

EFFECT OF AGGREGATE, CEMENT, AND MINERAL ADMIXTURES ON THE MICROSTRUCTURE OF THE TRANSITION ZONE

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ABSTRACT

This paper contains a review of the results from the studies at the University of California at Berkeley on various factors influencing the microstructure of the transition zone in concrete. Two types of aggregate, two different cement, and three mineral admixtures were investigated. Using cement paste-polished aggregate composite specimens cured up to three years, X-ray diffraction, scanning electron microscopy, and microhardness testing techniques were used for characterization of the transition zone.

Compared to the transition zone between a quartz aggregate and an ASTM Type I portland cement, transition zones with smaller and less preferentially oriented crystals of calcium hydroxide were obtained when using a Type K expansive cement, or limestone aggregate, or mineral additives, such as condensed silica fume, granulated blast-furnace slag, and fly ash.

INTRODUCTION

Beginning with Farran's work [1], there has been a growing interest in the study of transition zone between coarse aggregate and cement paste [2-14]. This is because many important properties of concrete, such as permeability, durability, and strength are controlled by the the transition zone characteristics. Due to differences in materials and characterization techniques although contradictory results on the transition zone microstructure are sometimes reported in the published literature, the studies described in this paper seem to confirm the following:

1. In concrete, the microstructure of hardened cement paste in the transition zone is different from the microstructure of the cement paste in the bulk matrix.
2. Compared to the bulk cement paste, the cement paste in the transition zone is characterized by higher porosity, and larger size crystals of hydration products.
3. Due to the inherent weaknesses in the microstructure as described above (#2) when a concrete is subjected to any internal or external stresses the microcracks form first in the transition zone.
4. The improvements in the properties of concrete from the use of mineral admixtures, modified cements, and certain aggregate types can be explained from the resulting pore refinement and grain refinement processes, which occur in the microstructure of the transition zone.

This paper contains a review of the results from the transition zone characteristics studies at the University of California at Berkeley. Two aggregate types (a quartz and a limestone), three mineral admixtures (a condensed silica fume, a fly ash and a granulated blast-furnace slag), and two cements (an ASTM Type portland cement and a Type K expansive cement) were used. Material characteristics, details of experimental procedure, and preliminary results were reported by the authors in earlier publications [14-18], and a summary was presented at the 8th International Congress on the Chemistry of Cements [15]. However selected data from the specimens cured for up 3-years period are presented here.

From tests on mechanical properties of concrete, it is difficult to evaluate the contribution of the transition zone, especially to establish that an observed improvement in cement properties can be directly related to pore refinement and grain refinement in the transition zone. This is because due to its small size the characterization of the transition zone is carried out at the microscopic level, whereas the overall assessment of concrete properties is carried out by macroscopic-level tests. One way to resolve this issue is to develop microscopic-level tests. Included in this paper are the results of microhardness tests on the interfacial quartz-portland cement paste film, which show that this type of test is promising for the development of microstructure-property relationships in the transition zone.

RESULTS AND DISCUSSION

The Transition Zone with Quartz Aggregate

With ASTM Type I portland cement and quartz the typical morphology of the cement-paste side of the transition zone, at relatively early age (28 days), is shown in Fig. 1. First, in conformity with the observations made by many researchers [3-7], a continuous and thin film of calcium hydroxide is formed at the surface. Below this film are found the other hydration products, such as CSH and ettringite, and large pores (Fig. 2).

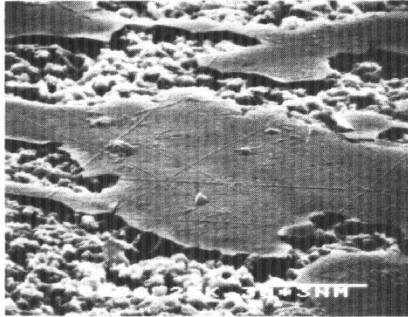


FIG. 1



FIG. 2(a)

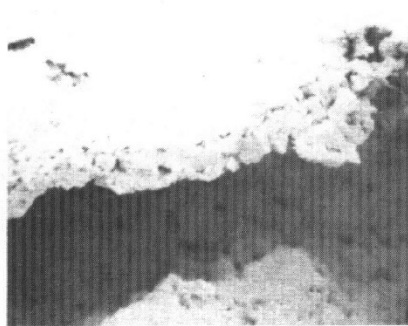


FIG. 2(b)

From X-ray diffraction analysis of the cement paste in the transition zone at various depths from the interface, it was concluded that: (a) the concentration of ettringite was the highest at the interface and decreased gradually as one moved away from the interface toward the bulk paste. (b) both the concentration and degree of preferred orientation (the intensity ratio between 00.1 and 10.1 peaks) of calcium hydroxide was maximum at the interface, and decreased gradually towards the bulk cement paste (Fig. 3).

