Pergamon

Cement and Concrete Research 29 (1999) 1099–1102

CEMENT AND CONCRETE RESEARCH

The use of scanning transmission X-ray microscopy for the real-time study of cement hydration

S.M. Clark[a,*], G.R. Morrison[b], W.D. Shi[b,1]

[a]*CLRC, Daresbury Laboratory, Warrington, WA4 4AD, United Kingdom*
[b]*Department of Physics, Kings College, Strand, London, WC2R 2LS, United Kingdom*

Received 30 September 1998; accepted 20 April 1999

Abstract

The use of scanning transmission X-ray microscopy for the real-time study of cement hydration is presented. The technique is illustrated with a study of the hydration of tricalcium silicate. Tubules emerging from C_3S grains were found to grow in a contorted fashion when the water-to-cement ratio was 3:1. This is in contrast to observations with larger water-to-cement ratios when the tubules were found to grow in a linear fashion. A scheme for the progression of the hydration reaction suggested by our observations is presented. The potential of chemical-state imaging was also explored and promises exciting possibilities for the understanding of cement hydration.

Keywords: Hydration; Reaction; C-S-H; Ca_3SiO_5

High resolution X-ray imaging of nonperiodic structures has seen much progress in recent years [1]. This is due largely to the development of X-ray microscopes. The advent of synchrotron radiation sources has provided intense tunable X-ray sources of high spectral brilliance that make X-ray microscopy a practicable technique, while the development of new microfabrication technologies has led to the production of Fresnel zone plates as diffractive X-ray focusing devices. The short wavelength and penetrating nature of X-rays means that X-ray microscopes can achieve higher spatial resolution than a visible light microscope, and can examine samples that are significantly thicker than would be possible with the transmission electron microscope, without the necessity of maintaining the sample in a high vacuum environment.

Most X-ray microscopes currently in operation use the soft X-ray region from about 100 eV to 1 keV. The tunability of the X-ray beam from a synchrotron source means that the operating energy can be chosen to optimise the contrast from a particular chemical component of the sample. In the case of cement samples the selection of an operating energy on the absorbing side of the calcium L absorption edge should enhance the contrast from calcium-containing material. Images taken at other energies around the L edge may allow more specific chemical information to be obtained, perhaps distinguishing between the calcium in CH, C_3S, and C-S-H. A further advantage is that the calcium L edge is at a lower energy than the oxygen K edge, so the absorption by water is relatively small and so it should be feasible to examine wet samples.

In this work we explore the potential of the scanning transmission X-ray microscope (STXM) for the study of cement hydration. A sample container suitable for wet samples was developed and images collected from hydrating C_3S samples. Differences between images collected at large and more realistic water-to-cement ratios are discussed and a scheme for the progression of the reaction is presented. Besides collecting images at one fixed wavelength, it is also possible to collect pairs of images at slightly different wavelengths selected so that the difference between the two images gives contrast that is proportional to the amount of a particular element in a particular bonding state. In particular, it might be possible to produce images showing the location of calcium atoms in different oxidation or bonding states. This technique, known as chemical-state imaging, was also explored and the potential of this technique for helping in the understanding of the mechanisms of cement hydration is discussed.

* Corresponding author. Tel.: +44-1925-603123; fax:+44-1925- 603124.
E-mail address: s.m.clear@dl.ac.uk (S. M. Clark)

[1]Present address is ACI Glass Packaging, 310-314 Ferntree Gully Road, North Clayton, Victoria 3168, Australia.

0008-8846/99/$ – see front matter
PII: S0008-8846(99)00091-5

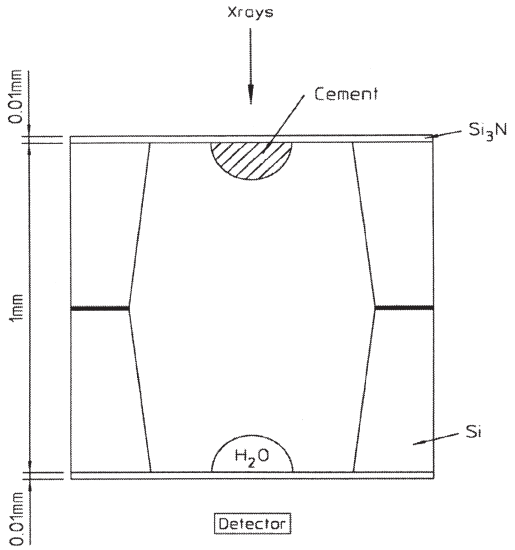

Fig. 1. Schematic diagram of the hydration cell.

