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Microstructural analysis of hardened alite paste

Part 1 *Porosity*

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New information about the pore structure of hydrating alite (impure tricalcium silicate) of 0.59 water : alite ratio has been obtained by examining polished cross-sectional surfaces with a scanning electron microscope. Micrographs were used to analyse quantitatively the volume of porosity which was impregnated with epoxy and these results were compared with independent measurements of porosity using volumetric technqiues. The results suggest that pores less than 50 nm diameter are not impregnated by epoxy and that they may be incorporated as part of the pore structure of the calcium silicate hydrate; however, only the finest of these pores may remain in pastes formed at low water : solid ratios. The calcium silicate hydrate formed in the late stages of hydration may not incorporate as much fine porosity as that formed during the early stages. The structure of the large "capillary pores" (i.e., pores greater than 50 nm diameter) changes with time from an open network to an array of disconnected pores. This study reveals that mature specimens are very heterogeneous and contain regions, hundreds of micrometres across, having few, if any, capillary pores. These regions are not found in young specimens.

1. Introduction

Complete microstructural evaluation of cementituous materials should ideally include quantitative measurements of features such as size, shape and location of all phases present, including pores. Usually the microstructure of both hardened portland cement and tricalcium silicate (C_3S) pastes [1, 2] have been studied by observing fracture surfaces with a scanning electron microscope (SEM). Fracture surfaces, however, follow the path of least resistance so that, in the case of these heterogeneous materials, rough surfaces are produced which are not representative of the average bulk material and do not allow quantitative analysis of the microstructure. Pores range in size from 10^{-10} to the order of 10^{-4} m and their structure is particularly difficult to evaluate from fracture surfaces. Polished surfaces have not been studied extensively because of difficulties in developing contrast between phases. Fluorescent dyes [3] were incorporated into epoxy which was impregnated into the paste, and subsequently polished thin sections were examined by optical microscopy, but this technique did not resolve much of the detailed structure of the fine porosity.

Preliminary results [4] using techniques described in this paper, help establish a relationship between porosity and diffusion of a fluid moving through the hardened alite (impure C_3S) paste. This paper discusses further observations about the quantity, structure, and distribution of porosity. Special attention is given to two classes of pores which are represented schematically in Fig. 1. Firstly, very fine pores are incorporated into calcium silicate hydrate (C-S-H), which is one of the solid phases present. The density of C-S-H depends on the volume of these pores. Secondly, there are pores which result because the quantity of solid product is almost never sufficient to fill all of the original water-filled space. The first, very fine type of porosity is often referred to as "gel porosity", or sometimes, "mesoporosity", "microporosity", or medium and small "capillary porosity". On the very finest scale, of the order of a few angstroms, there is interlayer space, which is an intrinsic part of the structure of calcium silicate hydrate and is often considered part of the "gel" porosity. In principle this space can expand and contract with the addition and removal of water and this is considered important to properties such as drying shrinkage. The second type of pore is larger and is often referred to as "macroporosity", or sometimes as large "capillary porosity". Because there is a smoothly varying pore size distribution there has been no clear distinction between these two classes of porosity. The number and size of pores associated with each type of porosity varies with many experimental variables such as reaction conditions, type of drying, and also measurement technique. With the help of microstructural observations, some of these distinctions are here analysed and discussed.

2. Experimental results

Selected characteristics of the alite used have been previously reported [4] and are shown in Table I. The material was hand mixed with water at a water : alite

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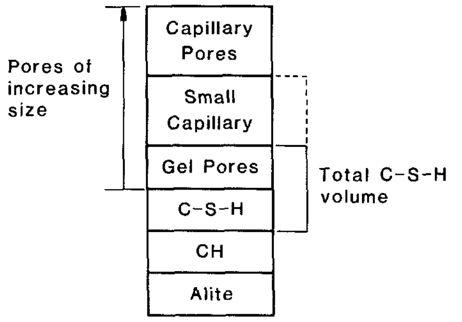

Figure 1 Schematic representation of volumes of all phases and pores present in alite paste. Distinctions between different porosities and between pores and C-S-H may be difficult to define. The volume of each type of pore changes with time. Dark areas are solid; white areas are porosity.

ratio of 0.59, sealed in a container, and rotated during setting. At an age of one day the paste was rigid enough to prepare specimens. Discs of 3 mm thickness were cut from the 10 mm diameter of cylinder of hydrated alite paste and at ages of 1, 3, 10, 28 and 203 days, the discs were immersed in methanol to stop hydration. After drying over silica gel under vacuum at 20° C for one day, the degree of hydration was determined by X-ray diffraction and by thermogravimetric analysis. These values could be used to calculate the volumes of alite and calcium hydroxide.

