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# Microstructural analysis of hydrated alite paste

## Part 2 *Microscopy and reaction products*

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The distribution and composition of the products of hydrating alite have been studied using a backscattered electron detector in a scanning electron microscope. Polished surfaces of specimens were examined and analysed quantitatively. Calcium hydroxide forms in the available water filled space. Calcium silicate hydrate appears to have several distinct morphologies, and their fomation can be associated with the different stages of the reaction. These observations are compared with classification schemes derived from fracture surfaces which heretofore have been the usual kind of specimen examined.

## 1. Introduction

Complete microstructural evaluation of hydrating cement systems should include quantitative measurement of features such as volume and morphology of all phases present, as well as information about the spatial relationship of solid reactants and products. For example, a question arises whether there is a difference between the structure of calcium silicate hydrate (C-S-H) that forms (i) inside and (ii) outside of the original alite grains. Although some results [1] suggest that there is a difference between "inner" and "outer" product, this has not been confirmed [2]. There is a related question of whether or not there is a difference in structure between product formed early and late in the reaction [1]. Fig. 1 illustrates the difference between these two reaction scenarios. Either different product types are separated by a boundary which is defined by the original anhydrous particle surface, Fig. 1a, or by the surface of the smaller particle which remains after hydration has consumed some of the original particle. We have studied both of these questions.

The composition of C-S-H has also been studied [2–13] using electron microscopy and although Ca : Si values average about 1.7, values range between 1.4 and 1.9. A possible explanation [2, 9, 10] is that tiny calcium hydroxide crystals are intermixed with C-S-H having a low Ca : Si ratio ($\sim 1.4$), and the measured value, therefore, depends on how many $Ca(OH)_2$ particles are included in an analysis. Other types of measurement [2] of the amount of $Ca(OH)_2$ produced from a given amount of tricalcium silicate, however, imply through stoichiometry that the C-S-H should have a Ca : Si ratio of between 1.7 and 1.8. This precludes the necessity of incorporating $Ca(OH)_2$ into C-S-H to account for measurements of high Ca : Si ratio, but means there must be present some C-S-H which has a low Ca : Si ratio to account for observed low Ca : Si ratios.

Many microscopic studies of fracture surfaces have attempted to characterize the microstructure of hardened cement pastes. Based on these studies classification schemes have been proposed for products formed during the hydration of tricalcium silicate ($C_3S$) [1] and Portland cement [14]. In the past, however, due to difficulties with imaging phases of cement from a polished surface, quantitative information about spatial distribution of products, which depends on a polished surface, has been lacking.

This paper reports results of a microstructural study of hydrating alite (impure tricalcium silicate) using backscattered electrons from a polished surface. In addition to providing a basis for quantitative image analysis these results give information on both morphology and chemical composition. They are compared with results obtained from observations of conventional fracture surfaces.

## 2. Experimental details

Both the materials used and the characterization of porosity are described elsewhere [15, 16]. The water : solids ratio is 0.59. Thermogravimetry was used to estimate the quantity of $Ca(OH)_2$ and quantitative X-ray analysis was used to estimate the quantity of alite. Additional techniques used in this investigation are as follows. The polished surface was examined in a SEM as follows: (i) directly, or (ii) after the cementitious material was lightly etched for 3 sec with ethanol containing 1% $HNO_3$. A Robinson backscattered electron detector was used in conjunction with a 30 keV electron beam. Micrographs obtain their contrast from differences in average atomic number and, therefore, different phases have different brightness. X-ray fluorescence has confirmed the following (see Appendix for explanation of brightness and composition): light greys are $C_3S$, medium greys are $Ca(OH)_2$, darker greys are C-S-H, and the darker areas are the epoxy used to impregnate the specimen. Fracture surfaces were also prepared.

