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Aspects of Portland cement hydration studied using atomic force microscopy

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Aspects of the mechanisms of hydration and microstructural evolution in Portland cement are still not fully understood. Atomic force microscopy (AFM) is in many ways a powerful tool for investigating changes in surface structure that accompany the hydration of Portland cement, especially because surfaces can be imaged under aqueous solutions at normal temperature, pressure and high magnification. We have investigated changes in the surface characteristics of sections of Portland cement clinker immersed initially in saturated calcium hydroxide solution which was then replaced by water, and in sucrose solution. In the case of the former, the observations are consistent with the early formation of a protective membrane and the subsequent growth of calcium silicate hydrate (CSH) structures by an osmotic process. The dissolution of the clinker in sucrose solution has also been directly observed. It is concluded that the use of AFM will help to resolve many questions relating to cement hydration.

1. Introduction

Portland cement was invented in the 19th century and its production now exceeds 10^9 tonnes per year. There is still debate as to the mechanisms of hydration, the evolution of the hydrated solid phases responsible for its consolidation and the effects of additives on these processes [1].

Portland cement consists of a number of chemical constituents of which the most important are the anhydrous compounds tricalcium silicate (C_3S or "alite") and dicalcium silicate (βC_2S or "belite") [2]. These two compounds constitute about 75% by mass of anhydrous Portland cement and their hydration provides about 70% by volume of the major bonding phase in the hydrated, set solid. This bonding phase is a calcium silicate hydrate (CSH) of somewhat indefinite composition which is largely amorphous. Calcium hydroxide is present as a major crystalline phase and minor phases are also present, including aluminate hydrates, but the properties of cement based products are largely dictated by CSH.

A characteristic feature of the kinetics of Portland cement hydration, as indicated by thermal history, is that an initial exothermic reaction on mixing with water is followed by a period of thermal quiescence, the so called "dormant period" (see Fig. 1). This is then followed some hours later by a second exothermic reaction accompanied by initial setting as indicated in Fig. 1. Hydrated phases, mostly CSH, form slowly and the material consolidates as space is filled with CSH and crystals of calcium hydroxide.

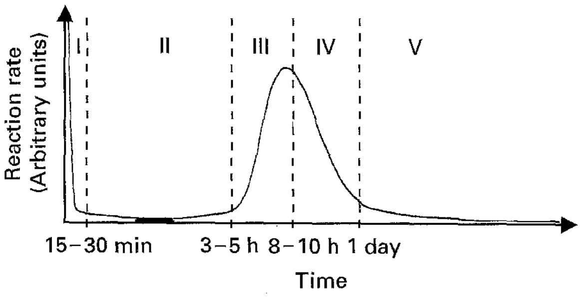

Figure 1 A typical schematic thermograph of the hydration of Portland cement. "I" is the pre-induction period (i.e. initial exotherm); "II" is the dormant period (i.e. time of thermal quiescence); "III" and "IV" is the setting period (i.e. second exotherm) and "V" is the diffusion period or the end of the thermal activity.

There has been much debate over the years as to the physicochemical events responsible for the onset and end of the dormant period and for the evolution of the varied morphology of the major hydrated material, CSH [1–5]. An early suggestion [3] was the formation of a protective membrane around the cement grains restricting the hydration reaction and initiating the start of the dormant period. The renewed reaction (i.e. the second exotherm), was then initiated by the breakdown of this protective membrane. This idea of a protective membrane and its rupture was re-visited by two groups independently in the late 1970s [4, 5] who drew attention to a remarkable similarity between morphological evolution in hydrating Portland cement and "silicate gardens" (see Fig. 2). In the latter,

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† Sadly deceased.

Editors note: I am very saddened by the sudden loss of Derek Birchall and acknowledge his outstanding contribution to the subject and this journal over many years.