The discs were impregnated under vacuum with a low viscosity epoxy resin and then, after curing, polished surfaces were prepared. Micrographs of polished specimens were taken to check for complete epoxy penetration. The surface was then deeply etched with a 50% hydrochloric acid which removed the cementitious material and left an epoxy replica of the impregnated pores. This was examined by secondary electrons in a SEM. Boundaries of the impregnated pores in the plane of polishing were traced from the micrographs, using a light box and tracing paper, to produce a black and white map of the original pore structure. Black areas represent solid material (unreacted alite, calcium silicate hydrate plus gel porosity as defined above, and $Ca(OH)_2$). White areas represent the porosity which was impregnated by epoxy.

Quantitative analyses of area fractions were carried out on the tracings at a magnification of 1000×, representing sample areas of $10^{-8}\,m^2$. A comparison of micrographs taken at several magnifications indicated that this magnification was a good compromise, resolving many important features, while still incorporating an adequate sample of the material. Both automatic image analysing and standard metallographic point counting techniques were employed for quantitative analysis of the fraction of pores, the assumption being that the material is isotropic, so that area fraction is equivalent to volume fraction. For boundaries with low contrast only the standard point counting techniques were used. When both techniques were employed they gave essentially the same results.

TABLE I Analysis of alite [4]. Composition (wt %)

SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3
25.45	0.10	1.20	71.74	1.25	0

Loss on ignition, 0.39%.
Density, $2190\,kg\,m^{-3}$.
Specific surface area, $365\,m^2\,kg^{-1}$.

Porosities were also determined volumetrically as described in [4]. In brief, butane adsorption was used to determine the volume of pores less than 50 nm in diameter. The difference between weights of samples saturated with water or methanol and oven dried samples was used to determine the total porosity. Methanol volumes are about 2% smaller than water volumes. The difference between the total porosity and the porosity of less than 50 nm diameter was the porosity greater than 50 nm diameter. The volume of C-S-H was determined by subtracting the volume of all other phases from the total volume. Pores less than about 5 nm diameter could also be determined with butane at a partial pressure of 40%. The value for these 5 nm diameter pores is, however, very approximate and it is probably more accurate to consider these fine pores to be associated with a volume which has different adsorption capabilities than larger pores. Although the pore size is ill defined, the volume is accurate within a few per cent. The surface area was determined from butane adsorption.

3. Results and discussion

Fig. 2 shows examples of porosity maps obtained by tracing micrographs. Results from quantitative image analysis of this type of micrograph are included in Table II. The values have a small error because of variation from one region to another and difficulties in defining pore boundaries. The error is likely to be larger in the 10 and 28 day old samples because of greater regional variation of the pore structure. For these older samples values for both local pore area and much larger areas of dense regions which contained no resolvable porosity were combined to obtain a value for average porosity. Standard deviation of several measurements suggest a worst case overall error of as much as 10%. These results, combined with results of volumetric analysis, which are also included in Table II, are interpreted in the following sections.

3.1. Pore size

The values in Table II indicate that a close correlation appears to exist between the volume impregnated by epoxy and the volume of porosity greater than 50 nm diameter as measured by volumetric techniques. This implies that pores less than 50 nm diameter were not impregnated whereas pores greater than 50 nm diameter were impregnated. Furthermore, the pore maps suggest that there is a fairly definite boundary between pores which are impregnated and those which are not. This suggests that the smaller pores are situated within, and are bounded by, hydrate particles which are predominantly C-S-H. In other words, these smaller pores are created as C-S-H is formed, while the volume of larger pores diminishes. In the carefully dried state of the specimens discussed here, therefore, the "gel" and /or small "capillary" pores might be considered to be all pores less than 50 nm diameter.