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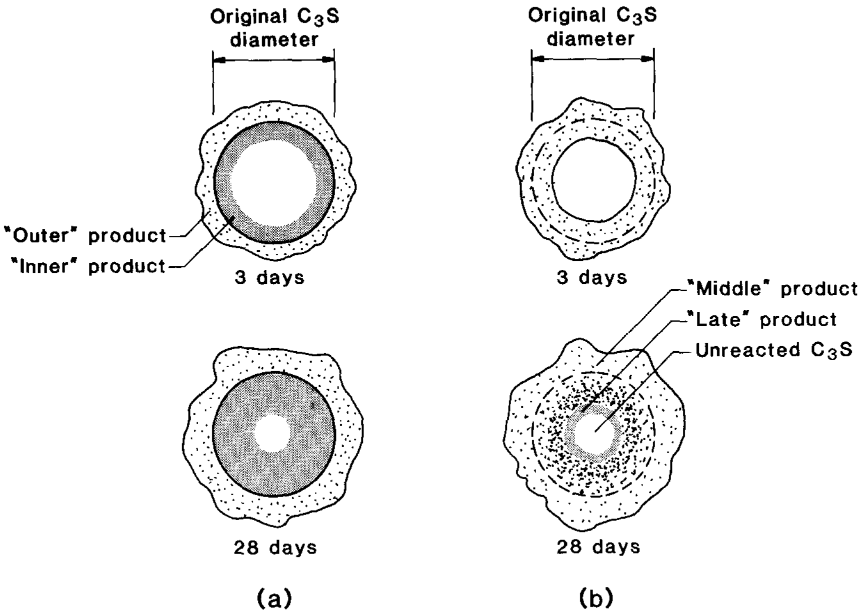


*Figure 1* Schematic representations for two types of hydration phenomena: (a) "inner" and "outer" products forming inside and outside of original anhydrous particle from the beginning of the reaction (b) "middle" product forms exclusively for the first several days and then "late" product forms, possibly along with the continued formation of "middle" products, after the first several days.

## 3. Results

Results of the quantitative analyses are summarized in Table I. Figs 2 to 5 show micrographs using backscattered electrons. The micrographs show good contrast separating alite, C-S-H, and $Ca(OH)_2$, but it is sometimes difficult to distinguish the precise boundaries which separate the C-S-H from the impregnated epoxy. Some specimens were reexamined after etching, which helped define the boundary of the epoxy. The micrographs reveal many changes as hydration proceeds.

### 3.1. C-S-H

At Day 1, Fig. 2, the micrographs show a structure which is composed of anhydrous alite particles, each surrounded by a thin, open, loosely compacted layer of C-S-H. Patches of C-S-H are sometimes separated from the more continuous layer surrounding alite grains. Although there is a variation from one point to another there is no consistent variation of brightness and morphology of C-S-H across the thickness of the layer. Many of the small particles of C-S-H do not have an alite core or the core is on a different plane.

At Day 3, Fig. 3, the product is thicker than at Day 1. As with the 1 day product, there is variation in brightness and morphology from one point to another, but there is no variation in the brightness or in the distribution of any microstructural feature which would define the former location of the original anhydrous particle. Most of the product in contact with the alite appears consolidated and does not contain visible porosity. Once again, smaller particles usually do not have an alite core.

At Day 10, Fig. 4, some new aspects of the microstructure are apparent. In addition to the structural characteristics seen in younger specimens, a few of the remaining alite grains, which are typically many micrometres in diameter, are surrounded with a thin layer of distinctly darker phase which is much more consolidated than the earlier product. The boundary between this darker phase and those described earlier, usually appears sharp and may represent the shape of the alite grain at some time between 3 and 10 days. Another feature, seen at lower magnification, is that a few regions, 60 to 100 $\mu$m across, containing no resolvable porosity, have formed.

At 28 days, Fig. 5, the space immediately surrounding many anhydrous particles appears to be filled with a dense, uniformly textured dark product. This product is not necessarily uniformly thick with some regions being very thin and others several micrometres thick. Again, the boundary between darker and lighter C-S-H is usually sharp. The small completely reacted grains never contain the darker phase. Micrographs obtained in an SEM using secondary electrons from lightly etched specimens, which rely on surface texture

TABLE I Volume fraction of solid phase in hardened alite

| | Age (days) | | | |
|---|---|---|---|---|
| | 1 | 3 | 10 | 28 and 203 |
| Degree of hydration | 0.22 | 0.30 | 0.50 | 0.83 |
| Volume fraction $Ca(OH)_2$ from thermal analysis | 0.045 | 0.063 | 0.097 | 0.160 |
| Volume fraction $Ca(OH)_2$ from image analysis* | 0.04 | 0.06 | 0.10 | 0.13 |
| Approximate number density of $Ca(OH)_2$ crystals $\mu m^{-2}$ | 0.002 | 0.005 | 0.005 | difficult to count |
| Volume fraction alite from X-ray analysis | 0.264 | 0.230 | 0.166 | 0.056 |
| Volume fraction alite from image analysis* | 0.25 | 0.22 | 0.15 | 0.085 |
| Volume fraction dark C-S-H image analysis | – | – | – | ~0.04 |
| Volume fraction C-S-H formed after 10 days, volumetric analysis | – | – | – | 0.12 |

*Average of 4 fields, $10^{-8}$ m$^2$ in area.