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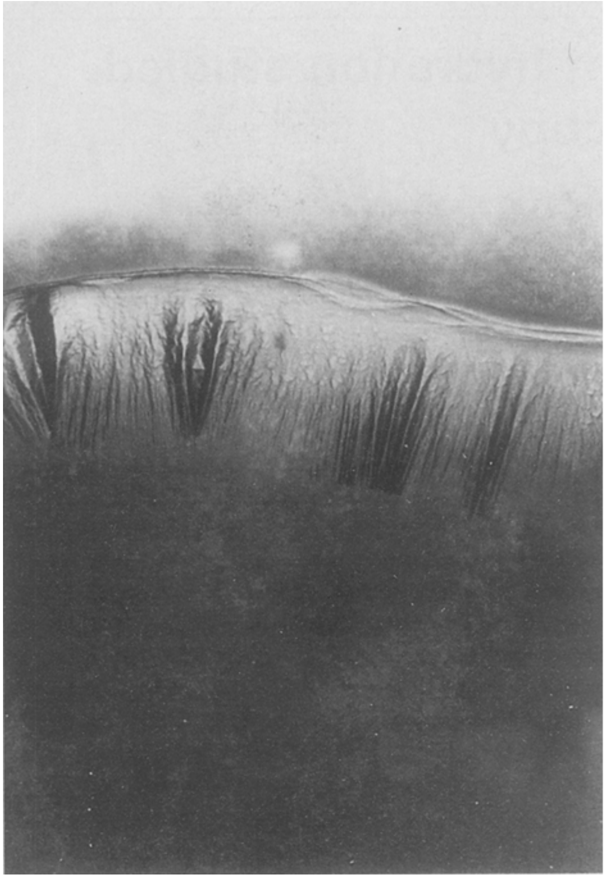

Figure 2 The soft, flexible membrane formed at the interface between solutions of Ca^{2+} and silicate anions. Puckering of the membrane illustrates its soft, flexible nature (optical microscope with immersion lens × 500). The conditions can be considered as reproducing the conditions at a C_3S/C_2S surface in which incongruent dissolution produces a low molecular mass silicate-rich surface in contact with calcium hydroxide solution.

a membranous sheath is observed to form around a crystal of either a M^{II} or M^{III} salt immersed in sodium silicate solution as shown in Fig. 3. Osmosis increases the pressure inside this membrane so that distortion and bursting releases the fluid within the membrane to form tubiform outgrowths, very reminiscent of the forms observed around hydrated cement grains, as depicted in Fig. 4. The various arguments supporting a membrane/osmosis model for Portland cement hydration are reviewed in reference [6].

There have been many microscopic studies [4, 7, 8] carried out over the years which have helped the understanding of the different hydration stages in the setting of cement. However, one of the problems with using conventional microscopy techniques, such as scanning electron microscopy (SEM) for example, is that observations are made in high vacuum. This dehydrating environment may destroy microstructural detail present in the normal wet condition with highly hydrated phases [9] and therefore, will not represent the natural state of hydrated cement. The development of the environmental SEM [10], has enabled samples to be imaged in the presence of water vapour. Meredith *et al.* [9] used such a technique to study the pre-induction and induction periods in the hydration of C_3S. They observed a thin amorphous,

Figure 3 Hydrous metal silicate, tubiform structures formed in a "silicate garden".