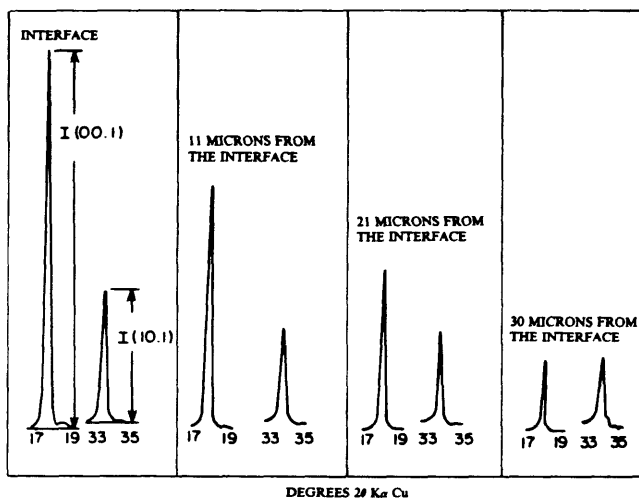


FIG. 3
XRD Analysis of the CH Preferential Orientation

The above observations can be explained on the basis of the "wall effect" at the interface, when an aggregate particle comes into contact with freshly mixed cement paste. This effect is responsible for local regions of high water-cement ratio, which are created when a fresh concrete mixture is consolidated after placement. The ions produced by the dissolution of cement grains easily diffuse to these high water-cement ratio areas present at the aggregate surface. From the solution which is supersaturated with respect to calcium and hydroxyl ions, first a precipitate of calcium hydroxide is formed as a coating on the aggregate surface. When the sulfate, aluminate, and silicate ions have also passed into the solution phase, the next products to precipitate out are the crystals of calcium hydroxide, ettringite, and C-S-H.

Compared to the bulk cement paste, the large size of crystal in the transition zone is due to the high water-cement ratio, which also accounts for the high porosity. This is because the crystal size is usually larger whenever there is more space for the crystal growth. Also, the Toulouse technique [8,9] for determination of the relative thickness of the transition zone assumes that the hexagonal sheet-like crystals of calcium hydroxide in the transition zone exhibit a preferential orientation, with their c-axis perpendicular to the aggregate surface. Scanning electron microscopic observations show that this may not always be true. However, from standpoint of mechanical characteristics of the transition zone what is important, is that in large cavities the hexagonal crystals of calcium hydroxide tend to stack up on top of each other and are preferentially oriented (with respect to each other).

The authors believe that, in addition to the large porosity, the presence of preferentially oriented and large crystals of calcium hydroxide with their poor intercry-

stalline bonding, is mainly responsible for the weak mechanical strength of the transition zone. Another source of weakness is the Hadley grains (hollow particles of cement from which the solid have been dissolved away) found in the transition zone (Fig. 4). Compared to the bulk cement paste, the presence of a relatively large number of the Hadley grains in the transition zone should not be surprising because of the high local water-cement ratio. Incidentally, the presence of the Hadley grains, and higher concentrations of ettringite and calcium hydroxide in the transition zone than in the bulk cement paste, provide a firm evidence that at least the early hydration reactions in portland cement paste are through solution.

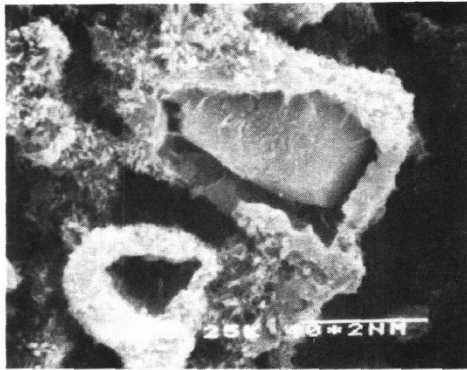


FIG. 4

The Transition Zone with Limestone Aggregate

At early ages, up to 28 days, the microstructure of the transition zone in the portland cement paste-limestone aggregate system was not different from the one already described with quartz aggregate. For instance, the transition zone typically contained a film of calcium hydroxide on the interface, underneath which were present clusters of large and preferentially oriented crystals of calcium hydroxide, and regions of high porosity.