The values for volume of the gel pores (less than 50 nm diameter) which are incorporated as a part of

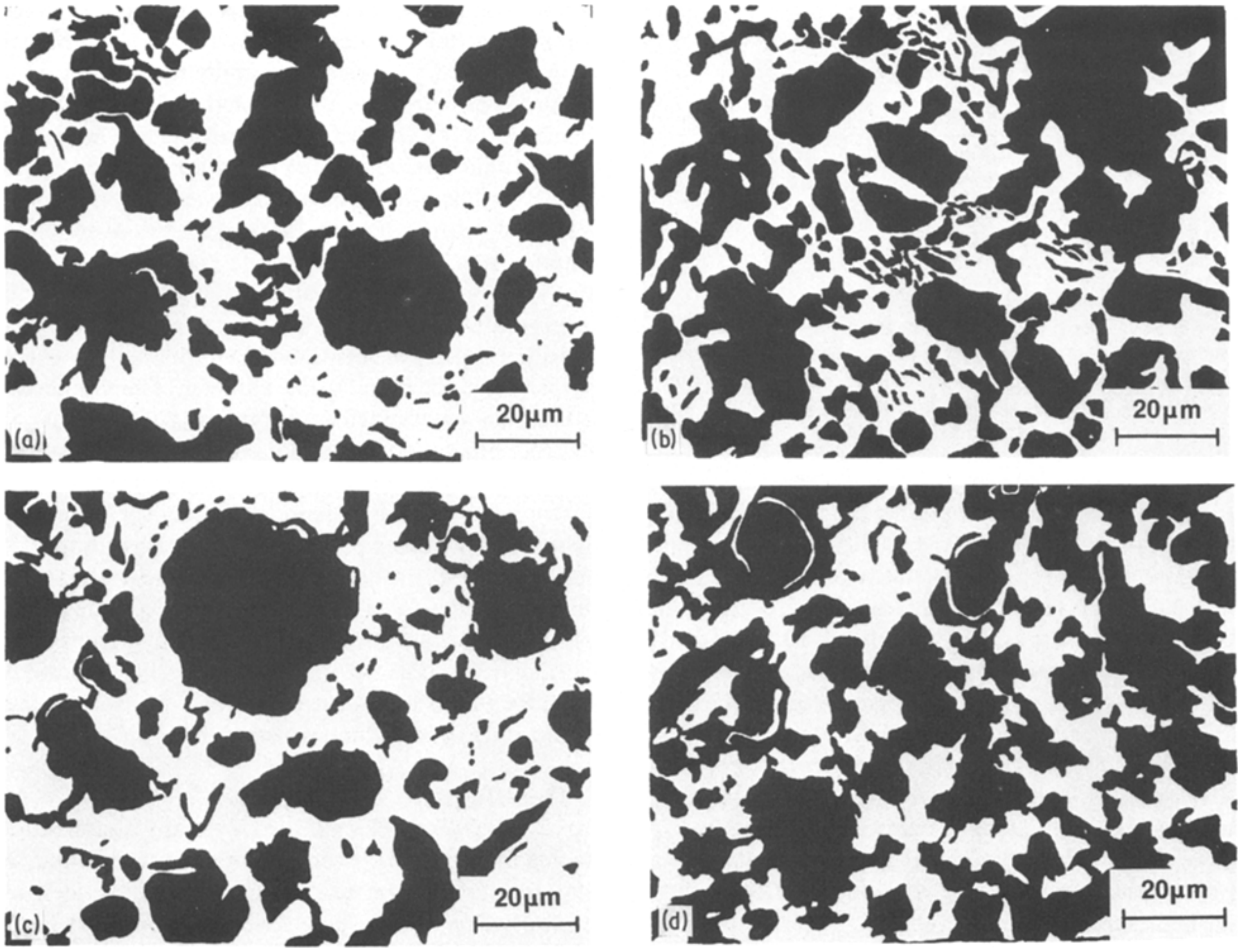

Figure 2 Pore maps of (a) 1 day, (b) 3 day, (c) 10 day and(d) 28 day specimens. Black-cementateous material; white-porosity.

the structure of C-S-H are shown in Table II. It can be seen that this volume does not increase significantly after 10 days. The calculated percentage porosity in C-S-H are also included in Table II. The percentage drops from 56 to 44% with time or degree of reaction. If the pores incorporated within the C-S-H are considered to be only those less than about 5 nm, then the calculated values are smaller, but the trend is similar, though less pronounced. There are three possible explanations which might account for the changes in porosity with ageing: (i) product could form and then, with ageing, the overall structure could collapse, removing some of the gel pores but apparently not changing the size of the larger gel pores present; or (ii) some of the smaller gel pores could be filled with additional product, leaving at least some of the larger gel pores unfilled; or (iii) during the "late" stages of reaction a product [5] could form which contains a smaller fraction of porosity and possibly a finer porosity than "early" product, resulting in a smaller volume fraction porosity. The third possibility would support the idea of "early", "middle" and "late" product [2, 5]

