHz). After this period the suspensions were dried overnight at 100–120°C. The resulting materials (an intermediate silicate, having a ratio $Ca/Si \cong 1.6$ and remaining hydroxides) were grounded and heated at 800°C, (heating rate of 30°C/min) and the solids were kept at this temperature for 180 min. FTIR (Spectrum One, Perkin Elmer) and X-ray diffraction (Shimadzu) were used to characterize the products. Further details are presented elsewhere [16, 17].

Hydration studies were carried out using FTIR spectroscopy and thermogravimetric analysis (TGA, Pyris 7, Perkin-Elmer). FTIR spectra were recorded using KBr discs and 16 accumulations. In TGA studies, about 8–10 mg were used in each analysis (heating rate of 40°C/min under nitrogen atmosphere) and the results are average of at least 3 different samples. For both methods, test specimen were prepared having a water/cement ratio = 0.50. Calcium silicates were sieved in order to have a particle size under 150 μm. Typically 1.00 g of each silicate and 0.50 g of water (distilled, fresh boiled) were used. After water addition the pastes were homogenized in polyethylene flasks and quickly transferred to closed recipients to avoid carbonation. The materials were kept at room temperature and relative humidity of 100% prior to analysis. After the desired period of time, the materials were broken and grounded to render powders suitable for each analysis. It is important to note that in earlier periods, i.e. less than one week, calcium hydroxide measurements were not fully reliable since there was observed a significant difference between individual measurements.

In mechanical analysis, sand-cement mortar specimens were prepared using washed natural sand with 2.57 fineness modulus (450 μm average particle size), water/cement ratio = 0.6 and sand/cement ratio = 3. The control specimens contain only commercial Brazilian slag-modified cement, type CPII-E32, which contains approximately 30% of granulated slag. Blast-furnace slag, a by-product of the iron-making process, is a non-metallic product, consisting essentially of silicates and aluminosilicates of calcium. In Brazil about 70% of commercial available cement is slag-modified type. Granulated blast-furnace, largely glassy, is produced by the rapid quenching of molten blast-furnace slag as it passes through water sprays, followed by water granulation over a spinning drum. The granules are added to the clinker before grinding. The two calcium silicates were used as partial replacement of commercial cement at two levels, 10 and 20% (mass relation). These silicates were sieved in order to have maximum particle size of 150 μm. Cylindrical

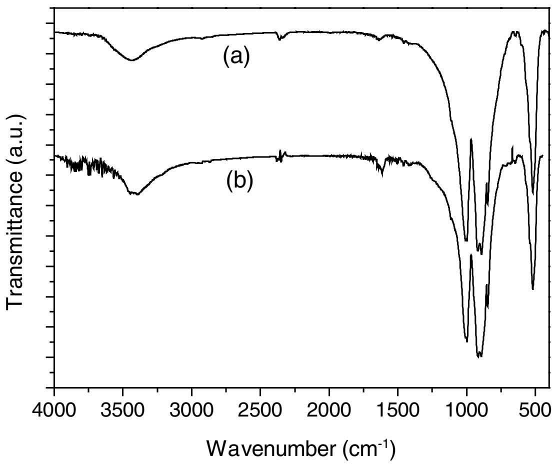

Figure 1 FTIR spectra of β-($Ca_{1.91}Ba_{0.04}$)SiO_4 (a) and β-($Ca_{1.96}Ba_{0.04}$)SiO_4 (b).

specimens measuring 3 cm in diameter and 4.5 cm in height (cured for 28 days at room temperature and relative humidity 100%) were used in accordance to ASTM C39-86, "Standard test method for compressive strength of cylindrical concrete specimens." Compressive strength results were obtained using a MTS 810 testing machine (Material Test System, Test Star IIs). A loading rate of 170 N/s, under load control, was used. Quintuplicate specimens were tested.

3. Results and discussion

The synthesis of both calcium silicates were completed at 800°C as evidenced by FTIR spectroscopy and X-ray diffraction. Fig. 1 shows the FTIR spectra obtained after heating the material at 800°C for 180 min.

In both cases the major peaks signaled are located at 1000 and 900 cm^{-1} (Si-O stretching modes) and 510 cm^{-1} (Si-O-Si bending mode). These peaks are characteristics of dicalcium silicate. Fig. 2 displays X-ray diffraction data confirming that the β phase was predominately obtained in both cases.

