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Cement and Concrete Research 35 (2005) 19–25

CEMENT AND CONCRETE RESEARCH

A soft X-ray microscope investigation into the effects of calcium chloride on tricalcium silicate hydration

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Received 21 November 2002; accepted 4 May 2004

Abstract

Calcium chloride ($CaCl_2$) is one of the most recognized and effective accelerators of hydration, setting, and early strength development in portland cement and tricalcium silicate (C_3S) pastes. The mechanisms responsible for this acceleration, as well as the microstructural consequences, are poorly understood. Soft X-ray transmission microscopy has recently been applied to the study of cementitious materials and allows the observation of hydration in situ over time. This technique was applied to the examination of tricalcium silicates hydrating in a solution containing $CaCl_2$. It appears that $CaCl_2$ accelerates the formation of ''inner product'' calcium silicate hydrate (C-S-H) with a low-density microstructure.

Keywords: Acceleration; Hydration; Microstructure; Admixture; Ca_3SiO_5

1. Introduction

Calcium chloride ($CaCl_2$) is one of the most effective accelerators of hydration and setting in tricalcium silicate (C_3S) and portland cement pastes. The accelerative power of this salt increases with increasing concentration, with a practical dosage being 1–2% by weight of cement. It has often been observed that $CaCl_2$ increases the rate of formation of hydration products, thereby increasing the rate of heat evolution during hydration. This acceleration is thought to occur by direct acceleration of the growth rate of calcium silicate hydrate (C-S-H), but the mechanism is not understood at the molecular level [1].

It is to be expected that accelerating the hydration reaction would affect the microstructure of the hydration products. Calcium chloride is known to increase the nitrogen surface area and pore volume of portland cement and C_3S pastes [2–4]. The effects of $CaCl_2$ on microstructure have been investigated using a variety of microscopy techniques. Early work using transmission electron microscopy (TEM) for samples less than 1 day old showed fibrous growths in the presence of $CaCl_2$ [5], forming in a cross-linked network in one case [6]. In contrast, further electron microscope work on samples with ages of 10–30 days described C_3S hydration products as small needles in the absence of $CaCl_2$, and ''crumpled foils'' or plates in its presence [2,7]. The use of scanning electron microscopy (SEM) allows a greater depth of focus; using this technique, researchers saw ''honeycomb-like'' morphologies of hydration products in the presence of $CaCl_2$ at ages of 3 h to 7 days [8–10], agreeing with the previous cross-linked observations. Ramachandran and Feldman [11] noticed that the morphology of hydration products (older than 1 day) varied depending on the amount of $CaCl_2$ added to cement pastes. In the absence of $CaCl_2$, needles of C-S-H and ettringite were the primary morphology observed. At a dosage of 1% $CaCl_2$, thin sheets of C-S-H appeared. Increasing the dosage to 2% consolidated the structure, and plates were observed. Addition of 3.5% $CaCl_2$

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doi:10.1016/j.cemconres.2004.05.016

resulted in a “spongy mass.” TEM on pastes older than 1 year showed similar results to the SEM studies—less fibrillar hydration products when $CaCl_2$ was present [12].

Transmission soft X-ray microscopy has recently been adopted for the study of cement-based materials [13–16]. The primary advantage of this technique is that it allows high-resolution (25 nm) images of wet samples at atmospheric pressure. Whereas optical transmission microscopy uses radiation in the visible light spectrum, soft X-ray microscopy (as its name implies) uses radiation in the soft X-ray regime, with wavelengths more than 100 times shorter. This enables the imaging of hydration products forming around cement grains in solution over time. This paper explores the results obtained using soft X-ray microscopy to study the effects of $CaCl_2$ on C_3S hydration.

2. Experimental

The soft X-ray microscope used in this study (XM-1) is located at beam line 6.1.2 of the advanced light source (ALS) at E.O. Lawrence Berkeley National Laboratory (LBNL) in Berkeley, CA, and is operated by the Center for X-ray Optics (CXRO). Synchrotron radiation is filtered by a plane mirror and soft X-rays (0.4–7 nm) are focused on the sample by using a condenser zone plate. A micro-zone plate is then used to focus the transmitted X-rays onto a CCD camera. The resulting images have magnifications of 1600–2400 × and a resolution as good as 25 nm. More detailed information about the microscope is reported elsewhere [17,18].

