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REVIEW ARTICLE

Interfacial Transition Zone in Concrete

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In fresh concrete a water:cement (W:C) ratio gradient develops around the aggregate particles during casting, resulting in a different microstructure of the surrounding hydrated cement paste. This zone around the aggregate is called the interfacial transition zone (ITZ). This review describes the formation mechanisms and the microstructure of the ITZ. The higher W:C implies a diffusion process during hydration, and this zone may be consequently described as a heterogeneous area with a porosity gradient and a complementary gradient of anhydrous and hydrated phases. By using very fine and well-dispersed mineral additions, the initial W:C gradient around the aggregates is lowered and the ITZ is densified. The microstructure of the ITZ may be improved in the vicinity of calcareous aggregate, which reacts with calcium aluminates of Portland cement paste, forming calcium carboaluminates. The overall engineering properties of concrete in relation to the ITZ are beyond the scope of this review. Nevertheless, the local properties of the interfacial zone are reviewed: the mechanical and the transport characteristics of the ITZ are discussed in relation to the porosity and connectivity of pores. ADVANCED CEMENT BASED MATERIALS 1995, 2, 30–38

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Concrete is usually modeled as a composite material to explain its behavior under mechanical, physical, or chemical stresses. According to this approach, a two-phase (aggregate and matrix) model is not generally adequate because the cement paste cannot be considered as a homogeneous phase. In fact, the microstructure of the cement paste is modified in the vicinity of the aggregate particles. Different terms have been used to refer to this zone; in this review it will be called the interfacial transition zone (ITZ). Many properties of concrete should be analyzed by considering it as a three-phase composite: aggregate, ITZ, and matrix.

The so-called wall effect has been extensively presented to explain the special features of the ITZ [1,2]. During casting, the spatial arrangement of anhydrous grains becomes looser in the vicinity of aggregate particles. Consequently, in fresh concrete the porosity and the W:C ratio increase from the bulk to the surface of aggregate particles. A complementary explanation has been proposed: during the vibration of concrete and before setting, microbleeding leads to an accumulation of water under the aggregate particles. Due to the first effect, the fresh cement paste which surrounds the aggregate grains exhibits a gradient of water and a complementary gradient of anhydrous cement. Due to the second effect, a certain heterogeneity of the gradient around the particles may be foreseen.

Only a few experimental data exist on the microstructure of fresh concrete. The wall effect has been confirmed by Escadeillas and Maso [3], who observed mortars by back-scattered electron imaging (SEM). The structure of fresh concrete has been frozen and the observation reveals excess porosity in the vicinity of the sand grains (Figure 1). This research also shows how the model of aggregate particles surrounded by an ITZ is a schematic one: when sand grains are close together, only a few small cement grains can be arranged together in this area, especially if they flocculate (i.e., in nonsuperplasticized, ordinary concrete).

This criticism of the model had been presented earlier by Diamond et al. [4] and Farran et al. [5], who observed or calculated that the average half-distance between sand grains and the ITZ thickness can be very close. Nevertheless, this image of a surrounding ITZ can be useful for understanding, and it has been used in some calculations presented in the rest of this review.

The review is devoted to the microstructure of the ITZ and its intrinsic properties. The microstructure of the ITZ formed around inert aggregates in OPC-based

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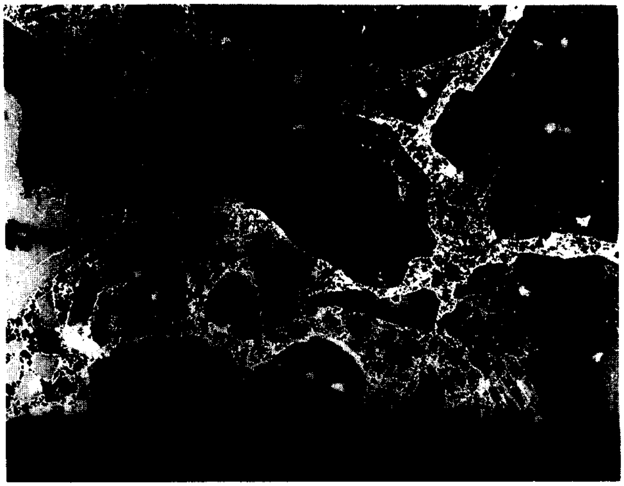

FIGURE 1. Packing of cement grains against the sand grains into fresh mortar. The excess of porosity in the vicinity of the sand surface is explained by a wall effect (from ref 3).

concrete is presented first, and then the influence of mineral additions is discussed. The characteristics of the ITZ may be affected by a chemical reaction between the aggregates and the cement paste. The reaction with calcareous aggregates, the most important nondeleterious reaction, is reviewed in detail. Finally, the intrinsic mechanical and transport properties of the ITZ are presented. The relationships between the bulk properties of concrete and the ITZ are not considered in this review.

