Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 30 (2000) 817–822

Proposed mechanism of C-S-H growth tested by soft X-ray microscopy

E.M. Gartner[a], K.E. Kurtis[b,*], P.J.M. Monteiro[c]

[a]*Lafarge, Laboratoire Central de Recherche, 38291 Saint-Quentin Fallavier, France*
[b]*School of Civil and Environmental Engineering, Georgia Institute of Technology, 780 Atlantic Drive, Atlanta, GA 30332-0355, USA*
[c]*Department of Civil and Environmental Engineering, University of California, Berkeley, CA 94720-1710, USA*

Received 19 November 1999; accepted 15 February 2000

Abstract

The reaction of silica particles in solutions saturated or supersaturated with respect to portlandite is observed by transmission soft X-ray microscopy, and a model for calcium silicate hydrate (C-S-H) growth is proposed which corresponds with the morphology observed in the X-ray images. These images show a product that consists of bundles of dendrites that appear to diverge as the growth process continues, resulting in the formation of a characteristic morphology which is narrowest in the middle and broadened at the end — the "sheaf-of-wheat" morphology. In many cases, the dendrites appear to be oriented about a common axis, and it is proposed that this axis corresponds to a common origin in a single crystalline nucleus. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Microstructure; Hydration; Calcium silicate hydrate; Pozzolanic reaction; Silica

1. Introduction

The "sheaf-of-wheat" morphology in cement-based systems is composed of branching, lath-like dendrites organized in a distinctive spherulitic or near-spherulitic pattern. This characteristic microstructure has been noted as a bottle-hydration product of both dicalcium silicate (C_2S) and tricalcium silicate (C_3S) [1], a product of the pozzolanic reaction of silica fume in concrete [2], and an early hydration product of type I cement [3]. Considering that these observations have been made after bottle-hydration, at paste/void interfaces, and at the aggregate/paste interfacial zone respectively, it appears that the sheaf-of-wheat morphology forms by the reaction of silica species and calcium ions in the presence of water in locations of relative emptiness which would allow such extensive growth. In cement based-systems, products formed as the sheaf-of-wheat morphology have been described as calcium silicate hydrate (C-S-H) precursors [1] or, more specifically, precursors to type I C-S-H [3].

Recent observations [4–6] of sheaf-of-wheat products formed during the reaction of silica particles in calcium-rich solutions pose interesting questions about the mechanism of C-S-H growth. Using transmission soft X-ray microscopy, Kurtis et al. [5] documented the evolution of the sheaf-of-wheat morphology and examined the microstructural features of the reaction product [4]. Examination of the microstructure development by X-ray imaging can provide additional insight for the evaluation of proposed growth mechanisms. The purpose of this paper is to reconcile the sheaf-of-wheat microstructure formed in hydrated systems containing both silica and calcium with possible reaction mechanisms.

2. Summary of proposed growth mechanisms

The mechanism of C-S-H growth in cementitious systems is a subject of considerable interest and is far from being well understood. C-S-H is a compound of varying stoichiometry, with a Ca/Si ratio generally between 0.8 and 2.1 and a highly variable water (H) content [7,8]. In Portland cement concrete, C-S-H may form the majority of the solid volume in the hydrated cement paste and is the primary strength-giving phase in the paste. C-S-H is one of the hydration products of calcium silicates in Portland cement and also forms through the pozzolanic reaction of reactive silicates, water, and lime.

Gartner and Gaidis [9] proposed that the hydration of C_3S, the archetype of the major cementing phase found in

---

* Corresponding author. Tel.: +1-404-385-0825; fax: +1-404-894-0211.

E-mail address: kkurtis@ce.gatech.edu (K.E. Kurtis).

