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THE MICROSTRUCTURES OF CEMENT PASTE IN CONCRETE

SUMMARY

A review and interpretation is provided of the current state of knowledge with respect to microstructures developed in Portland cement concrete under various conditions. Current developments in techniques for studying the microstructure are described. The microstructural elements in ordinary portland cement paste are illustrated, and the details of the developing processes of cement hydration are discussed. The early formation of shells around cement grains is illustrated, and the status of hollow hydration shells described. Because of their present widespread use in concrete, the influences on microstructure of incorporation of fly ash, silica fume, and slag are stressed. The special microstructures of the interfacial zones formed around aggregates and around steel and glass fibers in concretes are explored in detail in view of the importance of these special zones to concrete performance.

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FOREWARD

The present paper constitutes a review and personal interpretation by the writer of the progress made in the general area of hydrated cement paste microstructure since the preceding 7th International Congress in Paris in 1980.

At that Congress there was no specific principal report devoted to the microstructure of paste per se: rather, the subject was covered in part by Taylor and Roy (1) in their principal paper on "Structure and Composition of Hydrates" and in part by Sereda, Feldman, and Ramachandran in their principal paper on "Structure Formation and Development in Hardened Cement Pastes" (2). While both treatments provided significant microstructural coverage, both were primarily concerned with other, albeit related, aspects of cement paste. Contributions to the Paris Congress relating to paste microstructure were summarized by the writer in his General Report (3); there were comparatively few of these.

In the intervening years there has been a major increase in the availability of scanning electron microscopes, which continue as the primary tool for microstructural investigation in cement systems. In consequence, many more laboratories have facilities available for studies in this area, and there has been a corresponding increase in the number of papers published. The present review is not intended to be exhaustive, and because of the increased activity in this area a number of excellent papers will not be discussed.

In addition to the formally published literature, the writer is aware of two excellent recent Ph. D. theses devoted largely to paste microstructure, one by Scrivener (4) dealing primarily with cement paste per se, and one by Monteiro (5) dealing mostly with microstructural effects on concrete properties.

Despite this rise in research activity in the area, microstructures of cement paste systems are still not well understood by the general technical community. The difficulty of selecting the pertinent aspects of the microstructure of even a particular cement paste under investigation remains formidable; describing it in a publication so that it may readily be understood is even more difficult. A discussion the nature and magnitude of some of these difficulties was presented by the present writer in a recent treatment (6).

In that paper it was calculated that a set of 10 of the usual SEM micrographs taken in various places on a 1 cm square cement paste sample surface at 10,000x (a normal magnification for studying cement paste) provides a sampling of only 0.001% of the surface of that specimen. If the microstructure varies appreciably from place to place, as it ordinarily does, it is difficult to be sure that this limited sampling is adequate to insure that a proper representation of the structure has been secured.

Furthermore, each individual micrograph may reveal several different microstructural features. Picking out the pertinent points for discussion and then describing the structures ver-

bally is something of an art.

It is hoped that despite these difficulties the present paper may help to contribute to a more general understanding of cement paste as a material, as well as to an appreciation of the present state of knowledge of its microstructure.

It seems appropriate that before entering into the details, the writer specifically indicate something of his own biases concerning the subject. They include the following judgements:

1. The present writer feels strongly that the cement paste microstructures of primary importance are not those of laboratory mixed cement pastes but rather those microstructures actually present between sand grains and aggregates in concrete in service. The two may be similar, but they are certainly not identical.

2. Most of the lessons that can readily be learned from the study of the microstructures developed in pastes of pure cement minerals (e.g. C_3S) have by and large already been established, and future work on the development of microstructures should more heavily concentrate on cement, rather than C_3S, pastes. This is especially so in view of the fact that the cement hydration processes in concrete are strongly affected by chemical and other features not present in laboratory-mixed C_3S pastes.

3. There has also been something of a major change in concrete practice since 1980 in that "pure" portland cement concrete has become almost a rarity in many countries, most concrete now containing fly ash, slag, silica fume, or pozzolans of one type or another. Accordingly, the microstructures of cement pastes developed in the presence of these supplementary cementitious components are no longer a peripheral matter of interest primarily to specialists, but have become matters of central concern.

4. Cement paste microstructure needs to be understood primarily because of its influence on the behavior and properties of the concretes and other cement systems in which it is incorporated. However, the behavior may often be controlled by special microstructures that arise in specific locations in the system, rather than by the general or most prevalent microstructure. Illustrations in concrete include the special areas adjacent to aggregate interfaces, for example, or zones surrounding embedded steel reinforcement or prestressing cables. Another example is the special microstructure that wet exposure develops between individual glass fibers in strands of alkali-resistant glass fibers in GFRC (glass fiber reinforced concrete).

The remainder of the present paper will be devoted to a synthesis and interpretation of cement paste microstructures in the light of the extensive developments that have been recorded in the past six years.

INTRODUCTION

Hardened cement paste is a relatively inhomogeneous assemblage of particles, films, microcrystals, and other solid structural elements bonded together in a porous mass, and in its native state

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containing pore solution and some empty (air-filled) spaces. The non-solid components may be as important as the solid elements in some contexts.

On drying, much of the pore solution evaporates, shrinkage usually occurs, and ultrastructural details in certain particles may change irreversibly.

The air-filled spaces in the cement paste of partially dried concretes consist of two distinct classes of space: relatively large, mostly spherical entrained and entrapped air voids, usually lined with a smooth layer of calcium hydroxide; and smaller, geometrically complex "capillary" pores representing the residue of space between the original cement grains. "Capillary" pores resaturate readily; air voids do not. To avoid confusion, it is prudent to keep the distinction between the two classes clearly in mind, a caution that has not been universally adhered to in the literature.

"Capillary" pores tend to fill up to a greater or lesser degree with solid hydration products on continued hydration, and give way to still finer pores between hydration product particles and to some extent to "gel" pores within them. The boundary between ultrafine pores "between" and "within" C-S-H gel particles has never been conclusively established. Indeed, in a recent paper Taylor (7) stressed the point that the term gel porosity is a misnomer, because the water supposedly present in gel pores is in reality present in the hydrated phases. The subject remains an area of much controversy and confusion.

In concrete, cement pastes exist as relatively thin ribbons of material surrounding and separating sand grains and coarse aggregate pieces. As published measurements have indicated (8), in representative concretes the average spacing between adjacent sand grains at their narrowest separation is only of the order of 100 μm, about the magnitude usually ascribed to the sum of the two "aureoles de transition" thought to surround each aggregate grain.
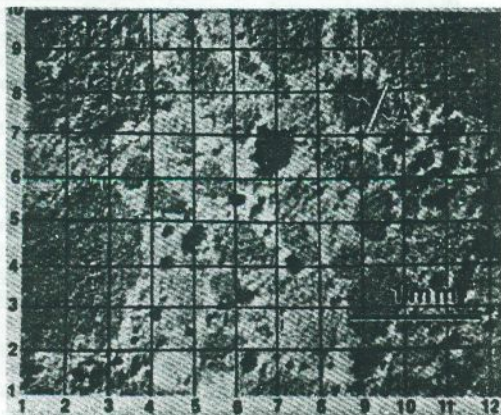

Fig. 1. Illustration of narrowness of paste ribbons in concrete.

Fig. 1, from (8), shows an area on a plane surface of a typical concrete; widths of the paste ribbons were measured on a statistical basis as controlled by the superimposed grid. The position marked "A" shows a typical measurement.

Although the ribbons of paste are narrow, individual cement paste particles are two orders of magnitude smaller yet, ranging in size from a fraction of a μm to several μm. Hence the term "microstructure" and the need for electron-based microscopes to investigate the details.

Cement paste arises as a direct result of the hydration of portland cement with a restricted amount of water. The microstructure varies greatly with the amount of water (more conventionally, with the water:cement ratio) used. The importance of this feature cannot be stressed too highly, both in terms of microstructure itself and in terms of the effects produced on many technical properties (strength, permeability, resistance to service-induced degradation) of the material in service.

The microstructure in a given system is also a function of time. Early age microstructural features develop rapidly on contact of the cement with water. These change with time on a scale of minutes or hours at first, and then more slowly over the first week or so after mixing. The hydration processes in most cement systems are rarely quite completed in practice; as hydration processes continue over periods of months or years, concomitant slow changes in microstructure may occur from deposition of late hydration products. Changes may also come about by solution and reprecipitation of certain previously-existing components independently of additional hydration.

Thus a specific cement paste or concrete hydrating under specific conditions generates not a single microstructure but a successive set of microstructures at progressive stages of development. To add to the complication, any given paste at a given age will be found to vary in microstructural details from place to place, reflecting variations in the local assemblage of the clinker grains that gave rise to the paste in each vicinity.

As a practical matter, the local variations may be adequately described by reference to only two or three typical local assemblages, which after a few days may not change very much with time. However, zones near aggregate interfaces and other special areas always require additional specific investigation to describe their pertinent features.

The writer considers that a proper microstructural description should consist of at least (a) a description of the various kinds of structural elements (particles, films, crystals, entrained air voids, etc.) that are present, together with some indication of their sizes and proportions, and (b) a description of their juxtapositions and mutual arrangements in space within the volume of the system. There may be several different typical assemblages of particles co-existing in different places within the cement paste; this fact should be duly noted, and the relative proportions of each estimated. Unfortunately, few, if any, "proper" microstructural studies meeting this standard have yet been published.

In the present state of the art, microstructural descriptions are ordinarily qualitative, and are necessarily quite subjective. However it appears

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that computer-based image analysis techniques may soon make quantitative descriptions more generally available.

Such computer-based image analysis programs should not be confused with more ambitious computer modelling programs. In the latter quantitative descriptions are derived by algorithms based on specific assumptions for successive periods of hydration under specified conditions. Such hydration modeling programs are currently being developed at several institutions, and the concepts involved have been discussed in some detail by Jennings et al. (9). A remarkable illustration of what can be done along these lines with current technology was presented by Jennings and Johnson (10), in terms of a simulation of the hydration processes and microstructural development in a C_3S paste.

Fig. 2, kindly supplied by H. M. Jennings, represents one output of such a program. The figure is a computer-drawn microstructural image in which the circles represent the original C_3S grains and the hexagons precipitating calcium hydroxide crystals. The original boundaries of the C_3 grains are depicted by the narrow white circles; the gray areas represent C-S-H gel deposited both within and external to the original grain boundaries. The figure represents the state of the system at a specific hydration time, and sequences of such figures can be produced to image the calculated microstructure at any desired age.
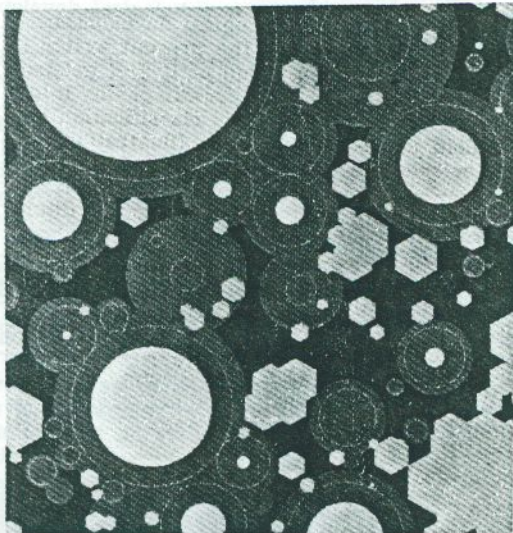

Fig. 2. Computer-drawn representation of a stage in C_3S hydration (H. M. Jennings).

While the concept and some of the specifics of such modelling of microstructural development can be extended to portland cement paste, such extension is extremely difficult because of the much greater complexity of the cement system, and success should not be expected in the near future.

Properly speaking, pore size distributions elements should logically form a part of a microstructural picture of a cement paste. However, historically such distributions have been developed using techniques (such as mercury intrusion porosimetry) that are separate from and do not correlate readily

with microscopic studies. Furthermore, a number of controversies have arisen relative to their interpretation. Because of these difficulties, pore size distributions will not be treated in detail in this review.