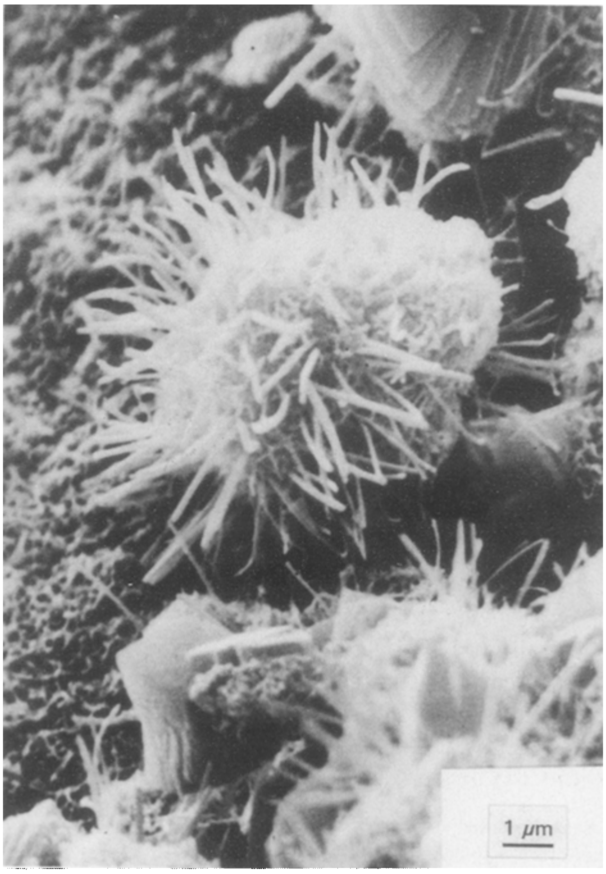

Figure 4 A hydrated cement grain at a W/C ratio of 0.6(× 4500).

membranous coating around a C_3S grain and showed that there was no significant microstructural change in the coating during the dormant period. However, they did not report on the microstructural changes that follow the end of the dormant period.

Another study has been carried out by Hall [11], who showed that atomic force microscopy (AFM) could also be used to observe surface changes of minerals during crystal growth, dissolution, adsorption or chemical reaction in aqueous environments. This technique differs from conventional microscopy techniques in that it uses a mechanical probe to feel and sense the sample surface in order to generate an image rather than use electron beams to create a magnified image. In particular, Hall demonstrated that Portland cement clinker could be imaged in water under ambient conditions. This set the basis for the current investigation. The purpose of this study was to demonstrate that the AFM could be used to study cement hydration in its natural environment during real time. We were also interested in observing the microstructural changes before and after the dormant period by modifying the solution in contact with the clinker surface.

2. Experimental section

2.1. Sample preparation

Samples of Portland cement clinker were obtained from Buxton Lime Industries Ltd. (see Table I for oxide composition) and cut into discs approximately 1 cm in diameter and 2 mm in thickness using a diamond saw. The underside of each specimen was sealed with a hydrophobic coating so that the hydrating liquid could not permeate through the porous cement clinker onto the optics of the AFM. Prior to examination, water was allowed to permeate and fill the porous clinker, the surface of which was then re-ground to expose anhydrous material, referred to as the dry, treated clinker surface from now on. The hydrophobic coating allowed the hydrating solution to be maintained in the AFM wet cell more easily, as it was found that samples previously not filled with water would absorb the hydrating solution from the wet cell. This created problems with the surface drying and image collection.

The aqueous phase in a normal cement/water mixture rapidly becomes saturated with respect to calcium hydroxide and to reproduce this, clinker sections were hydrated by immersion in saturated calcium hydroxide solution rather than in water to accelerate the hydration process.

TABLE I Weight percentages of the oxide components in the clinker

Oxide component	Weight(%)
Al_2O_3	5.05
SiO_2	21.11
CaO	62.93
Fe_2O_3	3.08
Free CaO	0.67
K_2O	0.85
Sulfur	0.39

2.2. Atomic Force Microscopy

A Nanoscope E contact AFM (Digital Instruments, Inc.) was used in this study. The D scanner (12 μm scan range) was chosen so that the scanner sensitivity gave atomic resolution [12]. Type 4 silicon nitride cantilever (a spring constant of $0.04\,\mathrm{N\,m^{-1}}$) was used so that the contact force between the tip and surface could be kept to a maximum and hence would not destroy any surface layers formed during hydration. A standard fluid cell [12] was used and no modifications to the set-up was required. All experiments were carried out at ambient conditions. Images were captured at regular intervals or after noticeable surface changes.

The following experiments were carried out using the AFM: (1) To examine a dry clinker surface pretreated as described above; (2) to observe the surface when immersed in a saturated calcium hydroxide solution as well as after the removal of this solution and its replacement with water; and (3) to image the surface immersed in a sucrose solution. This is of interest since it is known that the major components of Portland cement dissolve in sucrose solution [13]. No membrane can thus be formed as the clinker surface is etched.

