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Expansion mechanism and cementation in cured PFA–lime composites

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It gave me great pleasure to read the article by Wild *et al.* and it aroused my old interest in the structural habit of the hydration process. The present work has been designated a discussion, since it seems relevant to an understanding of the structures experienced in the work of Wild *et al.*, but it is more like a note, giving the Author the opportunity to air his *personal* views concerning the structural growth habit connected with cement hydration and silicate gardens.

Early researchers in the field of hydration suggested that colloidal particles of a small size were the building stones of hydration products, but the structural way in which they adhere together has only become clearer in the last decade. To my mind, one of the more interesting new discoveries within cement chemistry was the result of work by authors such as Double *et al.* and Birchal *et al.*,[1,2] who pointed to the special structural habit connected with 'silicate garden' growth. The growth of silicate gardens on the microscopic scale, which may be experienced by anybody possessing an optical microscope, is a spectacular sight which gives an insight into the mechanism of growth of structures connected with solid-state reactions of silicates.

The tendency to form small globular particles as a result of meeting with water is a characteristic of a wide range of silica or alumina-bearing hydraulic materials. The tendency of these particles to adhere together in the form of 'two-dimensional' elements (like sheets), envelopes around larger particles and tubular fibrils, results from favouring growth positions at the edge of growing structures, as opposed to adhesion at the plane.[3]

The tendency to form two-dimensional structures is again the reason for the ability to separate two opposing chemical domains. In silicate gardens these two domains are the inner and outer liquids separated by the enveloping membrane. The two domains, if mixed together by agitation, would result in the familiar random pattern of precipitated particles in aqueous suspension. The fact that envelopes are built from two-dimensionally adhering particles, prohibits such a 'first principle' chemical reaction, and is the key to understanding the dissipative structures connected with certain hydration mechanisms.[4]

When osmosis comes into play, the spectacular performance of structure-forming can take place. The route taken by the system, building up pressure due to osmosis, depends especially on the size of particles in the membrane. Small particles give rise to strong envelopes opposing the pressure build-up for a certain time, until some peculiar mechanism initiates bursting at points, leading to the fibrillar growth habit (Fig. 1).

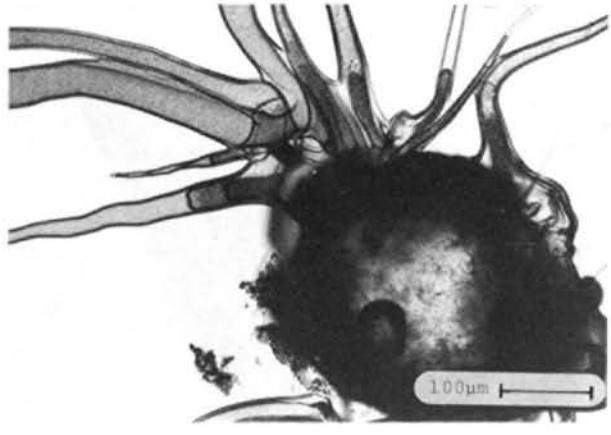

Fig. 1. Silicate garden seen under the microscope, by immersing a small crystal of dried ferrous sulphate heptahydrate in 20wt% sodium silicate solution (SiO_2/Na_2O = 3); the crystal appears as the dark sphere from which the fibrils grow

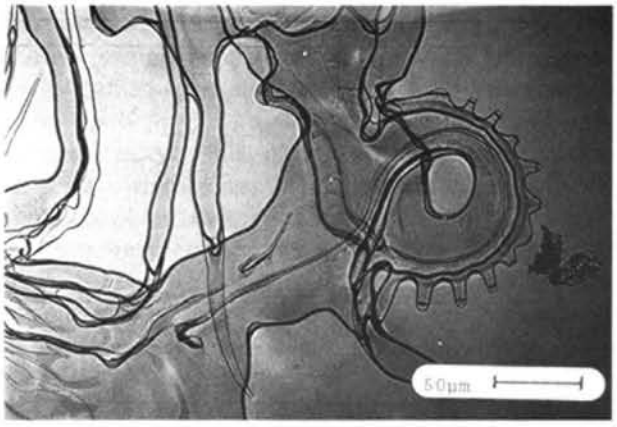

Fig. 2. Secondary fibrillar growth, away from the crystal (same composition as Fig. 1)

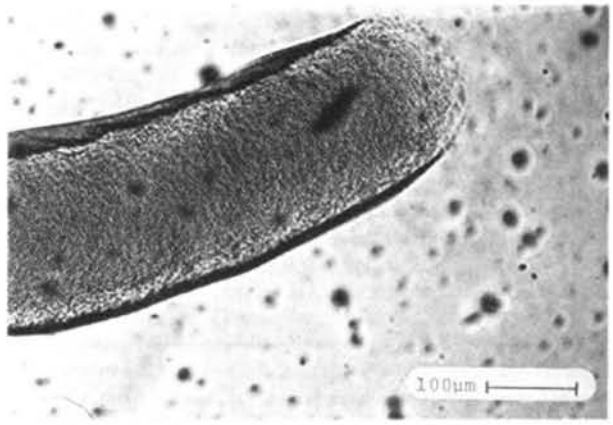

Fig. 4. Coarse colloidal precipitation with growth of large tubuls; ferrous sulphate heptahydrate in 5wt% sodium silicate solution

Weaker membranes, composed of larger particles, give way more easily and enlarge the membrane in a gradual way, retaining the spherical shape of the starting osmotic element. In between these extremes, structures of astonishing shapes may be seen (Figs 2 and 3).