TECHNIQUES OF INVESTIGATION

The sizes of the structural features in cement paste are such that the magnification capability of optical microscopes, however refined, are of little applicability, and electron microscopes of one kind or another are required.

Early work in the area was done by transmission electron microscopy (TEM), but long before the Paris Congress scanning electron microscopy (SEM) had effectively displaced TEM techniques for this purpose. The latter has major advantages in ability to handle large samples conveniently, and in ability to permit one to visualize depth and topography; this has more than made up for the more limited resolution offered by most SEM instruments.

Dalgleish and Ibe (11) developed effective procedures for ion-beam thinning sections of hardened cement paste for use in then newly-developed scanning transmission electron microscopy (STEM). In STEM examinations the image is formed by a raster technique, but is derived from electrons transmitted through very thin sections or films of materials, as in TEM. A combination of conventional fracture-surface SEM and ion-beam thinned STEM micrographs were used to provide a more definitive picture of the types of structures present.

Among the several possible imaging modes available in SEM is one in which the backscattered electrons are used to form the raster image. While the resolution is ordinarily not as high as the usual secondary electron images available from the same instrument, Scrivener and Pratt (12) have taken advantage of the differential element contrast capability available in this mode to produce extremely useful and informative backscatter electron image (BEI) micrographs of polished cement paste surfaces. These clearly delineate, for example, areas of calcium hydroxide crystals from areas of C-S-H gel, or areas of hydration product from areas of unhydrated clinker compounds. They can readily be used with image analysis techniques to produce quantitative estimates of the contents of specific components in the paste.

Barker at al. (13) illustrated the potential applicability for cement paste of a number of unusual microscopic technologies, including synchrotron topography and scanning acoustic microscopy, as well as BEI. At the same conference Barker and Barnes (14) reviewed and illustrated a variety of techniques for distinguishing phase composition of microstructural features within the SEM.

The continued utility of transmission electron microscopy, particularly if ion-beam thinned specimens, has been demonstrated by Groves (15).

All of the techniques mentioned so far necessarily involve drying of the paste specimen and exposure to high vacuum. The drying procedure itself may have unwanted effects, especially at very early ages. Orr (16) described a freeze-drying proce-

dure designed to minimize such difficulties. Possible effects of drying cement pastes on their microstructural characteristics were also emphasized by Parrott (17), who proposed a solvent replacement procedure followed by evaporation of the low surface tension replacement fluid used.

It is also possible to avoid drying, by imaging wet cement pastes in special wet cells using high voltage (transmission) electron microscopy (HVEM); instruments capable of doing this ordinarily operate at ca. 1 million electron volts and are available only in a few centers. Jennings et al. (18) combined HVEM observations with both conventional SEM and STEM observations of ion-beam thinned specimens, but unfortunately, only studied hydrating C$_3$S pastes. While the HVEM images are provided at high magnifications, their crispness and the ability to define detail are limited.

Use of a "wet cell" of an entirely different type within a standard SEM was reported by Diamond et al. (19). In this system the image is formed by backscattered electrons detected by a Robinson detector; the specimens themselves are completely saturated and are kept wet by a stream of water-saturated air pumped through the specimen chamber, which is isolated from the high vacuum electron column. The system was developed primarily for detection and observation of crack formation on paste and mortar specimens loaded in tension (20 - 22) and subsequently, in compression (23) within the SEM; its use and characteristic operating parameters were described in some detail by Diamond et al. (24).

Resolution in this system is adequate for observations of cracking and crack propagation, but not for proper study of microstructural details in cement paste. Micrographs taken at much more than 1,000x suffered from loss of resolution. A somewhat different kind of wet cell has recently been developed by Jennings et al. at the National Bureau of Standards for which a patent has been applied for (25); this device is said to be capable of securing useful micrographs of wet pastes at up to about 5,000x magnification, and thus does have the potential for study of cement paste microstructure.

MICROSTRUCTURAL ELEMENTS IN ORDINARY CEMENT PASTES

As is well known, portland cements hydrating under ordinary conditions give rise to several morphological forms of calcium silicate hydrate gel (usually abbreviated as C-S-H gel or even CSH); to calcium hydroxide; to ettringite or ettringite-like AFt phases; to calcium aluminate monosulfate hydrate or related AFm phases; and occasionally to small amounts of other phases, notably hydrogarnets. These, combined with residues of unhydrated clinker components and the pore spaces between (and possibly within) the solid particles comprise the microstructural elements making up cement paste.

It is usually considered that C-S-H gel makes up the largest proportion of the system, with calcium hydroxide of somewhat lesser importance, and the AFt and AFm phases being of relatively minor account. The total of these phases naturally increases with degree of hydration, as the propor-

tion of residual unhydrated cement diminishes. The relative volume of pore space also diminishes, but the degree to which the original water-filled space between the cement grains is filled depends strongly on the water:cement ratio.

Taylor (7) has recently calculated from experimental measurements the weight and volume proportions of each of the phases in several specific portland and portland-fly ash pastes. A w:c 0.5 portland cement paste hydrated for 3 months was found to have, in its saturated state, volume percentages of 40% C-S-H gel, 16% AFm product, 12% calcium hydroxide (plus 1% calcium carbonate carbonation product), a total of 8% of residual unhydrated cement, and a total of 24% of pore space. No attempt was made to define the relative proportions of the different C-S-H gel types. However, weight percentages in the saturated state, and volume and weight percentages in the dried condition were also estimated. The unexpectedly high content of AFm phase and the apparent absence of AFt product was not commented on.

The hydration processes, even if carried to completion, do not completely efface all traces of the original cement grains. As indicated by Taylor and Newbury (26) the original outlines of the clinker grains are substantially preserved and can be traced by Mg and Fe x-ray imaging.

Besides being the major component of the hydrated cement paste system, C-S-H gel is notorious for the variability of its morphological development. Approximately 10 years ago the present writer (27) proposed a rough classification of C-S-H gel particles observable in portland cement pastes into four morphological types. This classification seems to have held up reasonably well. Illustrations of Type I (acicular or lath-shaped), Type II (reticulated or honeycomb) and Type III (small disks or spheres) structures are common in current literature and are too numerous to cite individually. Various authors have also identified local regions of very dense "inner product" CSH as corresponding to the Type IV hydration product. This is more commonly seen when using specimen preparation techniques other than simple fracturing.

Illustrations of the several types are provided below. These are taken at relatively low magnifications to attempt to preserve an impression of the cement grain context in which they develop.

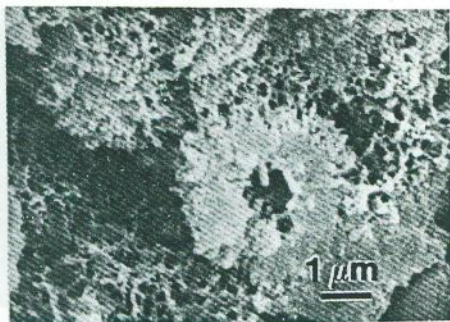Fig. 3. Type I C-S-H gel particles growing radially around cement grains.

Fig. 4. Type II C-S-H gel network; note the submicron size of the mesh, and the hollow hydration shell (early hydration).
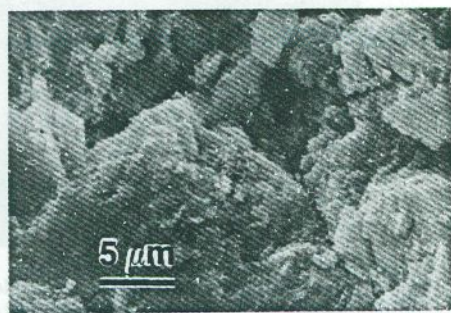

Fig. 5. Fine textured, almost featureless Type III C-S-H gel (late hydration).

Fig. 6. An "inner" hydration product cement grain residue showing dense Type IV morphology.

One of the peculiarities of portland cement paste is the degree to which the microstructure developed varies with relative amount of water-filled space in which the hydration processes take place, and also with chemical components that may dissolved in the water. The four C-S-H gel morphological types described by the present writer were meant to categorize the hydration product on conventional cement paste, and are certainly not the only morphologies that can be produced. This was illustrated profusely by Odler and Lin (28) who hydrated polished clinker surfaces in a various

free solution exposures, and produced a variety of well developed morphological types not usually seen in cement pastes.

A somewhat different classification of C-S-H gel morphological types, especially formulated to describe the sequential development of microstructural features in the early stages of C_3S (rather than cement) hydration, has been developed by Jennings et al. (29). The later stages described in this scheme correspond in substance, although not in nomenclature, to three of the four C-S-H gel types described by the present writer. Type III C-S-H gel was not observed in these studies.

The C-S-H gel types defined by the present writer were meant as shorthand descriptions of C-S-H gel morphologies as seen in scanning (or transmission) electron microscopy. These techniques ordinarily require that the cement pastes observed be pre-dried and evacuated before observations can be made. It has been suggested that Type I or fibrous particles, especially those produced in the earliest stages of hydration, may to some degree be artifacts of drying. These are said to be produced from preexisting colloidal or gelatinous crumpled films or foils which roll up or otherwise assume a fibrous morphology. Evidences for this point of view in the form of high-voltage transmission electron microscope pictures of wet C_3S pastes were published by Jennings et al. (18) and subsequently for both C_3S and C_2S pastes by Scrivener (4). The concept has been reviewed and restated by Jennings (29) in a recent review of cement microstructure development.

In these works as published, it is not exactly clear whether the authors ascribed such genesis to all Type I particles in hydrating C_3S pastes or only to those formed in the earliest stages of hydration. Jennings (30) indicated that the latter was the case in his experience; he considered that most of the Type I material formed in hydrated C_3S and in cement paste was not due to changes induced on drying, but preexisted as such in the undried pastes.

Lachowski and Diamond (31) made a study of fragments of cement pastes ground and examined in an analytical electron microscope and in an SEM. Composition was determined on appropriate very thin spots on the fragments, each of which was subsequently mounted for SEM work. It was hoped that information might be obtained on possible differences in composition between particles of C-S-H gel showing the different characteristic morphological types, but unfortunately, all of the C-S-H gel particles obtained for study were classifiable as Type III C-S-H gel. The compositional parameters still showed considerable variation, even from thin spot to thin spot on the same particle.

The work did provide an opportunity to image characteristic Type III gel at high resolution, and Diamond and Lachowski published several of such micrographs taken at up to 80,000x (32). Little additional detail could be gained, but it was clear that this gel consists of rounded nodules of the order of 0.2 μm, fused together to make up more massive particles.

C-S-H gel is not the only component in cement

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paste with a variable morphology. A considerable variation in morphology of calcium hydroxide is also present, although it has not been formally divided into classes and thus not always appreciated. Thin amorphous-appearing films that are flat or sometimes curved in complex fashions, thin linings of pores and coatings developed on foreign substances included within pastes, thin plates without specific recognizable interplanar angles, thin but clearly hexagonal plates, thick plates, massive layered structures incorporating CSH gel and other particles, and oriented multi-particulate deposits of several different morphologies have been seen by various investigators in cement pastes. This point has been recently emphasized by Shpynova et al.(33), who studied the range of variation of calcium hydroxide morphologies derived from CaO hydration under various conditions.

A few of these types are illustrated in Fig. 7 below, taken from the water-rich region of a four day old w:c 0.5 paste cast against a glass substrate. A thin film is visible to the right of "A", and thin hexagonal platy crystals ("B") and a large, euhedral hexagonal crystal ("C") are also visible. Micrographs showing other well-formed calcium hydroxide morphologies, developed especially near interfaces, will be presented later.
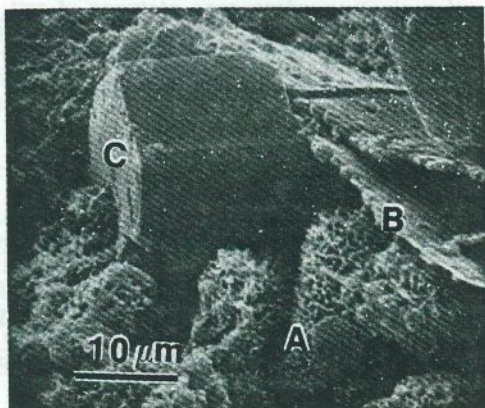

Fig. 7. Illustration of several Ca(OH)$_2$ morphologies

Much more representative of the usual status of most of the calcium hydroxide in mature pastes are the micrographs of Figs. 8 and 9 below. A "mature" paste microstructure is characterized by an intimate intermingling of layered deposits of calcium hydroxide and Type III C-S-H gel; indeed many instances of the layered calcium hydroxide crystals growing around and encapsulating pockets of gel (and other paste components) have been observed. The usual presentation of the layers in fractured pastes is approximately normal to the fracture surface, as in Fig. 8, but occasional fractures run along the layers, as seen in Fig. 9.