Microstructure of the ITZ between OPC Paste and Inert Aggregate Particles

The microstructure may be described in terms of (1) the porous microstructure, and (2) the hydration progress. The two approaches are obviously linked. Hydration in the vicinity of aggregate grains differs from the reaction which take place in the bulk paste because the W:C ratio is locally higher and because the growth and the nature of hydrates may be influenced by the surface and the chemical nature of aggregates. So the excess of porosity is both the cause and the consequence of the existence of the ITZ.

The evolution of the porosity will be presented first. The hydration process in the ITZ formed around inert aggregate grains will then be reviewed. Finally, the influence of the chemical reactivity of aggregates will be considered.

Porosity of the ITZ

The quantification of the porosity in the ITZ has been performed by means of two main techniques: image analysis of flat polished surfaces observed by SEM using back-scattered imaging, and mercury intrusion porosimetry (MIP). The first technique gives local data, whereas the second gives bulk information.

SEM STUDIES OF THE POROSITY IN THE ITZ. The observations made on flat sections of mortars or concretes allow one to determine the porosity as a function of the distance to the aggregate surface. Because the pore size measured in the two-dimensional images does not have a stereological nature, it is not possible to obtain the three-dimensional pore-size distribution using this technique.

Scrivener and Pratt [6] were the first to develop this experimental technique for analysis of the ITZ. The data presented in Figure 2 confirm the wall effect hypothesis [7]. With young OPC paste the porosity increases near the surface of the aggregate particles and the thickness of this disturbed area is 15 µm, the order of magnitude of the cement grain diameter (curve 1a). The main variations in porosity occur in the first 15 to 20 µm. When using silica fume and superplasticizer (curve 2), the porosity is approximately constant because the low packing of the cement grains in the ITZ is densified by the small particles of silica fume. The variation of the porosity decreases with age (curve 1b versus 1a) due to filling by hydrates.

The occurrence of microbleeding under aggregate particles and the resulting heterogeneity is not yet experimentally evident. Goldman and Bentur [8] report a difference in the top porosity, and the bottom porosity has been observed around 5 mm aggregates with W:C ratios as low as 0.2. Using a model aggregate enclosed in a cement paste, Hoshino [9] observed, on cut surfaces, the variation in penetration of red dye between the different parts of the specimen. He concluded that a considerable increase of the W:C ratio occurs under the aggregate before hardening. One the contrary, Scrivener and Pratt [2] observed relatively little differ-

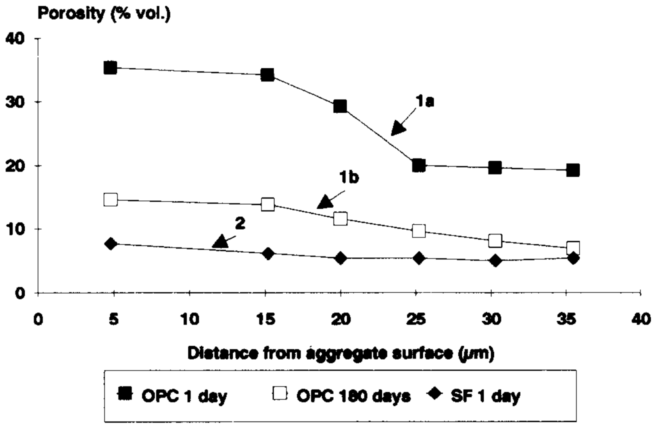

FIGURE 2. Effect of age and silica fume on the porosity in the ITZ (from ref 7).

ence in the microstructural gradients measured above and below aggregate particles at an overall 0.4 W:C ratio. This effect has to be clarified and it seems important to define the casting conditions as precisely as possible and to show the influence of the size of the aggregate particles and the W:C ratio.

MERCURY INTRUSION POROSIMETRY STUDIES OF THE ITZ. MIP is a technique which complements SEM studies on the porosity it allows the pore size determination. Nevertheless, one should keep in mind that the dimension of a pore is calculated from the value of the pressure using a cylindrical model of the microstructure. Another obvious but important point concerns the method of intrusion itself: the MIP assigns the volume of the larger pores to the pore entry necks. Consequently, the pore characteristics of the ITZ can only be revealed by MIP if they are connected to the external surface of the tested specimen. In other words, the pores of the ITZ can be characterized by their own dimensions using MIP if the ITZ porous system forms an interconnected cluster through the specimen. This has been well illustrated by Snyder et al. [10]. The evolution of the cumulative intrusion curves of the paste part of mortars presents a discontinuity between 45 and 48% in the volume fraction of sand (Figure 3). For the higher sand contents, ITZs are interconnected and a coarser family of pores can be revealed.

A geometrical model of percolation through ITZs has been presented by Snyder et al. [11]. Aggregate particles are modeled by spheres and ITZ by a layer around the grains. Interconnection can be studied as a function of aggregate volume fraction, gradation, and thickness of the ITZ. A typical result of this approach is reported in Figure 4.

A similar approach has been used by Bourdette et al. [12] for calculating the porosity of the ITZ in mortars.