At later ages (56 days or more), some manifestations of the development of a strong chemical bond between the aggregate and the bulk cement paste were on evidence. Firstly, unlike the cement paste-quartz aggregate system a part of the interfacial film tended to adhere strongly to the polished surface of the limestone aggregate during the process of separation of the cement paste from the aggregate. On the aggregate side, the result of etching of the calcite grain by the cement paste can be observed from the scanning electron micrograph shown in Fig. 5a. On the cement paste side of the interface, the products of the calcite etching can be seen imprinted on the calcium hydroxide film (Fig. 5b). A typical XRD analysis of the cement paste at the interface in a 1-year old specimen, showed a characteristic peak at $11.2^\circ 2\theta$ ($Cu-K\alpha$).

With portland cement and limestone aggregate Grandet and Ollivier [8] had also observed in the transition zone a peak at $11.2^\circ 2\theta$ ($Cu-K\alpha$), and attributed it to the formation of calcium carboaluminate hydrate. However, using a high-purity alite cement with marble aggregate, Monteiro and Mehta [15] found that as a result of chemical attack on the carbonate rock a basic calcium carbonate hydrate was formed, which improved the strength of the transition zone by grain refinement.

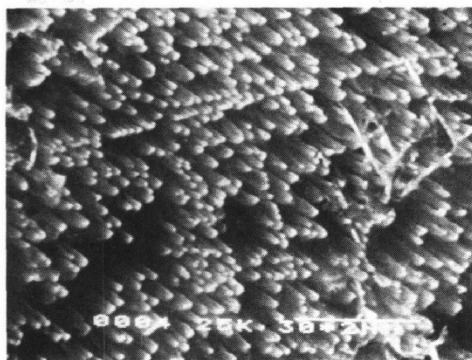


FIG. 5(a)

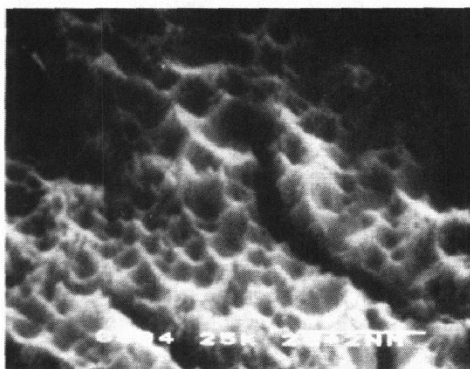


FIG. 5(b)

Compared to crushed sandstone aggregate, approximately 15% increase in the 56-day compressive strength of concrete was observed when crushed limestone aggregate of the same maximum size was used as coarse aggregate in a given concrete mixture [19]. Similarly, in the case of lightweight aggregates, it has been proposed [20] that a reaction between calcium hydroxide and the aggregate surface is responsible for the high strength of the transition zone, and the durability of reinforced concrete elements made with lightweight aggregate.

The Transition Zone with Type K Expansive Cement

The drying shrinkage cracking in concrete can be reduced or even eliminated by the use of cements, which form expansive hydration products. When concrete is adequately restrained it will get prestressed and will be able to withstand without cracking the tensile stresses produced by drying shrinkage. Many researchers, including Polivka and Willson [21] have reported that, in the range of 0.4 to 0.6 water-cement ratio, the compressive strength of concrete containing a Type K expansive cement (a portland cement containing an ettringite forming additive) is 25 to 40% higher than the corresponding portland cement.

To investigate the influence of the transition zone on the strength of expansive cement concrete the authors [17] made a Type K expansive cement was made from a mixture of alite (5600 g), $C_4A_3\bar{S}$ (400 g) and $C\bar{S}$ (720 g). Cement paste with a 0.4 water-cement ratio, was cast on the top of a polished surface of quartz aggregate. The vertical expansion of the cement paste was restrained by applying an external force on the composite system, which was maintained at 100% humidity.

