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Early age hydration of rice hull ash cement examined by transmission soft X-ray microscopy

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Abstract

Early age hydration of barium-doped β-Ca_2SiO_4 cement, produced from rice hull ash (RHA), is examined by transmission soft X-ray microscopy. Use of low-energy cements produced from by-product materials, such as the cement considered here, may be economically and environmentally advantageous. However, the hydration kinetics and morphology and composition of the products of RHA-based β-Ca_2SiO_4 cements have not been investigated. Observation of the early age cement hydration shows evidence of cement dissolution and hydration product formation, including the formation of Hadley grains. The rates of the reaction and amount product formed appear to be related to the hydrothermal processing temperature and the chemical composition of the cement. That is, more rapid hydration is observed for barium-doped RHA cements produced at higher temperatures and for cements produced with higher barium contents, within the ranges examined.

Keywords: Ca_2SiO_4; Hydration; Hydration products; Microstructure; X-ray microscopy

1. Introduction

The major components of ordinary Portland cements are the calcium silicates, tricalcium silicate (Ca_3SiO_5) and beta dicalcium silicate (β-Ca_2SiO_4). These two components together typically account for about 70% of cement by mass. Commercially, Portland cements are prepared by fusing raw materials containing calcium and silicon at temperatures ranging between 1450 and 1550 °C [1]. However, recently, a great deal of attention has been devoted to the preparation of cements composed of dicalcium silicate for several reasons, including lower energy consumption [2,3] and decreased "greenhouse" gas production. While production of Ca_3SiO_5, the principal component of Portland cement, requires 1810 kJ/kg, production of β-Ca_2SiO_4 is less energy-intensive, requiring about 1350 kJ/kg. Presently, manufacture of 1 ton of Portland cement produces 1 ton of the greenhouse gas carbon dioxide (CO_2) [4] by various reactions including the decomposition of limestone:

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2^{\uparrow} \tag{1}$$

This reaction is extremely endothermic and is responsible for much of the energy consumption in the cement kiln [5]. Thus, by decreasing the lime required for cement manufacture, more "environmentally friendly" cements are produced. In addition, dicalcium silicate cements are expected to demonstrate improved mechanical properties, increased durability, and decreased heat of hydration as compared to Portland cement.

Rice hull ash (RHA) has been used as pozzolanic replacement for cement in concrete [6], and recently, the viability of β-Ca_2SiO_4 cement production from RHA has been demonstrated [7]. However, the effect of parameters associated with the preparation of these cements on the cement hydration kinetics and morphology and composition of the hydration products has not been investigated. Composition and surface area are known to affect hydration rates of calcium silicate cements, but no clear relationship has been established between these parameters and rate of hydration. For instance, it is well known that the β-Ca_2SiO_4 hydration kinetics is much slower than those of Ca_3SiO_5. However, Ishida et al. [8,9] reported the hydrothermal synthesis of β-Ca_2SiO_4 and showed that its hydration similar to that of Ca_3SiO_5. This behavior is attributed to the large surface area, around 6 m^2/g. In this case, the synthesis is

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based on the thermal decomposition of hillebrandite, which is obtained under hydrothermal treatment of quartz and calcium hydroxide at 200 °C and 10 h. Ishida et al. [8,9] reported that β-Ca_2SiO_4 synthesized under these conditions presents a fibrous morphology, which is unusual for dicalcium silicate.

Many relatively new techniques have been used to study the hydration of cement, including neutron scattering [10], ^{29}Si NMR [11], and ESCA [12] among others. However, most of the techniques employed can affect the hydration process, because the reactions must be stopped prior to the analysis. This can be done using organic solvents, such as acetone or methanol, or by drying or heating the sample. Each of these processes may alter the morphology and composition of the hydration products, affecting interpretation of the results.

Recently, new characterization techniques have been applied to gain a better understanding of the cement hydration reactions. For example, the environmental scanning electron microscope (ESEM) avoids many of the sample preparation requirements of conventional SEM (e.g., drying) that had previously limited in situ hydration studies by electron microscopy [13] However, with both ESEM and SEM, the electron beam penetrates only a few microns below the sample surface, and analyses are consequently restricted to the surface and very near surface material.