For the sake of simplicity the hydration of both silicates will be described as:

$$2Ca_2SiO_4 + 4H_2O \rightarrow Ca_3Si_2O_7 \cdot 3(H_2O) + Ca(OH)_2$$

$$2Ca_{1.95}SiO_4 + 4H_2O \rightarrow Ca_{2.90}Si_2O_7 \cdot 3(H_2O) + Ca(OH)_2$$

TABLE I Hydration degree (%) for samples β-$Ca_{1.96}Ba_{0.04}SiO_4$ and β-$Ca_{1.91}Ba_{0.04}SiO_4$ after 60 and 270 days determined by TGA analysis

	Time (days)	
Sample	60	270
β-$Ca_{1.96}Ba_{0.04}SiO_4$	42 ± 5	72 ± 2
β-$Ca_{1.91}Ba_{0.04}SiO_4$	43 ± 4	72 ± 2

Based on these equations, the hydration degree for each silicate was determined by the amount of $Ca(OH)_2$ formed after 60 and 270 days. Although the mechanism involved and the resulting materials are probably much more complex than presented by the above equations, it seems to be a very reasonable indicative for the calculations and they are in good agreement with experimental results [7]. Fig. 3 shows typical TGA analysis for these samples after hydration period of 270 days. Table I presents the average hydration values obtained from TGA analysis. These results were obtained from the average of at least three analyses.

As it can be seen there is no significant difference in the hydration rates for both calcium silicates. Fig. 4 displays FTIR spectra for both samples after a hydration period of 270 days. In both cases, hydration degree increases as a function of time; also there is a broadening effect on the peak located at around 1000 cm^{-1} (silicate) and the increase of the peak located at 1500 cm^{-1} (due to the presence of calcium hydroxide) when compared to Fig. 1, for instance.

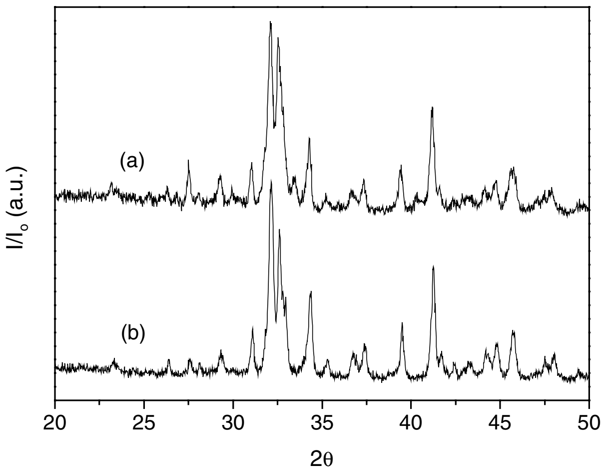

Figure 2 XRD for β-($Ca_{1.91}Ba_{0.04}$)SiO_4 (a) and β-($Ca_{1.96}Ba_{0.04}$)SiO_4 (b).

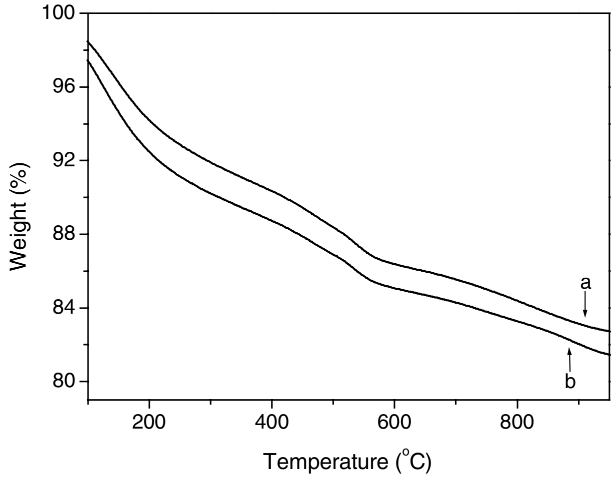

Figure 3 TGA curves for samples and β-($Ca_{1.91}Ba_{0.04}$)SiO_4 (a) and β-($Ca_{1.96}Ba_{0.04}$)SiO_4 (b) after 270 days of hydration.

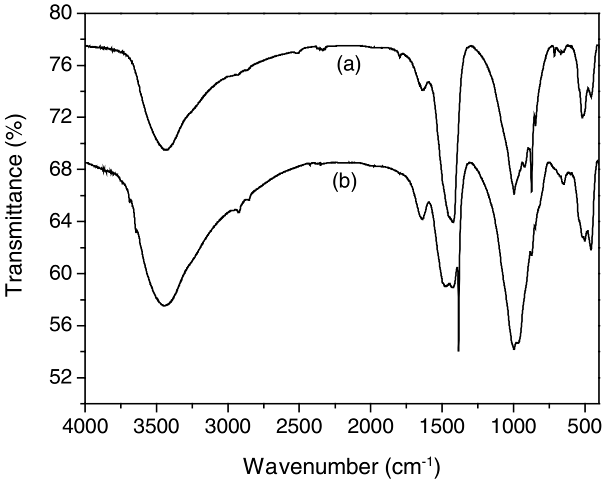

Figure 4 FTIR spectra for samples after 270 days hydration: (a) $(Ca_{1.91}Ba_{0.04})SiO_4$ and (b) $(Ca_{1.96}Ba_{0.04})SiO_4$.