PII: S0008-8846(00)00235-0

most Portland cements, is controlled by the growth of C-S-H which is initiated from relatively few nuclei that form almost immediately during the first wetting, and which then appear to follow crystal growth kinetics of a high order. However, it has been difficult for many to accept that an apparently amorphous or nearly amorphous phase [10] could exhibit growth kinetics associated with ordered crystals. In an attempt to reconcile the X-ray amorphous nature of the product with the high order (almost exponential) growth rates observed at early ages in C_3S hydration, Gartner [11] proposed that under lime-rich conditions, C-S-H grows as branching 'ribbons' that are based on layers similar to those of calcium hydroxide, but with silicate dimers attached randomly on either side that are capable of distorting the ribbons, leading to localized curvature. This proposed mechanism may be phenomenologically similar to a mechanism proposed by Williamson [1] who suggested that the microstructure is composed of silicate-covered calcium hydroxide lamellae. However, Williamson [1] also proposed that the microstructure resulted from "constitutional supersaturation" due to exothermicity of the hydration reaction coupled with the inverse temperature dependence of the solubility of the hydrates being formed. Gartner [11] proposed a different mechanism, suggesting that the branching process was essentially statistical, in that it was due to random local curvature on the growing sheets produced by random defects in the adsorption of silicate dimers onto the sheets. This was coupled with the assumption that the new ribbons could only nucleate on flat areas of existing sheets, leading to nano-crystalline regions, as shown in Fig. 1. Thus, a semi-ordered structure is generated which is essentially amorphous when analyzed by X-ray diffraction. In addition to explaining the high-order initial growth rates, such a mechanism can also help to explain the relatively high level of microporosity, which seems to be inherent in the C-S-H found in cement pastes.

Williamson's [1] model involving the constitutional supersaturation caused by the exothermicity of the hydration process might be considerably more important in the system he studied—the hydration of C_3S in a small drop of water—than in the present system which consists essentially of a pozzolanic reaction. This is because the enthalpy of the formation of C-S-H from calcium hydroxide and silica is relatively small, and the enthalpy of the precipitation of C-S-H from solution is probably close to zero. Williamson [1] likened the process to that of dendrite formation in the crystallization of metals or ice, but, in those systems, thermal effects are almost certainly much larger. The importance of the effect must depend on the ratio of the rate of heat release due to crystallization to the thermal diffusivity of the medium, and the rates of growth and heat release in the pozzolanic system studied here are much lower than those of the systems cited by Williamson, although the product morphology is the same [1].

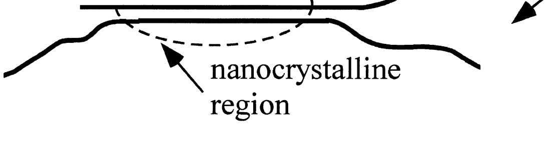

Fig. 1. Schematic of nanocrystalline region in C-S-H.

3. Model of proposed growth mechanism

It should be possible to model the C-S-H growth process that produces the sheaf-of-wheat morphology on the basis of some fairly simple assumptions. To develop a model, a simple system consisting of a spherical particle of amorphous silica suspended in a saturated calcium hydroxide solution is assumed. Under these conditions, the silica should start to dissolve immediately, giving a concentration gradient and a flux of silica into the solution away from the particle equivalent to a spherical source with a sink at infinity. For simplicity, it is reasonable to assume that the rate of silica dissolution per unit surface area of the particle should be constant (at constant temperature). Over short periods of time, the radius of the particle can be assumed to be constant, producing a roughly constant total silica flux during the period of interest.

Based on the known solubility of amorphous silica, the solution close to the silica surface should rapidly reach a concentration of several milliMolars. If the solution also contains significant levels of calcium and hydroxide (note that the solution need not be saturated with respect to portlandite (20 mM); a few milliMolars of $Ca(OH)_2$ will suffice), the phase diagram for the system [12] indicates that the solution should then be supersaturated with respect to C-S-H. Given that the solution itself contains little silica far away from the particle, the C-S-H supersaturation will be highest close to the silica surface; thus, nucleation of C-S-H would be expected there. Further, given that homogeneous nucleation is generally much slower than heterogeneous nucleation, it is almost certain that the first nucleus of C-S-H will actually form on the surface of the silica particle. Because of the high local silica concentration, this initial product is likely to be of C-S-H with a low Ca/Si ratio, perhaps, close to tobermorite composition, and, by analogy, probably having a basically orthorhombic symmetry [13]. Assuming that the initial nucleus remains firmly attached to the silica particle, and that the growing C-S-H initially retains the crystallographic symmetry associated with the orientation of the initial nucleus, the outward growth may occur in all directions, but will probably be preferred along either the *a*-axis or the *b*-axis (Fig. 1), thus, potentially producing a ribbon-like growth perpendicular to the *c*-axis.