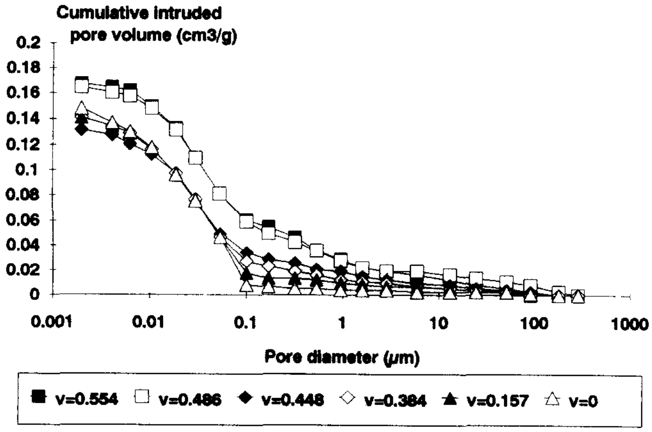

FIGURE 3. MIP cumulative curves of mortars containing different volume fractions of sand. A discontinuity in the evolution between the curves may be noticed for a sand volume concentration higher than 45% (from ref 10).

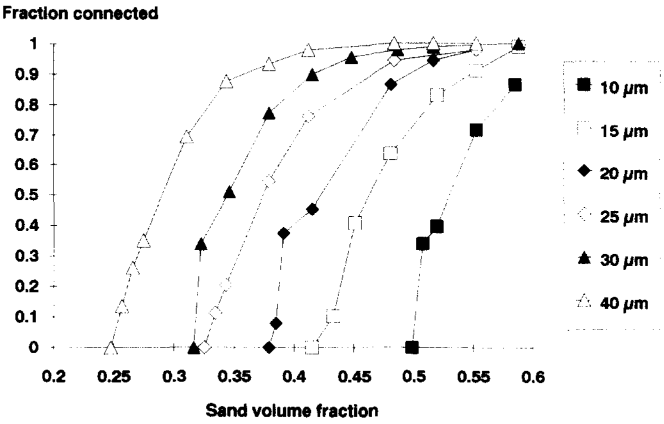

FIGURE 4. Influence of the ITZ thickness on the relation between the interconnected fraction of the ITZ and the sand volume fraction (from ref 11). Assuming a 20 µm ITZ thickness, the connection of the ITZ system appears for sand volume fraction greater than 38%.

The study of connectivity of the ITZ system is based on a different algorithm from that used by Snyder et al. [11], but the results are very similar. For example, the authors present results with a mortar in which the sand volume proportion is 52%. With a given sand gradation and assuming a 20 µm ITZ thickness, the fraction of interconnected ITZ is about 85% and it cor-

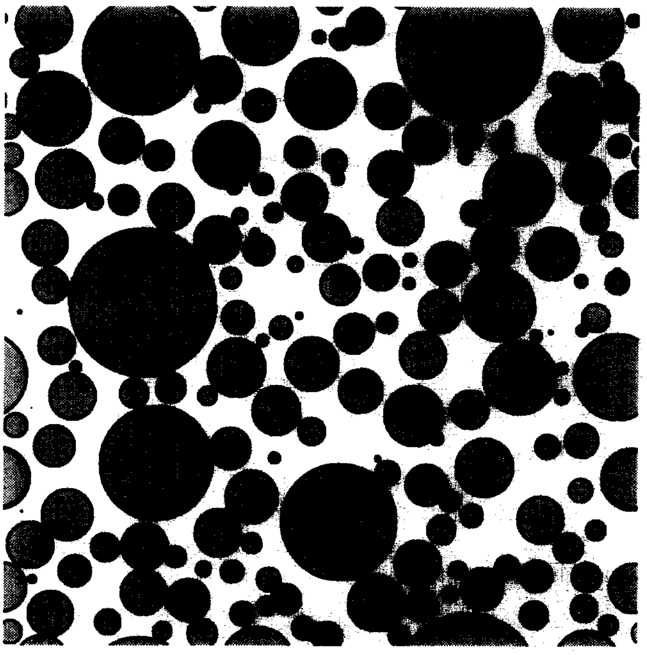

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FIGURE 5. Two-dimensional visualization of a mortar. The grains that belong to the percolating cluster are drawn in light gray and the other ones in dark gray. The traces of the ITZ, in black, have different thicknesses because they result from the intersection of a spherical shell with the cutting plane (from ref 12).

responds to a volume fraction of 5.7% in the mortar. A two-dimensional visualization of this mortar is presented in Figure 5. The porosity of the ITZ has then been calculated from MIP data and connectivity results. Figure 6 shows the two-pore systems of a pure cement paste and of a mortar paste (W:C = 0.4, hydrated for 3 months in lime water). The results of the porosity calculations are as follows: 19 ± 1% for the bulk paste and 48 ± 2% for the ITZ. The ratio between these two porosities is very close to the value proposed by Scrivener et al. from image analysis. Moreover, the porosity of the bulk is lower than that of the same W:C pure cement paste (22%). The effective W:C in the bulk paste of mortar is lowered by water enrichment in the ITZ. The evolution of ITZ porosity with time has been presented by Bourdette et al. [12], and this work shows that it decreases during maturation, whereas the bulk porosity remains constant (Figure 7). These trends can be explained by diffusion phenomena.