The main objective of this work is to gain insights about the hydration behavior of β-Ca_2SiO_4, doped with barium. The hydration of β-Ca_2SiO_4, studied at early ages (<2 h) using transmission soft X-ray microscopy, is described. Originally developed to study biological samples, transmission soft X-ray microscopy has recently been shown to be advantageous for the study of cement-based materials [14]. Soft X-ray microscopy allows high-resolution imaging of hydrated samples over time and permits complete, through-depth imaging of samples up to 40 μm thick. X-ray images of β-Ca_2SiO_4 obtained from RHA will be examined to provide information about the early product morphology and hydration mechanisms and to provide information about the effects of the cement preparation methodology (i.e., hydrothermal treatment temperature and amount of Ba^{+2} replacement) on its hydration.

2. Experimental

2.1. Characteristics of the RHA

Rice hulls provided by Wadhan Energy, California were the source of silica used in the manufacture of the cement. After washing in deionized water, the rice hulls were heated at 600 °C for 2 h, rendering RHA with a surface area of 21 m^2 g^{-1} as measured by BET (one point). RHA cements were prepared from the RHA, $BaCl_2 \cdot 2H_2O$, and CaO. All reagents were analytical grade. CaO was heated to 900 °C prior to use. Further details can be found in Ref. [7].

2.2. Hydrothermal treatment and characterization

The solids — RHA, CaO and $BaCl_2$ — were stoichiometrically weighed in order to obtain a mixture with ratio $(Ca+Ba)/Si=2$. $BaCl_2$ was introduced to distort the structure of the intermediate silicate; an “open” structure, obtained through by partial replacement of Ca^{+2} with Ba^{+2} in the silicate structure, can potentially lower the temperature necessary during thermal preparation. In addition, an open structure should lead to accelerated hydration. The Ba^{+2} replacements were made at 6%, 7%, 8%, 9% and 10%, relative to Ca^{+2}. Previously [7], it was found that the desired product could not be rendered using smaller amounts of Ba^{+2}. These mixtures were placed in sealed stainless steel capsules with an internal volume of 25 ml. Slurries were prepared using deionized water, and the desired solid/water ratio of 0.05 by mass was held constant. The capsules were placed in an oven preheated to the desired temperature (130 and 150 °C). A period of 20 min was considered enough to reach thermal equilibrium. After the required times of hydrothermal treatment, the capsules were cooled to room temperature and the samples were vacuum-dried at 130 °C for 24 h. Following the hydrothermal processing, the samples were heated up to 750 °C. The samples were characterized by X-ray diffraction (Siemens D5000, CuKα) and surface area. The main objective of this work is to gain insights about the hydration behavior of β-Ca_2SiO_4, doped with barium. The structure of the cements was found to be similar to that of β-Ca_2SiO_4 (file 9-351, I-33-B3 from JCPDS card). Further details can be found in Ref. [7].

2.3. Sample preparation for soft X-ray microscopy

X-ray imaging was performed using the transmission soft X-ray microscope XM-1 on beamline 6.1.2 of the Advanced Light Source (ALS), a third generation synchrotron facility located at Lawrence Berkeley National Laboratory in Berkeley, CA. The Center for X-ray Optics (CXRO) built XM-1 and operates and maintains the microscope. The X-ray optics and other features of XM-1 have been described by Meyer-Ilse et al. [15] Transmission soft X-ray microscopy is a high-resolution imaging technique which allows examination of wet samples over time under normal pressures, avoiding the introduction of artifacts to hydrated products by drying or pressure change [16]. In addition, internal structural features may also be examined. Because reactions can be imaged as they progress, transmission soft X-ray microscopy has been found to be useful for the study cement hydration and pozzolanic reactions [17,18].

Sample preparation procedures relevant to the study of cement-based materials at XM-1 have been previously described [14,17] and will be briefly summarized here. The RHA cements were imaged initially before the introduction of water to establish a basis for comparison with the hydration products. Dry samples were prepared by dusting the fine particles of each cement across a 120-nm-thick silicon nitride (Si_3N_4) window glued to the bottom half of the sample carrier. Wet sample chambers were prepared by dusting fine particles of each RHA cement across a silicon nitride window, and introducing a small (2–3 μl) drop of deionized, low resistivity (17.8 MΩ·cm) water. A second silicon nitride window was fitted on top of the sample in the sample chamber. To separate and prevent breakage of the windows, polystyrene beads of 6 μm nominal diameter were mixed with the water used in the sample preparation. The goal of this study is the characterization of early age hydration processes and products, and this simple method decreases preparation time, permitting more time for observation of initial stages of the formation. In addition, the problem of overlap that occurs when studying pastes is avoided, allowing the microstructure development to be observed and imaged more clearly.