TABLE II Volume fraction porosity in hardened alite*

	Age (days)			
	1	3	10	28 and 203
Degree of hydration (%)	22	30	50	83
Volumetric measurement of porosity (%)				
$d < 50\,\mathrm{nm}$	10	14	23	22
$d < 5\,\mathrm{nm}$	3	5	8	9
$d > 50\,\mathrm{nm}$	51	44	34	27
Image analysis of impregnated porosity (%)	55	44	38†	31†
Calculated vol % porosity within C-S-H:				
if include all pores $d < 50\,\mathrm{nm}$	56	54	54	44
if include only pores $d < 5\,\mathrm{nm}$	30	29	29	23
Density of C-S-H if pores are included and filled with H_2O ($\mathrm{kg\,m^{-3}}$)	1960	1990	2040	2060
Density of C-S-H excluding all pores ($\mathrm{kg\,m^{-3}}$)	2375 ± 70 (all ages)			

*Values taken from an average of four micrographs.

†Value takes into account large dense regions which account for 12% of area at 10 days and 26% of area at 28 days.

and is consistent with data showing that, beyond an age of ten days, the volume vacated by hydrating alite is almost sufficient to accommodate the volume of C-S-H and associated small pores as they form [4].

The size of pores which may be considered an indispensable part of the C-S-H formed in these reactions can be discussed in light of results reported here. First, if pores less than 5 nm diameter are filled with water of density 1000 kg m^{-3}, then the density of C-S-H plus water can be calculated, with the results shown in Table II. These values are very close to the values (1950–2070 kg m^{-3}) reported independently [6, 7] for saturated C-S-H. Secondly, "gel" porosity for Portland cement is often taken to be between 26% [8] and 28% [9] of the volume of C-S-H. These values have been correlated with low water : cement ratio and completely hydrated cement, and they are close to the values calculated here based on the assumption that the C-S-H contains only pores less than about 5 nm diameter. Since the results discussed above suggest that, the "gel" porosity includes the pores less than 50 nm diameter, for this high water to solid ratio paste, it seems likely that the size of gel porosity is variable. Since the volume of pores less than 5 nm diameter can be used to calculate a reasonable minimum "gel" porosity and saturated C-S-H density, particularly at younger ages, these small pores may be an essential part of "early" C-S-H. Product formed after 10 days may not contain as many of these pores but *all C-S-H must contain some porosity*. The pores between 5 and 50 nm diameter might be the pores which are sometimes referred to as small "capillary" pores.

The surface area, determined by butane adsorption, averaged 175 m^2 g^{-1} at complete hydration. The area is much higher for earlier stages of hydration, probably well over 250 m^2 g^{-1}, the exact value depending on how data of Parrott *et al.* [4] is extrapolated. These results seem consistent with the idea that C-S-H forms in constricted spaces at later ages.

3.2. Morphology of the capillary pore

The pore maps of Fig. 1 indicate that the larger pore structure changes significantly with time. At Day 1 the structure has smooth surfaces, consistent with the possibility [10] that early product is distributed fairly uniformly around the alite particles. In the polished plane there are many isolated islands of solid material which implies that nearest neighbour contact is often above or below the plane of observation, as illustrated in Fig. 3.

At Day 3 the pore structure becomes extremely "spongy", and solid material is apparently dispersed more widely into the original pores, about one quarter of which appear to contain this dispersed product.

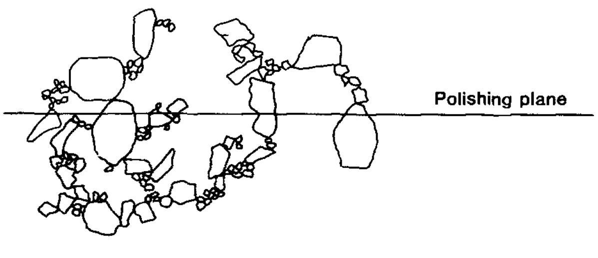

Figure 3 Schematic side view of particles illustrating polishing plane.

At Day 10 and Day 28 the solid again appears to be well consolidated. Long thin pores, which form a section of a circle within the solid material, are apparent at Day 10, and are common at Day 28. It is unclear whether these pores are artifacts of drying, or whether they are related to Hadley grains which are sometimes found in hydrated Portland cement.

The decrease in continuity of the larger pores as the alite hydrates has been discussed elsewhere [4]. Taken together with this work, we suggest that pores greater than 50 nm diameter appear to control diffusivity of fluids through the paste as has also been suggested by Mehta and Manmohan [11].