In silicate garden experiments under the microscope[5] the fibrillar habit seems to dominate at the start, when the largest difference occurs in the chemical composition between inner and outer liquid; this results in precipitation of the smallest particles. At a later stage larger tubular forms, limited in numbers, begin their slower extension into the outer liquid. These tubes may be so large in the case of silicate gardens that they actually use the upper and lower glass walls as confinements of the streaming inner liquid, together with walls consisting of the large precipitated particles.

Owing to the weakened osmotic drive at this stage, and the large size of the particles, this is the right time to study the mechanism of tubular growth in detail (Fig. 4). The two liquids meet at the tip of the tube, resulting in a cloud of precipitated particles in the form of a half-sphere. Particles are of the Brownian size and can be seen to exhibit characteristic motion, in addition to following the macroscopic movement of the advancing cloud. Particles at the 'north pole' will at some later stage find themselves at the 'equator', and now comes the time to decide whether to contribute to the wall-building or to leave as independent particles randomly traversing the ocean. Whether to stick or to leave depends on how near the particle gets to the tube wall. The particles sticking are seen at the last stage to be dragged towards the wall, and once captured they irreversibly become members of the wall-builders. The particles, not near enough to the drag from the wall-end are left behind to join later the random 'glue-builders' which probably contribute the greatest portion of strength, in the context of cement hydration.

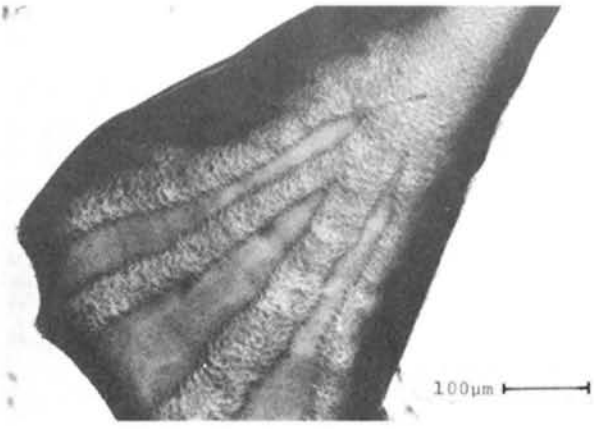

Fig. 3. Coarse colloidal precipitation around a ferrous sulphate heptahydrate crystal in 10wt% sodium silicate solution, giving rise to a 'duck-foot' pattern

In this picture there is no conceptual difference in topochemical growth and 'through-solution precipitation'. Some particles (maybe even the majority) are simply set free from the *statu nascendi* and coagulate at other places, depending on where they are taken by the random Brownian motion.

That abundancies of particles are set free is obvious from the beautiful tree-like pattern of colloidal particles adhering to the cover glasses. The structural habit of these coagulated precipitations is again proof of the preferential sites of adherence when these particles come together.

In one case the crystallization of a tree-like morphology was observed. The tree was amorphous from the beginning, as seen between crossed nicols. At a certain point the tree began to transmit light, as a result of incipient crystallization. The border between the amorphous and crystalline areas moved steadily ahead, and at the end the tree was completely ordered into one crystal. One amorphous particle after the other must have been pulled and reshaped so as to take part in the orderly pattern at molecular level called a crystal.

In my early days of physical chemistry I worked

with people on liquid models. I remember one saying 'If your model seems to work with water, forget about it. No model will ever picture the amazing capability of liquid water in forming liquid structures at the molecular level!'

Likewise I say 'If a theory tries to give a detailed account of what is going on during hydration at the colloidal level, forget about it. The structural behaviour of hydration is much too complicated for a model to be able to account for in detail!'

References

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Fig. 5. TEM micrograph of the reaction product from a PFA–20wt% lime–4wt% gypsum specimen cured for 18 hours at 90°C in 100% relative humidity

Reply by the author

I read the discussion contribution by Knudsen towards our paper with great interest. The analogy with silicate gardens is a very useful one in illustrating in a very elegant manner the way in which semi-permeable membranes develop and initiate osmosis, and the nature of the structures which develop. Also, the valuable early contributions by people such as Double and Birchall are often neglected by current workers in the field.

The observation by Knudsen that fine colloidal particles give rise to strong envelopes and that coarser colloidal particles produce weaker envelopes tends to be borne out by subsequent work carried out by myself.[1] That paper deals with the influence of gypsum on the microstructural development and expansion of cured PFA–lime mixes.

In that work we observed that the addition of calcium sulphate tended to promote membrane formation, osmotic swelling and expansion. The amount of expansion increased with an increase in gypsum content, up to a maximum value and then declined. In addition the amount of colloidal gel relative to fibrous gel also increased, and at high gypsum contents the size of the colloidal particles increased.

Also, we frequently observed tubular structures characteristic of those referred to by Knudsen as being typical of an osmotic process. The TEM micrograph in Fig. 5 below shows such tubes in the reaction product from a PFA–(20wt% lime)–(4wt% gypsum) specimen cured for 18 hours at 90°C in 100% relative humidity.

Although our work positively confirms that the presence of calcium sulphate in such systems promotes membrane development and the formation of globular colloidal particles, it does not explain the chemistry of this process and why it occurs. Possibly the final statement of Knudsen's discussion contribution should deter us from asking this question.

Reference

1. WILD S. *et al.* The influence of gypsum content on microstructural development, strength and expansion of cured PFA–lime mixes. *Adv. Cem. Res.*, 1990, **3**, 153–166.