Both dry and wet samples were observed at 2400 × magnification and using light of 2.4 nm wavelength (517 eV). This wavelength was selected to enhance contrast between the water and cement particles and developing hydrates [14]. Images were recorded by a thinned, back-illuminated CCD camera with 1024 × 1024 pixels of size 24 × 24 μm. The X-ray images were processed further to adjust contrast and to insert scale bars using Adobe Photoshop 4.0.1 and 6.0, Adobe Photodeluxe 1.0, and UNIX-based Interactive Data Language (IDL).

3. Discussion of early age hydration of RHA cements

The hydration of "pure" β-Ca_2SiO_4 can be roughly described by:

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

Any morphologicial difference between the dry powder and the cement powders in water can be directly associated to the hydration, which means, volume variation (anhydrate to hydrate) and the formation of $Ca(OH)_2$. On the other hand, due to the solubility of calcium hydroxide (1.13 g/l at 25 °C), this product can be dissolved as soon as formed, which prevents its visual observation in dilute (high water-to-solid) systems, such as those required for X-ray microscopy. Also, under ideal conditions, calcium hydroxide presents a hexagonal morphology. However, its crystallization can be altered accordingly to the environmental conditions. Based on these considerations, a discussion about the early hydration of the rice hull cements is presented for each set of samples.

3.1. β-($Ca_{1.88}$+$Ba_{0.12}$)SiO_4

X-ray images for hydration of this sample prepared with 6% Ba^{+2} and hydrothermal treatment temperature of 150 °C are displayed through Figs. 1 and 2. Comparing Fig. 1(a) and (b), which represent the same sample at the same site, but at different observation times (after 16 and 44 min hydration, respectively), shows that only small structural changes have occurred in the 28 min between imaging. For instance, from the decreasing density and size of the RHA cement particles, it appears that cement dissolution has progressed over this

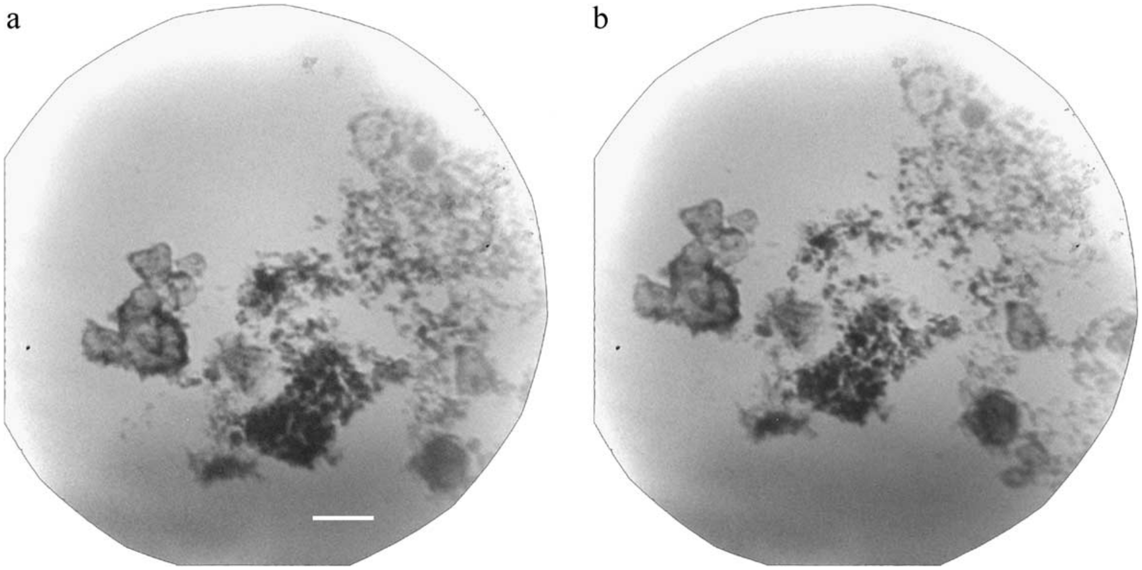

Fig. 1. X-ray images of β-($Ca_{1.88}$ + $Ba_{0.12}$)SiO_4 prepared with hydrothermal treatment of 150 °C in water (a) after 16 min and (b) after 44 min; images were taken with exposure times of 22.330 and 29.610 s and beam currents of 312.2 and 269.0 mA, respectively.