Of great interest is the demonstration by Groves (34) using TEM of ion-beam thinned specimens of low water:cement ratio cement pastes that embedded in the dense Type III C-S-H gel structure are very small microcrystalline clusters of calcium hydroxide, only about 100 A thick and stacked normal to the local c-axis direction but in a two-dimensionally random array. Such very small stacks are not generally observed using SEM,

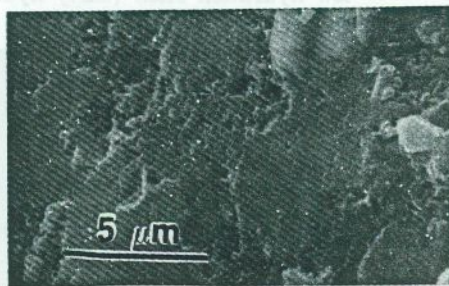Fig. 8. Typical intermingling of layered calcium hydroxide with Type III C-S-H gel.

Fig. 9. Exposure of calcium hydroxide along the layer, showing the intermingling.

The interspersion of calcium hydroxide in much larger crystals with C-S-H gel on a much coarser scale was a feature in the investigation of Marchese (35); this author examined fracture surfaces of old, but higher water content cement pastes using EDXRA and paired examination of each matching side of the fracture surfaces produced.

Calcium aluminate hydration products, while quantitatively less important and geometrically less complex, may be important features in the development of microstructure in certain types of cement pastes, notably expansive cement; and of course are of major concern in sulfate attack and perhaps in other secondary degradation processes.

Ettringite-type (AFt) crystals are usually elongated particles, sometimes roughly circular in cross section, sometimes bounded by plane surfaces. Hollow or partly hollow particles have been observed. Ettringite particles show some variation in size and may show considerable variation in aspect ratio, short, stubby rods being reported to occur under some conditions. Monosulfate-type (AFm) crystals are almost invariably small thin hexagonal plates, found in local clusters of relatively few particles, with a characteristic edge-to-face contact between adjacent plates.

Fig. 10 provides some indication of the morphologies of these phases, although the figure itself was taken from a paste composed entirely of high-calcium fly ash and water, rather than a cement paste. The spheres are obviously fly ash particles, the rods are ettringite, and the thin plate ("A") is an AFm phase.
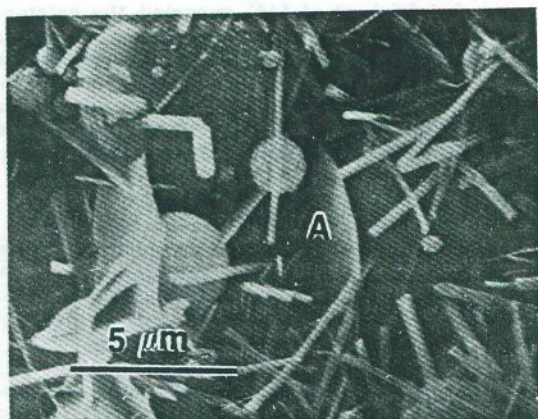
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Fig. 10. Morphologies of AFt and AFm phases developed in a fly ash paste.

The development of C_3A and C_4AF products independently with and without sulfate, and in cement pastes were studied using a wet cell in a HVEM by Scrivener and Pratt (36); the importance of the solution sulfate concentration at the time of hydration in determining the product morphology was stressed. Of possibly greater importance were the observations of the influence of the presence of C_3A in the development of hollow shell hydration grains, as discussed subsequently.

Ettringite is of course much more important as a microstructural element in expansive cement than in conventional portland cement systems. Ogawa and Roy (37) studied the formation and morphology of ettringite produced in pastes whose main component was the type K expansive compound, $C_4A_3\bar{S}$; early ettringite seemed to occur as small irregular particles; later deposition occurred as a radial zone of elongated crystals around the hydrating grains, with expansion said to commence when these zones intersected each other.

All of these microstructural units exist in and are characteristic of cement paste in concrete that has been hydrated under ambient conditions. As is well known, high temperature curing and especially autoclaving, can result in substantial changes in the compositions and microstructures of the products formed. Autoclaving, especially, generates an entirely different class of hydration product, comprising well crystallized calcium silicate hydrates and other compounds. The details of microstructures developed under these conditions are not considered further in this review.

UTRASTRUCTURE OF CEMENT PASTE STRUCTURAL ELEMENTS

The crystal structures of calcium hydroxide, ettringite, and calcium monosulfate hydrate components of cement paste are well established, and while the latter two are subject to significant atomic substitution, there is little fundamental uncertainty as to their structure on a scale below that visible in conventional scanning or transmission electron microscopy.

This is of course not true for C-S-H gel; the degree of crystallinity in this material is so poor that conventional structural analysis procedures are useless. Indeed, it is not at all clear whether the different C-S-H gel morphological types represent materials with significant ultrastructural (or even compositional) differences, or whether they are different morphological forms of quite the same substance.

The chemistry, water content, and internal structures of C-S-H gel particles have been reviewed intensively by Taylor in the 1980 Paris Congress (1) along with similar treatments of the AFt and AFm phases. A more recent summary (38) was provided by this author as part of a series of instructional modules in cement science. The chemical composition of C-S-H gel particles is found to be variable, with mean Ca:Si ratio of 1.4 to 1.6 in different mature cement pastes; individual analyses may depart fairly widely from these mean values. Substantial, but variable amounts of aluminum, iron, and sulfate ions are also usually found. The ascertainable water content of the solid hydration product particles is significant, but varies with type of drying. As mentioned previously, crystallinity is very badly expressed, with only two or three weak x-ray diffraction peaks discernable. The silicate anions are partly polymerized in the structure of the C-S-H gel, the degree of polymerization increasing with age.

Very recently, Taylor (39) has presented evidence for a proposed C-S-H gel ultrastructure consisting of disordered layers, most of which are structurally imperfect jennite and others structurally imperfect 1.4nm tobermorite.

In addition to the above characteristics and others enumerated by Taylor (38), it is well established by a variety of techniques that C-S-H gel particles possess a large internal surface. While the geometrical details of the internal surface are not, in the present writer's opinion, adequately understood, Winslow (40) has recently shown that the fractal surface dimensions of cement pastes are very high (2.95 to 3.09 in his measurements), indicating a very rough and irregular arrangement of this internal surface structure.

In the absence of hard structural information, a number of so-called "models" of C-S-H gel based on inferences from measured properties have been proposed, illustrated repeatedly in review publications, and discussed frequently. The writer does not feel that any of these are sufficiently well based to be of serious consequence to the present microstructural treatment, and they will not be considered further.

ORIGIN AND ARRANGEMENT OF MICROSTRUCTURES IN CEMENT PASTES

In this section the writer hopes to convey some picture of the microstructural patterns observed in cement paste, and an indication of the current state of efforts to understand its origin and development.

Cement paste arises as a result of hydration reactions taking place in cement mixed with a limited amount of water. Hydration reactions begin almost immediately, but ordinarily slow down though a period of only minor activity, during which mutual adjustments of the arrangements of cement grains

and other particles can take place. A surge in rate of hydration is then ordinarily experienced, which is shortly followed by setting; the mobility of the system is then essentially lost.

The development of the hydration product structure can conveniently be divided into three parts: (1) the earliest stages of hydration in which the focus of activity is confined to the actual surfaces and near-surface mix water surrounding the individual cement grains; (2) a later stage, in which hydration products project into or are deposited within the solution-filled space between the cement grains, meet, and start to form a coherent skeletal structure which then stabilizes grain-to-grain arrangements and results in setting; and finally (3) the remainder of the hydration processes, during which the skeletal structure fills in with additional hydration product generated from within the original outlines of the cement grains. The first two stages occur during the first hours of hydration, with the third stage comprising most of the actual period of active hydration.

The details of the first stage are perhaps little influenced by the water:cement (w:c) ratio, but the morphology produced in the second and third stages are to a large extent dominated by this parameter. The same cement can produce distinctly different microstructural assemblages depending on the amount of water-filled space available. The point was illustrated with respect to a "low porosity" cement by Diamond (41), and has been more recently re-expressed with respect to C_3S paste by Abo-el-Enien (42). Even compaction of an already-mixed paste followed by vacuum removal of excess water squeezed out of the system was found by Bajza (43) to change the character of the hydration products that were subsequently deposited; after effective compaction little of the usual massive calcium hydroxide crystal deposition could be detected.

In discussing the initial hydration stages, the floc structure of fresh cement paste should not be ignored. As is well known, ordinary portland cement mixed with water, in the absence of superplasticizers or special dispersants, invariably forms floc structures. Visible sedimentation of these flocs can be seen in diluted pastes; the counterpart of this in concrete is bleeding. The individual flocs may range up to several hundred μm in size, and may be composed of many individual clinker particles. They involve relatively close contacts between some portions of the clinker grains, but contain substantial pocket of empty (water-filled) space; additional water filled spaces occur between adjacent flocs. On setting, these spaces become "capillary" pores. In typical concretes batched at high water:cement ratios, these subdivide but remain incompletely filled despite long-continued hydration.

The nature of the surfaces of ground cement grains undoubtedly influences early hydration profoundly. Little is known about these surfaces. They would be expected to be comprised more or less randomly of patches C_3S and C_2S, with occasional narrower exposures of zones of the smaller interstitial C_3A - ferrite assemblages, depending on how the specific clinker fractures in the grinding process. It is expected that many surfaces may be contaminated with smeared depo-

sits of gypsum or hemihydrate because of the universal intergrinding of this softer component. Dalgleish et al.(44) reported the existence of smeared surfaces on the particles of as-received cement of one type of the three examined, but not on another. They were not able to determine the nature of the smearing material. Gypsum is known to dissolve only slowly in mix water, and smeared surface deposits, if present, may remain for some hours.

The local availability of gypsum smeared onto some cement surfaces combined with surface exposure of at least local areas of interstitial C_3A may account for recent observations that suggest that one of the earliest recognizable hydration responses is the formation of an amorphous or gelatinous film around some grains with a composition approaching that of AFt (45). Indeed, hollow sacs and hollow tubules of gelatinous material having such composition have been observed to form by several authors, including Barnes et al. (46) and Pratt and Jennings (45). The "glutinous films" reported as the earliest products by Orr (47) may fall into this category, although no chemical information was provided by this author.

On the other hand, Dalgleish et al.(44) reported etch pitting on clean surfaces of a cement that did not have a smeared deposit as its earliest hydration response, followed by subsequent development of deeper pitting and deposition of possible hydration products on some areas; other areas remained smooth and seemingly unaffected in the same period. There is no indication, in this detailed description of the earliest hydration morphology, of any "glutinous film" formation, nor of crinkled films and foils that have been variously reported. This may be a consequence of the specimen preparation procedure used, which involved freeze drying.

After a few hours Dalgleish et al. reported that small regular individual particles of "calcium hydroxide and/or AFt" morphology appeared widespread over the surface of one cement, followed by generation of a fibrous deposit of C-S-H appearing to arise from a filmy layer on the surface. AFt products seemed more plentiful in the initial deposits around grains of the other two cements examined, but by four hours "all of the cements...showed particle surfaces entirely covered by product."

The next step in the sequence seems clear, and has been remarked as an important step in the hydration process since its first clear description by Hadley (48) as early as 1972. A micrograph taken from this work is provided as Fig. 11. It was evident from Hadley's results that by 1 day many grains in near-aggregate surface zones investigated by him had formed thin (1 μm thick) shells, and that the enclosed clinker grains had subsequently dissolved away, leaving a large gap or in some cases a completely hollow shell.