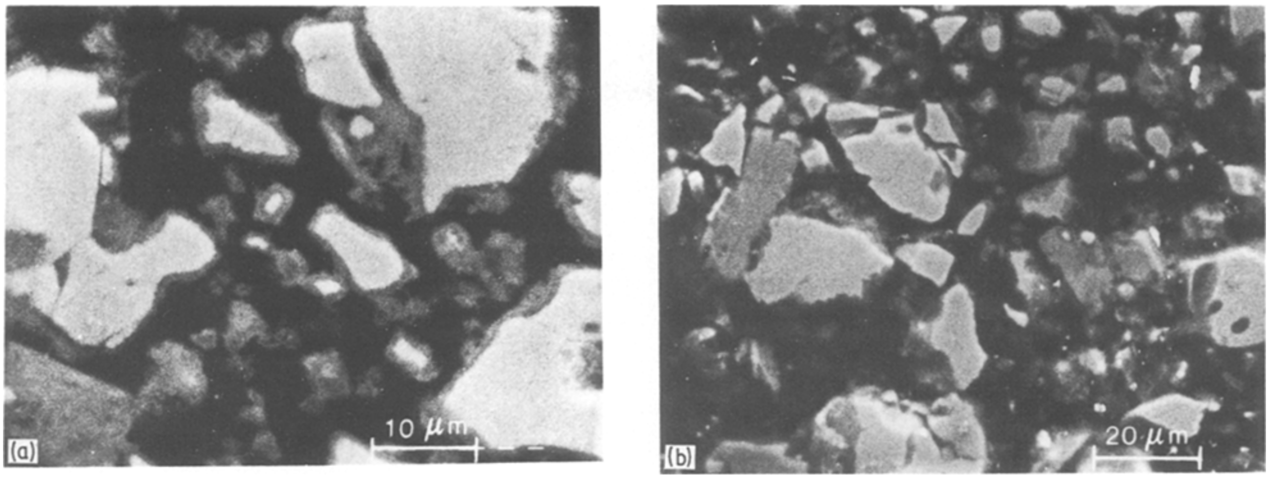


*Figure 2* Micrographs of 1 day specimen, using backscattered electrons, of polished alite. White–$Ca(OH)_2$; light grey–alite; medium grey–$Ca(OH)_2$; darker grey–C-S-H; darkest grey–epoxy.

for contrast, confirm that this darker phase consists of reaction product. Frequently there is a gap between this uniform product layer and the "outer" products which were probably formed earlier, and this gap is filled with epoxy. The 28 day specimens also contain very large low porosity regions, Fig. 6, many hundreds of micrometres across. These regions contain mostly C-S-H, with some alite and $Ca(OH)_2$ distributed throughout.

### 3.2. $Ca(OH)_2$

At Day 1, crystals of $Ca(OH)_2$ are not perceptibly elongated and range in size from very small, i.e. the limit of resolution, to about 10 μm across. The smaller crystals are often difficult to distinguish and there appears to be a diversity of number and size of crystals depending on the region considered. A rough estimate of the number density of crystals, as well as their volume fraction, is included in Table I. The number density of crystals is an upper limit because of the necessary assumption that apparently separate crystals are not joined outside of the plane of polishing which is, of course, not always true.

At 3 days, the number of resolvable $Ca(OH)_2$ crystals has increased and at least two types of morphology can be identified. Long thin crystals, 10 μm across and often 50 μm long, can be found in many of the relatively open regions. Most of the surface area of these crystals is free, i.e., not in contact with other solid material. Bulkier crystals are found in regions which appear to be more congested. These crystals have little or no free surface area as they appear to grow around other material.

