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Studies of the growth of "silicate gardens" and related phenomena

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Various growth morphologies obtained in "silicate gardens" are described and the influence of salt type and silicate concentration are examined. It is demonstrated that these growths develop by an osmotic mechanism based on the semipermeable properties of the silicate gel membrane precipitated between the metal ion and the silicate. The osmotic effect is not confined to silicates but also includes aluminates and ferrocyanides – and in general, it probably applies to systems where a continuous colloidal gel membrane is precipitated between two aqueous solutions of differing compositions. The implications in relation to certain practical problems (i.e. the hydration of Portland cement, the corrosion of metals in an aqueous environment) are considered.

1. Introduction

Many people will be familiar, if only as a diverting experimental exercise, with the fascinating forms of growth that occur in so-called "silicate gardens" – obtained when sodium silicate solution (water glass) is seeded with crystals of a variety of water-soluble metal ion salts. The experiment has often been described in chemical textbooks (as much for its curiosity value as anything else, see, for example, Sherwood Taylor [1]) and it is clear that the effect has been known for many years. Source references to systematic studies on these growths are, however, difficult to trace. One of the first of these would seem to be the article by Clunies Ross published in 1910 which sets out the recipe for producing such gardens and describes, in almost botanical terms, the types of growth obtained from more than twenty different metal ion salts [2]. More importantly, a mechanism is proposed to explain the phenomenon. This is seen as an osmotic process depending on the semipermeable character of the gelatinous membrane precipitated around the seed crystal when it comes into contact with the silicate solution.

Experiments by Hazlehurst [3] confirm these observations and also make the point, previously noted by Copisarow [4], that similar "structural precipitates" can be obtained not only from silicate solutions (although these produce the most striking effects) but also from alkaline solutions of oxyanion species such as aluminates, borates, zincates, stannates, phosphates, chromates and from ferrocyanide, oxalate and even sodium carbonate solutions. In spite of this apparent chemical diversity, the common feature would seem to be the precipitation out of solution, by combination with the metal ion of the seed salt, of a coherent and continuous membrane which, by virtue of its colloidal gel character, has inherent osmotic properties.

Clearly, one is not dealing with a conventional crystal growth problem such as is normally encountered in the precipitation of solids from aqueous solution – nor should the effect be treated simply as a curiosity piece. It is perhaps surprising that so little work has been done to investigate these growths more thoroughly since they provide a relatively simple and, certainly, very graphic method of obtaining information about the chemical and physical properties peculiar to inorganic colloidal gel systems. This article seeks to remedy the situation to some extent and also attempts to show how these studies could provide some insight into more obviously practical problems which involve precipitation of colloidal matter from aqueous solution – notably in the hydration of Portland cement and in the corrosion of metals in aqeous media.

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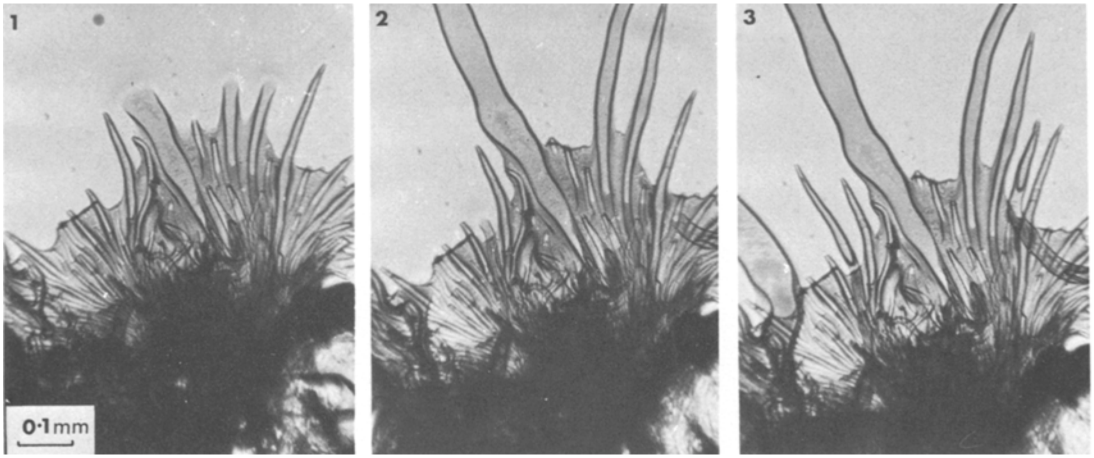

Figure 1 Sequence showing the development of a "silicate garden" from a crystal of cobalt nitrate immersed in dilute aqueous sodium silicate solution. Optical micrographs at 10 sec intervals.

2. Silicate gardens

2.1. Growth morphologies

The typical growth sequence of a silicate garden is illustrated in Fig. 1. In this instance, the seed crystal is cobalt nitrate and the pictures are obtained from a cell comprising two glass cover slides sealed round their outer edges and viewed in the transmission optical microscope. The sodium silicate solution* (diluted 1:5 with water) is injected into the cell with a hypodermic syringe, the seed crystal being previously sandwiched between the glass slides.