In 1978 Barnes, Diamond and Dolch (49) concluded that hollow shell grains occur in bulk paste as well as that formed in aggregate-influenced zones, and that such grains constituted the vast majority of grains so fractured that the interior was visible. The paper concluded with the implication that the formation of such grains was an intrinsic part of

the normal cement hydration process that should not be overlooked in modelling the hydration process. The present writer is gratified that this is finally being recognized.
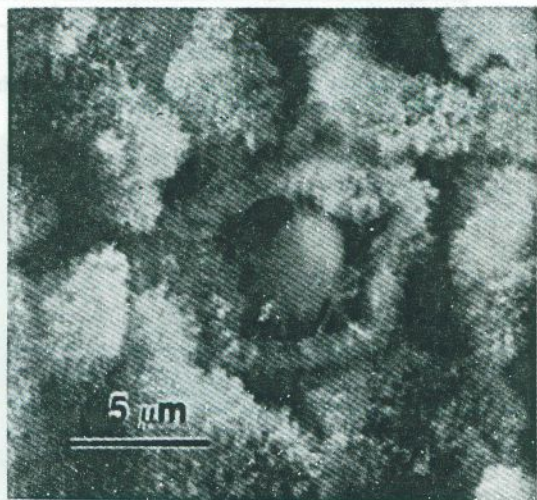

Fig. 11. Hydration shell and remnant grain (w:c 0.5 paste cast on glass slide, 1 day). Fig. 13 from the thesis of Hadley, 1972 (48).

Hadley originally considered the structure of the shell to consist of an inner layer of oriented and stacked platelets of calcium hydroxide deposited first on the cement grain, with an outer shell of C-S-H gel. He found AFt rods and platelets of AFm projecting inward from the shells into the empty space formerly occupied by cement grains, and occasionally rods projecting outward.

Subsequent work suggests that the shell structure is less regular than Hadley supposed, and is principally C-S-H rather than calcium hydroxide. However, the local composition and to some extent the local appearance at high magnification may vary from place to place around the perimeter of a given shell. Many shells seem to be slightly incomplete, in that small holes or thin spots can be detected through which solutions can apparently diffuse easily.

In recent work, the formation of such shells starting around 12 hours after the beginning of hydration was clearly described by Dalgleish et al.(44), with a micrograph taken at this time showing detachment of the shell from the hydrating cement core. The feature was even more prominent at 18 hours, and a STEM micrograph of an ion-beam thinned specimen taken normal to the shell at this time showed an apparent thickness of approximately 0.5 μm, and a gap of almost this extent.

Further details of such shells were provided recently by Pratt and Ghose (50), along with confirmation of their status as intrinsic features of the normal cement hydration process.

On further hydration it was proposed by Pratt and Ghose (50) that there is a progressive inward thickening of most shells, from an early thickness of the order of 1-2 μm at ca. 12 hours, to up to 5 μm at 4 days, and possibly exceeding 10 μm after

7 days. This does not seem to have been the usual case in the writer's experience and that of his colleagues.

For example, none of the shells rescorded in the original work of Hadley (29) much exceeded 2 μm in thickness, and the pastes examined were up to 14 days old. In the Ph. D. thesis of Barnes (51) cement mortar specimens were examined after a 14-day hydration period; residual shell thicknesses observed in hollow shell grains (for example in his Figs. 266 and 267) did not appear to appreciably exceed 2 μm.

With the recognition that definite shells of hydration product surround individual cement grains after a few hours of hydration, the subsequent processes of hydration and microstructural formation can be subdivided; attention should be paid separately to what happens on further hydration within the shell, and what happens to the space between shells. Attention to the latter will be postponed.

It is evident that the shells do not constitute impenetrable barriers to the outward flow of dissolved clinker components, since as hydration proceeds the outside capillary space progressively fills up with freshly-deposited hydration product. Thus residual clinker cores necessarily get smaller as hydrations continues, and many disappear.

There seems to be some difference of opinion, however, on what else happens within the perimeter of the shell.

It is worth restating at this point that according to Taylor and Newbury (26) the original boundaries of the cement grains in old pastes can be established by electron probe microanalysis imaging of the distribution of Mg. Thus one can establish the inner boundary of the original shell as deposited around a given clinker grain.

Once the shell has been deposited, some cement grains empty out their contents quickly and become fully hollow. Other hydrating grains do not; instead hydration is accompanied by deposition of dense hydration product just inside of, and contiguous with, the inside of the shell. Various workers report that in such grains the shell plus dense hydration product thus gets thicker as the core gets smaller, with only a small gap being observed between the augmented shell and the core.

According to Pratt and Ghose (50) this narrow gap as observed by conventional SEM procedures may be an artifact of drying. In any event, these authors have clearly depicted the formation of the dense inner deposit of hydration product within the shell. This interior hydration product is apparently C-S-H gel without visible particulate structure, presumably the Type IV gel.

Scrivener and Pratt (52) suggested that if the shell is tight, calcium hydroxide necessarily formed by the C_3S hydration reaction will be dispersed in microcrystalline form through this dense inner CSH product. The hydration product in any case may not be homogeneous; zones of iron-rich material interpreted as relicts of interstitial material almost unmoved from their original locations within

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cement grains have been reported by Taylor
and Newbury (26).

Some uncertainty exists in understanding why some
clinker grains hydrate in the first mode, i.e. so
as to form hollow shells, and others in the second,
so as to form dense inner product. Scrivener (4,
p. 155) suggested that it is only the smaller
clinker grains that form completely hollow shells,
with hollow grains larger than 5 μm never being
observed. The basis for the distinction is thus
suggested as being the size of the individual
grain; some subsequent authors have accepted this
as a working criterion. This may not be correct.
Hollow grains have been observed in the writer's
laboratory by Hadley (29) and by Barnes (51) in
the 10 to 15 μm size range, without any attempt to
select or look for especially large hollow shells.
Indeed, the stereo pair of a completely hollow shell
grain published as Fig. 3 of (49) is about 12 μm.
in diameter.

A fairly revealing hollow shell micrograph taken
from Barnes (51) is reproduced as Fig. 12 below.
The paste had a w:c ratio of 0.65 and was
hydrated 1 day. Energy-dispersive x-ray analysis
of the residual core at Point 1 indicated that it
was C_3S (Ca:Si atom ratio 2.88). Point No. 2 on
the smooth area of the shell yielded a Ca:Si of
4.36, with some sulfur being detected (Ca:S 0.22)
The shell at this point is thus mostly C-S-H gel
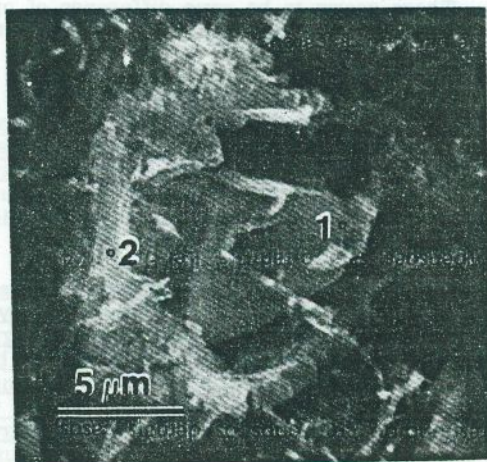with a little bit of $Ca(OH)_2$.

Fig. 12. Partly hydrated hollow-shell grain (w:c
0.65 cement paste, 1 day).

Instead of hollow-shell hydration being a mode
restricted to small grains, our interpretation in the
past has been that it is a function of local space
external to the grains, i.e. local water:cement
ratio. Hollow-shell grains were first located in
connection with studies of the aggregate cement
interfacial zones, where high local water contents
are common. In a small casual experiment carried
out some years ago the writer found that pastes
mixed at very high water contents, such as w:c
0.7, produced large numbers of hollow-shell grains
easily visible on fracture surfaces; in contrast
pastes mixed at very low water contents were
almost entirely unproductive of such observations.

If this concept is correct, the implication is that

clinker grains hydrating in wet environments will
tend to "leak" dissolved material which precipitates
as hydration product in the external spaces if
such spaces are plentiful; if they are scarce, i.e.
the cement grains are closely packed, this becomes
progressively more difficult, and precipitation
of hydration product necessarily tends to ensue
within the shells as inner product.

Fig. 13 below provides an illustration of hollow
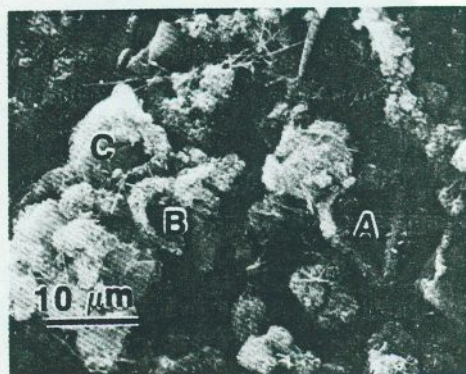shell development in a very wet paste.

Fig. 13. W:C 0.70 cement paste, 1 day, showing
three nearby hollow shell grains.

It is also possible that the effectiveness of the
shells as a partial barrier may depend in part on
the individual layout of the clinker compounds on
the surfaces of each grain; for example, if the
shall requires a film of calcium aluminate sulfate to
deposit on, as seems possible, grains with little
C_3A exposure on the surface may not form a com-
plete film and hence give rise to "leaky" shells.

It may be useful at this point to remark that the
hollow shell mode of hydration apparently depends
on the presence of calcium aluminates and gypsum,
and is not found, for example, in C_3S-water
pastes. Classical studies of C_3S hydration have
thus been misleading indicators of what to expect
with cement hydration.

It is now appropriate to return to consideration of
that part of microstructure development that con-
cerns deposition of hydration products in the
"capillary" spaces between the clinker grains.
This has been more easily followed in microstructu-
ral studies, and generally more familiar.

The scenario is approximately as follows. Early
C-S-H Type I fibers and ettringite rods are sup-
plemented rapidly by calcium hydroxide deposition;
reticulated (Type II) C-S-H zones appear, and
adjacent shells start to become tied together. Thin
calcium hydroxide plates grow and then thicken
and the characteristic layered $Ca(OH)_2$ morphol-
ogy starts to be seen; deposition of fine-particle
Type III C-S-H gel starts to overlay and obscure
some of the earlier deposits; now-massive deposits
of calcium hydroxide continue to grow and start to
intrude around and encapsulate local regions of
C-S-H gel, and the particle outlines start to
become more difficult to see, especially in low
water:cement pastes.

The processes naturally vary in detail from place
to place in a given paste, and the rate of deposi-

tion of product is naturally conditioned by the cement used and by the local environment.

Illustrations by the writer of the mature product morphology have appeared in Refs. 6, 27, and various other places, and by many other authors in a variety of publications.

The extent to which the morphology attains maturity is frequently not uniform over the entire paste or concrete system. In consequence several different local morphologies may simultaneously persist. As indicated in (6), a generally dense paste marked by extensive infilling of Type III C-S-H gel and massive intergrown calcium hydroxide deposits may often contain pockets of entirely different and "looser-textured" morphology. In these pockets individually discernable Type I particles and ettringite rods persist, patches of the Type II network structure remain, and visual space between particles makes their individual identifications easy. Broken hollow-shell (Hadley) grains may be seen in such pockets, and local clusters of thin AFm plates may occasionally be detected. Few of these features can be seen in the denser, more mature regions of the same paste.

This localization of the microstructural development pattern is perhaps a consequence of the restriction of movement of dissolved cement components before they precipitate as hydration products as emphasized by Taylor and Newbury (26); the generalization they arrived at was that "a substantial proportion of the precipitation occurs within distances below a few μm or even a few nm" from the staring site in a clinker grain.

PASTE MICROSTRUCTURE IN THE PRESENCE OF SUPPLEMENTARY CEMENTITIOUS COMPONENTS

Supplementary cementitious components or mineral admixtures include, but are not restricted to such substances as slag, silica fume, fly ash (pfa), and ground natural pozzolans incorporated in concrete either as factory blended cements or as materials batched separately into the concrete. These components by their mere physical presence naturally affect the development of paste microstructure; most also enter into chemical responses with the developing hydration product system.