The structure of $Ca(OH)_2$ at 10 and 28 days is similar to that at 3 days except that the crystals are often densely packed together. At 28 days it is often

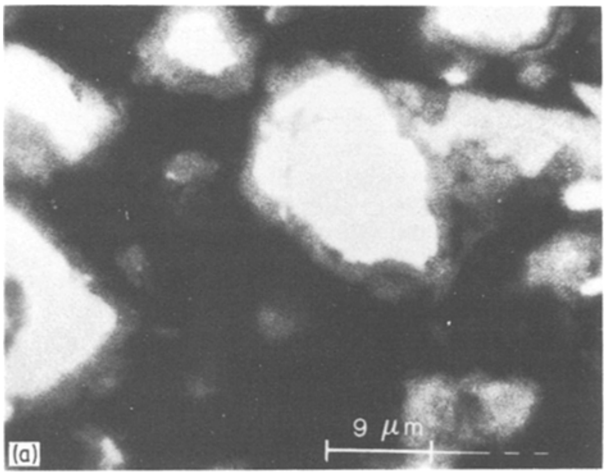
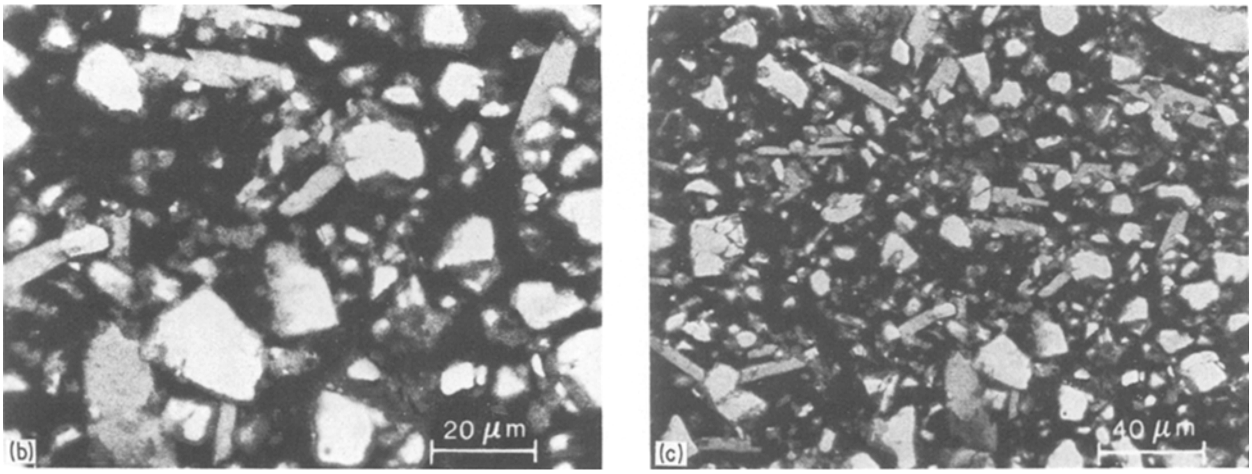


*Figure 3* Micrographs of 3 day specimen, using backscattered electrons, of polished alite. White–$Ca(OH)_2$; light grey–alite; medium grey–$Ca(OH)_2$; darker grey–C-S-H; darkest grey–epoxy.