The formation of C-S-H requires diffusion of silica through the solution to the unblocked growth sites, which will tend to move further and further away from the silica source. Clearly, then, there will be a point in time at which the rate of diffusion of silica towards these growth sites will limit the growth rate of the C-S-H. Since by this time, it appears that the surfaces of the original silica particle will be at least partially covered with C-S-H, it can also be assumed that the rate of diffusion of silica will be further reduced by the tortuosity of the path it must follow to escape from this C-S-H shell. The further the C-S-H extends from the original particle, the less silica will be available, and the higher the Ca/Si ratio will be. The resulting C-S-H will then be of the type typical of high-lime solutions. For example, C_3S hydration produces C-S-H with Ca/Si of at least 1.4 [13]. A product formed in this manner would have an increased tendency for missing silicate groups and thus, for localized curvature and porosity. It seems reasonable to suppose that the absence of silicate groups between two ribbons may allow separation, much as is shown in Fig. 1. This will ultimately lead to a multiplicity of ribbons that, if they twist to some extent, will tend to lose most of their original orientation, except perhaps for some residual orientation in the direction of the fastest growth direction. It might also be imagined that the relative excess of dissolved silica which is to be expected in the free solution found in the central plane normal to the axis of the sheaf might cause curvature of the growing ribbons on average away from the axis, if a relative imbalance of silicate ion adsorption on one side of the ribbon should cause warping by mechanical stresses, as proposed earlier. Regardless of this detail, if the sheets tend to separate from one another due to missing silicate ions, their orientation with respect to the original axis will become less and less well-correlated, which might explain the "unfurling" of the sheaf at the ends.

The system considered above consists of a silica particle suspended in a saturated calcium hydroxide solution—a simple system effective for describing the proposed growth mechanism. However, the sheaf-of-wheat morphology has also been observed in Portland cement systems [1,3]. In these systems, the proposed mechanism of C-S-H growth would be relevant to the hydration of small, relatively isolated calcium silicate particles suspended in a fairly dilute medium, as would exist during early hydration. The system considered above consists of a silica particle suspended in a saturated calcium hydroxide solution—a simple system effective for describing the proposed growth mechanism. However, the sheaf-of-wheat morphology has also been observed in Portland cement systems [1,3]. In these systems, the proposed mechanism of C-S-H growth would be relevant to the hydration of small, relatively isolated calcium silicate particles suspended in a fairly dilute medium, as would exist during early hydration. While the concentration gradient would be not quite the same as in the simple silica–lime system described above, product nucleation at only a very a small number of sites on the particle surface could lead to growth in preferred orientations, resulting in products exhibiting the sheaf-of-wheat morphology.

In summary, the proposed C-S-H growth mechanism that results in the sheaf-of-wheat morphology can be described by the following, according to the model above.

- An initial product nucleates on the silica surface. This initial product is essentially crystalline, with a low Ca/Si ratio, probably similar to tobermorite.
- Outward growth of this product continues in all directions, but is favored along either the *a*-axis or the *b*-axis.
- As growth continues further from the silica source, the products formed have a higher Ca/Si ratio due to the lower silica and higher calcium concentrations.
- The lower silica content at the growing extremities produces silicate defects between the lamellae, resulting in "unfurling" of the sheaf at the ends, leading to the appearance of ribbons "bundled" at the center. However, the absence of significant supersaturation with respect to portlandite will not allow the sheets to convert to portlandite. The growth rates become limited by the rate at which silica can diffuse to the growing extremities.
- Increased silica concentrations around the central plane of the sheaf tend to cause the ribbons to grow towards that area, resulting in a spherulitic morphology.

If the type of growth mechanism described above is accepted, it is easy to recognize the possibility of a relatively high degree of correlation in the orientation of the dendrites or laths produced, resulting in the sheaf-of-wheat morphology.

4. Soft X-ray microscopy of the sheaf-of-wheat morphology

4.1. Description of soft X-ray microscopy technique

X-ray imaging was performed using the transmission soft X-ray microscope XM-1 on beam line 6.1.2 of the Advanced Light Source (ALS), a third generation synchrotron facility located at the E.O. Lawrence Berkeley National Laboratory (LBNL). Soft X-ray wavelengths range from 1 to 50 nm, or 50 to 100 times longer than hard X-rays and 50 to 100 times shorter than visible light. The Center for X-ray Optics (CXRO) built XM-1 and operates and maintains the transmission soft X-ray microscope. The X-ray optics and microscope features have been described by Meyer-Ilse [15] and Meyer-Ilse et al. [14,16].