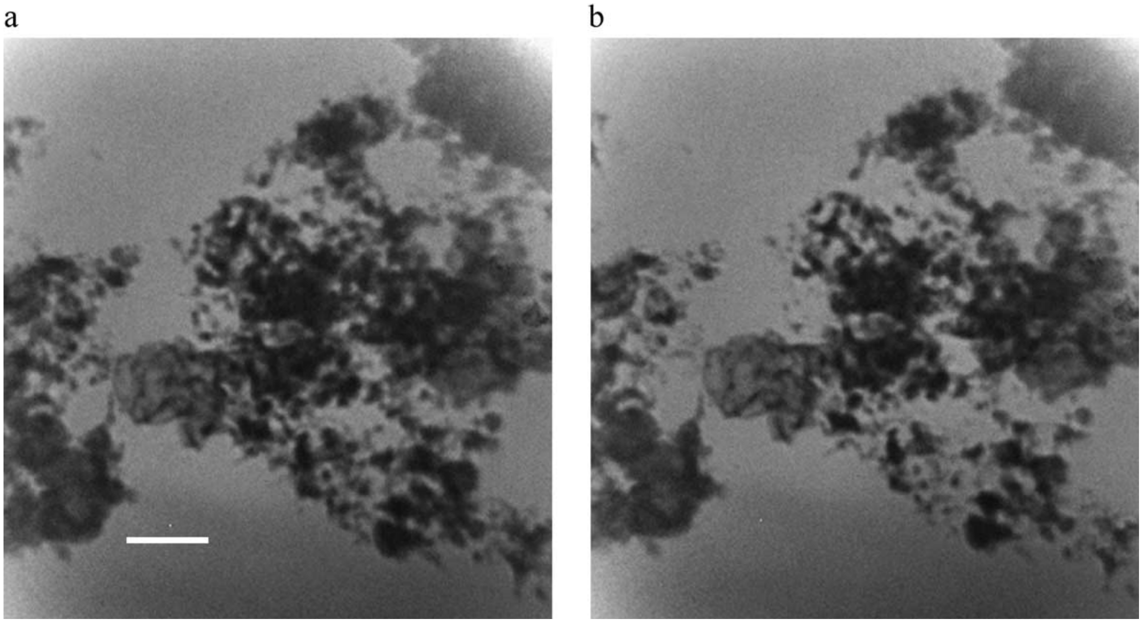

Fig. 2. X-ray images of β-($Ca_{1.88} + Ba_{0.12}$)SiO_4 prepared with hydrothermal treatment of 150 °C in water (a) after 30 min and (b) after 34 min; images were taken with exposure times of 27.576 and 28.072 s and beam currents of 288.5 and 283.7 mA, respectively.

time period. However, few changes in the relative density or volume of hydration products are apparent. The hydration products can be identified by the clear morphological differences between these structures and the dry particles of cement, as imaged in Fig. 3. The particles imaged in Fig. 3 are representative of each of the cements synthesized.