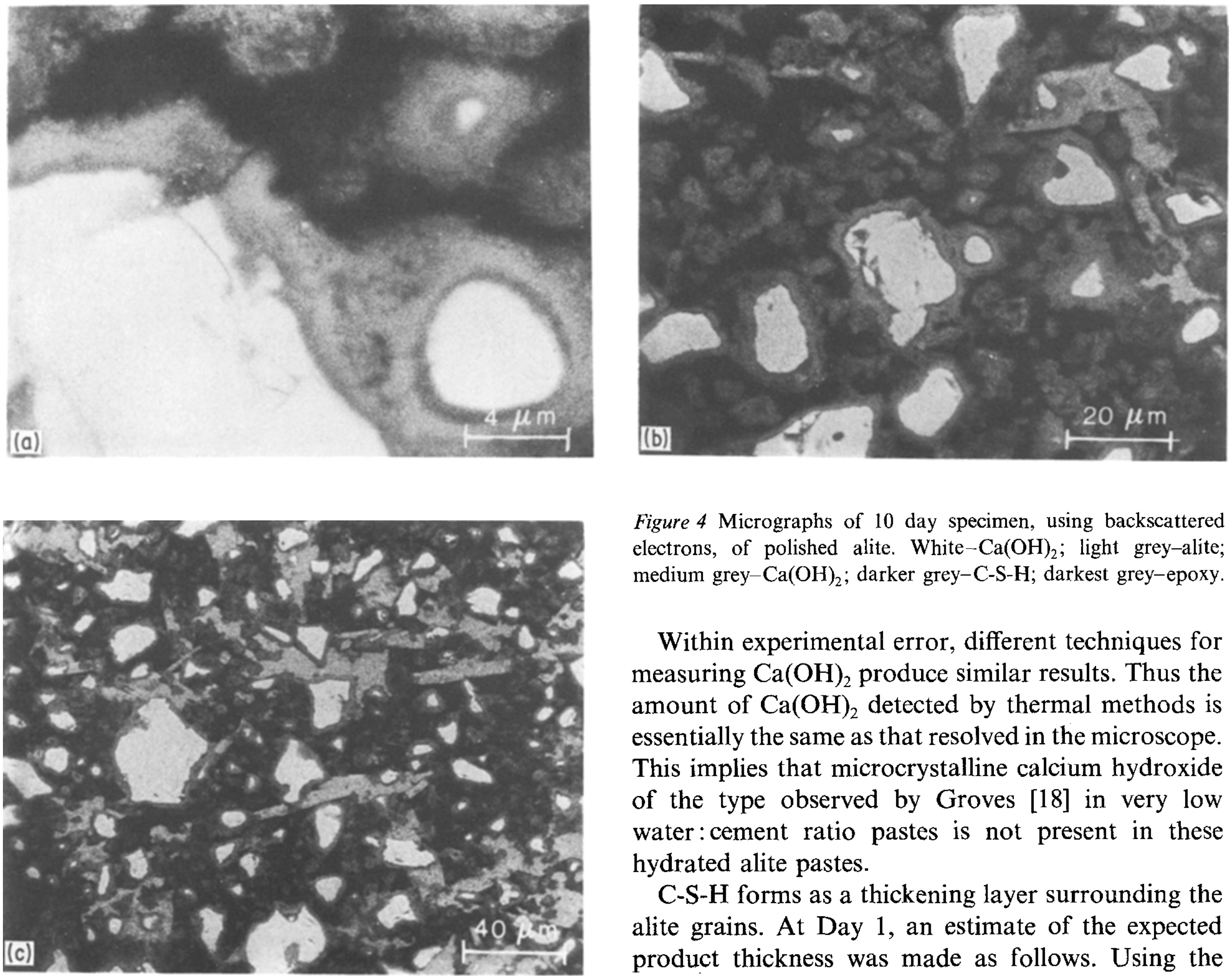


*Figure 4* Micrographs of 10 day specimen, using backscattered electrons, of polished alite. White–$Ca(OH)_2$; light grey–alite; medium grey–$Ca(OH)_2$; darker grey–C-S-H; darkest grey–epoxy.

difficult to detect individual crystals and even a rough estimate of the number density of crystals is not possible.

The density in number of remaining alite crystals can be determined. At 3 and 10 days there is approximately one $Ca(OH)_2$ crystal for every five alite grains, implying that there are relatively few nuclei of $Ca(OH)_2$ and these grow into large crystals. Compared to 28 days, no additional hydration was observed at 203 days.

## 4. Discussion

Backscattered electrons from epoxy impregnated polished surfaces of alite paste have produced micrographs with resolvable contrast between phases. Quantitative image analysis, Table I, of these micrographs reveals that the volume of alite and $Ca(OH)_2$ are nearly the same as the volumes determined from X-ray and thermal analysis. The smaller alite grains are consumed during the early stages of hydration while the larger grains react only partially before hydration stops.

Only a few $Ca(OH)_2$ crystals grow per each alite particle. First they appear as small crystals, and then as long thin crystals some of which finally fill all of the available volume. These observations are similar to those reported by Berger and McGregor [17]. The reason why some crystals grow and fill available volume, while others appear to avoid contact with C-S-H, is not known.