For soft X-rays to be transmitted through a sample of cementitious material, its thickness must be limited to 10 μm. This restricted thickness demands that dilute suspensions of cement and water be examined. To mimic cement pore solutions more closely in these dilute systems, the mixing water was saturated with calcium hydroxide and gypsum. Without such an approach, we might expect excessive dissolution of the anhydrous particles due to the high dilutions used. The presaturation with respect to calcium hydroxide was intended to prevent excessive dissolution of the C_3S. Presaturation with respect to gypsum was intended to prevent excessive dissolution of the aluminate phases in portland cement samples and was used in this examination for consistency with portland cement studies.

Solutions were made with distilled water that was boiled before use to eliminate any dissolved carbon dioxide. After cooling to room temperature, 0.4 g anhydrous $CaCl_2$ (Mallinckrodt Baker) was dissolved in 100 ml water (resulting in a concentration of 36 mM, and equivalent to 2% by weight of C_3S at water-to-cement ratio $w/c = 5$). The

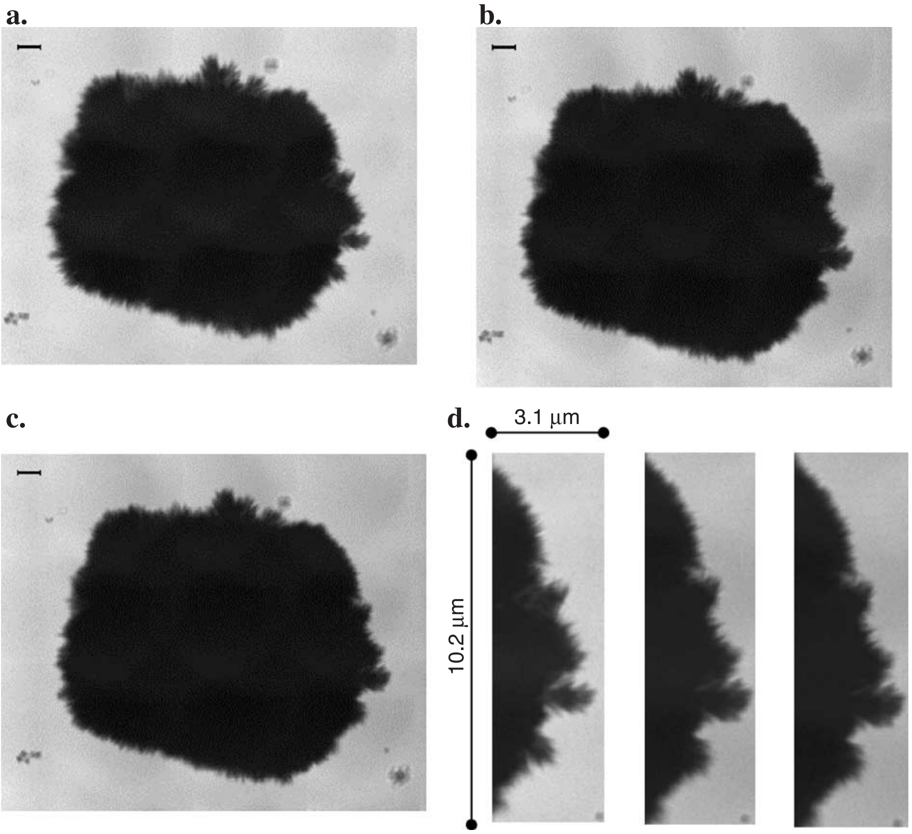

Fig. 1. C_3S in solution saturated with calcium hydroxide and gypsum, scale bar = 1 μm, (a) 20 min after mixing, (b) 93 min after mixing, (c) 115 min. (d) Detail of (a)–(c).

solutions were supersaturated by adding 3.5 g $Ca(OH)_2$ (Sigma-Aldrich) and 1 g $CaSO_4 \cdot 2H_2O$ (Sigma-Aldrich) for every 100 ml of water. The mixtures were shaken in a sealed polyethylene bottle, allowed to settle overnight, and then 14 ml of the supernatant was pipetted off for each sample to obtain a saturated solution. Care was taken not to disturb the solids at the bottom of the bottle and to minimize exposure to air.