X-ray images show that when dry the RHA cements are very fine (0.2–0.4 μm diameter) particulate materials of relatively uniform size and density, rather than the more unusual fibrous morphology reported in Refs. [8,9]. Thus,

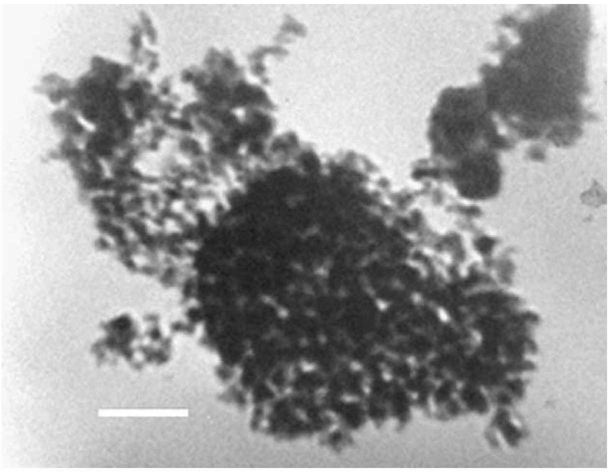

Fig. 3. X-ray image of dry powdered β-($Ca_{1.88} + Ba_{0.12}$)SiO_4 prepared with hydrothermal treatment of 150 °C; the image was taken with an exposure time of 10.606 s and a beam current of 375.8 mA.

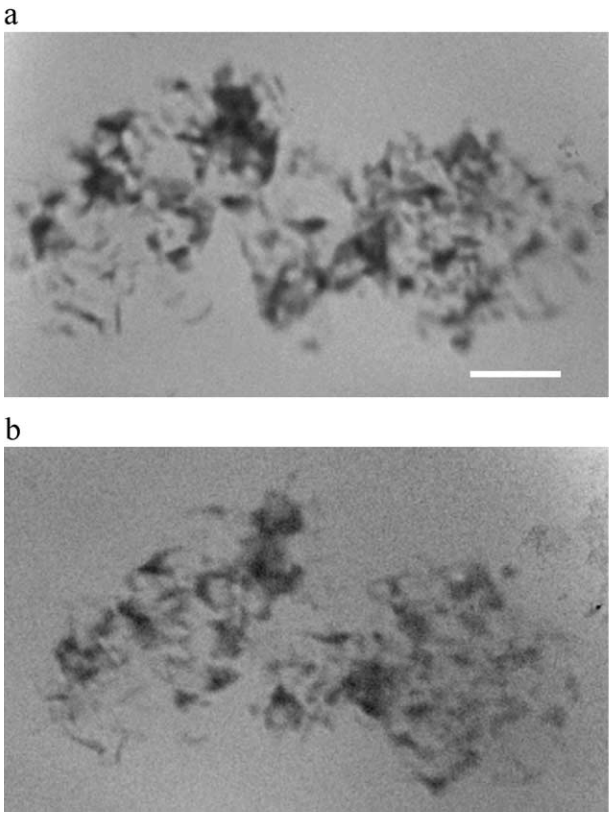

Fig. 4. X-ray images of β-($Ca_{1.84} + Ba_{0.16}$)SiO_4 prepared with hydrothermal treatment of 130 °C in water (a) after 15 min and (b) after 25 min; images were taken with exposure times of 34.353 and 5.922 s and beam currents of 174.0 and 168.6 mA, respectively.