Within experimental error, different techniques for measuring $Ca(OH)_2$ produce similar results. Thus the amount of $Ca(OH)_2$ detected by thermal methods is essentially the same as that resolved in the microscope. This implies that microcrystalline calcium hydroxide of the type observed by Groves [18] in very low water:cement ratio pastes is not present in these hydrated alite pastes.

C-S-H forms as a thickening layer surrounding the alite grains. At Day 1, an estimate of the expected product thickness was made as follows. Using the surface area and density of alite, a characteristic radius for starting alite particles (one that produces the measured surface area of starting material) could be calculated from data presented in Part 1 [15]:

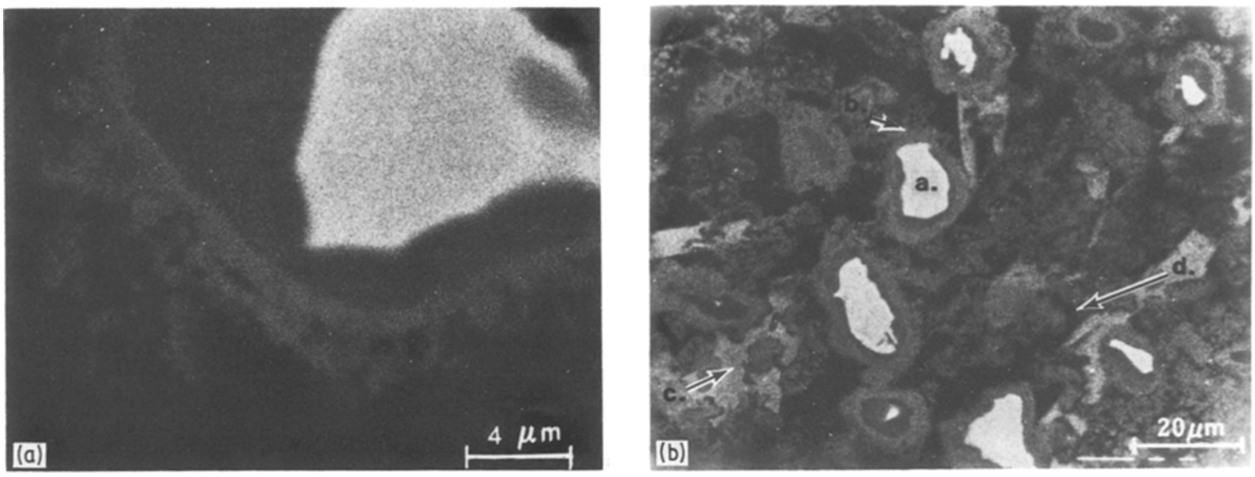
$$r = \frac{(3)\text{ volume}}{\text{surface area}}$$

$$= \frac{3\text{ (mg)}}{\text{(density) (surface area)}} = 2.6\,\mu\text{m}$$

where volume and surface area are specific quantities.

If the products, including accompanying "gel" pores, are assumed to be roughly 2.5 times as voluminous as the starting alite (from [16]), then, at 22% reacted, a uniform layer would be about 0.5 µm thick, having consumed alite to a depth of ~0.26 µm. (The calculated value does not change much even if the surface is considered flat.)

This value is the same as that reported [1] from observations using a high voltage electron microscope (HVEM). Thus the layer is thin, which is consistent with the extremely weak nature of the bulk material. The product thickness (i.e., layer thickness) in Fig. 2, however, sometimes appears to be thicker than 0.5 µm in some places. This can be explained by reference to Fig. 7 which shows that, in a plane, the thickness can appear much greater than the radial, or equatorial thickness, if the particle centre is above or below the plane of observation. Because the HVEM technique used did not disrupt individual particles the equatorial product thickness is observed. Product which apparently has no anhydrous core results either from