Microstructural studies on the transition zone by X-ray diffraction and scanning electron microscopic analyses showed that, when expansive cement was used, the formation of the continuous calcium hydroxide film and preferentially oriented crystals was prevented. Instead, a large amount of ettringite and randomly oriented calcium hydroxide were formed (Fig. 6). This change in the microstructure of the transition zone is considered to be responsible for the stronger transition zone and better mechanical properties of Type K expansive cement concrete, when compared to portland cement concrete.

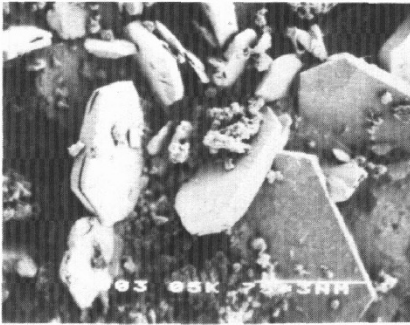


FIG. 6(a)

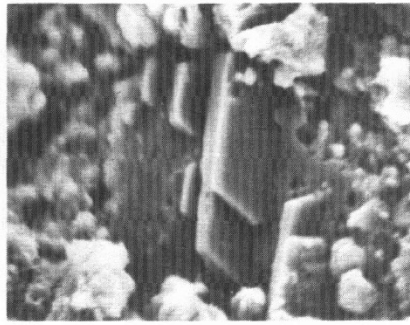


FIG. 6(b)

The Transition Zone with Mineral Admixtures

An ASTM Type I portland cement, and commercially available fly ashes (a Class F and a Class C), granulated blast furnace slag, and condensed silica fume -- all meeting standard specifications prevalent in the North America -- were utilized for making the blended portland cements of this study. The fly ash dosage was 20% by weight of cement; the slag and silica fume were used in two different dosages (10 and 30 weight percent for the slag and 5 and 16 weight percent for the silica fume). Due to the extremely small particle size of silica fume ($0.1 \mu m$ average diameter), a high-range water reducing admixture was used as a plasticizer for blended cements containing 16% silica fume replacement. Only a summary of the conclusions from this work is given below.

Compared to the reference portland cement, it is concluded that generally the blended cements are able to produce a remarkable reduction in the relative thickness of the transition zone (as measured by the Toulouse technique), thus contributing to the overall homogeneity and improved strength characteristics of the cement paste-aggregate system. The degree to which this effect is realized varied with the characteristics of the individual mineral admixture, its dosage in the blended cement, and the age of curing. The reduction in the transition zone thickness may be explained from several phenomena, such as lower permeability of fresh concrete (less accumulation of bleed water at the aggregate surface), the presence of numerous nucleation sites for crystallization (which would help the formation of smaller crystals of cal-

cium hydroxide which would have less tendency for preferred orientation), and a gradual densification of the system from the hydration products from the slow pozzolanic reaction between calcium hydroxide and reactive silica.

The silica fume ($20 \text{ m}^2/\text{g}$ surface area) was found to be the most effective in reducing the transition zone thickness, from about $50 \text{ }\mu\text{m}$ (no admixture present) to less than $8 \text{ }\mu\text{m}$. From scanning electron microscopic investigations it was evident that some silica fume particles reacted quickly during the early stages of hydration while others remain only partially reacted even at later ages (Fig. 7). Some silica fume particles or their pseudomorphic hydration products appear to become engulfed in the calcium hydroxide film. This may have the effect of reinforcing the film, because generally cracks were found to go around these silica fume inclusions. It is however interesting to point out that despite a considerable reduction in large pores and preferentially-oriented crystals of calcium hydroxide in the transition zone, some unreacted silica fume particles and large crystals of calcium hydroxide were always found to be present at the interface, even in the specimens containing 16% silica fume.