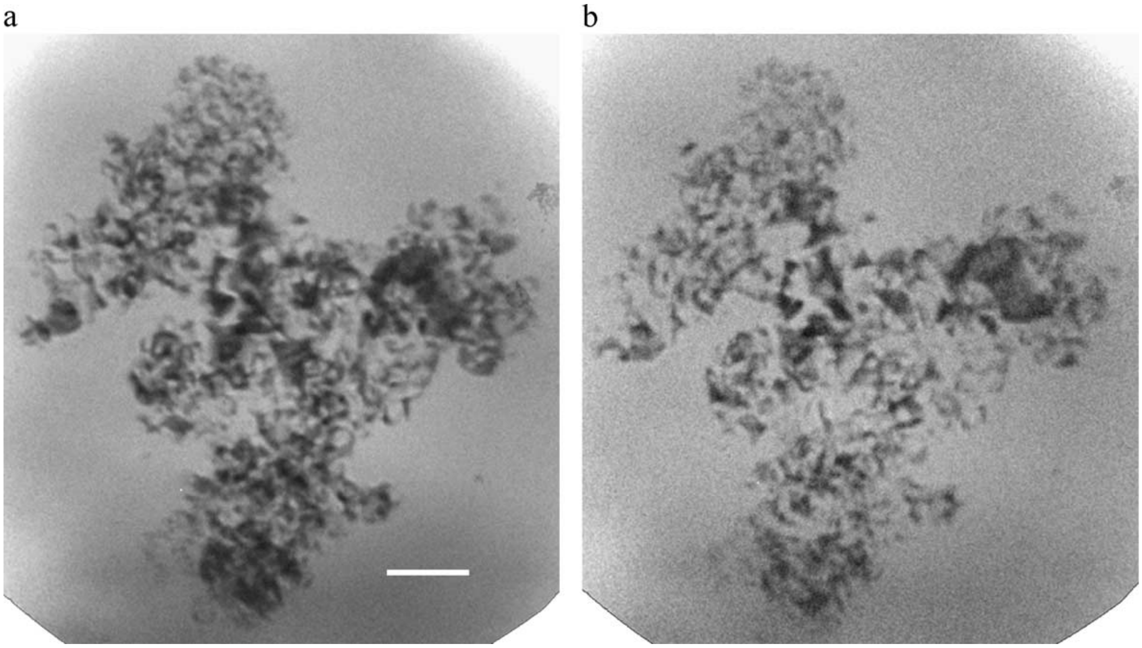

Fig. 5. X-ray images of β-$(Ca_{1.84}+Ba_{0.16})SiO_4$ prepared with hydrothermal treatment of 130 °C in water (a) after 21 min and (b) after 26 min; the images were taken with exposure times of 34.852 and 5.933 s and a beam current of 171.4 and 168.3 mA, respectively.

by comparing the dry particles in Fig. 3 with the images in Fig. 1, some evidence of hydration is found, including dissolution and precipitation. However, these images also indicate that the hydration kinetics is very slow in this system. Fig. 2(a) and (b), X-ray images of the same site after 30 and 34 min hydration, respectively, also presents the similar trends.

In fact, for "pure" β-Ca_2SiO_4, it is well known that the hydration process is much slower than that of Ca_3SiO_5. Many characteristics may influence the overall kinetics, including surface area, degree of crystallization, and morphology. Although the X-ray images do not provide direct information about the hydration mechanism, it can be suggested from these observations that the hydration occurs

Fig. 6. X-ray image of β-$(Ca_{1.84}+Ba_{0.16})SiO_4$ prepared with hydrothermal treatment of 150 °C in water after 20 min; the image was taken with an exposure time of 12.753 s and a beam current of 233.8 mA.

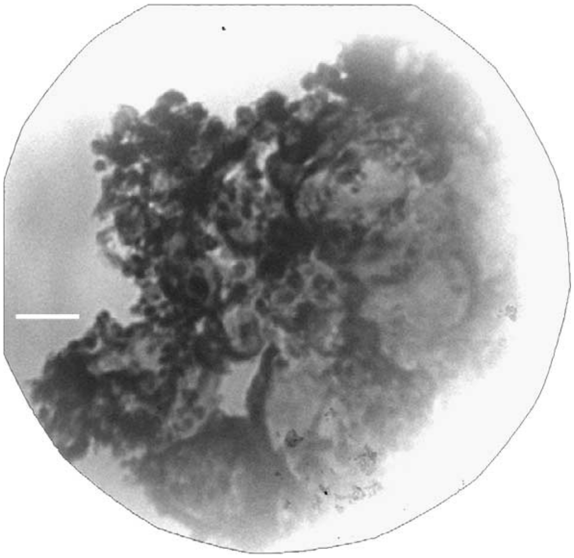

Fig. 7. X-ray image of β-$(Ca_{1.84}+Ba_{0.16})SiO_4$ prepared with hydrothermal treatment of 150 °C in water after 30 min; the image was taken with an exposure time of 18.016 s and a beam current of 221.0 mA.