Some conclusions from this first part can be made: (1) the porosity is higher in the ITZ than in the bulk (two to three times more); and (2) the pores are coarser in the ITZ. These features can be explained by a poor arrangement of cement grains in the vicinity of the aggregate particles.

Microcracking at the interface may appear due to shrinkage or mechanical loading. This feature depends on several parameters, such as the nature and the intensity of the loading, the elastic properties of the aggregates, and the paste. Its consequences on the mechanical performances and the durability are obvious, but their description is beyond the scope of this review.

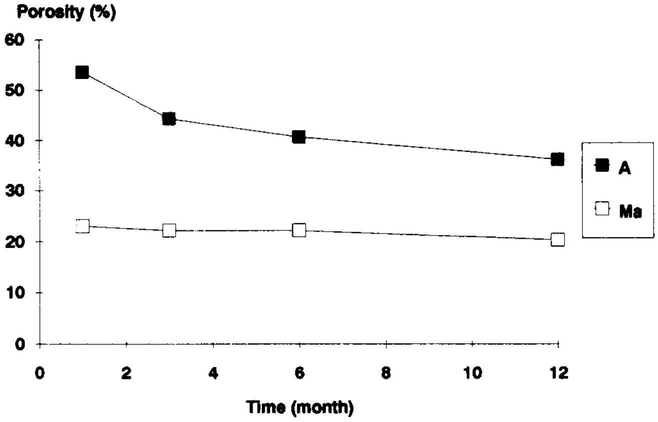

FIGURE 7. Evolution of ITZ porosity (curve A) and of cement matrix of paste mortar porosity (curve Ma) with the age of mortar (from ref 12).

Hydration into the ITZ

Farran [13], a pioneer in the ITZ research, was the first to observe a zone exhibiting a different mineralogical composition at the interface of aggregates. His research was done on a composite model which consists of cement paste cast against a flat face of cylindrical aggregate. To explain these differences, it is necessary to consider the progress of hydration from the beginning (i.e., the initial state of the paste in the ITZ). As a first step, hydration into the ITZ formed in the vicinity of inert aggregates will be reviewed. In a second step, the influence of the reaction of aggregate with the paste will be presented. Concerning this last part, the review is limited to the principal case of a nondeleterious reaction which occurs in Portland cement-based concrete: the reaction with calcareous aggregates.

Due to the wall effect and microbleeding, a gradient of porosity and a complementary gradient of anhydrous cement grains exist. The concentration of C_3S has been studied by Ollivier [14] using the composite model and X-ray diffraction analysis (Figure 8). Scrivener et al. came to the same conclusion using SEM (scanning electron microscope) observations and im-

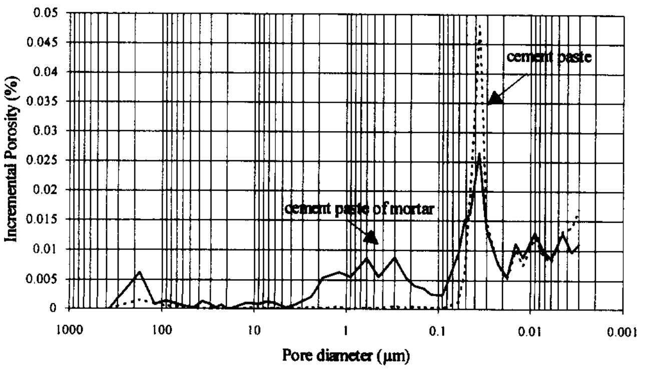

FIGURE 6. Incremental porosity distribution of pure cement paste W:C = 0.4 and cement paste of mortar (3 months old). A new porous volume in excess for the pores bounded by 0.045 and 0.1 µm may be observed (from ref 12).

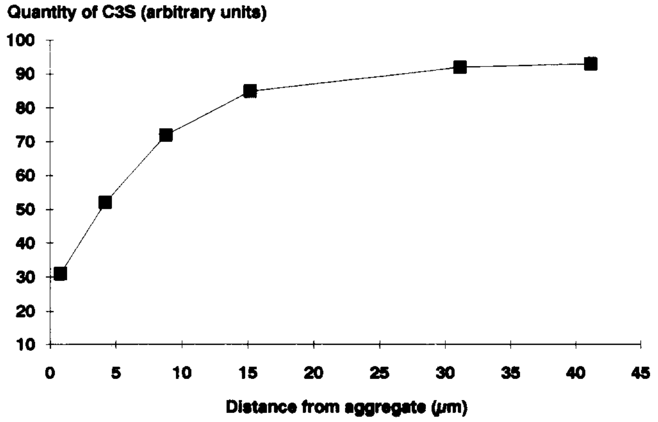

FIGURE 8. Variation in C_3S concentration in OPC paste cast against a flat aggregate (W:C = 0.5 after 10 days) (from ref 14).

age analysis on the model [15] or on concrete specimens [16]: "the package of cement grains results in microstructure gradients extending some 50 μm from the interface into the cement paste in which the amount of anhydrous cement decreases as the interface is approached" [2].