When the crystal becomes immersed in the aqueous silicate solution it begins to dissolve and, almost simultaneously, is enveloped by a gelatinous coating of precipitated hydrous cobalt silicate. After a short induction period, the envelope is observed to swell and burst open intermittently and, from the points of rupture, develop thin fibres which on close inspection are seen to have tubular cross-sections. These tubes may grow to lengths over a hundred times their initial diameter if allowed to develop freely. They tend to taper in diameter as they increase in length and eventually close to a point. The intermittent rupture of the coating and subsequent fibrillar growth continues until the seed crystal is completely dissolved within the initial gel envelope. The radial pattern of growth emanating from the original seed has an almost organic appearance and the term "garden" in this context seems a very appropriate description.

A wide variety of water-soluble metal ion salts (except those of group 1A of the Periodic Table) show this type of growth although, depending on the conditions, the rate of growth and size and shape of the excrescences may differ considerably. Variables include the cation/anion type and the concentration of the silicate solution. The latter is an important factor. As Fig. 2 illustrates, for a given salt type there is an optimum range of concentrations that produces the capillary growth most effectively. In concentrated solutions of silicate, a dense, tight-fitting shell is formed around the seed crystal and this seems to rupture only with difficulty to produce secondary growths. At the other extreme, as the solution is made more dilute, the gel membrane takes on an increasingly "elastic" character. Fibrillar growth gives way to globular excrescences formed by repeated rupture and rehealing of the gel coatings (Fig. 3). Finally, with increasing dilution, there comes a point where the precipitated material fails to cohere properly and instead forms a flocculent spongy mass around the dissolving seed crystal.

The relative effects of permutations in the cation and anion type of the seed crystal are difficult to categorize in any systematic manner, even on a qualitative basis. However, under equivalent conditions (of silicate concentration, temperature, etc.), differences in the pattern of growth are observable. The identity of the metal ion of the salt seems to be a dominant factor in determining the morphology, scale and rate of growth of the fibrous material. This is perhaps not surprising since the initial membrane and the secondary growths are formed by precipitation between the

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*B.D.H. sodium silicate solution (S.G. 1.54) which contains a range of silicate species, largely *ortho*- and *meta*-silicate.

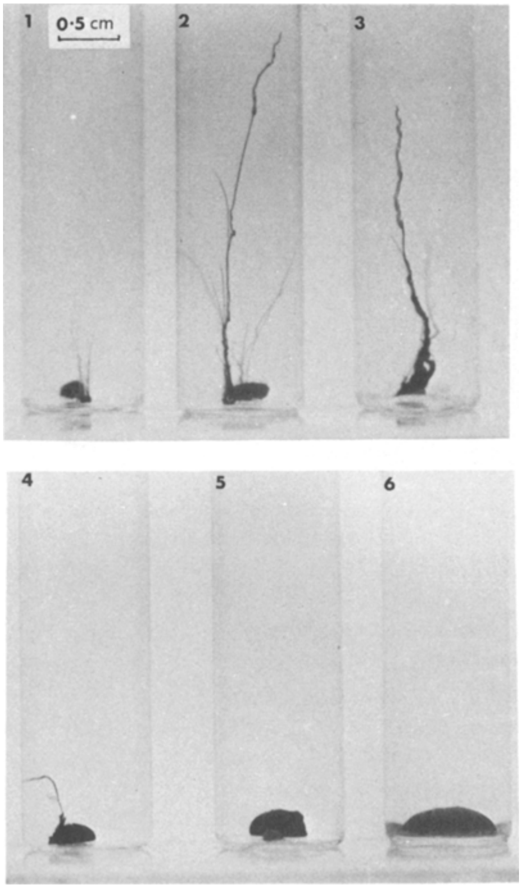

Figure 2 "Silicate garden" growths from cobalt nitrate crystals in sodium silicate at different concentrations. Water glass (7 M with respect to silica) was diluted by the following amounts: $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$, $\frac{1}{64}$.

metal ion and the silicate in solution. Changes in the metal ion type must necessarily alter not only the chemical character but also the physical properties of the precipitated material. Thus, for example, while cobalt salts tend to produce relatively coarse regular fibres, other salts such as those of Cu and Fe often give a dense mass of very much finer, hair-like fibres (Fig. 4). The scanning electron micrographs in Fig. 5 show the microstructure of these tubular fibres in greater detail. Other types show very convoluted forms of fibrous growth often with branched junctions, and in some cases rope-like arrangements consisting of a number of intertwined fibres (Fig. 6). In salts with a common metal ion but differing anionic species, the pattern of growth seems to be rather similar in each case, although differences in the rate of growth are distinguishable. To some extent, this effect may be attributable to differences in the aqueous solubility of the crystals in question. In any case, the detailed processes by which these growth forms develop must involve a complex series of interacting effects.