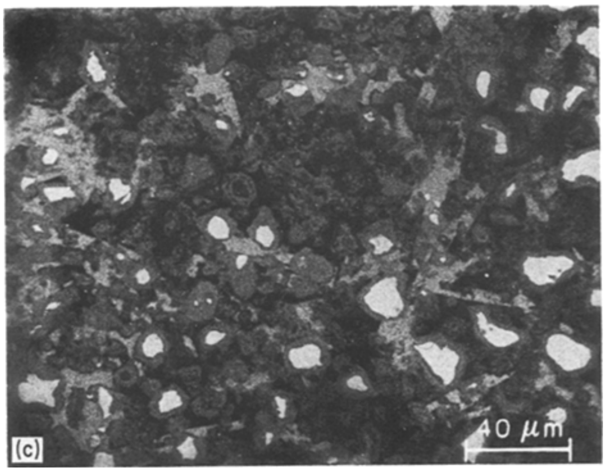


*Figure 5* Micrographs of 28 day specimen, using backscattered electrons, of polished alite. White–Ca(OH)$_2$; light grey–alite; medium grey–Ca(OH)$_2$; darker grey–C-S-H; darkest grey–epoxy.

complete hydration of smaller particles, or because the plane of observation does not pass through the anhydrous core. Thus, caution must be used when estimating product layer thickness from polished surfaces.

The C-S-H adjacent to the large "capillary' porosity, which is observed from the earliest stages, appears only loosely consolidated and often not directly associated with the product that is closer to the alite grains. This structure is compatible with the fibular, Type I or Type 1 [1, 14] material often seen on fracture surfaces. Closer to the alite grain, the C-S-H appears fairly well consolidated. This structure is compatible with irregular, flattened grains or partially crumpled sheets, Type III or 3 [1, 14], seen on fracture surfaces. There is no regular variation of brightness, and therefore of composition, across the thickness of C-S-H. Sometimes, but not always, there appears to be a well defined boundary between the above two types of texture. The outer material, Type 1, does not appear to increase in thickness with time, remaining between 1 to 4 μm from day one. The irregular nature of the boundary between the two types does not indicate the location of the original alite surfaces. These observations are compatible with the idea [1, 19] that these morphologies are derivatives of one type of C-S-H (perhaps a phase), which has been called "middle" product. In this hypothesis it is proposed that the different morphologies may result from different amounts of available free volume.

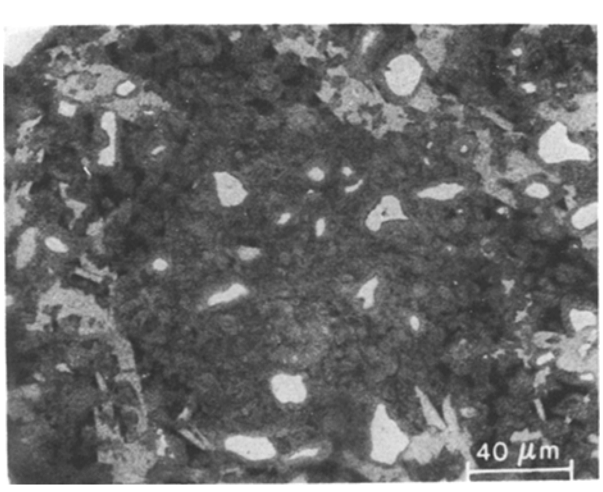


*Figure 6* 28 day specimen containing large dense region.

28 day specimens contain some grains in which the innermost region surrounding alite cores is both texturally and compositionally different from C-S-H discussed above. It appears very smooth and dark and has a well defined sharp boundary between it and the material observed in younger specimens. The lack of uniform thickness suggests that different regions grew at different rates. The sharp boundary has been observed in transmission electron micrographs [1, 20]. This dark inner phase may be a dense, gelatinous inner product, described as Type IV [14] or Type 4 [1] C-S-H, seen on fracture surfaces. Quantitative image analysis, Table I, indicates that this material accounts for only about 4% of the volume. Calculations of expected brightness (see the Appendix) suggests that the Ca : Si ratio of 1.5 or less is a possibility, particularly if the product formed earlier has a ratio of 1.8. Thus, the presence of this dark material could account for the variable composition observed for C-S-H, precluding the necessity of fine CA(OH)$_2$ being embedded in C-S-H.