The hydration of the cement and the resulting features in the ITZ may be described by considering diffusion of ions and spatial constraints. As large areas filled with water are available in the vicinity of the aggregate particles, the hydration happens mainly following the Le Châtelier mechanism. Then, after the dissolution of anhydrous compounds, the more mobile ions move under the influence of concentration gradients (i.e., from the bulk to the interface. In OPC, Na^+, K^+, SO_4^{2-},$Al(OH)_4^-$, and CA^{2+} ions diffuse faster. The mobility of silicate ions is lower and they diffuse more slowly from the silicate grains to the aggregate surface [1].

This ion diffusion phenomenon may be illustrated by comparing the amount of hydrates with the amount of anhydrous material as a function of the distance to the aggregate. Results have been extensively published from studies made on both composite models [16–18] and on concrete specimens [2]. A very comprehensive presentation of such experimental investigations has been presented by Scrivener and Pratt [2] (Figure 9). The figure shows the amounts of CH and C-S-H calculated as being in excess of the amounts expected if all the hydration products were precitated in the immediate vicinity of the anhydrous cement from which they formed. The redistribution of portlandite appears clearly. The redistribution of C-S-H is less marked due to the lower mobility of silicate ions.

The evolution of the profiles between 28 days and 1 year is not similar for the two hydrates: the diffusion of calcium ions seems to be more influenced by the packing in the ITZ during hydration than the silicate ions do.

Another example of this diffusion process is the evolution of the $CaO:SiO_2$ ratio detected in the ITZ by microprobe analysis. Such a study has been made by Yuan and Odler [19] in the interfacial zone between marble and tricalcium silicate paste (Figure 10): in the vicinity of the aggregate, the C:S ratio is much higher than 3, the C:S ratio of the anhydrous silicate. In the bulk paste and to about 120 μm from the interface, the C:S ratio is equal to 3: a migration process of Ca^{2+} and OH^- ions is proposed by the authors to explain their results. Moreover, the C:S ratio of C-S-H found in the interface is in the range 3.5 to 4 instead of 1.5 to 2 in the bulk paste, probably because very small crystals of portlandite are intermixed with C-S-H in the ITZ.

The concentration profiles obtained for ettringite are very similar to portlandite ones (Figure 11) because the crystallization of both takes place during the first steps of hydration from very mobile ions. As well as the porosity, the main variations in ettringite or CH concentrations occur in the first 15 to 20 μm. When the ITZ microstructure is densified by means of silica fume additions, for example, the W:C ratio gradient is lowered and the possibilities of diffusion are reduced also. Such

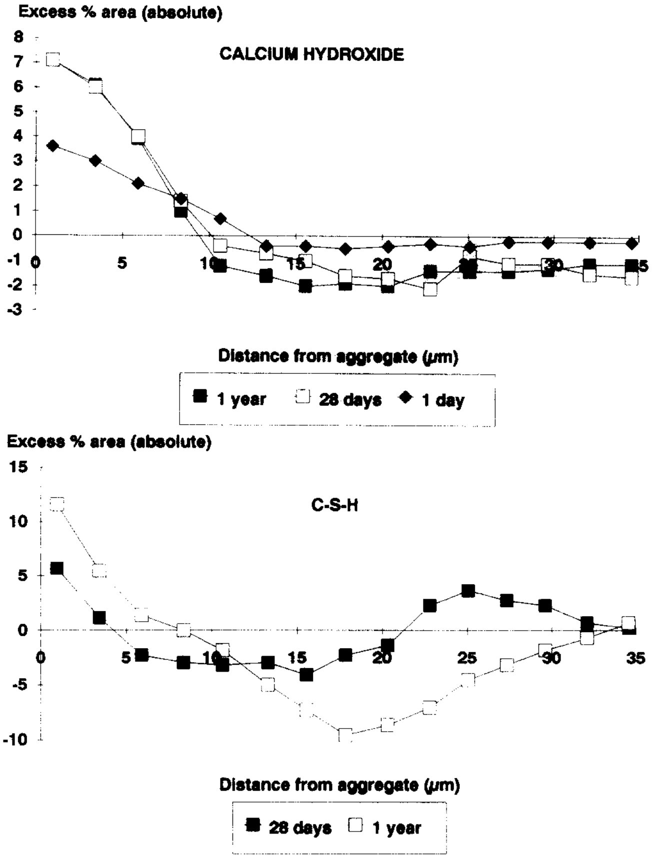

FIGURE 9. Redistribution of CH and C-S-H into the ITZ (from ref 2).