For this study, triclinic C_3S (Construction Technology Laboratories) was mixed with saturated solutions in an initial w/c of 5 by weight. After briefly shaking the sample to ensure mixing, 2 ml was removed and centrifuged so that only small grains of C_3S (<10 μm) remained in the supernatant. One drop of the supernatant was placed on silicon nitride membranes and sandwiched between stainless steel plates of the sample mounting cell. Rubber O-rings in the steel plates prevent evaporation and carbonation. Using this procedure, one may take images as soon as 10 min after mixing.

The images taken have a field of view of approximately 10 μm in diameter. To observe larger areas, several images were taken over a grid in the area of interest. A custom autocorrelation process was then used to create a larger, composite image using montage alignment [19]. The images shown in this paper were chosen for their clarity out of several showing similar phenomena.

3. Results

Fig. 1 shows images of C_3S grains hydrating in a solution saturated with calcium hydroxide and gypsum. Hydration products with a "sheaf-of-wheat" morphology, as described by Gartner et al. [13], form immediately after mixing (Fig. 1a). These products are similar to those seen and described as "fibrillar" in Refs. [2,5,8,9,12] and were originally thought to be a form of C-S-H [13]. However, we have recently found similar products in supposedly pure saturated calcium hydroxide solutions, leading us to pose the question of whether they might not be closer to calcium hydroxide than to C-S-H. They could perhaps be a form of calcium hydroxide modified by small amounts of dissolved silica, which is a known inhibitor for portlandite crystallization. Further work is required to determine their true composition. Interestingly, the morphology of these hydration products changes almost insignificantly over the first 2 h (Fig. 1b and c), the most obvious growth occurring in the area enlarged in Fig. 1d.