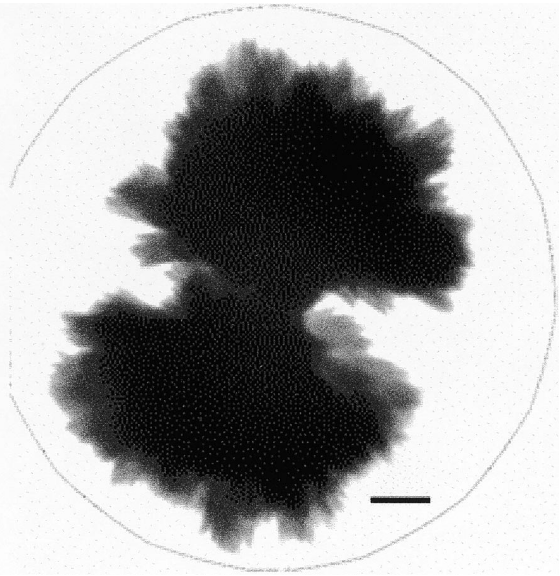

Fig. 2. X-ray image of the sheaf-of-wheat product formed by the reaction of silica fume in saturated $Ca(OH)_2$ solution for 1 h. The image was taken with a 180 s exposure time with a beam current of 203.2 mA at an original magnification of 2400×. Scalebar = 1 μm.

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 [17]. In addition, internal structural features may also be examined. While XM-1 was originally designed to examine biological samples, the microscope has been found to be advantageous for the study of ongoing reactions in cement-based systems, such as cement hydration, pozzolanic reaction, and alkali–silica reaction [6].

4.2. Sample preparation

Sample preparation procedures relevant to the study of cement-based materials at XM-1 have been previously described [4–6] but will be briefly summarized here. Chemical grade silica gel (60–200 mesh) and silica fume (obtained from Elkem) were reacted with calcium-rich solutions, including saturated $Ca(OH)_2$ (pH = 12.4) and 0.7 M NaOH + 0.1 M $CaCl_2$ (pH = 12.6). All solutions were made from reagent-grade chemical and deionized, low resistivity (17.8 $M\Omega \cdot cm$) water at room temperature. The water contained 50–200 ppb Si based on ICP-OES at wavelengths of 212.412, 251.612, and 288.158 nm. Solutions were prepared and stored in Nalgene flasks, and to avoid carbonation, solutions were used with several hours of preparation and were filtered to 0.2 μm just prior to use. Fine particles of the siliceous material were dusted across a silicon nitride window, and a small (2–3 μl) drop of the calcium-containing solution was introduced. A second silicon nitride window was fitted on top of the sample in the sample chamber, and the chamber was mechanically sealed with screws and a rubber O-ring to prevent evaporation. The sheaf-of-wheat morphology develops rapidly, and this simple method decreases preparation time, permitting more time for the observation of initial stages of the formation. In addition, the problem of overlap that occurs when studying pastes is avoided, allowing the microstructural development to be observed and imaged more clearly.