The scanning electron micrographs in Figs. 5 and 6 show that the fibres have a closely knit granular texture on a fine scale. X-ray diffraction on a variety of fibres prepared in this fashion gives no sharp reflection peaks but a diffuse background scattering consistent with a colloidal material of largely amorphous character. For a calcium-silicate coating, transmission electron microscopy of a fragment (Fig. 7) shows it to be composed of a coagulated mass of small rounded particles with

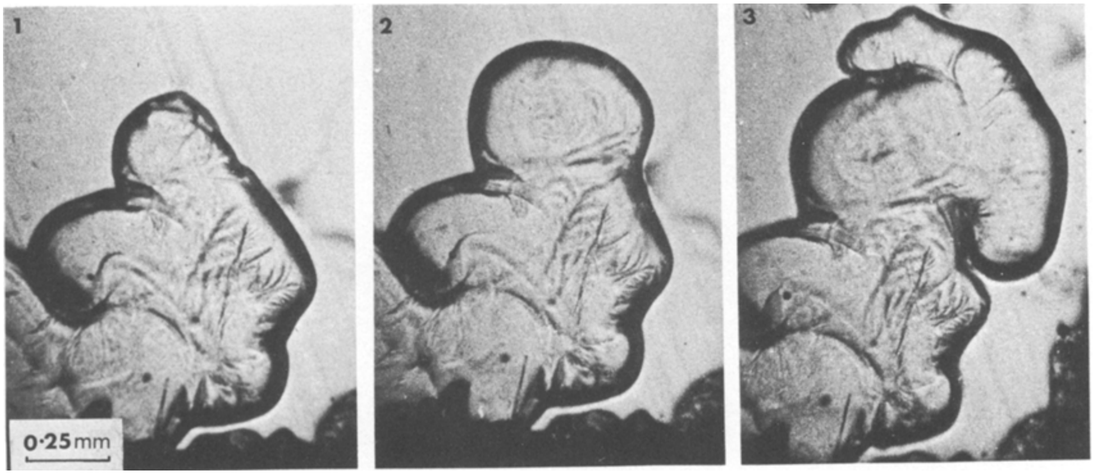

Figure 3 Sequence showing globular growths from an expanding gel envelope around a calcium chloride crystal immersed in dilute aqueous sodium silicate solution. Optical micrographs at 2 sec intervals.

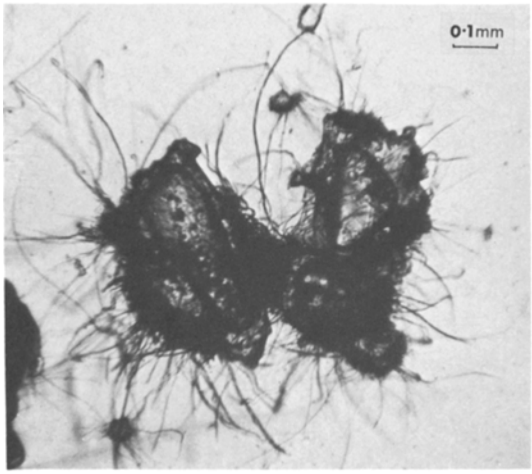

Figure 4 Fine hair-like fibres grown from ferrous sulphate immersed in dilute aqueous sodium silicate solution. Optical micrograph.

sizes ranging from about 200 to 1000 Å diameter. Whether these particles themselves are made up of smaller adhering units is not clear.

Chemical analysis of growths obtained in silicate gardens and of precipitates formed by combination of aqueous solutions of the salt and of sodium silicate, indicate that the compositions (metal ion to silicate ratio) are variable. Indeed it has proved impossible to obtain reliable estimates of the compositions because of the tendency of the constituents to leach out during repeated washing of the precipitates. Clearly, one is not dealing with chemical components of fixed and reproducible stoichiometry.

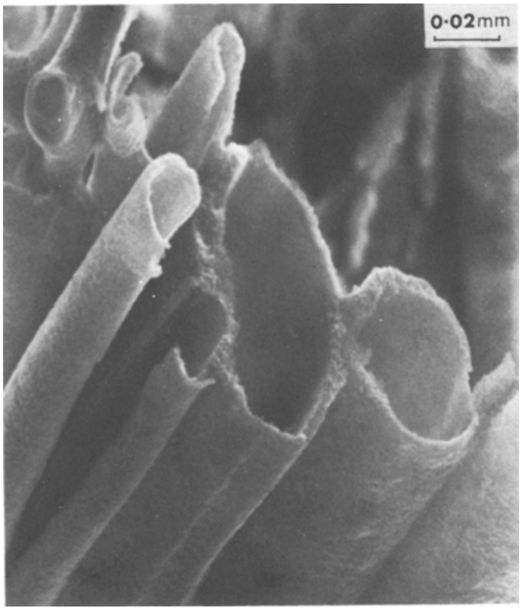

Figure 5 Scanning electron micrograph showing hollow fibres in a "silicate garden" grown from ferrous sulphate and dilute sodium silicate solution.

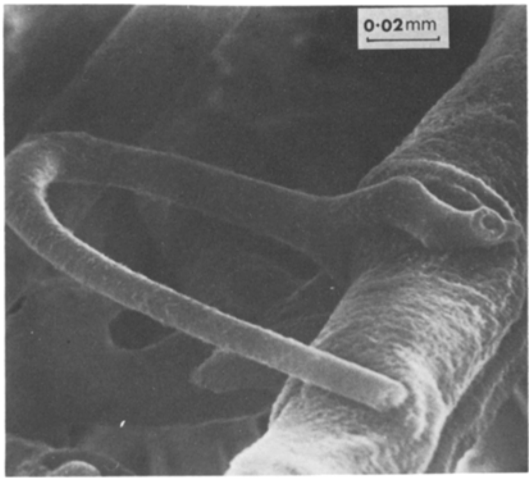

Figure 6 Branching of fibres in a "silicate garden" grown from ferrous sulphate and dilute sodium silicate solution. Scanning electron micrograph.