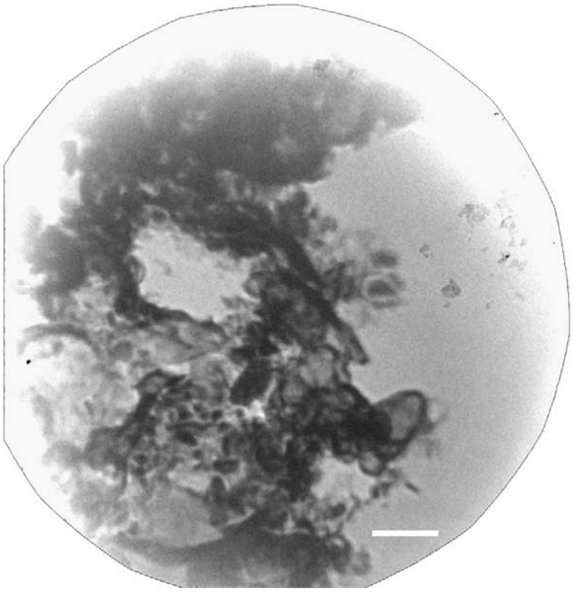

Fig. 8. X-ray image of β-($Ca_{1.84}+Ba_{0.16}$)SiO_4 prepared with hydrothermal treatment of 150 °C in water after 32 min; the image was taken with an exposure time of 18.232 s and a beam current of 218.8 mA.

initially at the grains surface while the inner structure remains anhydrate. Such a process would result in the hollow "tubules" of product or reaction coronas observed in the images of the hydrated cement (Figs. 1 and 2). Similar descriptions are found in literature for Portland cement hydration, where hollow shells or Hadley grains have been observed at early ages and in mature systems [19–21].

3.2. β-($Ca_{1.84}$+$Ba_{0.16}$)SiO_4

Figs. 4 and 5 show the hydration behavior of an RHA cement prepared with 8% Ba^{+2} with hydrothermal treatment at 130 °C. Fig. 4(a) and (b) and Fig. 5(a) and (b) show morphological aspects similar to that presented in Fig. 1, although the amount of solid material in Fig. 4 is much smaller (this may be related to sample preparation). Fig. 4(b) shows a clear reduction in that material over the 12-min period between imaging at this location. Similar observations are made in Fig. 5(b), where a substantial decrease in solids present occurs between Fig. 5(a) and (b), taken 5 min later. The loss of particle density over these time periods indicates that dissolution of the initially present sample has occurred. The dissolved material could be β-($Ca_{1.84}+Ba_{0.16}$)SiO_4, calcium hydroxide, although no hexagonal plates can be identified, or $BaCl_2$, which was added during the cement preparation. In addition, no evidence of hydration product formation is apparent in these images, while at similar ages, Hadley grains were already visible in the β-($Ca_{1.88}+Ba_{0.12}$)SiO_4 sample (Fig. 1(a)). The behavior observed in Figs. 4 and 5 may be associated to the so-called induction period, which occurs during the hydration of Portland cement. The induction period may be more lengthy for the β-($Ca_{1.84}+Ba_{0.16}$)SiO_4 (with hydrothermal treatment at 130 °C) sample examined here than for the β-($Ca_{1.88}+Ba_{0.12}$)SiO_4 sample prepared with hydrothermal treatment at 150 °C.

3.3. β-($Ca_{1.84}$+$Ba_{0.16}$)SiO_4

Figs. 6–8 show the hydration behavior of the above sample prepared with 8% Ba^{+2} with hydrothermal treatment performed at 150 °C. Examination of these images shows that the temperature during the hydrothermal processing is very important. The sample is well represented by Figs. 6–8 where each shows the development of the characteristic hollow microstructure observed in Figs. 1 and 2. However, the products formed in greater abundance and with greater density in this sample. In addition, these products were noted at hydration times as early as 15 min, indicating that the hydration, in this case, is much faster, than for the sample prepared at 130 °C examined in Figs. 4 and 5. It is believed that higher temperature of the hydrothermal treatment may lead to a better crystallization and faster reaction rates.

4. Conclusions

β-Ca_2SiO_4 cements were prepared from RHA; the preparation method was varied according to the hydrothermal treatment temperature and the amount of barium chloride included. Hydration of the RHA-based cements was examined by X-ray microscopy, which indicated that the hydration rate and the volume of products formed are related to the preparation method. RHA cements processed at higher temperatures (150 °C vs. 130 °C) reacted more rapidly, with products visible through X-ray microscopy at earlier ages. In addition, the amount of Ba^{+2} appears to affect the rate of reaction. Comparing samples prepared with 6% and 8% Ba^{+2}, both with hydrothermal treatment at 150 °C at similar ages, uniformly shows much greater product density for the cement with the higher Ba^{+2} content.

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