As a general principle the writer considers that microstructure-forming processes respond to all aspects of the internal environment during hydration. Many of these may be changed by the incorporation of supplementary components.

A number of effects are possible, which may conveniently be grouped as follows:

(a) Physical effects accompanying the introduction of the particles of the supplementary component. These are mostly in the same size range as cement grains, except for silica fume. The typical particle size of most silica fumes is perhaps two orders of magnitude smaller than that of cement grains. The numbers of such particles added in any real application are thus immense compared to the number of cement grains, and so-called "filler effects" have been extensively discussed in the technical literature.

(b) Physicochemical effects are possible, especially manifesting themselves in modifications of the floc structure. As an illustration, Helmuth (54) recently proposed that many fly ashes reduce water demand by a deflocculating effect resulting from their finest particles becoming adsorbed on or stuck to large cement grains.

(c) Chemical effects, which may take place directly or indirectly. For example, species such as alkali sulfates present as coatings on a few fly ashes dissolve quickly and greatly modify the alkalinity and sulfate content of the mix water and thus the pattern of early hydration (55). Acceleration of the early hydration of several cement components by seemingly "inert" low calcium fly ashes has been reported (56). Chemical effects may be indirect, in that they can involve reactions with hydration products rather than with the hydrating cement grains. An obvious examples is late stage "pozzolanic" reaction with previously deposited calcium hydroxide.

On a somewhat different level are effects produced by chemical admixtures used, sometimes at a high dosage level, together with a supplementary component. The obvious examples are the effects resulting from high dosages of superplasticizer in silica fume concrete or in certain high strength fly ash bearing concretes. It appears that certain combinations together produce major effects on the microstructure that would not be present if either were used independently.

Microstructural Effects Of Fly Ash Incorporation

Fly ash or pfa, unlike many other supplementary components, is a highly inhomogeneous material. It is composed of individual particles that are collected, rather than being ground from a larger mass, and these particles are not alike. Rather, each particle is derived independently from an individual ground fragment of coal being carried on an air stream, isolated from its neighbors. Its composition, and thus to some extent its behavior in cement systems, may be different from its neighbor. This tends to make microscopic interpretations of the general effect of adding a given fly ash to cement rather difficult; different particles do different things.

Different fly ashes also vary considerably from one source to another, depending both on the coal being burned and the details of the power plant operating system.

A distinction is customarily made between low-calcium content fly ashes derived mostly from bituminous coals and high-calcium ashes from sub-bituminous and lignite coals. This is operationally (if not by definition) the distinction between the "Class F" and "Class C" pozzolans of ASTM C 618. The microstructural implications of this dichotomy are not yet clear. Much work has been done over the years with low calcium fly ashes, but the effects of the high calcium fly ashes on cement paste microstructure have only recently begun to be documented.

The apparent physicochemical effect of some fly ashes on the floc structure of cement paste has already been mentioned.

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With respect to what happens to the fly ash particles themselves, a considerable body of information has developed. It appears that one of the first recognizable responses is the deposition of a thin duplex film of calcium hydroxide topped by a sparse layer of C-S-H gel on their surfaces. This seems morphologically and compositionally identical to the duplex film known to be characteristically deposited on other inert components (glass, aggregates, etc.) incorporated in cement paste or concrete.

Diamond et al (57) provided micrographs showing almost complete early coverage of fly ash particles by such films; similar coverage on some particles but not on others was reported by Ghose and Pratt (58) and Pratt (50). An interesting paired TEM and SEM view of such a structure was provided recently by Blaschke (59) in his Fig. 12.

The next stage in the response seems to be a densification and modification of this early duplex film into a fairly tight and dense shell, apparently by continued deposition of both C-S-H gel and calcium hydroxide. The latter sometimes deposits in a particular "stacked plate" morphology. A clear illustration of this phenomenon is present in the micrographs of Halse et al. (60). The thin film covering the large fly ash sphere in their Fig. 4 (taken at one day of hydration) is peeled back exposing the duplex film laterally; in Fig. 6, after 7 days, the film has densified into a clearly-defined shell visible particularly clearly around the bright fly ash sphere in the upper part of the figure. Another clear illustration of shell formation was provided in Fig. 7 of the paper by Montgomery et al (61).

Sometimes the original duplex film persists without appreciable densification into a shell; such lack of densification seems evident in the persistence of the duplex film appearance in Figs. 14 at 3 days, and 15 at 14 days in the pastes of Ghose and Pratt (58).

Meanwhile, the usual processes of cement hydration occur on the cement grains, including the development of shells around them and the formation of Hadley grains, as seen for example in Fig. 9 of Ghose and Pratt (58). An interpretation relating occurrences of these microstructural development in fly ash cement pastes with calorimetric responses was recently provided by Halse et al. (62).

Replacement of a significant proportion of cement with fly ash entails a practical risk that unless the fly ash itself contains a quickly available source of calcium sulfate, the gypsum balance in the system may be affected. This may influence both setting and the early hydration responses. It is possible to add gypsum along with the fly ash, and Huang (63) has explored the microstructural and other consequences of so doing. He found evidences of earlier production of gel around fly ash spheres when gypsum was added, and a general appearance of enhanced pozzolanic reactions at intermediate ages.

Whether gypsum is added or not, sooner or later reaction commences on the glass-rich surfaces of some, but not all of the fly ash spheres; this is despite the fact that they are covered by a duplex film or a shell. The reaction is evidenced first by light etching, and as the etching progresses the outlines of crystals of mullite and quartz embedded within the fly ash glass start to become visible. The progressive development of this process of removal of glass and exposure of embedded unreactive crystals is very clearly illustrated in the micrographs constituting Fig. 7 of Halse et al.(60).

It should be mentioned that some fly ash spheres are of radically different composition than most. Many fly ashes contain some content of iron-rich spheres contain extensive embedded magnetite-type iron oxides and only a little glass. The glass may also be iron rich. Such glass reacts only very slowly, but eventually exposes crystals of embedded iron oxides quite different in appearance from the usual mullite or mullite and quartz crystals uncovered in the majority of spheres. Other iron-rich spheres seem not to react at all.

As cement hydration processes proceed and additional hydration products are laid down, the formerly isolated shells surrounding the fly ash spheres tend to become bound together in the developing interconnected structure of the densifying cement paste. Calcium hydroxide may be locally deposited, and sometimes is seen to partly surround and specifically encapsulate fly ash spheres within their shells. A striking illustration of this was provided by Montgomery et al. (61) in their Fig. 4.

This tieing in of shells to the densifying cement paste skeletal structure seems to occur at the same time that progressive dissolution occurs from reactions at the fly ash surfaces within the shells. At least in some cases this leads to gaps developing between the progressively reacting fly ash grain and its surrounding shell, seemingly analogous to gaps developing in hollow-shell hydration of cement grains. Pratt (56) reported that such hollow-shell development in fly ash grains seemed particularly prominent where fly ash spheres had been surrounded by massive layers of calcium hydroxide.

The presence of gaps is also evident in results of Jawed and Skalny (64) and Chanda and Bailey (65).

In a rather unusual study by Montgomery and Diamond (66), the propagation of cracks induced by mechanical loading was studied in the SEM for special pastes in which large fly ash cenospheres were prominent components. Despite the relatively thin walls of the hollow cenospheres, the advancing cracks almost inevitably went around them rather than through them. The paths were clearly between the cenospheres and the lime-rich shells that surrounded them. This may have been due to the existence of such gaps, which were evident once the crack had passed.

Away from the fly ash grains themselves, it appears that the general cement paste microstructure that develops when fly ash particles are used is not dissimilar to that of plain cement paste. However the partly-reacted (and occasional completely unreacted) fly ash particles are a prominent feature, particularly obvious because of their characteristic spherical shape.

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It is generally appreciated that the presence of fly ash both limits the amount of calcium hydroxide that deposits in the early stages of hydration and subsequently results in removal of some of the previously deposited calcium hydroxide. The locations and microstructural features of the removal process, that is, the pozzolanic reaction per se, have not to the writer's knowledge been adequately documented.

As mentioned previously, the specific effects of high calcium fly ashes on the microstructure of cement systems has received attention only recently, in part because they have only recently come into general use. A considerable body of information is now developing.

Grutzeck et al.(67) reported unusual shell formations observed on incorporating high calcium fly ash with an oil-well cement hydrated at 38° C. The shells were dense, radially oriented bundles of C-S-H gel. It is not certain whether these and other observations would be reproduced using their fly ash with ordinary cement under a more conventional hydration regime.

Scheetz et al. (68) studied a number of unusual combinations of materials, including one that involved a high calcium fly ash, with a Class H oil-well cement in the joint presence of an expansive additive, NaCl, and a superplasticizer. Several unusual microstructural features were observed, including extensive development of ettringite both inside of and outside of the separated outer shells around the fly ash spheres. Again the relevance of these features to conventional cement paste morphologies with high calcium fly ashes remains to be established.

Somewhat more conventional fly ash concretes containing high calcium fly ashes were studied by Baker and Laguros (69). They confirmed that duplex films deposit and are evident on fracture surfaces early in the hydration processes with high-calcium fly ashes as well as with low-calcium ashes. They found that after 7 days many smooth-surfaced spheres were observed to be projecting upward from the general fracture surface, with corresponding empty sockets observable on the opposite fracture surface. This is presumably due to the development of a gap between the sphere and its shell, similar to those reported for low-calcium fly ash pastes.

Pistilli (70) provided a number of micrographs of the paste structure in concretes batched with a high content of high calcium fly ash with and without water reducer. While the focus of the investigation was on the air-entrainment characteristics of the various mixes, enough detail can be seen in the micrographs to suggest that the microstructure developed did not differ radically from that customarily seen with low-calcium ashes.

Very recently Mills (71) examined cement hydration products incorporating high-calcium fly ash and found results similar to those previously discussed; that is, development of thin reaction shells around the fly ash spheres, opening up of a gap between these shells and the underlying spheres, and the eventual envelopment of some of the fly ash grains in calcium hydroxide. Mills called attention specifically to the very prominent early

precipitation of ettringite near the fly ash particles, and on a more general note, to the possible unbalancing of the C_3A and gypsum characteristic of portland cements by uncontrolled addition of fly ash as a mineral admixture.

The papers cited above, and others, represent a response to the growing importance of the use of fly ash in concrete. However, many details remain to be unravelled. The writer was disappointed in the almost complete lack of study of microstructure among the reports presented at the just-concluded 2nd International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete in Madrid. Of the many papers on fly ash in concrete, only that of Tenoutasse and Marion (72) on Belgian fly ashes, provided information on microstructure.

In addition to their influences on the microstructures of "bulk" cement pastes, fly ashes also influence the special microstructures developed at such critical locations as cement-aggregate interfacial zones. Consideration of these effects will be found in the section of this paper dealing with such special microstructures.

Microstructural Effects of Silica Fume

While the volume of concrete produced with silica fume is very much less than that produced with fly ash, the modification and potential improvement of properties is so great that silica fume concrete commands great international interest.

The microstructural effects to be expected depend on the relative amount of silica fume used with the cement, and more importantly, with whether or not the silica fume is accompanied by an effective dosage of superplasticizer or water reducer. Such accompaniment produces a synergistic deflocculating and dispersing effect, which results in fluidity at very low water contents, and which changes the structure of the resulting paste significantly. In the absence of a dispersing agent, silica fume adds significantly to the cement water demand so that high water contents must be used, and a very different microstructure develops.

A number of workers have documented the dense final structure that develops when silica fume is used with effective superplasticizers, but only a little information is available on the early stages of cement hydration with silica fume under these conditions. Grutzeck et al.(73) investigated the response of silica fume itself to immersion in dilute (but saturated) solutions of calcium hydroxide. They found that some silica dissolves quickly and reprecipitates as a silica-rich gel layer on the surfaces of the remaining undissolved fume particles, which then become agglomerated. With time, this layer of reprecipitated silica reacts further to produce C-S-H gel.