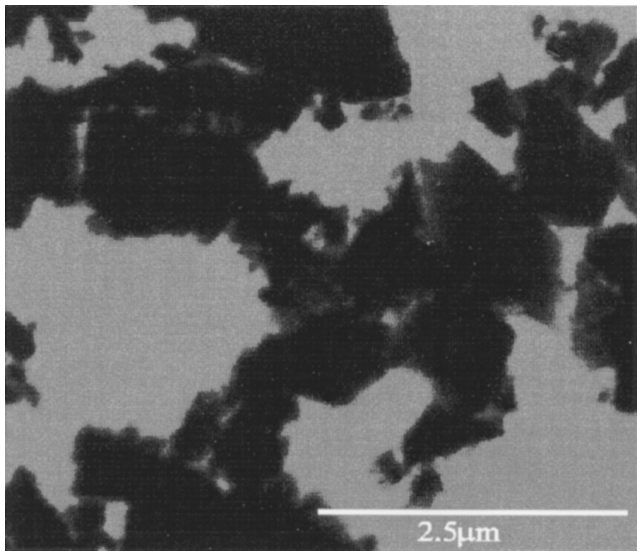

Fig. 2. STXM image of hydrating C_3S taken after 40 min of hydration.

1. Methods

The X-ray microscopy was carried out using the STXM located on beamline 5U2 of the Synchrotron Radiation Source (SRS) at the CLRC Daresbury Laboratory [2,3]. The SRS operates with an electron beam of energy 2 GeV and a stored current of around 200 mA. On beamline 5, a 10-period undulator enhances the emission in the soft X-ray region, and a plane pre-mirror directs the radiation along branch 5U2. A particular X-ray energy is selected using a cylindrical grating monochromator, which produces focusing and dispersion in a vertical plane at an exit slit about 2.5 m from the grating. The grating has a period of 540 lines/mm, and the chromatic resolving power of the monochromator is typically about 500 at energies around 350 eV, when a 50-μm exit slit is used. The exit slit acts as the effective source for the zone plate-focusing element of the STXM. The zone plate was about 150 μm in diameter, with an outermost zone width of just under 40 nm, giving an image resolution better than 50 nm. The zone plate produces a focused X-ray probe that is scanned in raster fashion over the sample, using a three-axis stage to scan the sample through the fixed X-ray beam. The X-ray photons transmitted by the sample are counted by a gas-flow proportional counter, and the recorded counts used to set the brightness level of pixels on an image framestore. A photon-counting system such as this provides a dynamic range that is limited only by the time that can be devoted to data acquisition. In practice the proportional counter becomes nonlinear at rates around 10^5 Hz, and pixel dwell times are typically 20 ms, so recorded counts per pixel are usually a few thousand. Fine scans are controlled by piezoelectric transducers with a minimum step size of 10 nm and a maximum field size of 40 μm. Larger areas up to 4 mm in size can be explored by a stepper motor-driven course stage. The whole process of monochromator control and image acquisition was controlled by a PC, with a menu-driven user interface.

The samples of tricalcium silicate used in these studies were from one batch prepared by Blue Circle Cement Ltd. High resolution powder diffraction [4] has shown that the C_3S was of a single phase and of type T_3, with unit cell parameters: $a = 11.6292$ Å, $b = 14.1456$ Å, $c = 13.6412$ Å, $\alpha = 105.5°$, $\beta = 94.702°$, $\gamma = 90.0°$, similar to those determined by Golovastikov [5]. The course of hydration of this material has also been well characterised by a number of diffraction techniques [6].