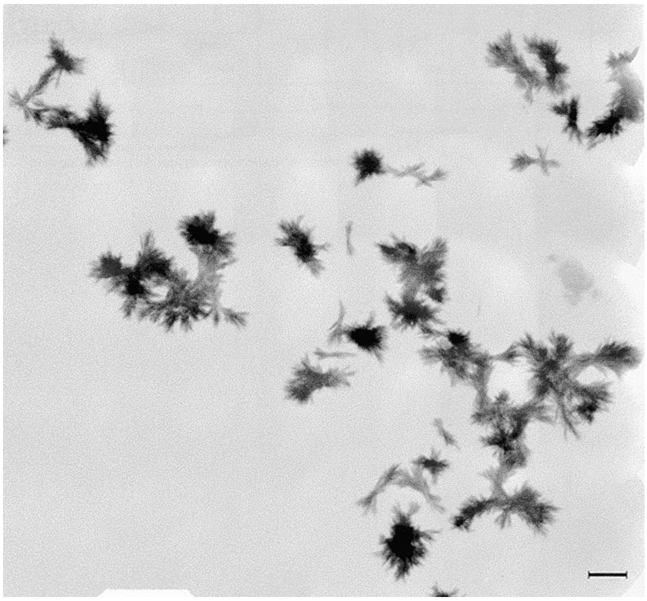

Fig. 3. Tiled X-ray images of chemical grade silica gel after 2 h in saturated $Ca(OH)_2$ solution shows numerous products with the sheaf-of-wheat morphology. The images were taken at an original magnification of 2400×. Scalebar = 2 μm.

Samples of chemical grade silica gel and silica fume in calcium-rich solutions were observed at XM-1 at 2400 × magnification and using light of 2.4 nm wavelength (517 eV) to enhance contrast between the solution and the developing hydrates [6]. X-ray images are recorded by a thinned, back-illuminated CCD camera with 1024 × 1024 pixels of size 24 × 24 μm. Images were processed further to adjust contrast and to insert scale bars using Adobe Photoshop 3.0 with Intellihance and UNIX-based Interactive Data Language (IDL). In addition, IDL was used to create tiled images, which are composite images formed from many individual images fitted together. Tiling is useful when the features of the sample are better observed over a larger field rather than a single image where the field is a ~ 10 μm diameter circular region.

5. Discussion: X-ray images and the proposed mechanism of growth

Soft X-ray microscopy of several low solid-to-solution systems (described above) containing fine siliceous particles in calcium-rich alkaline solutions demonstrate that the sheaf-of-wheat morphology is a typical early hydration product in these systems. The X-ray image in Fig. 2 shows a rather dense sheaf-of-wheat structure formed after 1 h reaction time between silica fume and saturated $Ca(OH)_2$ solution. The structure is characteristic of the morphology with the lath-like particles that form the structure roughly oriented about a central axis. Similar morphology is generated by the reaction of chemical grade silica gel and saturated $Ca(OH)_2$ solution. Fig. 3 is a tiled image of the products of that reaction after 2 h. The tile shows numerous products with the sheaf-of-wheat morphology singly and in clusters, demonstrating that the microstructure forms ubiquitously by the reaction of siliceous particles in saturated $Ca(OH)_2$ solutions.

The morphology observed in these X-ray images corresponds to the proposed C-S-H growth mechanism described previously, and they provide indirect evidence for the near-crystallinity of the C-S-H formed under these conditions. The tiled X-ray image in Fig. 3 shows a large number of the sheaf-of-wheat structures, and many are composed of dendrites that are roughly oriented around a common axis—a circumstance that is hard to explain unless they share some sort of common crystalline origin close to the neck of the sheaf. It seems very unlikely that the silica particles from which the C-S-H originates can have any very strong external field, such as a magnetic or electrostatic field, with the kind of axial symmetry which might offer an alternative explanation for this type of morphology. Knowing that the silica particles themselves are truly amorphous, and assuming that the effect is simply related to the growth of C-S-H in an essentially isotropic medium, one is forced to conclude that the observed preferred orientation of the fibers around a common axis has its origins in a common nucleus of some kind. That is, all of the fibers in a single oriented bundle can trace their origins to a single nucleus. Examination of the structures under polarized light shows that the sheaf-of-wheat structure formed by the reaction of chemical grade silica gel or silica fume and saturated $Ca(OH)_2$ exhibit birefringence, with portions of the sheaf-of-wheat structure going into extinction every 90°. Birefringence is characteristic of optical anisotropy, providing additional evidence of the near-crystalline ordering of the laths in the sheaf-of-wheat morphology. The preliminary data indicate some degree of common orientation within the structure, but further work is planned to obtain more precise information on the nature and degree of this common orientation.