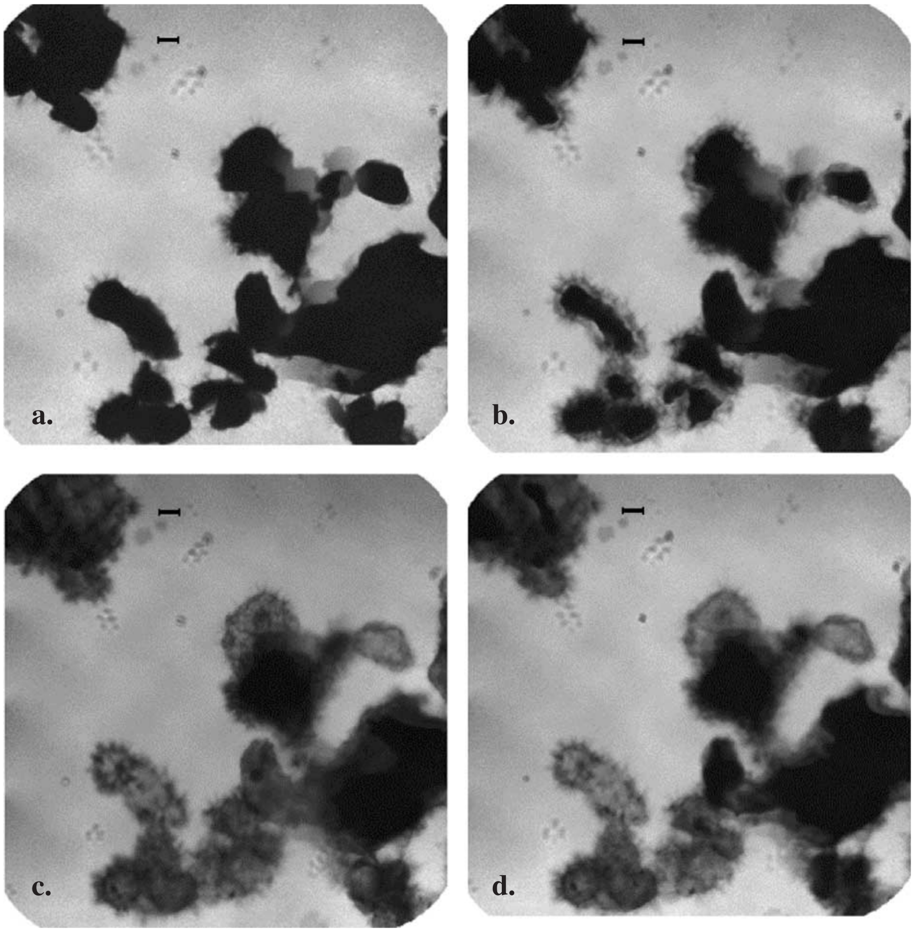

Fig. 2. $C_3S + 2\%$ $CaCl_2$ in solution saturated with calcium hydroxide and gypsum, scale bar = 1 μm, (a) 18 min after mixing, (b) 80 min, (c) 120 min, (d) 155 min (shadows seen in (a) are artifacts of the montage alignment).