2.2. Osmotic driving force for growth

As has been noted, Clunies Ross proposed an osmotic mechanism to explain the growth of silicate gardens [2]. The essential point is that the colloidal gel envelope formed on first contacting the seed crystal with the silicate solution, has semipermeable properties. Since this membrane separates two solutions of different compositions and

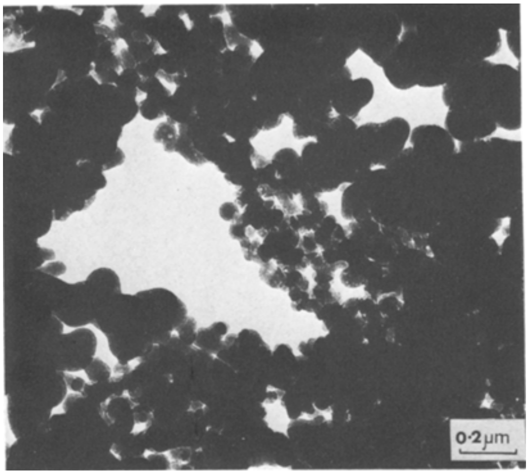

Figure 7 Transmission electron micrograph of calcium-silicate-hydrate gel formed from calcium chloride in 1.2 M sodium silicate solution.

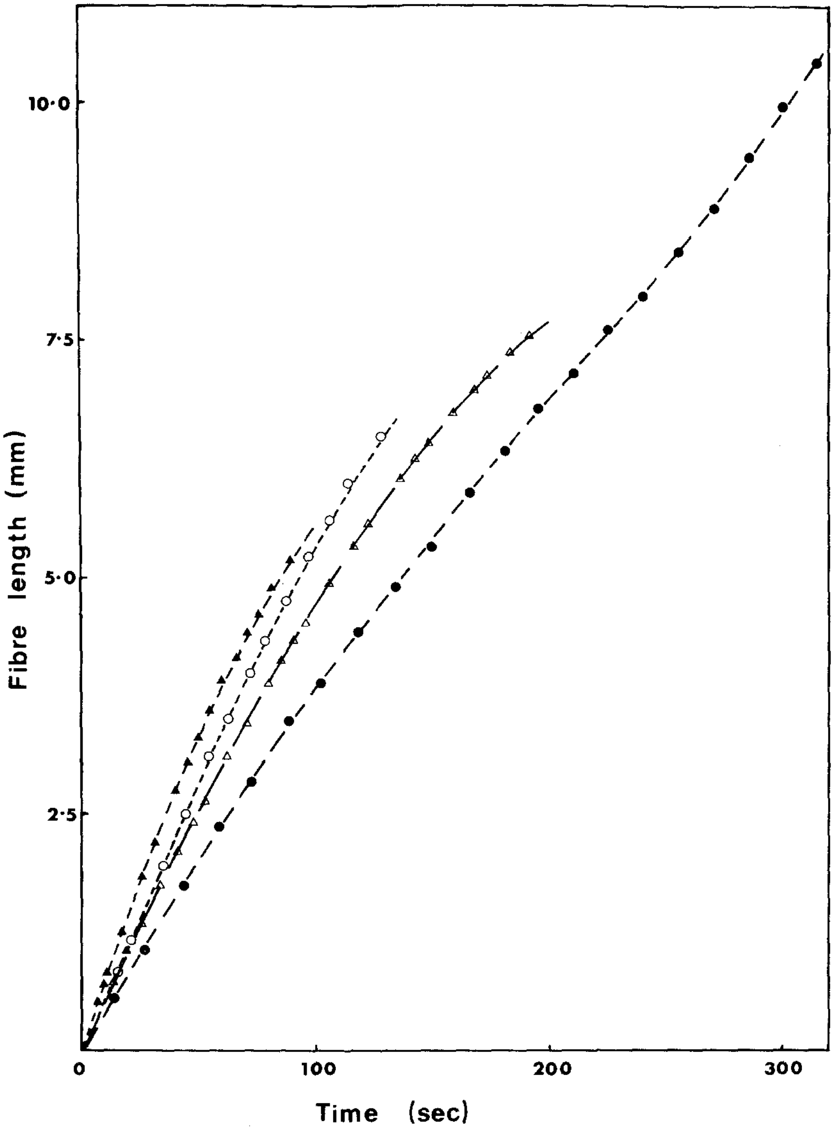

Figure 8 Fibre length as a function of time for a silicate garden grown from cobalt sulphate crystals in 1.2 M sodium silicate solution.

concentrations (a concentrated solution of the metal salt inside, a dilute solution of sodium silicate outside) preferential inward diffusion of water will give rise to an osmotic pressure within the envelope. Eventually, the envelope is ruptured locally at weak points and jets of solution from the dissolving seed crystal are ejected into the surrounding silicate solution. If the conditions are right, secondary precipitation of the hydrous metal ion silicate occurs as a continuously growing tubular wall. The initial membrane acts as an "osmotic pump": the seed crystal continues to dissolve, the salt solution flows up the tupe and precipitation occurs by an almost steady state process at the periphery of the tube at the end remote from the original seed crystal.