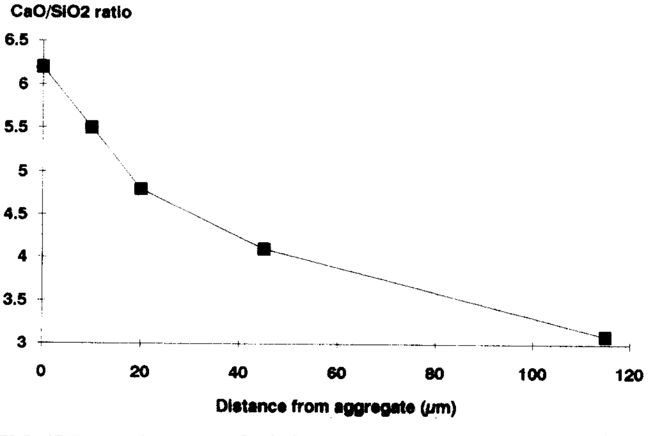

FIGURE 10. Average CaO/SiO_2 molar ratio of the hydrated C_3S paste as a function of the distance from the marble-paste interface (from ref 19).

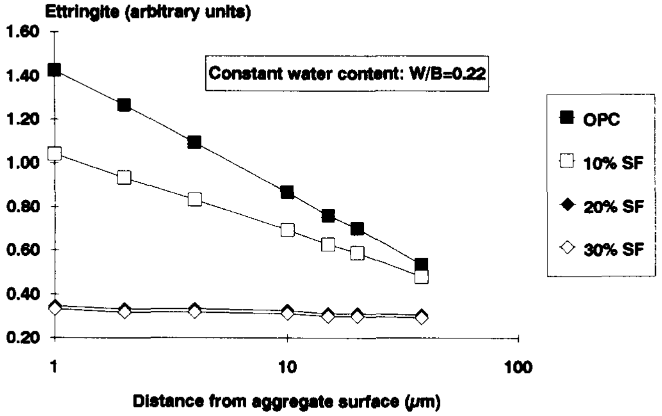

FIGURE 11. Concentration profile of ettringite into the ITZ as a function of silica fume substitution (from ref 23). When packing in the vicinity of aggregates is improved, the W:C ratio gradient decreases and then the diffusion of ion toward the surface of the aggregate.

an analysis may be confirmed by the modification in the ettringite profile with the silica fume content (Figure 11 [20]).

Morphology of Hydrates in the ITZ

The morphology of hydration products in the ITZ has been extensively studied. As many investigations have been published, this review is focused on the most important results. Using a geometrical model, Barnes et al. [21] have detected a duplex film. This film is typically 1 to 1.5-μm thick. The inner part which is formed in direct contact with the aggregates is portlandite and the outer part is C-S-H gel. The CH film is preferentially oriented with the c-axis normal to the aggregate. SEM investigations made by these authors and many others have shown that hydrate crystals are well formed and larger than in the bulk paste. The preferential orientation of portlandite in the ITZ has been studied by XRD (X-ray diffraction) with a method proposed by Hadley [22] and developed by Grandet and Ollivier [23]. In this technique, the CH orientation is characterized by means of an orientation index defined from the ratio between two XRD reflections. According to this method, the ITZ thickness is the distance to the aggregate in which the orientation index is higher than in the bulk. For OPC paste the typical thickness defined in this way is about 50 μm.

Influence of Mineral Additions on the ITZ Microstructure

Mineral additions may have some influence on the development of the microstructure in the interfacial zone because of two main factors: (1) a densification of the packing of the particles if the size of the additions is much finer than the size of the cement grains; and (2) a modification of the hydration process. These two factors may act simultaneously. It is then difficult to analyze their individual effect and the choice made in this review of the influence of mineral additions is to present successively the influence of the ultrafine additions and then the influence of the fine additions whose size is similar to the cement grains.

Influence of Ultrafine Additions

As mentioned by Goldman and Bentur [8], silica fume grains may be considered as a microfiller. Their influence in reducing the porosity and the W:C ratio gradients in the ITZ has been discussed earlier in this review. These reductions have been presented as a proof of the existence of a wall effect. When using very fine alumina grains as another microfiller, Hanna [20] has shown that the filling effect into the ITZ as well as in the bulk paste is due to the size of the finer particles, this effect being effective if the particles are deflocculated (i.e., when superplasticizer is used). A similar conclusion has been presented by Goldman and Bentur [8] using very fine carbon black grains.

Moreover, a pozzolanic reaction takes place with silica fume, and calcium hydroxide is consumed in the bulk paste as well as in the ITZ [24,25]. This modification of the microstructure in the ITZ has been proposed to explain the enhancement of the compressive strength of concrete. In fact, it seems that the main factor is the filling effect because the strength increase is similar with silica fume and inert alumina [26] or carbon black [8] grains.