3. Results

3.1. Hydration in saturated lime solution

The dry, treated clinker surface shows polishing striations (see Fig. 5(a) and (b)), which have destroyed the grain boundaries observed in samples which have not been polished. A rapid change in the nature of the surface microstructure was observed immediately after the saturated lime solution was introduced into the wet cell. Fig. 6(a) shows an image of this soft surface 20 min after exposure to saturated lime solution. A pore in the clinker surface can be seen in Fig. 6(a) (i.e. the darker region of the micrograph), but the area to the right of this pore clearly shows enhanced surface details. The section highlighted in Fig. 6(a) has been magnified and is shown in Fig. 6(b). From the image, the surface appears to be undulating. It is interesting to point out that the surface protuberances observed in Fig. 6(b) are similar in structure to the underlying surface of hydrated cement grains shown in Fig. 4.

It was also found that the "setpoint" (i.e. a voltage which is proportional to the constant contact force the tip exerts on the surface) had to be decreased and therefore the force required to obtain a reasonable image was reduced as well. This transition is consistent with a change in the nature of the clinker surface from a hard solid to a soft, readily deformed material. Table II shows typical changes in the setpoint voltage with hydration period. No image can be collected at the start of the experiment because it takes about 5 min to set up the AFM. It can be seen from Table II that after 15 min contact time, the voltage decreased

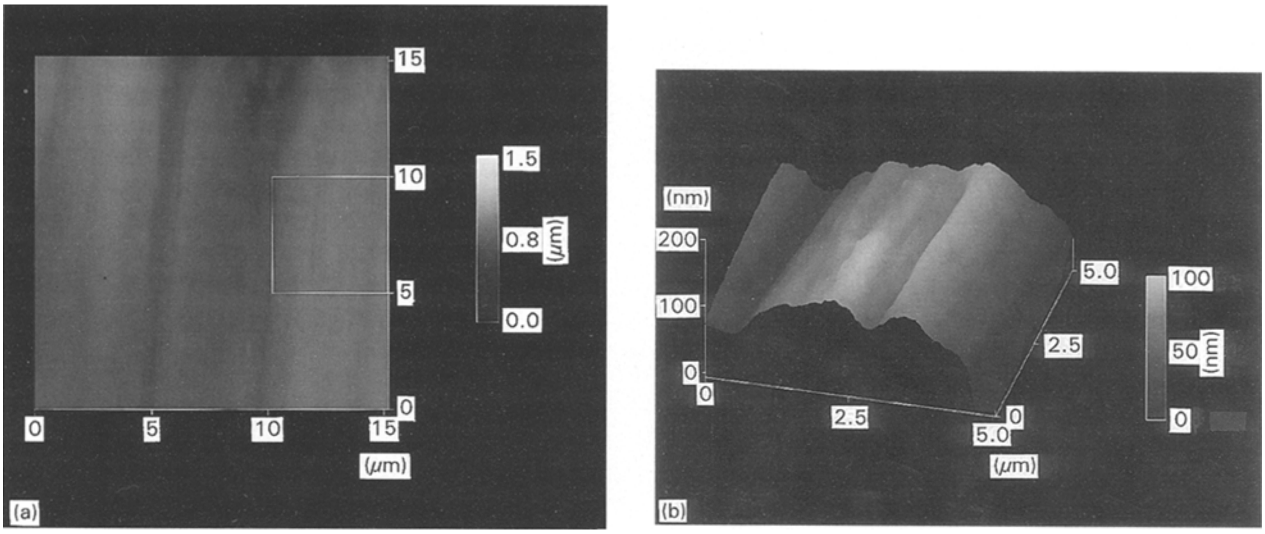

Figure 5 (a) An AFM image of the surface of a dry, treated clinker sample, and (b) enlarged area of the region outlined in (a).