To obtain a regularly shaped tube obviously requires the establishment of particularly stable conditions (solution concentration profiles, flow rate, etc.) at the growing tip. Any tendency for the end of the tube to be blocked by precipitated material during growth would give rise to convoluted and irregularly branched forms. Extreme non-steady-state forms are exemplified by globular growths such as those illustrated in Fig. 3. Once a tube has been established, its subsequent rate of growth and probably also its diameter will be determined largely by the rate of flow of the solution up the tube. For a given osmotic pressure differential, one would expect that as the tube extends in length, increased viscous drag within the capillary would

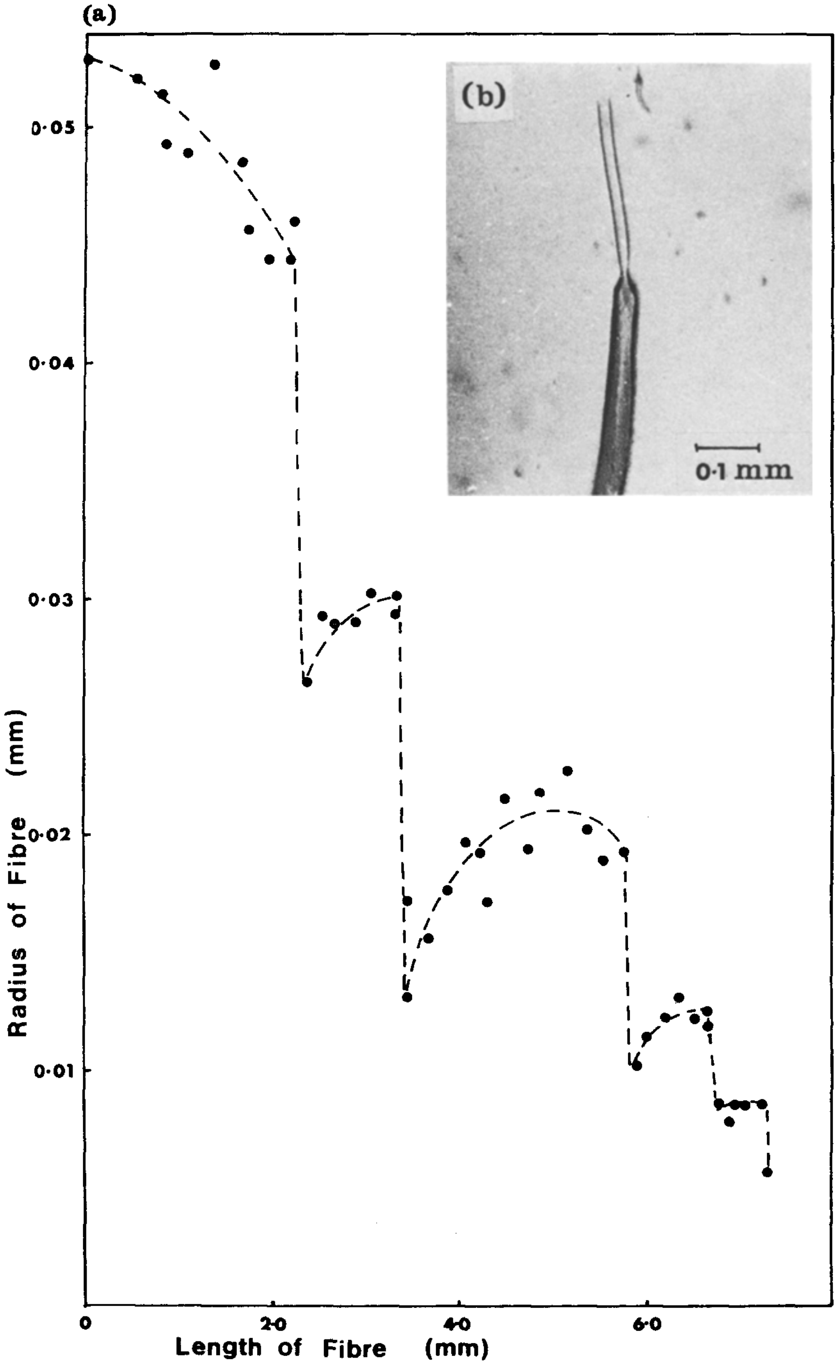

Figure 9 (a) Graph showing a stepped reduction in fibre radius with increasing length, for a silicate garden grown from cobalt sulphate in 1.2 M sodium silicate solution. (b) Optical micrograph illustrating the reduction in fibre diameter.

decrease the flow rate (according to a Poisseuille-type relation) leading to a slowing down of growth with concomitant reduction in diameter of the tube. In practice, however, the situation is complicated by variations in the osmotic driving pressure within the initial gel envelope. The graph in Fig. 8 shows that, in general, there is a reduction in growth rate with time, but clearly the effect is not readily quantifiable. Although in most cases the diameter of the tube decreases regularly with length, in some instances one observed sudden reductions in diameter giving a stepped or shouldered appearance to the tube (Figs. 9a and b). These occur because of sudden drops in the flow rate