This darker region of C-S-H occurs only in older specimens and never around smaller grains which have been completely hydrated during the early stages of reaction; also there is a well defined and sharp boundary between it and product formed earlier. These observations are similar to the schematic of

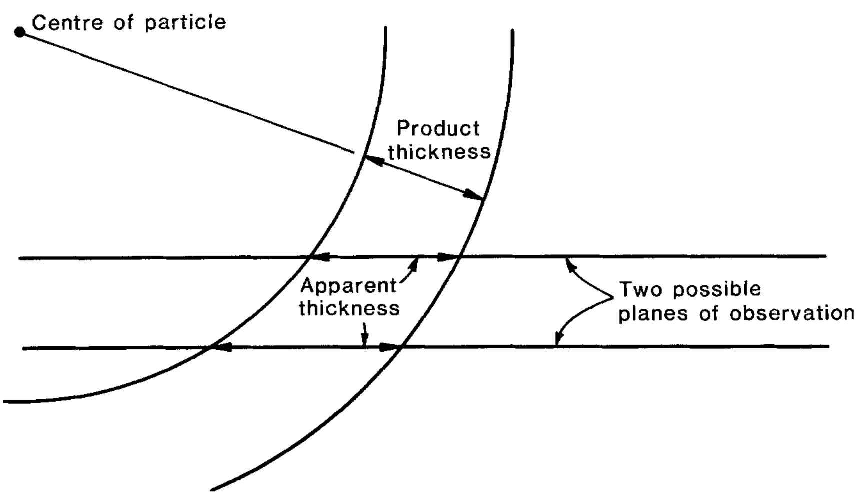


*Figure 7* Schematic representation of a particle which has been sliced on an arbitrary plane.

Fig. 1b and therefore support the concept of "early", "middle" and "late" products [1]. The existence of the sharp boundary between "middle" and "late" products could be interpreted as suggesting former presence of the surface of the original anhydrous particles, but this possibility is negated by the lack of the inner phase in younger specimens and the lack of a dark phase in small grains. Time or, perhaps more accurately, the degree of hydration and the C-S-H coating thickness, controls the type of product. The time when the "late" product appears may depend on variables such as initial water : solids ratio, particle size distribution and temperature. It is also possible that sharp compositional distinctions diminish over a period of years which would account for the observation [2] that there is no distinct "late" product after an extended period.

As was also indicated in the study of pore structure, Part 1, results reported here indicate that large, relatively dense regions are apparent at 28 days. Although these regions contain some $Ca(OH)_2$ and alite, they are primarily C-S-H. The uniformity of the density of this C-S-H over large regions, which stands in contrast with the situation in earlier samples, suggests that some C-S-H may have been transported from other regions. These regions seem to be a new feature of the microstructure. Many similarities with electron micrographs of fracture surfaces suggest, however, that they may be the same as the common Type III [14] or Type 3 [1] product; and if so, this study has revealed new characteristics of these types, namely that they can form into large regions.

## 5. Summary

Micrographs which provide new information were obtained from polished surfaces of hydrated alite specimens using backscattered electrons in a scattering electron microscope. Quantitative image analysis of the phases present produced results which agree well with other analytical techniques. These observations were compared with information obtained from fracture surfaces. The main observations of this study can be summarized as follows:

1. Calcium hydroxide appears to form in available free volume, growing into larger crystals which can sometimes engulf C-S-H. The number density, size and shape of the crystals varies from one region to another.
2. During the "early" states of reaction there does not appear to be any sharp boundaries between different types of C-S-H. Different morphologies may be variations of the same type of C-S-H.
3. At later ages there is a sharp boundary between "late" product and product which formed at earlier ages.
4. At 28 days hydration the overall microstructure contains large, pore-free areas of solid material, composed mostly of C-S-H and some $Ca(OH)_2$ and alite.

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## Appendix

If a material is a homogeneous mixture of several elements a backscatter coefficient can be calculated [21, 22] as

$$\eta_{\text{mix}} = \sum_i \eta_i C_i \qquad \text{(A1)}$$

where $C_i$ = weight fraction of element $i$ and $\eta_i$ = backscattering coefficient for element $i$.

The results of this calculation for several solids are listed in Table AI. The larger the value of $\eta_i$ the brighter the image. X-ray microanalysis confirmed these results and no inconsistencies were found.

TABLE AI Backscattering coefficients for several compounds which may be found in hydrating $C_3S$

| Compound | $\eta$ |
|---|---|
| $C_3S$ | 0.178 |
| Alite* | 0.176 |
| $Ca(OH)_2$ | 0.168 |
| $C_{1.75}SH$† | 0.16 |
| $C_{1.5}SH_2$† | 0.14 |

*Composition given in Table I, Part 1 [15].
†Brightness depends only weakly on water content.

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