Influence of Fine Additions

The influence of fly-ash and slag additions on the ITZ microstructure has been extensively studied by Carles-Gibergues [27]. During the first days, the influence of these additions is poor because the wall effect is not affected. Some minor differences can be underlined: for example, microbleeding can be more important with slag additions increasing the ITZ thickness. These additions may act as nucleation sites; the crystallization of portlandite is therefore more disoriented. The pozzolanic reaction in the presence of fly-ash has no particular effect in the ITZ. The influence of calcareous fillers on the ITZ structure has not been extensively investigated. It could be assumed that the packing around aggregate particles is not affected, the size of these additions being the same of cement grains. With a higher W:C ratio in the ITZ, calcium aluminate hydrates are formed more easily instead of ettringite, and the reactivity of calcareous fillers is enhanced [28]. A positive consequence of this reaction is the formation of calcium carboaluminate, which fills in the porosity of the ITZ (see below).

Hydration into the ITZ around Calcareous Aggregates

The microstructure in the ITZ may be affected by a chemical reaction of the aggregate with the cement paste. Deleterious reactions such as the alkali-aggregate reaction are beyond the scope of this review. The effect on the ITZ characteristics of the most important beneficial reaction which takes place at ordinary temperature, the reaction between calcareous aggregates and OPC paste, is presented here.

The reactivity of calcareous aggregates with Portland cement paste has been presented by Farran [13]; a chemical reaction takes place between calcite and the paste, resulting in a superficial etching. The hydrate which reacts is calcium aluminate hydrate, forming calcium carbo-aluminate $C_3A.CaCO_3.11\ H_2O$ [29] (Figure 12). This reaction is limited to the interfacial zone due to the low mobility of carbonate ions. Jambor [30] has shown that the reaction leads to an improvement of the compactness of the paste. One can then expect a resulting improvement of the properties of this ITZ around calcareous particles. Moreover, the etching of aggregates may result in a certain enhancement of the bond. A similar reaction involving the same chemical products has been observed with high alumina cement [31,32], but an alternative explanation of the reaction with calcite particles has been described By Monteiro and Mehta [33]: etching of aggregates is also observed with alite paste. According to these authors, calcite reacts with calcium hydroxide, resulting in the formation of a calcium carbonate with a variable composition, $CaCO_3$-$Ca(OH)_2$-H_2O. The experimental facts seem to be convincing in the two approaches, but this point has yet to be clarified.

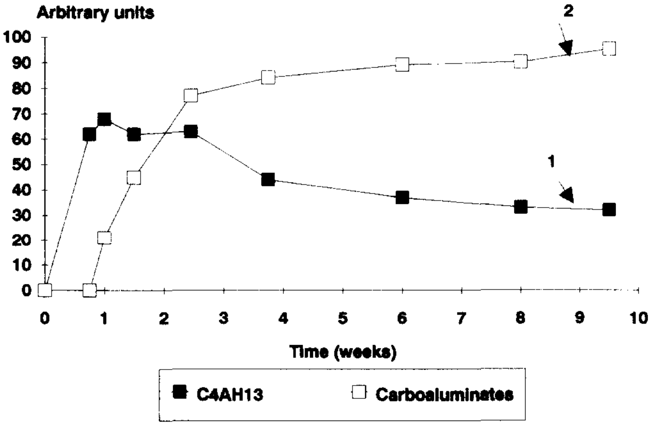

FIGURE 12. Evolution with time of the amounts of calcium aluminate hydrate (C_4AH_{13}, curve 1) and carboaluminate (curve 2) in the vicinity of a marble particle. W:C ratio of the OPC paste = 0.50 (from ref 14).

Local Properties of the ITZ

The mechanical and transport properties of concrete have been extensively studied in relation to the characteristics of the ITZ. This is beyond the scope of this review. Our objective is to review the intrinsic mechanical and transport properties of the ITZ. The coarser porosity and the presence of easily cleavable and highly soluble CH crystals can obviously affect the performances of the ITZ.

Different studies have proved that the mechanical properties of the paste are locally affected by this extra porosity. Among many others, Perrin [34] has observed a lack of cohesion in the ITZ by the replica-TEM technique. Lyubimova and Pinus [35] mentioned a drop in microhardness values in the ITZ around inert aggregates. On the contrary, a higher microhardness in the vicinity of aggregates (5 to 10 μm to the interface) and a lower microhardness at a distance of 25 μm from aggregates have been measured with calcareous rocks. The abrasion resistance is lower in the ITZ than in the bulk [36]. The bond strength between particles and cement paste is obviously a local property which involves the characteristics of the ITZ, including the chemical reactivity of aggregates. The bond strength between aggregates and cement paste has been investigated by Zimbelmann [37], and the typical behavior is reported in Figure 13. The physical adhesion with inert aggregates increases with time (curve 1). With limestone aggregates, further adhesion is measured due to the chemical reaction or to epitaxial growth (curve 2).