X-ray images have also been made of the early stages of the sheaf-of-wheat development. Two images shown in Fig. 4 show the evolution of the sheaf-of-wheat morphology around a single silica particle during the reaction of chemical grade silica gel in a solution of 0.7 M NaOH + 0.1 M $CaCl_2$ —a solution significantly supersaturated relative to portlandite. In this case, it appears that there

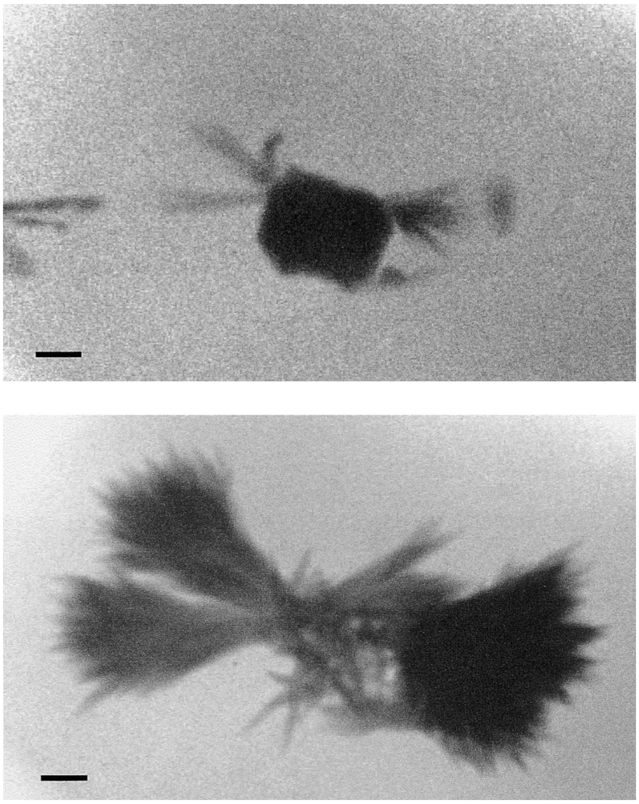

Fig. 4. Two X-ray microscopy images of the evolution of the sheaf-of-wheat morphology during the reaction of chemical grade silica gel in a solution of 0.7 M NaOH + 0.1 M $CaCl_2$ after 10 min (a) and 19 min (b). Exposure times for the X-ray images measured 3 and 36 s with beam currents of 347.3 and 335.7 mA, respectively. Original magnification was 2400×. Scalebar = 0.5 μm.

are at least three differently oriented groups of dendrites on the surface of the original particle during the initial stage of the product formation where dendrites form nearly perpendicular to the surface of a seed particle (Fig. 4a). When considering the initial product nucleation described in the model presented here, it is possible that more than one nucleus will form on the same silica particle. This likelihood will depend on a variety of factors, including the size of the particle and the inherent growth rate of the C-S-H relative to the nucleation and diffusion rates. If the growth rate is high relative to the nucleation rate, but the reaction rapidly becomes diffusion-controlled over distances similar to the average initial particle diameter, then, it is quite likely that most of the particles will only give rise to one nucleus because the local supersaturation will fall rapidly as the C-S-H grows. Assuming that the pure sheaf-of-wheat morphology is indicative of a single nucleus per silica particle, the relative number of particles generating this morphology might be used as an indication of the relative probabilities of single vs. multiple nucleation events per particle under the experimental conditions used. In the case of the reaction of chemical grade silica gel in a solution of 0.7 M NaOH + 0.1 M $CaCl_2$, the higher calcium concentration may increase the probability of multiple nucleation sites per particle seen in Fig. 4.

An X-ray image made 9 min later (Fig. 4b), shows that much more product has formed. The location and orientation of the initial product formation appears to influence the orientation of the products formed subsequently. The dendrites formed during the 9-min interval between X-ray images are oriented similarly to those that initially nucleated, implying that growth from an existing group preponderates over secondary nucleation.

6. Conclusions

X-ray images indicate that the sheaf-of-wheat morphology forms from the reaction of silica particles in calcium-rich solutions. Specifically, the morphology has been observed during the reaction of silica particles in saturated $Ca(OH)_2$ solution and 0.7 M NaOH + 0.1 M $CaCl_2$ solution. In these systems, the morphology is characterized by bundles of lath-like particles or dendrites that originate from the silica surface and appear to be crystalline or nearly crystalline. These dendrites are often oriented about a single common axis, which is consistent with the concept that all the dendrites in such a group originated from a common initial nucleus. Far from the silica surface, the dendrites separate and become more and more poorly aligned with initial orientation, broadening the ends of the sheaf-of-wheat structure. This type of growth can be explained by a mechanism similar to that proposed by Gartner [11], in which random silicate ion vacancies on the surfaces of the calcium hydroxide ribbons that make up the backbone of each dendrite cause the ribbons to curve and to separate from one another.