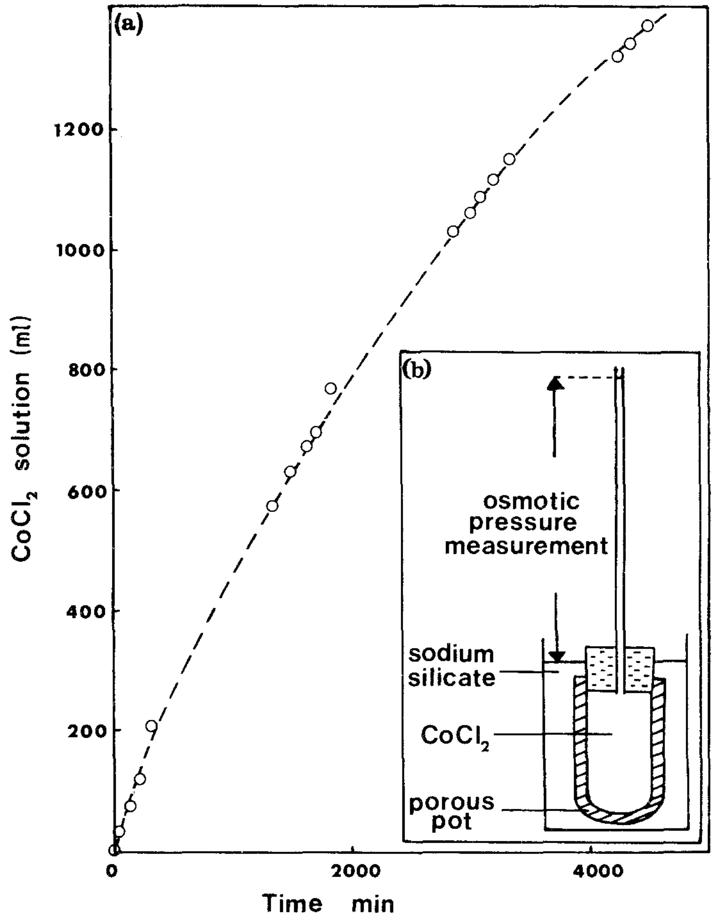

Figure 10 Pfeffer experiment to illustrate the semipermeable nature of the colloidal gels. (a) Graph showing pressure rise as a function of time. (b) Schematic diagram of apparatus used.

brought about by the release of internal pressure when new growths are nucleated by ruptures in the primary envelope.

The osmotic activity of the precipitated gels can be demonstrated by an experiment similar to that originally designed by Pfeffer (see Taylor's Treatise on Physical Chemistry [5]). Instead of the conventional copper ferrocyanide, a membrane of the metal ion silicate is precipitated within the walls of a porous clay pot. The pot is filled with a concentrated solution of the metal ion salt and sealed with a stopper into which is inserted a long vertical capillary tube. The pot is then placed in a bath containing aqueous sodium silicate solution and, after allowing for pressure and temperature equilibration, the differential diffusion through the membrane is measured by the rise in liquid level within the capillary tube (Fig. 10b). The results of such an experiment are shown in Fig. 10a. There, the rise in liquid level corresponds to the development of an osmotic pressure of about $\frac{1}{6}$ atm and from the graph it is clear that the pressure is still rising after 75 h. Attempts to measure pressures much higher than this invariably failed because of leaks that eventually developed in the membrane within the porous pot. The experimental arrangement is, in a sense, a large-scale model of a silicate garden and the observations would seem to confirm the correctness of the mechanism proposed by Clunies Ross.

3. Other related systems

Since the development of an osmotic pressure depends on the difference in chemical potential of species in solution on either side of a membrane, it is perhaps not surprising to find that, by adjusting the concentrations appropriately, equivalent growths can be obtained when the constituents in a silicate garden are reversed, i.e. when a grain of soluble silicate is immersed in a dilute solution of the metal ion salt. The example in Fig. 11 shows both globular and tubular growths from a calcium-silicate "reverse" garden. The splitting and collapse of the envelopes evident in the micrograph are effects due to drying of the specimen under vacuum.

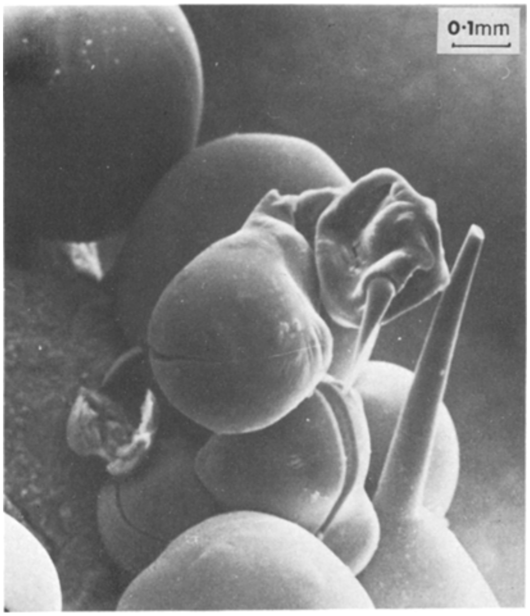

Figure 11 Scanning electron micrograph of globular and tubular growths in a "reverse silicate garden" grown from sodium metasilicate crystals in 0.5 M calcium chloride solution.