Subsequently Grutzeck et al. (74) studied early microstructural development in pastes made with Class F (oil well) cement and several varieties of silica fume or ferrosilicon dust. Agglomerations of remnant fume were identified after some weeks similar to the gel-bound fume agglomerations that had been described earlier (73), but not in all cases. C-S-H gel similar in appearance to Type III gel in ordinary cement pastes were observed

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growing on agglomerated spheres. Only a trace of calcium hydroxide was left unreacted in these cement pastes at 28 days; at higher temperatures of hydration no calcium hydroxide was seen even at 7 days.

The mature paste structure produced in low water content pastes batched with silica fume and super-plasticizers has been studied by a number of authors. Essentially the same picture is presented by all of these, including Aitcin et al. (75), Dingsoyr et al. (76), Marusin (77), Regourd (78, 79), and Regourd et al. (80). Where more than a minor amount of silica fume is used, the paste microstructure developed is completely different from that of ordinary cement paste. The structure is variously described as "dense", "amorphous", "of high compacity", etc. The basic structure appears to be that of Type III C-S-H gel particles but packed into an unusually dense array, with only rare and isolated small gaps. Type I elongated and Type II network or reticulated C-S-H gel morphologies are never seen. Large masses of layered calcium hydroxide intergrowing around and encapsulating C-S-H gel, a prominent feature of ordinary mature cement paste, are rarely seen, although in systems with smaller amounts of silica fume x-ray diffraction usually indicates that some $Ca(OH)_2$ persists. The boundaries between individual small Type III C-S-H gel particles are indistinct, as though the particles have partly fused, and in many systems a bright sheen seems to overly some or all of the fracture surface. This could perhaps represent residual "silica gel" of the type described by Grutzeck et al. (73,74).

The microstructure may be affected by surprisingly small amounts of silica fume. Regourd et al. (81) investigated the microstructure of mortars with 30% of slag, fly ash, or pozzolanic component, and 5% silica fume incorporated as a supplementary admixture to improve the strengths and mechanical properties of these systems. Only slight changes in the microstructure were observed with the slag system, which was already dense; with pozzolans and fly ash, some densification of the structure was observed; with inert components such as quartz and crystalline slag, a considerable benefit was realized, and the paste structure was significantly densified.

In addition to the major effects of silica fume on "bulk" microstructure, significant effects are reported on the microstructure of the interfacial regions surrounding aggregates; these will be discussed later.

There is a tendency to ascribe the rather strong effects on bulk microstructure described above to a specific response induced by the silica fume, rather than to the combined effects of silica fume and the superplasticizer. This tendency is reinforced by the results of studies like that of Marusin (82) which show negligible microstructural effects by superplasticizers alone. However, the writer is not sure that the structure induced by the silica fume-superplasticizer combination is specifically attributable to the silica fume, or indeed is uniquely dependent on the presence of the fume.

For a number of years the writer and other investigators have been examining the properties of gypsum free "low porosity" concretes, which are formulated at low water contents using conventional ground portland cement clinker without gypsum addition. Paste w:c ratios of around 0.20, and concrete w:c ratios of around 0.25 can be effectively batched in the resulting highly deflocculated system. The deflocculation (and control of set) are effected by a combination of admixtures, usually including a lignosulfonate and an alkali carbonate or bicarbonate. These systems achieve strengths and technical properties similar to those obtained with silica fume-superplasticizer combinations but involve no necessary supplementary cementitious component; fly ash is sometimes used to improve rheology, but it is not necessary.

Investigations of the microstructure of mature paste in these systems have been carried out by Diamond and Gomez-Toledo (83), and more recently by Coleman (84), Skvara and Zbuzek (85,86), and Subba Rao et al.(87), among others. The characteristic microstructure developed in these systems on maturity is extremely similar to that reported for dense silica fume concretes; the same dense, apparently partly fused Type III C-S-H gel morphology, the same absence of layered calcium hydroxide masses, and as documented by Coleman (84), a similar sheen over at least some regions of the fracture surface examined.

In (83) it was shown that the same ground clinker-admixture combination that produces this dense microstructure when hydrated at low water contents, produced normal cement hydration product microstructures in the agglomerations developed on bottle hydration (w:c 10). The bottle hydration provides a large volume of available space to deposit hydration products; paste hydration at low water contents provides only a minimum of such space, and indeed hydration usually stops short of completion for lack of space. These considerations suggest that the dense microstructure produced in low porosity concrete, so similar to that produced in silica fume-superplasticized concrete, might be a normal response to the restricted hydration space conditions rather than to specific chemical features of the hydration system.

Very recently a new but related gypsum-free low porosity system consisting of ground clinker treated with polyphenol sulfonate and alkali carbonate was described by Skvara and Rybinova (88); this appears to develop the same type of dense microstructure as the previous systems described.

MICROSTRUCTURAL EFFECTS OF SLAG

Slag, more specifically ground granulated blast furnace slag, has been used for many years as a supplementary cementitious material with generally excellent results. The percentage of slag ordinarily used is much higher than used for fly ash or silica fume; a significant portion of the C-S-H gel generated in such concretes made with slag cement or separately-batched slag must be due to hydration of the slag component itself.

Regourd (89) provided some information on paste microstructure in her principal paper on the structure and behavior of slag-portland cement hydrates at the Paris Congress. An early development of large amounts of ettringite, widely dispersed and derived from the alumina in the slag was noted;

phases. The C-S-H gel developed was described as compact, well-crystallized, and dense.

Recent microstructural studies of slag-containing systems include that of Tanaka et al. (90), a study by Marchese (91), and a previously-mentioned study by Regourd et al. (81).

Tanaka et al. (90) depicted the development of a skeleton hydrated layer rich in MgO on the surfaces of the slag grains: at a later stage this layer converts to a denser "inner hydrated layer" which remained distinct from the bulk paste deposited by the cement.

The differing mature microstructures developed by plain portland cement and slag cement were compared by Marchese (91); the denser character of the slag-containing system was apparent.

Regourd et al. (81) studied a 30% slag system and a corresponding 25% slag - 5% silica fume system. At 28 days the slag system appeared to show a fairly dense microstructure, but some open voids and some zones could be seen of less dense C-S-H material in a pattern resembling Type II gel. Around residual slag grains a 1-μm thick rim or zone consisting of very small "tangled thin plates" were observed, with an unremarked but extremely obvious gap of about the same thickness separated this from the residual slag particle. When silica fume was incorporated with the slag the rim zone was found to be denser and the general C-S-H gel appeared to be significantly denser as well.

In general it appears that slag cements do indeed generate a significantly more compact paste microstructure than do plain portland cements, but more porous local patches of what appears to be fine-textured Type II C-S-H gel may be found, as well as some other residual open space. The microstructure is definitely less compact than that occurring in dense superplasticized silica fume or gypsum-free low porosity systems.

MICROSTRUCTURE OF SPECIAL "MDF" SYSTEMS

The microstructure of special ultrastrong MDF systems developed by Birchall and associates and described in a number of publications, has been investigated by Groves (92) and by Sinclair and Groves (93). These systems are hardly cement pastes in the conventional sense. They are characterized by an extremely limited extent of hydration, and by the fact that the hydration products are embedded in and entwined with a continuous polymer matrix. MDF pastes made with portland cement show no fibrous C-S-H gel products, and the calcium hydroxide generated is microcrystalline; those made with calcium aluminate cement generate an amorphous hydration product said to have a CaO:Al$_2$O$_3$ ratio of about 1.

MICROSTRUCTURE IN SPECIAL ZONES

Without doubt the most important special zone of cement paste microstructure is that of the zone near the surface of contact with aggregates and sand grains in concrete. The influence of this zone on the behavior of concrete is considerable, and significant work has been done toward defining it and describing its characteristics. Other special zones of importance include the region around included steel (fibers, strands, or reinforcement) in concrete, and the special local zone developed within and around glass fiber strands in glass fiber reinforced concretes.

THE AGGREGATE INTERFACIAL REGION AND THE "AUREOLE DE TRANSITION"

The concept that the cement paste developed around coarse aggregate pieces in concrete is somewhat different in structure than bulk cement paste has been held for many years. Early work defined the transition zone, or as viewed in two dimensions on a section, the "aureole de transition", as a region extending radially outward from the aggregate surface and gradually merging into the bulk paste microstructure over a distance of perhaps 50 μm.

The prevalence of calcium hydroxide in this region was observed many years ago. Maso and his associates at Toulouse early established by x-ray diffraction that the apparent amount of calcium hydroxide and its degree of preferred orientation (with c-axis normal to the surface) diminishes with distance from the aggregate surface. The thickness of the zone through which calcium hydroxide preferred orientation can be measured is customarily taken as the size of the aureole de transition and the limit of the region of paste affected by the aggregate.

However, detailed studies have shown that the special microstructure developed in paste within the affected zone is complex (and variable). Differences between the microstructure of such zones and "bulk" cement paste microstructure are more extensive and profound than simply the presence of extra, well oriented calcium hydroxide in the former.

Pertinent developments in this area prior to 1980 were appropriately reviewed in the Paris Congress principal paper by Maso (94). Another review to 1980 was provided by Struble et al. (95). Subsequently a considerable body of work was reported at the Colloque International "Liaisons Pates de Ciment Materiaux Associes" held at Toulouse in 1982. A spate of recent papers and the previously mentioned thesis of Monteiro (5) have been produced since then.

Early work at Purdue University included theses by Hadley (49) and Barnes (51). This work and its extensions, taken together with the steady progress of developments by members of the Toulouse group and others, provide a reasonably consistent and well-documented picture of the details of the processes of microstructural development near an aggregate interface for conventional flocculated fresh cement paste. The following summarizes the present writer's understanding of the general effects encountered.

(1) Fresh cement paste is ordinarily flocculated, and consists of multi-particle flocs that are often up to several hundred μm in extent and roughly spherical in shape. The flocs, held together by VanderWaals' (dispersion) forces at points of close contact between adjacent clinker grains, are strong enough to resist dispersion by

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mechanical agitation while concrete is mixed, and to some extent to resist changes in shape on con-solidation. In consequence, cement grains pack against aggregate surfaces poorly, leaving exten-sive areas of high local water content both between grains within flocs, and between adjacent flocs.

(2) As a result of early calcium hydroxide supersaturation in the mix water, there is a ten-dency to rapidly precipitate a layer of calcium hydroxide, ca. 0.5 μm thick, on aggregate sur-faces exposed to the mix water; this layer is in the form of a film that is crystalline to x-ray diffraction but without visible crystalline bound-aries along its surface.

(3) Due perhaps to poisoning by dissolved silica, this film does not increase in thickness appreciably with time. Instead a thin single layer of short fibrous C-S-H gel in open parallel array develops on its paste-facing surface, with the fibers extending roughly normal to the film. The thickness of the combined or "duplex" film so created is usually no more than 1 μm. The C-S-H layer may densify somewhat with time with the individual fibers becoming more closely spaced, or the fibers may join at apices to create a layer with a morphology approaching that of network (Type II) C-S-H gel.

(4) The film may not form over all areas of aggregate surface in contact with the fresh paste; the proportion of areas covered with pastes of lowered calcium hydroxide producing capacity, e. g. slag cements, may be significantly reduced.

(5) Depending on age, nature of the aggre-gate, and circumstances of fracture, if fracture takes place at or near the original interface the film may be mostly retained by the aggregate or it may remain mostly bonded to the paste side. Even if it follows the latter mode, its adhesion to the aggregate may be sufficiently strong that it may carry some of the aggregate with it.

(6) This duplex film has been seen to deposit on aggregates of a variety of compositions, on silica glass, on alkali-resistant glass fibers, on steel, on polytetrafluoroethylene ("Teflon") , plastic, etc. Thus its deposition is not a consequence of any reaction with a particular kind of surface, but rather is the normal result of nucleation on any surface in contact with a super-saturated liquid.

(7) This thin duplex film is not the "aureole de transition" or the interfacial zone, which typically is 40 or 50 μm thick; rather it consti-tutes only the thin boundary element in closest contact with actual aggregate surface.

(8) On the cement paste side of the duplex film is the volume of space of high local water content described previously. The relatively sparsely packed cement grains in the flocs in this volume of space hydrate so as to produce large populations of hollow shell grains; thus most of the hydration products deposit in the water-filled space between the shells rather than within the shells.