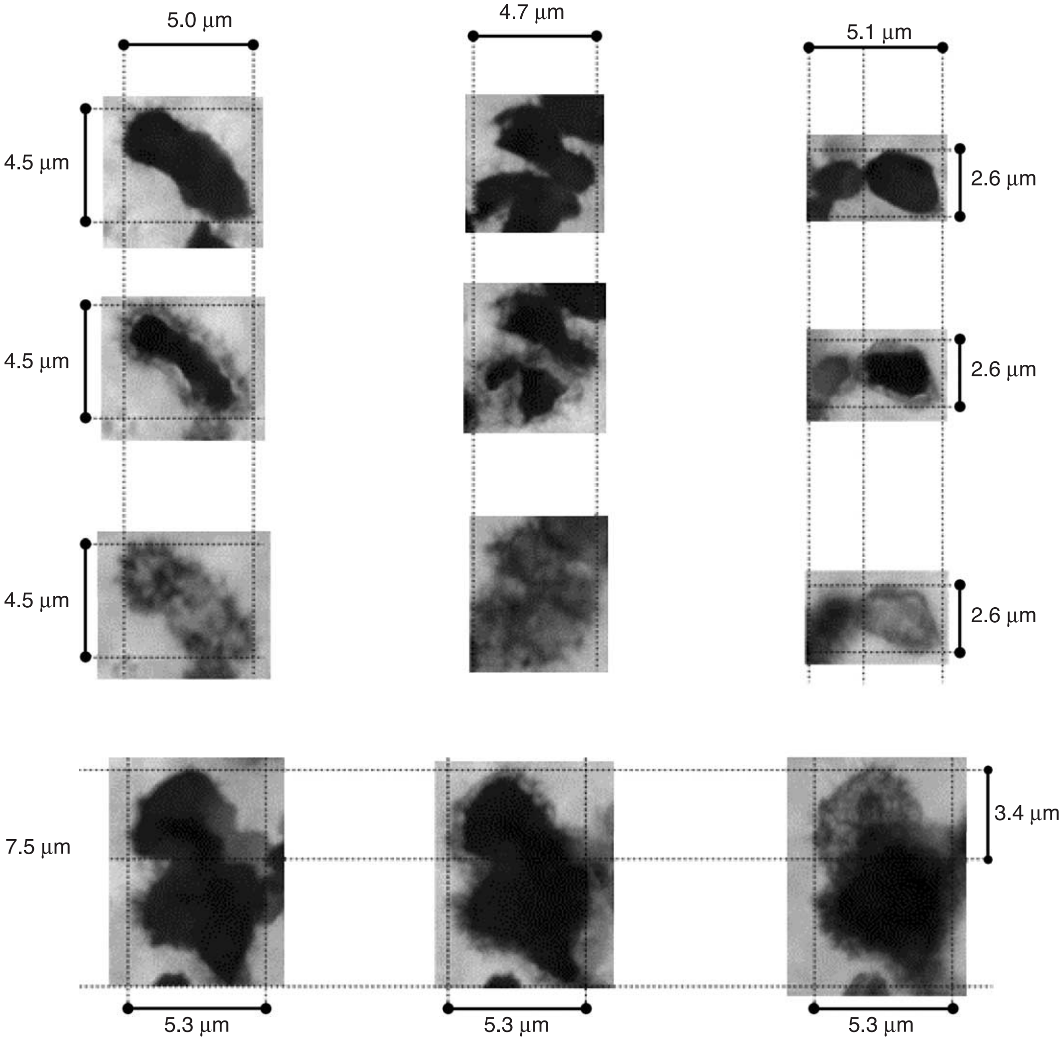

Fig. 3. Details of grains and their morphological changes over time (from Fig. 2).

Images of C_3S hydrating in the presence of $CaCl_2$ are shown in Fig. 2. Very small needlelike hydration products form early on (Fig. 2a). With time, however, the morphology of the hydration products diverges from that seen in Fig. 1. An amorphous phase begins to form, interspersed with the crystalline needle phase (Fig. 2b). This phase may be synonymous with the "honeycomb" or "spongy mass" seen by previous researchers [8–11]. It should be noted that most of the amorphous hydration products form within the boundary of the initial grain (Fig. 3). In some cases, the original grain reacts completely. However, some hydration products are seen to bridge spaces between grains, indicating that some products are forming outside of the original grain boundary as well.

Fig. 4 shows more images of C_3S hydrating in solution containing $CaCl_2$. In this case, fibrillar hydration products form both outside and inside the grain and the amorphous products seen in Fig. 3 are absent. In both cases, however, hydration products seem to be growing rapidly inside the grain, with a lower density than the original anhydrous grain.

4. Discussion

4.1. Hydration products

C-S-H that forms within the original boundary of a hydrating cement grain is often described by the term "inner product" [20]. This is in contrast to that forming through solution in the spaces between grains, called "outer product." In Figs. 2 and 3 it appears that hydration products are forming both within the cement grain and on the surface. Because compositional analysis cannot presently be done with this soft X-ray microscope, it is impossible to say whether these products are C-S-H or calcium hydroxide, or a mixture of the two. It is likely that the amorphous "inner product" formed within the volume of the original grain is C-S-H; but, following our earlier comments, the needles forming on the surface of the grains, which will be assigned to the "outer product" category, could be either C-S-H or a modified form of calcium hydroxide. As the outer product needles also appear in