A more interesting variation is an "aluminate garden" obtained when a salt crystal is immersed in dilute sodium aluminate solution. In the example in Fig. 12, the rupturing of the membrane has not led to secondary tubular growths but has caused surface eruptions leaving a pockmarked/cratered effect. A tubular growth in a reverse aluminate garden is shown in Fig. 13a. The outer surface of the tube is covered by irregular foil-like material (Fig. 13b) which is identifiable by X-ray diffraction as a crystalline calcium aluminate hydrate. It seems to be the case in these aluminate gardens that the gelatinous calcium aluminate first precipi-

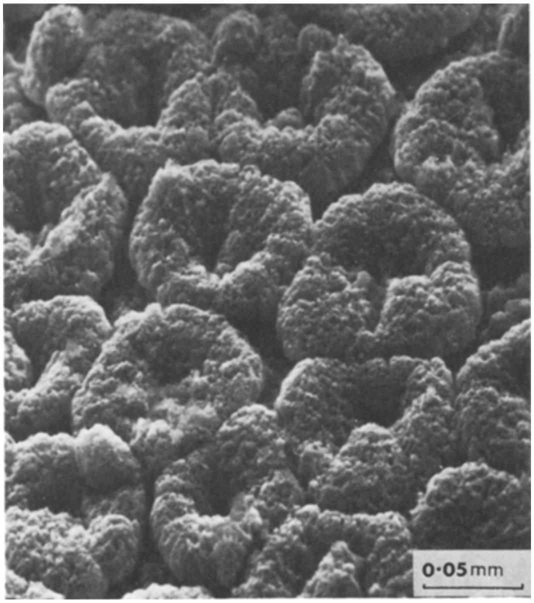

Figure 12 Scanning electron micrograph of an "aluminate garden" from calcium nitrate crystals in 0.6 M sodium aluminate solution.

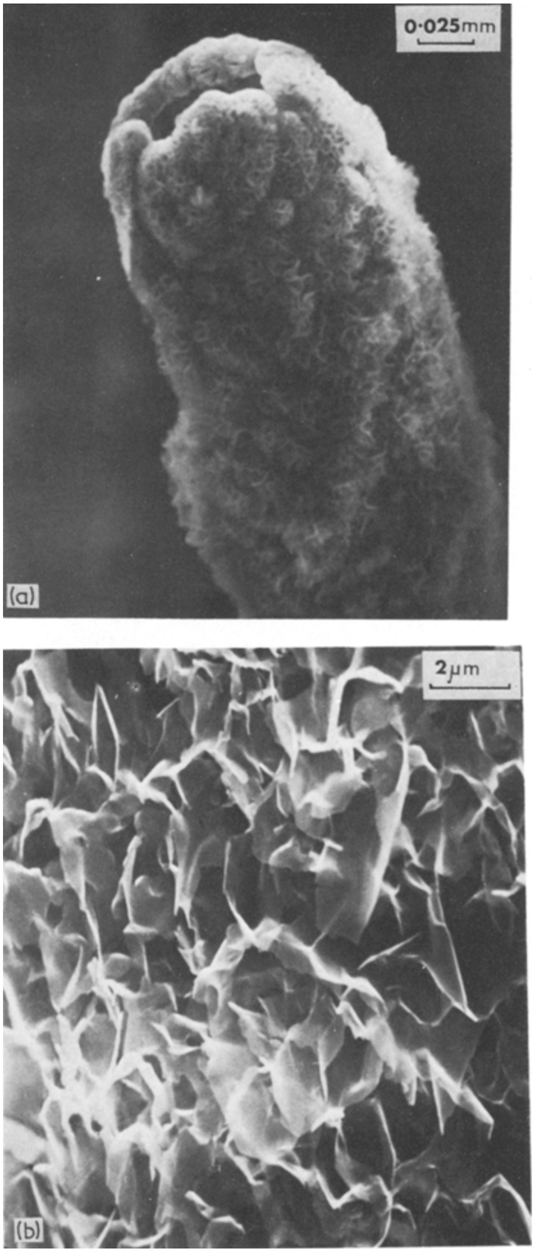

Figure 13 Scanning electron micrographs from a "reverse aluminate garden" from sodium aluminate crystals in 0.2 M calcium nitrate solution. (a) Tubular growth. (b) Detail of foil-like material on the surface of the tube.