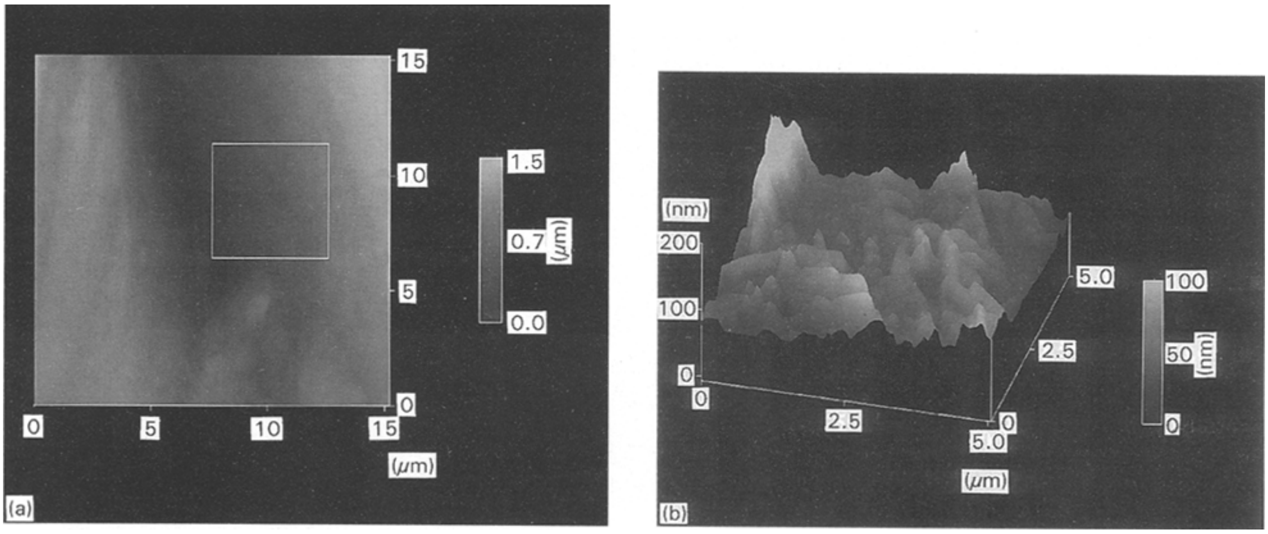

Figure 6 (a) An AFM image of the clinker surface after 20 min contact with a saturated lime solution; (b) area highlighted in (a) magnified in order to show the presence of an undulating CSH sheath.

TABLE II Changes in the setpoint value, a voltage proportional to the force the tip exerts on the surface, as a function of hydration time

Time in contact with lime (minutes)	Setpoint voltage (V)
0	–
5	− 5
12	− 7
20	− 9
45	− 7
240	− 7

from − 5 V to − 9 V, indicative of the surface becoming softer. Further evidence for the formation of a soft surface is that when a force greater than − 5 V was applied during the first 45 min of hydration, the image became streaked and image collection was poor. Thereafter, the setpoint was decreased to a constant value of − 7 V and remained at this voltage for 4 h, suggesting that the surface thickened with exposure to the saturated lime solution. There were no appreciable surface changes observed with the AFM images captured after 20 min and up to 4 h hydration in saturated calcium hydroxide solution. The times at which the setpoint voltages were changed experimentally on the AFM are similar to the times of the different cement hydration steps shown in the thermal history profile in Fig. 1. On the basis of this information, it was assumed that a soft and membranous surface had indeed been formed.

This being the case, the replacement of the saturated calcium hydroxide solution with water would be expected to provide an "osmotic kick", such that distortion/rupture of the membrane would occur, visible as eruptions and outgrowths. Although the soft membrane was found to form fully after 20 min hydration (see Table II), the saturated lime was withdrawn and replaced with water after 50 min, in order to ensure that the membrane had sufficiently developed. During the changing of the solution, the clinker surface was never allowed to dry *in situ*. It was observed that