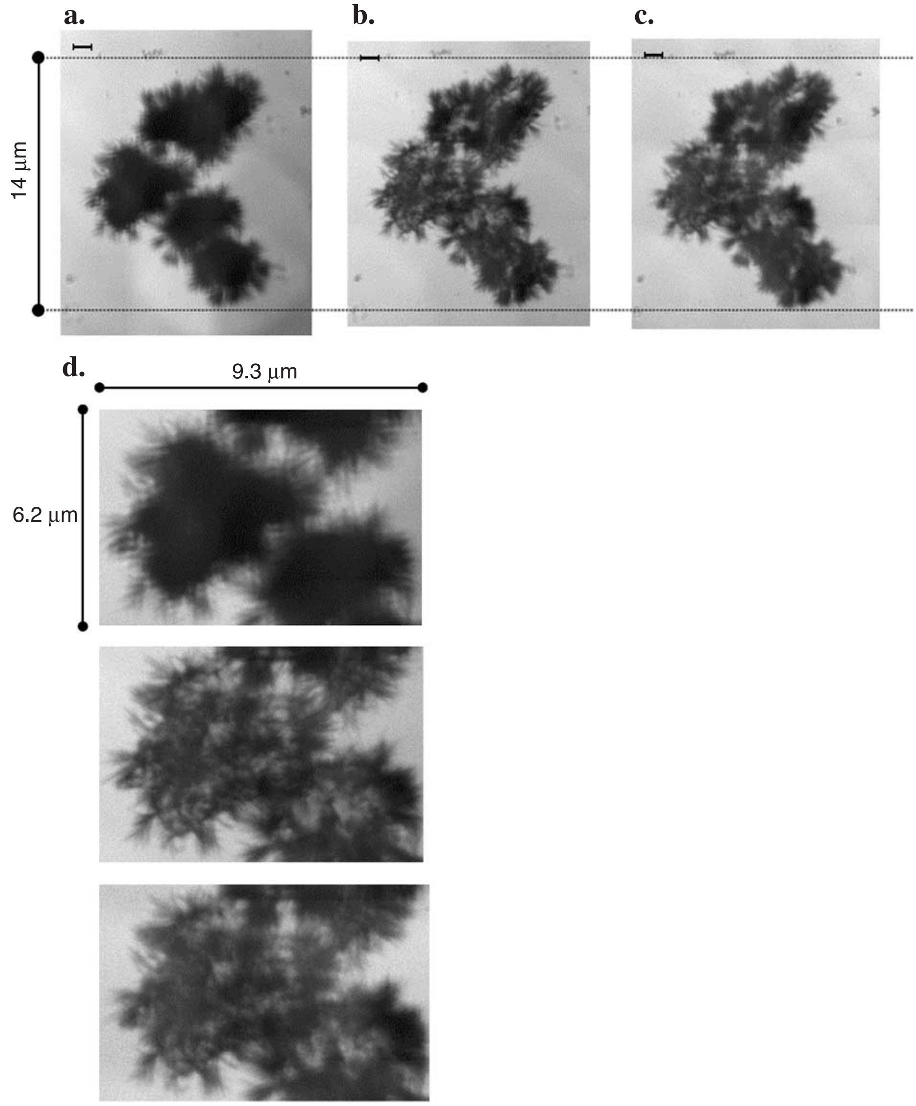

Fig. 4. $C_3S + 2\%\ CaCl_2$ in solution saturated with $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$, scale bar = 1 μm, (a) 30 min after mixing (slightly out of focus), (b) 65 min, (c) 158 min, (d) enlarged portion of (a), (b), and (c).

the control sample (Fig. 1), it appears that $CaCl_2$ primarily increases the rate of inner product formation. Inner product has not been seen in any of the neat C_3S samples tested to date. It is of interest to note that these inner hydration products are less dense (more X-ray transparent) than the hydration products seen in the unaccelerated systems shown in Fig. 1.

The "pseudomorphic" hydration that results in inner product C-S-H is essentially a leaching process, i.e., the inner product that forms is presumably calcium-poor relative to the anhydrous material. Given the high dilutions necessitated by the X-ray transmission microscopy technique, it is very possible that this leaching process is rather exaggerated compared to what would in principle be observed in cement pastes made at the much lower w/c typical of concrete applications. Since it is known that calcium hydroxide is the main component that leaches out of the anhydrous grains during cement hydration, we did take the precaution of using a presaturated calcium hydroxide solution as the dilution medium to minimize this type of artifact. Nevertheless, calcium hydroxide supersaturations of 2–3 generally occur at fairly early ages during OPC hydration [21] and we cannot preclude this possibility in our experiments, implying that the loss of calcium could still be much greater than would be expected in more concentrated suspensions. Moreover, any loss of calcium hydroxide due to carbonation, or complexation by the admixtures used, would tend to enhance the leaching effect.

4.2. Proposed mechanism

Researchers examining the effects of salts on portland cement and C_3S hydration have arrived at the following

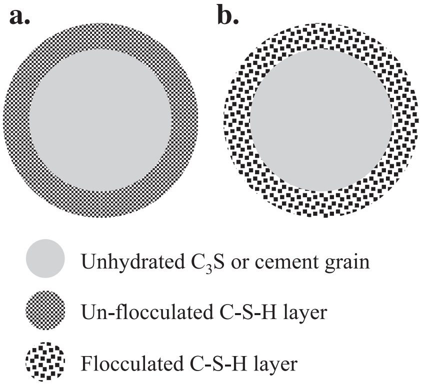

Fig. 5. Effects of accelerating ions on flocculation of C-S-H, (a). unflocculated system, (b) flocculated C-S-H as may occur in the presence of $CaCl_2$.