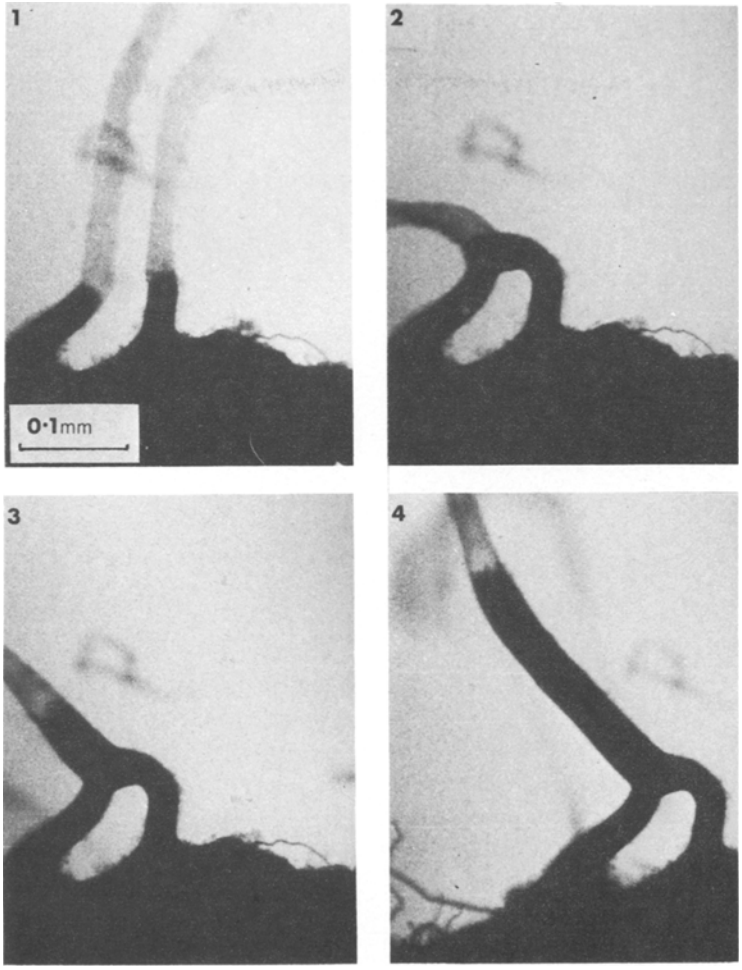

Figure 14 Sequence showing the growth of tubes from the surface of a mild steel plate immersed in a solution of potassium ferrocyanide and sodium chloride. Optical micrographs taken at 2 sec intervals.

tated rapidly crystallizes *in situ* as growth proceeds. This tendency towards crystallization presumably destroys the membrane character of the original gel and it is possibly for this reason that the aluminate gardens do not grow as effectively as silicate gardens – the latter retaining their colloidal fine structure even on standing for long periods.

Finally, to illustrate the range of chemical conditions that can produce these types of growth, in the ciné sequence of Fig. 14 are shown two tubes (subsequently joining to form a single tube) growing off the surface of a polished plate of mild steel immersed in aqueous potassium ferrocyanide solution. The solid material precipitated is a colloidal ferri-ferrocyanide and the process by which the tubes grow is evidently much the same as occurs in the case of silicate gardens.

4. Discussion

The feature that these systems have in common is the precipitation out of aqueous solution of a membrane which has selectively permeable properties. In silicate systems, the variability in chemical composition implies no fixed chemical identity and precipitates of this type are probably best described as "mixed hydrous oxides" of the metal ion and the silica [6]. Britton [7] found a close correlation between the pH at which an insoluble metal silicate is precipitated and the pH of hydroxylation of the cation, i.e. a metal ion will not combine with silicic acid at a pH much below that at which its hydroxide is formed.

The fact that a range of chemical combinations can produce the effect would seem to indicate that the inherent osmotic activity is not so much due

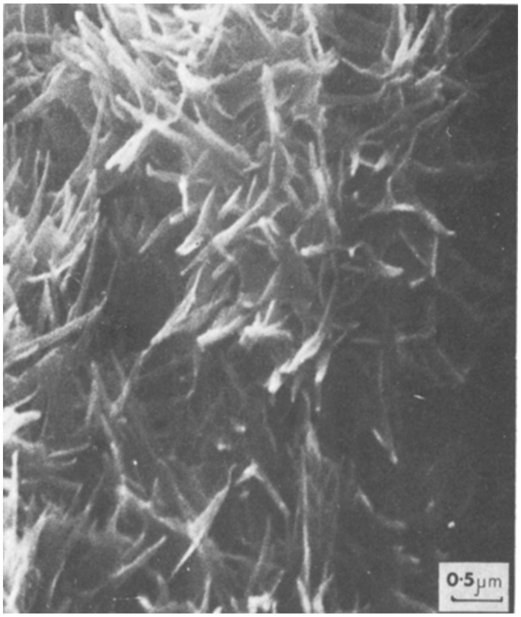

Figure 15 Scanning electron micrograph showing fibrillar growth produced during hydration of tricalcium silicate – the major constituent of Portland Cement.

to the particular chemical composition but rather to the physical characteristics of the precipitated material – essentially, the coagulation of very fine particles (with large surface areas and unsatisfied surface forces) into a coherent solid which can act as a selective "sieve" between solute and solvent species in aqueous solution.

Two practical examples where one might be concerned with situations like this are in the corrosion of metals in aqueous solutions and in the hydration of cement. It is beyond the scope of this work to try to elaborate on detailed processes which might be involved in these reactions, but it is worth noting that the sequence in Fig. 14 illustrates what is essentially a corrosion process. It sometimes appears to be the case that the corrosion products formed on the surface of a metal are colloidal in character and continued reaction requires (a) some kind of preferential diffusion process through this protective skin, and (b) the spalling of the skin from the metal by pressures generated within it, to expose fresh metal to the aqueous environment. It is interesting to speculate whether such pressures might have an osmotic origin, by virtue of the membrane character of the protective skin.

The main consituents in Portland cement are reactive calcium silicates which combine with water to form an ill-defined colloidal calcium-silicate-hydrate gel (conventionally referred to as C-S-H gel). This gel, by progressively filling the spaces between the cement grains, forms a cohesive matrix that gives rise to the development of strength of the paste. In many cases, the C-S-H gel grows from the surface of the cement grains as interlocking fibres (Fig. 15) which apparently have a tubular cross-section on a fine scale. The development of osmotic pressure within the C-S-H gel coating surrounding the individual cement grains has been postulated as a driving force for the hydration reaction [8] and mechanisms have been proposed to explain the hydration sequence and morphological development of the hydrate by an osmotic mechanism invoking analogies with the processes occuring in the growth of silicate gardens [9–11].

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