(9) After a day or two have elapsed, a new thin secondary layer of calcium hydroxide, typi-cally about 3 μm thick, develops immediately under the duplex film, that is, on the paste side. This is seen as a layer of thin, closely stacked calcium hydroxide crystals in parallel array, with their faces oriented at an acute angle with the duplex film. This layer is usually incomplete, but it serves as something of an intermediate layer between the very thin duplex film and the sparsely populated region below.

(10) Larger, individual, euhedral tabular-shaped crystals of calcium hydroxide may also develop at about the same time below this second-ary layer, and many of these crystals may be oriented so that the c-axis is parallel, rather than normal to the surface.

(11) Despite the fact that the clinker grains in the sparsely-populated zone below the secondary calcium hydroxide layer are depositing their hydration product largely into the empty spaces between the shells, the local volume of such space is so great that much of it remains empty even after nearly all of the cement hydration has taken place. This sparsely-occupied space subsequently "attracts" further deposits of calcium hydroxide in various forms, and of ettringite. The process of accumulating these later deposits extends over a period of weeks rather than days. The mass of calcium hydroxide accumulated seems far greater than the mass of ettringite, which is only occasionally encountered.

(12) These late calcium hydroxide deposits often appear as arrays of layered crystals, tens of μm long, and quite thick. They surround and encompass previously deposited hydration prod-ucts. They may extend fairly deep into the paste, and only gradually give way to the usual C-S-H gel - Ca(OH)₂ bulk paste microstructure.

(13) These late calcium hydroxide deposits are not rigorously oriented with their c-axis normal to the interface. Arrays of large crystals locally parallel to each other are usually seen, but they vary in orientation with respect to the surface, some even having their c-axis parallel to rather than normal to the surface.

There is seeming conflict between the statements above and the usual picture, based on x-ray dif-fraction, of preferential calcium hydroxide orienta-tion with c-axis normal to the surface. This apparent conflict is resolvable by attention to x-ray diffraction theory. The SEM results show the presence of increased numbers of large calcium hydroxide crystals near the interface, occurring locally parallel to each other but at varying orientations. Only those crystals which happen to be oriented with c-axis normal to the surface of a specimen (assumed parallel to the aggregate) can contribute to the enhanced basal x-ray diffraction peak; the others simply do not register. Thus while there are extra crystals oriented parallel to the aggregate surface, there are also extra crys-tals oriented in other by directions as well.

(14) Smaller interfacial zones of similar structure may be expected to surround smaller coarse aggregate pieces and sand grains. The mutual orientations of these zones to each other and to that of any large aggregate piece in the vicinity may be complex.

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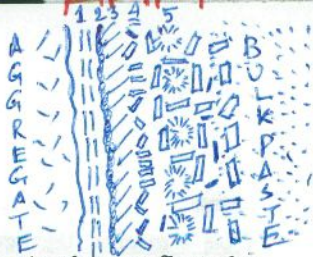
A { 1 = 0.5 μm thin film of CH (xtalline to X-ray) } Duplex Film
   2 = 0.5 μm thin film of CSH

B { 3 = Secondary CH 3μm thick at acute angle to duplex film
   4 = Large, euhedral, tabular CH, some with c axis ‖ interface

C 5 = Hollow shells, Large CH, few AFt, high porosity, w/c

While some of the statements above reflect the current general consensus, others may be controversial or poorly understood. It seems appropriate here to provide at least some visual indications of the basis for these generalizations.

Fig. 14 below, taken from the thesis of Barnes (51) shows the paste-facing surface of a duplex film formed when a cement paste specimen was cast against a glass microscope slide. The film remained attached to the glass slide on parting, and the view is looking down on the glass slide and its attached film. The sparse layer of short, fibrous C-S-H gel is immediately visible, and the underside of the film of calcium hydroxide may be seen in spots where the gel is particularly sparse.
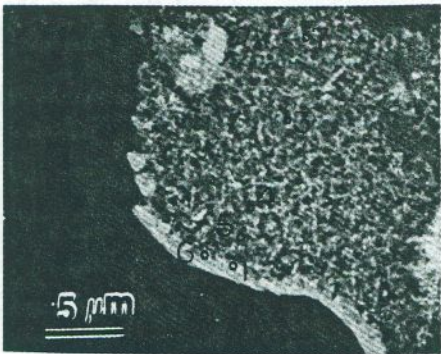

Fig. 14. Duplex film, C-S-H side upward. Paste cast against glass at w:c 0.65, 1 day.

The paste side uncovered by removal of the duplex film is shown, also for a 1-day old w:c 0.65 paste, in Fig. 15 below. The calcium hydroxide side of a portion of the duplex film is visible as the gray area marked "1" in the upper left of the figure. The exposed paste underneath is sparsely occupied by hydrating cement grains. Partly hollow hydration shells are visible at "A and "B", and in various other places, and "C" seems to mark a very large and fully hollow shell.
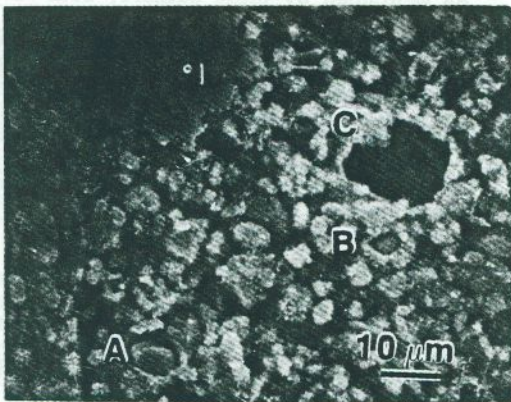

Fig. 15. Poorly-populated zone of paste immediately underneath a duplex film. (w:c 0.65 paste, 1 day, cast against glass).

Fig. 16, taken of a w:c 0.5 paste hydrated for 4 days, reflects the subsequent formation of the

layer of secondary calcium hydroxide under the duplex film. The calcium hydroxide side of the duplex film is the uniform gray surface present over the upper and leftmost parts of the micrograph. Where it has been stripped away the underlying structure of the paste is visible. The layer of secondary calcium hydroxide referred to previously is the bright region marked "A". The area marked "B" represents still sparcely-filled space at levels below the secondary calcium hydroxide deposit, starting perhaps 2 or 3 μm below the surface.
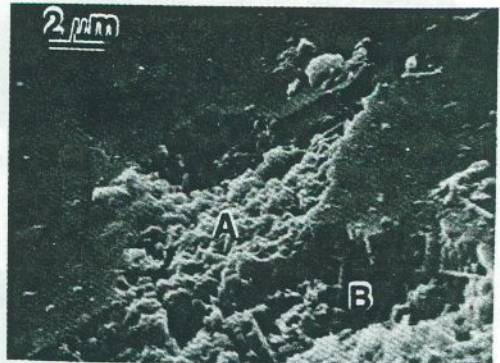

Fig. 16. Detail of secondary calcium hydroxide layer in paste cast against glass (w:c 0.5, 4 days)

A better view of the secondary calcium hydroxide layer ("A") and of the extent of empty space in the paste below it ("B") can be seen in Fig. 17 below.
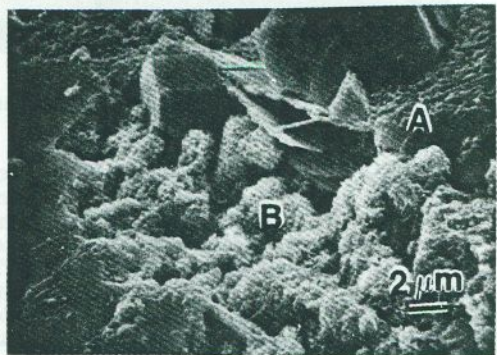

Fig. 17. Another view of a paste immediately below the duplex film.

An idea of the eventual deposition of calcium hydroxide in this sparsely-filled zone, and indications of the differing orientations of the calcium hydroxide that may develop are provided in Figs. 18 and 19.

Variations in the general pattern described above may be expected depending on various factors including the specific characteristics (and possible chemical reactivity) of the aggregate itself, the water:cement ratio, the effects of superplasticizers or superplasticizer-silica fume combinations in deflocculating the paste, the nature and amount of supplementary cementitious components or inert fillers used, and many others.
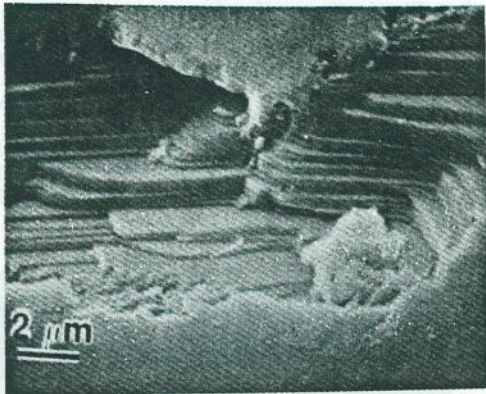
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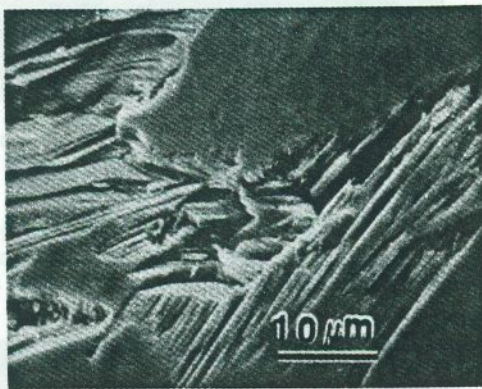Fig. 18. W:C 0.5 paste cast against glass, 30
days old.

Fig. 19. W:C 0.5 paste cast against glass, 30
days old.

The study of the interfacial zone has involved a
number of specialized techniques, including appli-
cations of both x-ray diffraction and scanning
electron microscopy. An exposition of the special
x-ray diffraction technique developed at Toulouse
was provided at the Paris Congress by Grandet
and Ollivier (96) and a more general review of
applicable techniques was provided by Carles-
Gibergues et al. (97).

The sequence of events that constitute the steps
taking place in the formation of the interfacial zone
were reviewed by Ollivier and Grandet (98). Their
synthesis is different in some details from that
provided above by the present writer. The impor-
tance of the influence of the early hydration
reactions, especially the C_3A reactions that
produce early deposition of ettringite, was
stressed by them. They considered that there is
a competition of sorts between radial ettringite
growth around nuclei, and oriented calcium hydro-
xide development in the near-aggregate region of
the interfacial zone.

Subsequently Monteiro and Mehta (99) studied the
variation of ettringite concentration with distance

from a granite aggregate surface as a function of
time. They found that early (1-day) ettringite
deposition is pronounced in the region closest to
the aggregate; the content appeared to reduce
linearly with distance over a zone of about 100 μm,
where its content became negligible. At later ages
a substantial and uniform concentration developed
in the region beyond about 35 μm from the aggre-
gate, but the region closer to the aggregate conti-
nued to be somewhat enriched with ettringite in
comparison.

The influence of seepage of the mixing water in
practical concrete on the development of the inter-
facial zones around aggregate pieces was stressed
by Hoshino and Tomabechi (100).

A number of recent studies have documented vari-
ous departures and variations from the general
pattern of the duplex film and the features of the
interfacial zone as described above.

The special effects that may mark the interfacial
zone developed with limestone aggregates are of
major importance, in view of the widespread use of
limestone aggregate in concrete. Early reports of
stronger bond formation and local chemical reaction
were summarized by Monteiro and Mehta (101).
Some of these involve local formation of calcium
carboaluminate at the interface; for example Gran-
det and Ollivier (102) demonstrated such formation
from previously-formed hemicarboaluminate in the
zone adjacent to the aggregate surface, and corre-
sponding etching of the aggregate.

Such reactions might readily disturb either pre-
viously deposited interfacial features or modify
those that would develop subsequently. This may
provide an explanation for the failure of Struble
and Mindess (103) to find any trace of the
expected duplex film between the paste and lime-
stone aggregate that they investigated; rather,
these authors found "a somewhat continuous layer,
several microns thick, of apparently parallel
calcium hydroxide crystals at the interface." This
is apparently the secondary calcium hydroxide
layer pictured in Figs. 16 and 17 above.