sequences of cations and anions, ranked in order of their effectiveness as accelerators [22–24]:

$$Ca^{2+} > Sr^{2+} > Ba^{2+} > Li^{+} > K^{+} > Na^{+} \approx Cs^{+} > Rb^{+}$$

$$Br^{-} \approx Cl^{-} > SCN^{-} > I^{-} > NO_3^{-} > ClO_4^{-}$$

It is clear from these series that calcium chloride is an extremely effective accelerator. Attempts have been made to correlate these ionic rankings to the diffusivity of ions [25], pH of the solution [6], or the solubility of calcium hydroxide [26], but the results have been inconclusive. More promising is the observation that the series are very similar to the Hoffmeister (lyotropic) series, which describes the ability of ions to affect the flocculation of hydrophilic colloids [23,24]. The more effective accelerating ions increase flocculation of colloidal particles. In the case of cement or C_3S hydration, the C-S-H forming on the surface of the particles would be more flocculated in the presence of these ions. Thus, the structure should contain larger pores, allowing easier pathways for diffusion through the layer of C-S-H forming around the particles (Fig. 5) and more rapid hydration during the early stages of the diffusion-controlled period. This would be consistent with the observation that calcium chloride not only accelerates the rate of setting and hardening, but also increases the maximum hydration rate achieved (frequently referred to as the principal heat peak in an isothermal calorimetry curve) [1].

A consequence of the theory that $CaCl_2$ increases flocculation of C-S-H is that the C-S-H forming around the hydrating particle would have inhomogeneous areas of high density and low density (Fig. 5b) rather than a homogeneous dense structure (Fig. 5a). The resolution of the images shown in Figs. 2–4 is not high enough to observe such flocs of C-S-H. However, on the scale seen by soft X-ray transmission microscopy, a flocculated structure should have an overall less dense appearance than a nonflocculated one. Figs. 1–4 demonstrate this point. Furthermore, easier diffusion of water into the hydrating particle and calcium and silicon ions away from the particle not only increases the rate of the hydration reaction, but should decrease the density as well. Ions can travel further and have more space for hydration. A more open or less dense C-S-H formed in the presence of $CaCl_2$ is confirmed by surface area measurements [4]. Furthermore, the honeycomb morphology seen by SEM is indicative of a more open microstructure [8–10].

The mechanism proposed above relates mainly to the influence of the structure of inner product C-S-H on diffusion rates of ions and water through its structure. During the diffusion-controlled period of hydration, it is assumed that the rate is controlled either by diffusion of calcium and silicate ions out of the grain, or by diffusion of water into the grain [1]. One question that remains to be answered, however, is that of the fate of the outer product. In the current study, we have not observed a lot of outer product, perhaps because our observations were limited to early ages. The high dilutions necessary during the actual observations mean that the outer product may be very dispersed and not easily observable at early ages, despite the fact that calcium chloride is assumed to accelerate its growth. However, we have observed outer product growth under different conditions, as will be reported in a subsequent paper.

5. Conclusions

Soft X-ray transmission microscopy offers the possibility of examining hydration of grains of cementitious materials in situ over time. The chemical composition of the systems examined by this technique can be easily altered with chemical admixtures. Results from the examination of C_3S hydrating in a solution containing $CaCl_2$ show that this accelerator increases the rate of formation of inner product C-S-H. Furthermore, this C-S-H is less dense than in a control sample. The accelerative power of $CaCl_2$ may come, at least in part, from its ability to flocculate hydrophilic colloids, such as C-S-H, facilitating diffusion of ions and water through the initial C-S-H layer due to an increased mean pore diameter, and thus allowing a higher rate of hydration during the early diffusion-controlled period.

Acknowledgements

Funding for this project was provided by Lafarge, Laboratoire Central de Recherche, France. Research at XM-1 is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract DE-AC 03-76F00098. The authors also gratefully acknowledge the help of V.H.R. Lamour and A.L. Pearson.

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