Acknowledgments

The authors are grateful to Werner Meyer-Ilse of the Center for X-ray Optics, for his expertise in X-ray microscopy and for use of XM-1, and to Angelic Lucero of the Center for X-ray Optics and the Lawrence Berkeley National Laboratory, for her assistance in generating the tiled image in Fig. 3. Research at XM-1 is supported by the United States Department of Energy, Office of Basic Energy Sciences under contract DE-AC 03-76SF00098.

References

[1] R.B. Williamson, Constitutional supersaturation in Portland cement solidified by hydration, J Cryst Growth 34 (1968) 787–794.

[2] A.M. Rashed, The Microstructure of Air-entrained Concrete, UC Berkeley Dissertation, 1989.

[3] D. Zampini, S.P. Shah, H.M. Jennings, Early age microstructure of the paste–aggregate interface and its evolution, J Mater Res 13 (7) (1998) 1888–1898.

[4] K.E. Kurtis, P.J.M. Monteiro, J.T. Brown, W. Meyer-Ilse, Imaging of ASR gel by soft X-ray microscopy, Cem Concr Res 28 (3) (1998) 411–421.

[5] K.E. Kurtis, P.J.M. Monteiro, J.T. Brown, W. Meyer-Ilse, Analysis of deterioration products developed in large concrete dams by high resolution transmission soft X-ray microscopy, J Microsc, in press.

[6] K.E. Kurtis, Transmission Soft X-ray Microscopy of the Alkali–Silica Reaction, UC Berkeley Dissertation, 1998.

[7] E. Henderson, J.E. Bailey, The compositional and molecular character of the calcium silicate hydrates formed in the paste hydration of $3CaO{\cdot}SiO_2$, J Mater Sci 28 (13) (1993) 3681–3691.

[8] P.K. Mehta, P.J.M. Monteiro, Concrete: Structure, Properties, and Materials, 2nd edn. Prentice-Hall, Englewood Cliffs, NJ, 1993.

[9] E.M. Gartner, J.M. Gaidis, Hydration mechanisms, I, J.P. Skalny (Ed.), Materials Science of Concrete, Am Ceram Soc 1 (1989) 99–125.

[10] P.C. Hewlett (Ed.), Lea's Chemistry of Cement and Concrete, 4th edn. Arnold/Wiley, New York, 1998.

[11] E.M. Gartner, A proposed mechanism for the growth of C-S-H during the hydration of tricalcium silicate, Cem Concr Res 27 (5) (1997) 665–672.

[12] H.M. Jennings, Aqueous solubility relationships for two types of calcium silicate hydrate, J Am Ceram Soc 69 (1986) 614.

[13] H.F.W. Taylor, Cement Chemistry, 2nd edn. Thomas Telford, London, 1997.

[14] W. Meyer-Ilse, H. Medecki, J.T. Brown, J.M. Heck, E. Anderson, C. Stead, A. Stead, T. Ford, R. Balhorn, C. Petersen, D.T. Attwood, X-ray microscopy in Berkeley, in: J. Thieme, G. Schmahl, E. Umbach, D. Rudolph (Eds.), X-ray Microscopy and Spectromicroscopy, Springer-Verlag, Heidelberg, Germany, 1998, pp. I3–I11.

[15] W. Meyer-Ilse, X-ray microscopy and microanalysis, Encyclopedia of Applied Physics, VCH Publishers, New York, in press.

[16] W. Meyer-Ilse, H. Medecki, L. Jochum, E. Anderson, D. Attwood, C. Balhorn, R. Balhorn, M. Moronne, D. Rudolph, G. Schmahl, New high resolution zone-plate microscope at beamline 6.1 of the ALS, Synchrotron Radiat News 8 (3) (1995) 29–33.

[17] J.M. Heck, W. Meyer-Ilse, J.T. Brown, E. Anderson, H. Medecki, D.T. Attwood, Resolution of XM-1, in: J. Thieme, G. Schmahl, E. Rudolph, D. Rudolph (Eds.), X-ray Microscopy and Spectromicroscopy, II130–II135.