Hydration of the alite has virtually stopped by 28 days in spite of the availability of water and pore space. Possibly hydration is impeded by the reduction in the finest pores of the C-S-H gel that surrounds the residual alite, producing a diffusion barrier which prevents further reaction.

3.3. Pore distribution

At 1 and 3 days, the structure in any given field of 100 μm cross-section, shows little or no variation from one part of the specimen to another. At Day 10, however, regions as large as 100 μm diameter, which are impregnable by epoxy, have begun to appear. Micrographs taken at lower magnification, Fig. 4, indicate that these relatively dense areas account for about 12% of the overall volume. At Day 28 they have grown to many hundreds of micrometres across and they occupy about 26% of the overall volume. These regions have not been, heretofore, explicitly identified, probably because they are not obvious on fracture surfaces.

4. Summary

Polished specimens impregnated with epoxy and deeply etched to remove cementatious material can be examined with a scanning electron microscope to provide new information about the pore structure of hydrating alite. This study shows that some of this information can be quantified and used to help interpret data on pore size from volumetric techniques. In the future many more aspects of the pore structure, such as connectivity, shape, etc., should also be examined quantitatively. The present findings are summarized as follows:

1. In carefully dried, relatively high water : alite paste specimens, pores of less than 50 nm diameter appear to be the part of the structure of C-S-H referred to as "gel" pores. Their number increases with extent of reaction. Of these pores, those larger than 5 nm may be removed in pastes having low water : cement ratios but those smaller than about 5 nm are difficult to remove. Product formed after 10 days hydration has a smaller percentage of pores having less than 50 nm diameter than does early product. Either the product formed in the later stages of reaction contains few, if any, of these "gel" pores; or some pores collapse or fill in as reaction continues. The largest pores, "capillary" pores, decrease in volume fraction with increased

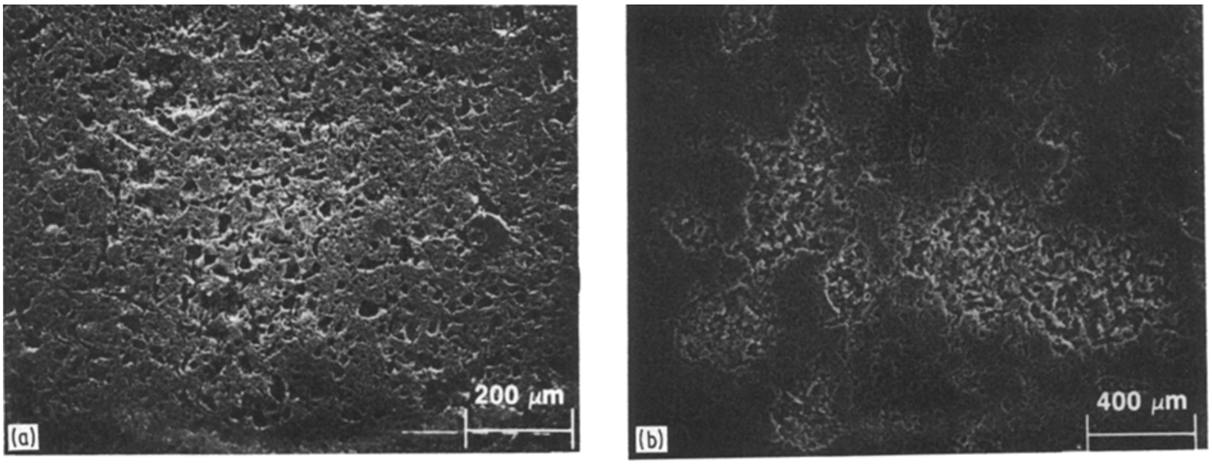

Figure 4 Low magnification of (a) 10 and (b) 28 day specimens. Heavily etched regions are regions where epoxy could not penetrate, i.e., these were dense regions.

degree of reaction. This change with time may help define the meaning of "capillary" porosity.

2. Between one and three days hydration there is little variation in the structure from one field of view, 100 μm across, to another. At day 10 non-uniform structures begin to appear as regions which are of the order of 100 μm across form, and are impenetrable by epoxy. At day 28 these regions are many hundreds of micrometres across.

3. For specimens prepared with the relatively high water : cement ratio investigated here, the reaction virually stopped at 28 days despite the availability of water and large pore space.

4. The continuity of the larger pores decreases with age as the hydrate coatings around the alite grains thicken, confirming an earlier result [4].

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