Great care was taken when preparing hydrating mixtures to avoid contamination from the air. Preweighed samples of C_3S and distilled deionised water were mixed for 5 min inside a nitrogen-filled glove bag before a small amount of the paste was placed inside the sample holder. The sample holders were made from silicon wafers, with thin, X-ray transmissive windows made of 100-nm-thick silicon nitride membranes (Fig. 1). A small sample of the hydrated cement was placed on the window facing the X-ray beam, with a small reservoir of water also being left in the cell. The holders were carefully sealed while still inside the glove bag to ensure that air was excluded during the collection of the STXM images, and all data were collected at room temperature, with a water-to-cement ratio of 0.5. A series of images were collected over a 48-h period, and some X-ray absorption spectra were collected from particular locations on the samples to investigate the feasibility of chemically sensitive imaging.

2. Results

Images collected during the early images of hydration showed clusters of C_3S grains with regions containing clear

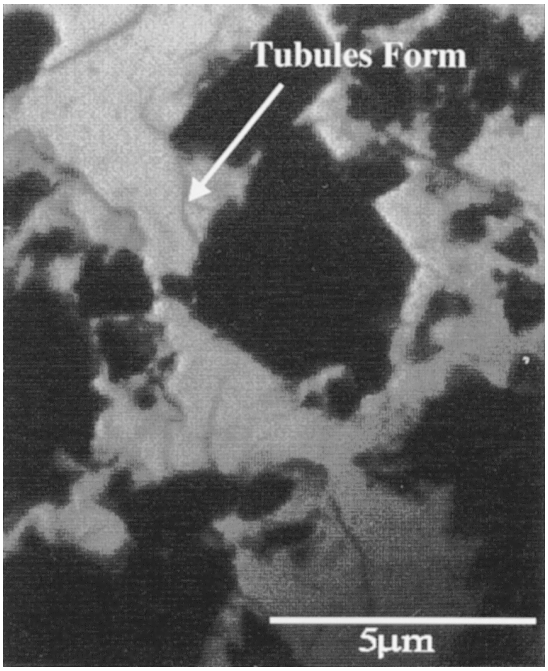

Fig. 3. STXM image of hydrating C_3S taken after 24 h of hydration.

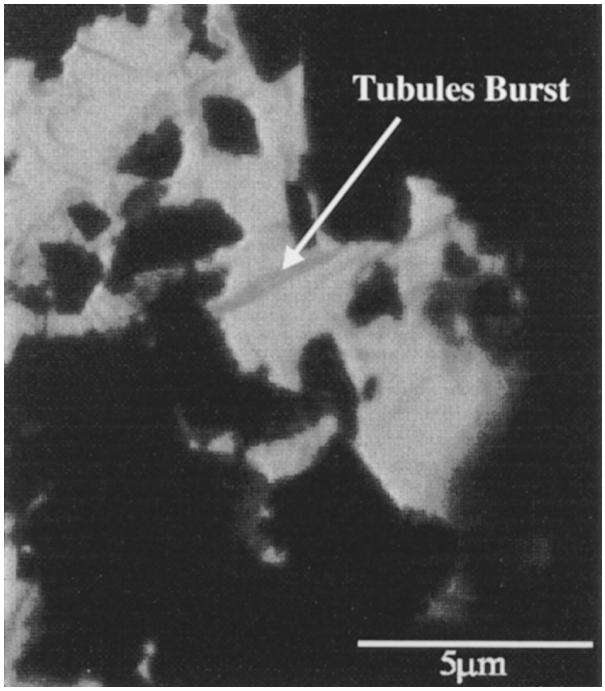

Fig. 4. STXM image of hydrating C_3S taken after 48 h of hydration.

water between them. As time progressed, a film of material appeared to form around the C_3S grains (Fig. 2). This film has quite low image contrast when imaged at an energy greater than the calcium L absorption edge, suggesting a low mass thickness of calcium. Thereafter, tubules are seen to grow from the C_3S grains into the intergrain area (Fig. 3). Images taken at energies above and below the calcium L edge suggest that these tubules contain significant amounts of calcium. Their rather convoluted form differs quite markedly from the very straight tubules observed previously [7] in samples prepared with a large excess of water (typically 5:1 water-to-cement ratio). The previous study also showed that crystals with a hexagonal morphology reminiscent of CH crystals formed at the ends of the tubules. This was not clearly observed in our study. Our latter images showed the tubules apparently splitting open to give wispy sheetlike structures (Fig. 4).