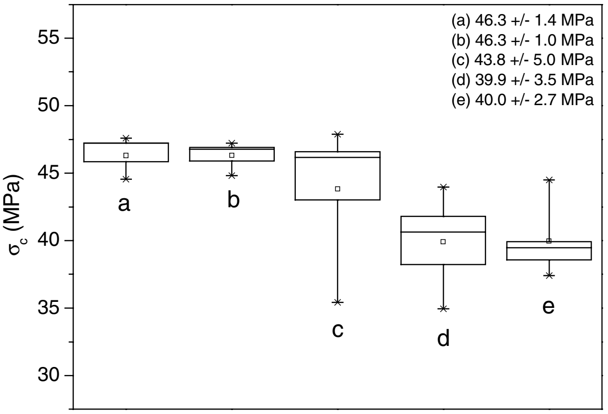

Figure 5 Box plots of compressive strength for mortar test specimen prepared with blends of commercial Portland cement and the two calcium silicates, at replacement levels of 10 and 20%. (a) control - prepared only with Portland cement; (b) β-$(Ca_{1.91}Ba_{0.04})SiO_4$ - 10%; (c) β-$(Ca_{1.96}Ba_{0.04})SiO_4$ – 10%; (d) β-$(Ca_{1.91}Ba_{0.04})SiO_4$ – 20%; (e) β-$(Ca_{1.96}Ba_{0.04})SiO_4$ – 20%. Quintuplicate specimens. Legend indicates the average and standard deviations on the compressive strength results.

Although FTIR analysis were conducted in a qualitative way it shows that calcium hydroxide is always present as result of hydration during the whole period studied. For instance El-Didamony [20] has found that β-Ca_2SiO_4 releases calcium hydroxide but it is consumed latter, probably due to formation of calcium carbonate and/or the formation of hydrates having higher Ca/Si ratio. It was also found that the presence of admixtures may have an important effect on the overall presence of calcium hydroxide. The experiments presented here were designed to avoid carbonation of samples which, as pointed by Taylor [13], may produce important distortions in the results. This is especially important in laboratory-scale experiments. Also, Ishida [21] studied the hydration of β-Ca_2SiO_4 obtained from the thermal decomposition of hillebrandite and in this case calcium hydroxide was almost absent during the process. The results presented here show that the calcium silicates obtained from rice hull ash hydrates rendering calcium hydroxide as product; furthermore it is present at all periods of time.

Compressive strength, σ_c, measurements are presented in Fig. 5. A box plot is an effective visual representation of both central tendency and dispersion. Box shows 50% of the data, the small square indicates the average, the median is shown as a line across the box (or on its horizontal bounds) and the vertical line contains the other 50% of the data and the minimum and maximum data values on its edges. The length of the vertical line indicates visually how far from the middle of the distribution the extreme values are. Also, inside the figure there is an insert displaying the respective values for average compressive strength and standard deviation for each sample.

Compressive strength results show that at 10% of substitution level both silicates present a behavior quite similar to control specimen, although the silicate having ratio $(Ca+Ba)/Si = 2$, presents a higher degree of dispersion. For instance, the standard deviation for this sample is 5 MPa, while for reference is just 1.4 MPa (insert, Fig. 5). On the other hand, when substitution level reaches 20% there is a decrease in the compressive strength of about 10%, in average, in relation to control specimens. This behavior can be attributed to the intrinsic lower hydration rate of dicalcium silicates. At relatively low-replacement levels, it does not interfere with mechanical properties of test specimens; on the other hand, increasing amounts of these calcium silicates cause a small reduction. Since these experiments were carried out after 90 days the hydration rate of both silicates can be estimated to be around 50%. At this point, an important issue should be stressed. The maximum particle size of both silicates used in these experiments was 150 μm. The average and particle size distribution have an important effect on hydration rate and typically cement particle size is less than 100 μm [22]. It has a deleterious effect both on hydration and mechanical resistance. Higher hydration degrees could be attained by reducing the silicates particle size. Since we were primarily concerned with the comparative behavior among these samples, the particle size parameter was not fully exploited in this work.

4. Conclusions

The synthesis of the two calcium silicates was completed at 800°C. The hydration degree for each silicate, determined by the amount of $Ca(OH)_2$ formed, was followed by TGA and FTIR analysis. After 60 days, a hydration degree of 43 ± 4% and 42 ± 5% was obtained for the β-$Ca_{1.91}Ba_{0.04}SiO_4$ and β-$Ca_{1.96}Ba_{0.04}SiO_4$ silicates, respectively. The hydration degree reaches 72 ± 2% for both silicates after 270 days.

At relative low—replacement level, 10%, the compressive strength of the specimens containing β-$Ca_{1.91}Ba_{0.04}SiO_4$ remained similar to the control. The reduction of 10% in compressive strength for the specimens with substitution level of 20% indicates a nonlinear decrease in mechanical strength with the increase of synthetic silicate amount replacement.

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