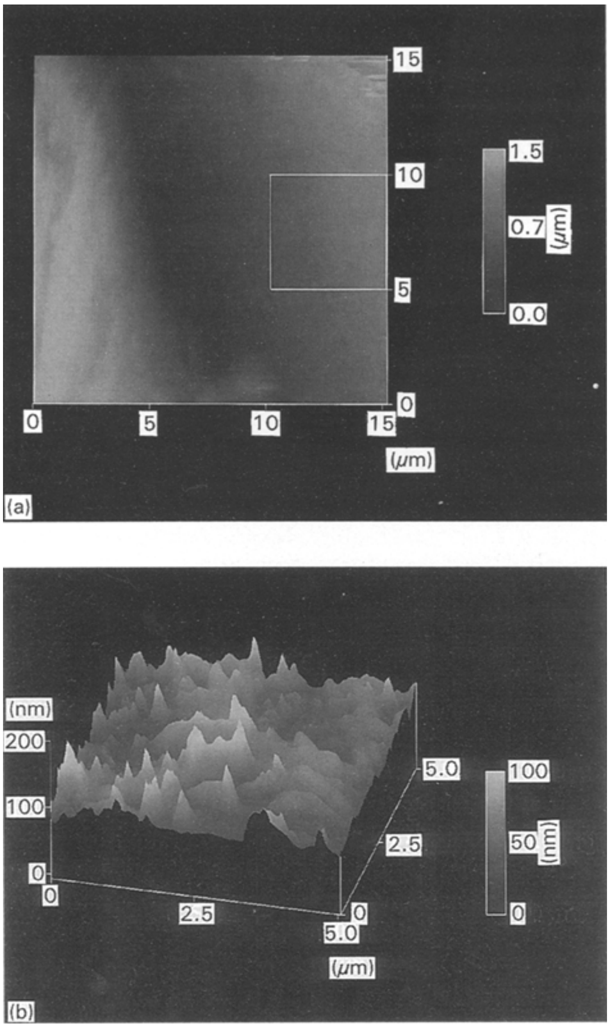

Figure 7 (a) The clinker surface 5 min after the calcium hydroxide solution was changed to water; (b) section outlined in (a) magnified, illustrating the effect of the "osmotic kick" on the CSH membrane. Note: The protuberances are clearly visible on the clinker surface.

changing the solution in contact with the clinker surface perturbed the surface microstructure, making comparison of similar areas before and after the "osmotic kick" irrelevant. It was also experimentally difficult to image exactly the same area on the clinker surface, as that shown in Fig. 6(a), due to thermal drift.

Fig. 7(a) shows an AFM image 5 min after the change from calcium hydroxide solution to water. The streaks in the figure and the fact that the setpoint was always at the lowest possible setting of − 10 V during the experiment, suggests that the surface is softer in nature after dilution with water. It is not evident from Fig. 7(a) that there is a significant microstructural change on the surface. However, magnifying an area as outlined in Fig. 7(a), shows that pronounced surface protuberances and excrescences have developed after dilution. It was also observed that the image became streaked after 15 min contact time with water, suggesting that the projections had grown and erupted, forming soft, flexible, raised structures making image collection impossible. For this reason, the continued growth of the projections observed in Fig. 4 could not be seen with the AFM.

3.2. Hydration in sucrose solution

It is known that sucrose inhibits the formation of solid phase of calcium hydroxide and CSH [13], so that C_3S and βC_2S phases dissolve congruently in sucrose solution. Sucrose is thus a hydration accelerator, although setting is retarded. Thus, in the presence of sucrose, no membrane can be formed and the major components of Portland cement (i.e. C_3S and βC_2S) dissolve to give high levels of Ca^{2+} and Si in the cement aqueous phase, with no dormant period. This was indeed observed to be the case, when a section of clinker was exposed to a 50 mM sucrose solution. Fig. 8 shows the surface of the clinker after 105 min immersed in the sucrose solution. Etching of the surface at the grain boundary interfaces is apparent with grains within the polygranular clinker becoming prominent. After 17 h of contact time with sucrose, these features become rounded as seen in Fig. 9. These observations support the conclusions of chemical studies [13], indicating that the major components of Portland cement dissolve congruently in sucrose solution.