By using a static X-ray probe, it is also possible with the STXM instrument to measure the X-ray transmission of a small region of the specimen as a function of wavelength. Fig. 5 shows spectra collected in this manner for two regions containing what we believe to be CH crystals and C-S-H gel. The absorption peaks in the spectra are caused by excitation of calcium electrons. The peak at about 347 eV can be assigned to an electron transition to the $2p^5\ ^2P_{3/2}\ 4s^2\ 3d[1/2]_1$ state. The peak at about 349 eV is due to a transition to the $2p^5\ ^2P_{3/2}\ 4s^2\ 3d\ [3/2]_1$ state and the peak at about 352 eV is due to a transition to the $2p^5\ ^2P_{1/2}\ 4s^2\ 3d\ [3/2]_1$ state [8]. Clear differences between these two spectra are apparent in the 347 eV region. This could be due to differences in the bonding or the local environment of the calcium ions, and suggests that the STXM could be used to distinguish between calcium ions in different chemical environments within the hydrating matrix.

3. Discussion

A summary of the STXM observations is contained in Fig. 6. It seems that the hydration process can be divided into five stages. Stage 1 involves immersing the C_3S particles in water. Stage 2 sees the growth of a surface layer on each C_3S grain, which is depleted in Ca and made up of a large number of small needle-shaped crystals. This may be the protective layer known as the first Stein hydrate [9], which is thought to cause the dormant period. Stage 3 involves the growth of tubules from the C_3S grains into the intergrain region. These structures may be what is known as

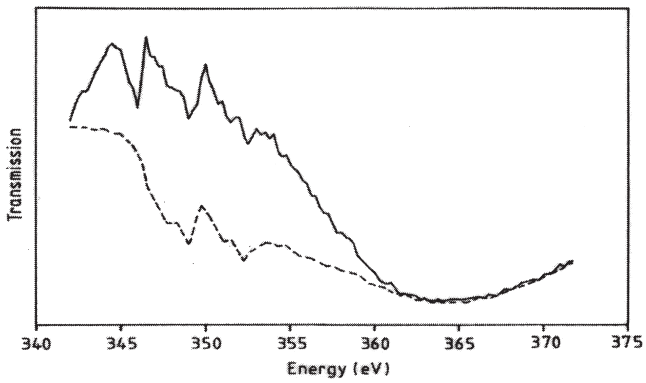

Fig. 5. X-ray absorption spectra collected from CH (- - - -) and CSH (—) portions of the hydrating C_3S sample.

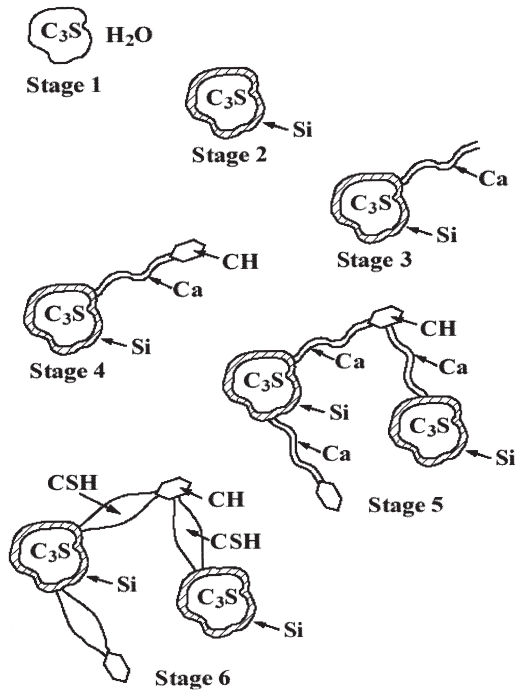

Fig. 6. Schematic summary of the STXM observations.