The transport properties may be affected by the ITZ

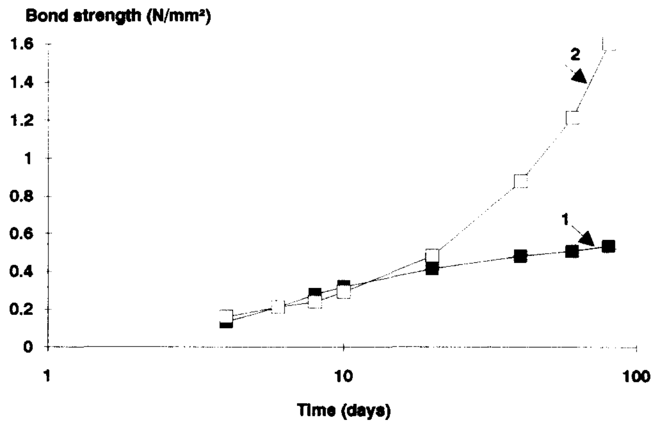

FIGURE 13. Bond strength between Portland cement paste and granite (curve 1) or limestone (curve 2) polished aggregates (from ref 37).

microstructure. The water coefficient of permeability of cement-rock composites has been measured by Skalny and Mindess [38]. The coefficient of permeability is essentially constant with time in tests on quartz and limestone themselves. However, tests on either pure cement paste or cement-rock composites showed that the apparent water permeability decreases for several days before reaching a stable value corresponding to an established regime in the specimen. The test results suggest to the authors that the ITZ itself does not appear to play a significant role with regard to water permeability, but no comparative values of the permeability are given in the reference [34]. A similar conclusion has been obtained by Wakeley and Roy [39]: the contact zone between different rocks or mortar does not provide a preferred pathway for water flow. These data are not in a good agreement with mercury intrusion porosimetry experiments in which widening of the larger pathways is explained by the existence of an interconnected cluster of ITZ. In fact, it seems difficult to measure the flow in excess through one ITZ in a permeability test because its thickness is extremely thin in comparison with the overall dimension of a specimen.

The chloride diffusion coefficient of the ITZ has been estimated by Breton et al. [40]. The transport of chloride ions has been studied, first by diffusion and second under the action of an electric field. The results show an increase of the diffusivity in the ITZ: assuming a 100 μm ITZ thickness, the diffusion coefficient is 12 times greater than the bulk cement paste one.

The overall engineering properties of concrete obviously depend on the local properties of the ITZ, but the analysis of the consequences of the microstructure on the bulk properties is not so easy. For example, the oxygen diffusion coefficient of concrete depends on the diffusion coefficients of the three phases: the aggregate, the paste, and the ITZ. It depends on the aggregate concentration and the ITZ thickness, and it depends also on the interconnection of the ITZ [41]. These relations between the properties of concrete and the characteristics of the ITZ are extensively studied because their knowledge could be an efficient way for improving the material or for fitting it to specifications in a more economical way.

Conclusion

The geometrical arrangement of cement grains in water, whether flocculation occurs or not, will be disturbed in concrete by the presence of aggregates. This involves a wall effect creating a gradient for water concentration in the cement paste and thus a W:C ratio gradient. In its initial state, the latter is infinite on contact with aggregates and tends toward a lower limit than its theoretical value calculated from the quantities of water and cement introduced into the concrete.

This perturbation, which is most significant on a thickness of 15 to 20 μm around the aggregates and equal to the mean diameter of the cement grains, has a number of consequences on the microstructure of the hydrated cement paste in the vicinity of the aggregates. These consequences are as follows:

1. The relatively large dimension of the spaces remaining vacant for the formation of the first hydrates, together with the significant variations in mobility of ions resulting from anhydrous compounds, leads, during hydration, to preferential crystallization of hydrates corresponding to the more mobile ions, ettringite and portlandite, according to the Le Chatelier hydration process.
2. A locally greater W:C ratio with fewer nucleation sites results in a minimum of germs and formation of larger, better-formed, and preferentially oriented crystals in contact with aggregates.
3. Finally, as the pores to be filled in are larger, the porosity, at all ages, will remain higher.

Thus, a zone where the paste has a microstructure different from the surrounding bulk exists around the aggregate particles. The microstructural characteristics of this zone vary gradually from the surface of the aggregates. The phenomenon therefore clearly involves an ITZ.

The consequences of initial geometrical perturbation on the microstructure have in turn an effect on the properties of the ITZ, which is mechanically less resistant than the bulk. The first microcracks resulting from mechanical or hygrothermal action will appear in this zone. If the ITZs surrounding the aggregate particles are connected, as is the case in concrete, transfers will be facilitated, particularly by diffusion. These transition zones will thus provide the main route for penetration of chemically aggressive ions.

Superplasticizers and ultrafine additions will reduce the largest spaces, with the former closing grains and the latter multiplying nucleation sites. The microstructural differences between the paste in the ITZ and that in the bulk will be lowered. High performance concretes are directly derived from an understanding of this phenomenon.

When aggregates are superficially soluble in the interstitial solution (mainly by action of alkali), the ions coming from the aggregates can combine, in the transition zone where they are in highest concentration, with the more mobile ions coming from cement grains. This is the case with limestone aggregates with the formation of carboaluminates.

While the mechanisms and the microstructures they generate are now well known, the influence of such factors as the size of aggregate particles, for example, remains to be defined. But the main questions which are yet to be answered are centered on the quantification of mechanical and transfer properties in the transition zone.

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