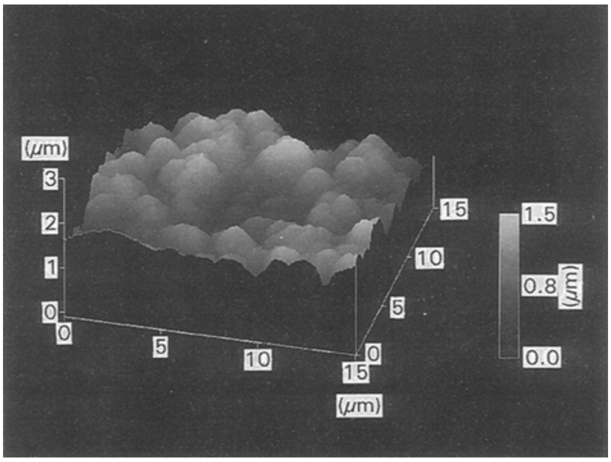

Figure 8 An image of a clinker sample after 105 min immersion in a sucrose solution. Individual grains are emphasized as grain boundaries are etched.

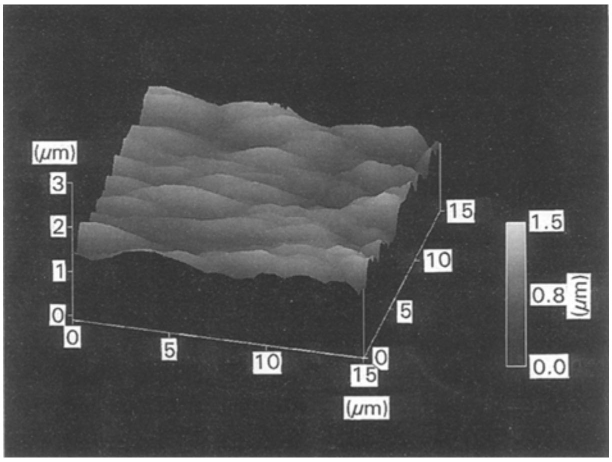

Figure 9 The clinker surface after 17 h exposure to a sucrose solution, showing a flatter surface with etched intergranular boundaries and smoother protruding grains.

4. Discussion

At least two observations within these experiments, using AFM, strongly support a membrane/osmosis model for cement hydration and subsequent morphological development. The first is the indication, from the changing scanning conditions (i.e. setpoint voltage), of the transformation of the clinker surface from a hard to a soft, deformable surface following exposure to saturated calcium hydroxide. The second is the dramatic development of surface features which rapidly follows the replacement of the saturated calcium hydroxide solution with water. It is difficult to invoke a conventional crystal growth mechanism to account for accelerated growth on dilution of a system, whereas rapid growth is predicted in a system in which the osmotic disruption of a semipermeable membrane is the driving force. The enhanced growth of hollow, tubiform excrescences from cement grains on dilution of the aqueous environment has been previously observed [14]. There is now a body of evidence [4, 5, 6] supporting the formation of a membrane and its osmotically-driven rupture, a key process in the initiation and end of the dormant period and much of the subsequent morphogenesis of hydrated phases.

AFM observation of the surface of Portland cement clinker immersed in sucrose solution provides a direct observation of dissolution of the material as indicated by grain boundary etching and by the gradual rounding of grain surfaces towards a progressively flatter topography.

5. Conclusion

These experiments demonstrate the utility of AFM as a means of directly observing events at Portland cement surfaces under realistic conditions. The technique promises to throw new light on hydration mechanisms and on the effect of additives. The present experiments lend support to membrane formation provoking the dormant period and to osmotic engorgement and membrane distortion/rupture as a fundamental mechanism responsible for the morphogenesis of the major binding phase, CSH. At the highest resolution in these experiments, the membranous material appears to consist of roughly spherical particles of the order of 10 nm diameter and thus accounting for its semipermeable nature (see also Fig. 2).

Acknowledgements

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