C-S-H type I [10] or the second Stein hydrate [9], which marks the end of the dormant period. Stage 4 sees the formation of CH crystals at the end of the tubules and stage 5 involves the bursting open of the tubules to give a fine sheet-like structure in the intergrain region. This fine sheet structure may be equivalent to C-S-H type III or C-S-H type IV [10]. The final structure contains four distinct regions containing solids, C-S-H formed initially, C-S-H formed later, and voids, perhaps containing water. These last two structures may correspond to the gel pores and capillary pores described by Powers [11]. It seems apparent from the STXM observations that the long fibres that grow from the C_3S grains are involved both in the nucleation of CH crystals in the intergrain region and in the formation of intergrain C-S-H when they burst. Since tubules seem to be dense in Ca, they may well be involved in the transport of Ca ions from the C_3S grains to the growing CH crystals, as suggested by osmotic pumping models for the hydration of cement pastes. It has been suggested that a break up of the initial C-S-H coat causes the end of the dormant period [10,12]. No such breakup was observed. The tubules emanating from the C_3S grains were observed to be straight in a paste with a high water-to-cement ratio but convoluted in a paste with a low water-to-cement ratio. This may be due to more complex chemical gradients in the denser pastes, perhaps caused by convection due to the larger heat output of the greater amount of hydrating material. This suggests that tubule growth, and therefore setting time, relies not only on the composition of the hydrating particle but also on the makeup of the intergrain water.

4. Conclusions

We have shown in this work that the STXM is capable of forming high resolution images of structures in hydrating cement pastes, with realistic water-to-cement ratios, held in an environmental cell to ensure isolation from the air. The STXM observations are summarised Fig. 6. These conclusions in general support an osmotic pumping-type model of cement hydration. The difference in X-ray absorption of Ca atoms in different chemical environments suggests that the STXM might allow us to map out the distribution of calcium atoms in different oxidation or bonding states throughout a hydrating paste in much the same way that elemental distribution can be mapped out by an electron microprobe. This would give us a very detailed picture of the chemistry of cement hydration on the nanoscale and could potentially revolutionise our understanding of the mechanisms underlying cement hydration.

Acknowledgments

We wish to thank the EPSRC for the provision of beam time on station 5U2 at the Daresbury SRS.

References

[1] D. Sayre, H.N. Chapman, X-ray microscopy, Acta Cryst A51 (1995) 237–252.
[2] J. Kirz, C. Jacobsen, M. Howells, Soft X-ray microscopies and their biological applications, Quart Rev Biophys 28 (1995) 33–130.
[3] G.R. Morrison, S. Bridgwater, M.T. Browne, R.E. Burge, R.C. Cave, P.S. Charalambous, G.F. Foster, A.R. Hare, A.G. Michette, D. Morris, T. Taguchi, P.J. Duke, Development of X-ray imaging at the Daresbury SRS, Rev Sci Instrum 60 (1989) 2464–2467.
[4] S.M. Clark, Development of an energy-dispersive powder diffraction facility for the study of chemical reactions and phase transitions, Ph.D. thesis, University of London, 1990.
[5] R. Golovastikov, R. Matveeva, N.V. Belov, Crystal structure of the tricalcium silicate $3CaO{\cdot}SiO_2{=}C_3S$, Sov Phys Cryst 20 (1975) 441–445.
[6] S.M. Clark, P. Barnes, A comparison of laboratory, synchrotron and neutron diffraction for the real time study of cement hydration, Cem Conc Res 25 (3) (1995) 639–646.
[7] G.R. Morrison, J.T. Beswetherick, M.T. Browne, R.E. Burge, R.C. Cave, P.S. Charalambous, P.J. Duke, G.F. Foster, A.R. Hare, A.G. Michette, D. Morris, A.W. Potts, T. Taguchi, Development and applications of the King's College/Daresbury X-ray microscope, in: X-ray Microscopy in Biology and Medicine, K. Shinohara, K. Yada, H. Kihara, T. Saito (Eds.), Japan Scientific Societies Press, Tokyo, and Springer-Verlag, Berlin, 1990, pp. 99–108.
[8] M.W.D. Mansfield, The Ca_1 absorption spectrum in the extreme ultraviolet: Excitation of the 2p subshell, Proc Roy Soc Lond A 348 (1976) 143–151.
[9] H.N. Stein, J.M. Stevels, J Appl Chem (London) 14 (1964) 338.
[10] S. Diamond, Hydraulic cement pastes: Their structure and properties, Proceedings of a Conference at University of Sheffield, Cement and Concrete Association, Wexham Springs, April 1976.
[11] T.C. Powers, Physical properties of cement paste, Proc Symp Chem Cement, Washington, 1960, 2 pp. 577–613.
[12] T.C. Powers, Some physical aspects of the hydration of portland cement, J Res Dev Labs Portland Cement Ass 3 (1) (1961) 47–56.