As mentioned by these authors, both Langton and
Roy (104), and Conjeaud et al (105) had pre-
viously found duplex films at interfaces with
limestone. Subsequently Monteiro and Mehta (106)
clearly documented the early development of such
films by cement pastes surrounding limestone
aggregate, although the films may have been dis-
continuous and incomplete. Subsequent severe
chemical etching of the underlying calcite was
shown to take place, presumably destroying the
duplex film in the process.

Monteiro and Mehta then duplicated these observa-
tions using a C_3S paste rather than a cement
paste; this led to their suggestion that the etching
reaction is not due to carboaluminate formation,
aluminum being absent in this case. Rather they
tentatively attributed it to the formation of an
unusual basic calcium carbonate with a variable
composition approximating $CaCO_3$-$Ca(OH)_2$-H_2O. It
appears to the present writer that the duplex film
might be the prime local source of the $Ca(OH)_2$ for
such a reaction, if it occurs.

A contribution toward the understanding of the

geometry of interfacial zones in real concrete has been provided recently by Monteiro et al. (107). Following up the early indication by Barnes et al. (108) that interfacial zone features do develop around sand grains, and the more recent measurements of Diamond et al. (8) which disclosed the likelihood that the interfacial zones of adjacent sand grains in concrete overlapped, these authors confirmed that sand grains as well as coarse aggregate pieces create interfacial zones around themselves. They indicated that the mutual intersections of zones around adjacent particles might interfere with the orientation of calcium hydroxide around any given grain. This might modify the measured size of the zone, if calcium hydroxide orientation is used as the measurement criterion for size.

Other recent studies of "normal" interfacial zone development and properties were reported by Zimbelman (109), Xie (110), and Skalny and Mindess (111).

The properties of the zone naturally reflect the specific physico-chemical regime under which it develops. Massazza (112) demonstrated that on autoclaving at 180°C, quartz, feldspars, and several varieties of glass aggregate react with the cement paste and develop an interfacial structure dominated by 1.1nm tobermorite laths; this interfacial zone is harder (and stronger) than the bulk autoclaved paste. In some systems the initial interfacial product is hydroxyellastadite, which then transforms to tobermorite. Limestone aggregates apparently do not develop such a zone.

Somewhat less drastic changes accompany the substitution of Type K expansive cement for ordinary portland cement, as reported by Monteiro and Mehta (113). The duplex film formed is discontinuous, and large tabular hexagonal crystals of calcium hydroxide with a nearly random orientation develop adjacent to it. A concentration of ettringite near the actual interface was demonstrated, but the apparent amount of ettringite formed here seems somewhat less than might have been expected.

Changes are also expected to accompany replacement of some of the portland cement with supplementary cementitious components. Carles-Gibergues et al. (114) described various effects of different systems. Fly ash containing many plerospheres absorbed enough mix water to lower fluidity of the paste near the aggregate surface and reduce the thickness of the measured aureole de transition; high calcium fly ashes, acting as plasticizers, increased fluidity and thus increased the thickness of the zone. Silica fume, used by itself, decreased fluidity and reduced the thickness. Somewhat surprisingly to the writer, but in accord with results obtained by Barnes (51), blends with slag behaved little differently than unmodified portland cements. Silica fume was found to cause progressive replacement, with time, of the calcium hydroxide in the interfacial zone with secondary C-S-H gel derived from the pozzolanic reaction; in consequence, the calcium hydroxide-rich layer was reduced to a narrow zone extending only a few μm from the aggregate.

Recently Huang and Feldman (115) indicated that with time, mortars containing silica fume showed an unexpected increase in mercury-intruded pore volume attributed to pores of 100 to 1000 nm. The time involved was commensurate with the time over which the pozzolanic reaction might proceed. These authors attributed the increased pore space in this size range to space generated by consumption of some of the lime deposited in the interfacial zone, presumably to form C-S-H gel with a coarse ("discontinuous") pore structure. Similar results were subsequently reported by Feldman (116).

The results cited above with respect to silica fume refer to systems of relatively high water content without the dispersive effect of the high dosage of superplasticizer ordinarily used in practice. In contrast to these modest effects, dispersed, superplasticized silica fume systems develop an entirely variant local structure near the interface. As shown clearly by Aitcin et al. (75), Dingsoyr et al. (76), Regourd et al. (80), and others, in such systems, while there may have been a duplex film or a thin layer rich in calcium hydroxide at early ages, after appreciable hydration the paste is fully dense and tight right up to the true interface, and neither calcium hydroxide, ettringite, nor empty space can be seen.

MICROSTRUCTURE OF PASTE ZONE SURROUNDING STEEL AND OTHER METALS

Steel is incorporated in concrete as reinforcement, as prestressing cable, and occasionally as steel fibers. Galvanized steel (presenting a zinc surface to the concrete) and other metals are occasionally used in concrete for special purposes. The interfacial structures developed next to such surfaces are of interest both for their effects of bond and mechanical properties, and for their possible influences on corrosion behavior.

The microstructure of the interfacial zones formed around steel fibers was profusely illustrated by Bentur et al. (117) and shown to have features in common with zones around aggregate particles. The usual duplex film was found, but this was surrounded by a zone of 10 to 30 μm thickness occupied by massive calcium hydroxide. This massive calcium hydroxide layer was not continuous parallel to the fiber, but was interrupted at intervals by more porous areas.

Beyond this massive calcium hydroxide layer, these authors found a highly porous layer of loose C-S-H deposits, through which induced cracks usually preferred to travel. The pattern of crack propagation induced in steel-fiber reinforced pastes was separately reported by Bentur et al. (118) and Bentur and Diamond (119), and shown to be in part a consequence of this microstructural development.

The interfacial zone around steel fibers in mortar was investigated by Sun et al. (120) using microhardness measurements. They concluded, in excellent agreement with the pattern described by Bentur et al. (117), that the thickness of the transition zone was approximately 40 μm, and that the weakest layer was about 25 to 35 μm from the steel surface.

Monteiro et al (121) investigated the reinforcing steel - cement paste interface from the corrosion point of view, in the presence of added chloride.

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Pastes with and without silica fume were compared,
with the pastes examined being spontaneously
parted from the steel by drying shrinkage. The
duplex films were clearly evident, although these
authors suggest that "the interfacial film consists
of large CH crystals", rather a contradiction in
terms. The silica fume appeared to make little
visible difference in the microstructure, but
apparently induced greater corrosion.

The formation of the transition zone developed
around galvanized steel was studied by Arliguie
and Grandet (122). A relatively thick chemically-
perturbed zone was found to develop, with crys-
talline calcium hydrozincate formed close to the
zinc interface, a layer containing zinc hydroxide
further away, and a still further layer deficient in
calcium hydroxide. The pattern is modified some-
what if calcium chloride is present, due to the
prior formation of zinc hydroxychloride at the zinc
surface (123).

Microstructural responses induced in pastes of C$_3$A
(124) and C$_3$S (125) to incorporation of iron,
copper, or zinc wires were studied by Tashiro and
co-workers.

MICROSTRUCTURE WITHIN AND AROUND
GLASS FIBER STRANDS IN GLASS FIBER
REINFORCED CONCRETE SYSTEMS

Glass fiber reinforced concretes (or more properly,
mortars) have been increasing used for special
purposes, notably architectural panels and other
thin-sheet applications. A major limitation on their
even wider use has been the reduction in ductility
and strength accompanying exposure to wet condi-
tions in service, despite use of alkali-resistant
glass compositions. This special durability problem
was the subject of a recent international symposium
in Chicago (126).

It appears from results of Bentur (127), Bartos
(128), and others, that while alkali attack on the
glass may in fact take place to some degree over
prolonged periods, the basic problem is micro-
structurally related. Glass fibers are customarily
provided in strands of about 200 individual 10 to
12 μm-thick fibers, which are chopped to short
lengths and incorporated in the cementitious prod-
uct mix. The narrow spaces between the parallel
fibers, typically no more than a μm or two in
width, do not admit cement particles, but become
sites for deposition of massive calcium hydroxide
and sometimes C-S-H gel. Mills (129) has shown
that calcium hydroxide seems to show a marked
preference for deposition such fibers rather than
on other available surfaces.

As a result of this deposition within the strands,
individual fibers become tightly bound to each
other and locked to the surrounding cement paste.
This results in loss of strain capacity; the individ-
ual fibers can no longer pull out independently,
nor can they bend individually to accept off-axis
stresses.

Fig. 20 depicts the empty space between the indi-
vidual fibers in GFRC that has not become
embrittled; Fig. 21, the appearance of typical
calcium hydroxide deposits that surround the glass
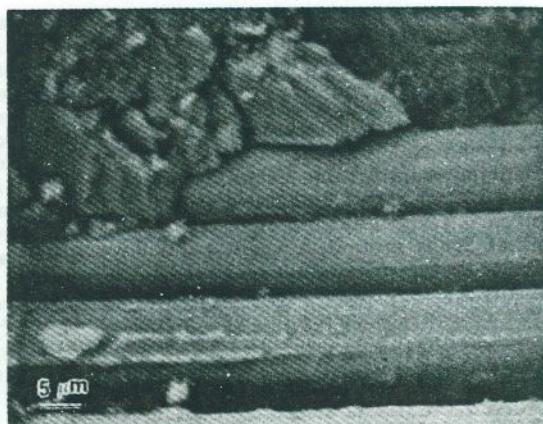fibers after long exposure to wet conditions.

Fig. 20. View showing empty space between glass
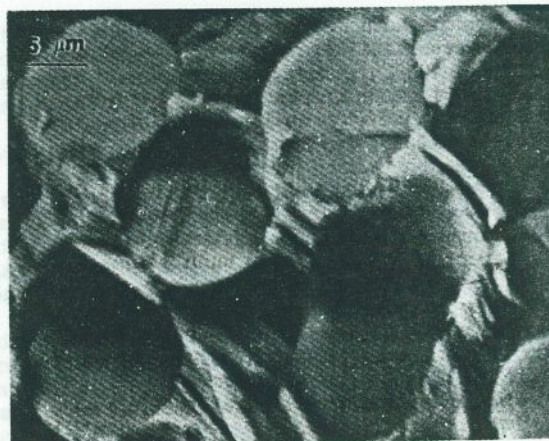fibers in GFRC that has not been
embrittled.

Fig. 21. Morphology of calcium hydroxide deposits
surrounding glass fibers in weathered
GFRC.

Bentur and Diamond (130) have studied the details
of the response of the fibers in cement paste to a
crack induced by compact tensile loading within
the SEM. The details of the pullout and
subsequent fracture of the fibers are clearly
conditioned by the pre-existing microstructure of
the region surrounding the strand and of the
spaces within it.

A number of systems to reduce this effect have
been proposed. Majumdar and Stucke (131) have
reported details of the microstructural development
in and around the strands when supersulfated
cement is used instead of portland cement. Ettrin-
gite deposited early in this system eventually
carbonates, and the spaces become filled with
deposits of gypsum and calcite.

Microstructural details of another system for
improving the durability of GFRC developed by
Bentur and Diamond (132) were recently
described. This system involves direct incorpora-
tion of a dispersed slurry of silica fume by wick-
ing action into the inter-fiber spaces before the
strands are included in the GFRC product. The
prior presence of the silica fume appears to pre-

vent the subsequent deposition of calcium hydroxide in these spaces, and beneficially modifies the microstructure of the hydration products immediately surrounding the strand.

The GFRC symposium proceedings also include microstructural characterizations by Kumar and Roy (133) of glass fiber strands incorporated in several blended cements and subsequently autoclaved, and a study by Cohen and Constantiner (134) of microstructural effects accompanying use of cements with additions of alkali sulfate and of silica fume to the matrix mixture.

CONCLUSION

It is evident from the great mass of information cited that significant progress has been made in understanding the development of the microstructure of cement paste in concrete, including pastes incorporating fly ash, silica fume, and other supplementary components, and including the special microstructures developed near aggregate interfaces, around steel, and in other special zones. The application of such understanding for the production of stronger and more durable structures and concrete products offers a further challenge that is just beginning to be met. Perhaps by the time of the next Congress it may be appropriate to provide for a review on the applications of microstructural knowledge to practice, rather than on microstructure per se.

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