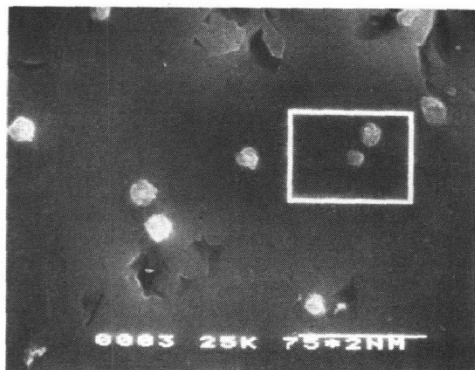


FIG. 7

The ground ($500 \text{ m}^2/\text{kg}$ Blaine) granulated blast-furnace slag was not effective in reducing the transition zone thickness at 10% level of cement replacement, but was found to be quite effective at 30% level (Fig. 8), and curing ages of 7 and 65-days [18]. Since 30% slag is not sufficient to remove most of the calcium hydroxide present by pozzolanic reaction, the improvement in the transition zone characteristics was attributed largely to the nucleation of randomly oriented calcium hydroxide crystals on the fine particles of slag. Both the fly ashes (approx. $400 \text{ m}^2/\text{kg}$ Blaine) were effective only after prolonged curing (28-days or more). As with the silica fume, the three years old specimens containing fly ash showed partially hydrated fly ash particles existing side by side with large crystals of calcium hydroxide. The acicular products of the fly ash hydration and pozzolanic reaction seem to be quite effective in reducing the presence of large pores in the transition zone (pore refinement). There is some evidence that Class C produced more acicular hydration products (Fig. 9).

Microhardness Tests

Using Vickers Pyramid, the microhardness analysis was limited to the interfacial film between the quartz aggregate and the ASTM Type I portland cement paste.

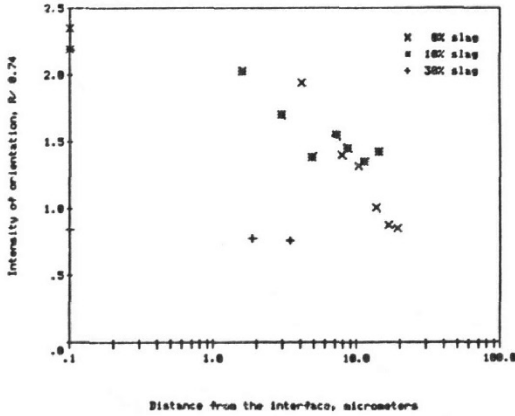


FIG. 8
Orientation of Calcium Hydroxide Crystals for and Slag Cement Pastes at Age 65 days

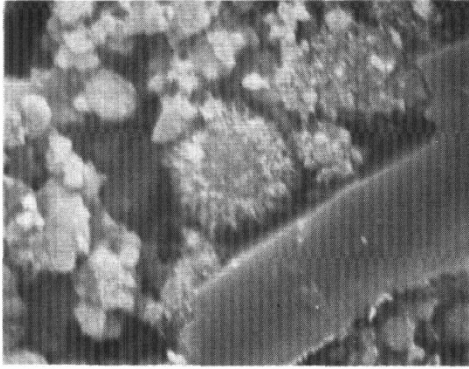


FIG. 9

A typical impression of the Vickers Pyramid on the interfacial film of a 30-day old specimen is shown in Fig. 10a. The impression was sharp and well defined, and there was no radial cracking. Different loads (P) were used to obtain corresponding values of the width of the indentation $2a$. From a load versus indentation width plot, the reproducibility of the microhardness data seems to be good. Hardness (H) of the film was found to be $(6.34 \pm 0.17) 10^5 \text{ kg/m}^2$. No cracks were obtained for any load level, but material displacement was noted (Fig. 10b), when a load greater than a threshold limit (30 kg in this test) was applied.

In the 1-year old specimen, the cracks did appear on indentation (Fig. 10c). The 1-year old interfacial film gave a hardness of $(7.89 \pm 0.40) 10^5 \text{ kg/m}^2$, -- an increase of about 25% when compared to the 30-day old film.

The development of cracks on indentation motivated an exploratory excursion into a possible method of determining the fracture toughness of the transition zone. The word exploratory should be emphasized because really the technique is applicable to homogeneous materials, whereas the transition zone has many heterogeneous

characteristics. According to Anstis et al. [22], the fracture toughness (K_c) can be derived from an indentation test by using the relationship: $K_c = \delta_v P (E/H)^{1/2} c^{-3/2}$, where δ_v is a constant for the Vickers radial cracking (a value of 0.016), P the applied load, H the material hardness, E the elastic modulus, and $2c$ the crack width. Assuming 50 GN m^{-2} elastic modulus and applying this equation to the results of the indentation test on the 1-year old transition zone the calculated value for fracture toughness is $0.07 \text{ MN/m}^{3/2}$, which is not far different from the value ($0.1 \text{ MN/m}^{3/2}$) reported by Hillemeier and Hilsdorf [23], using a CT specimen. Fig.10d shows that the crack pattern can be more complicated than assumed by the constitutive relationship of the type discussed here.

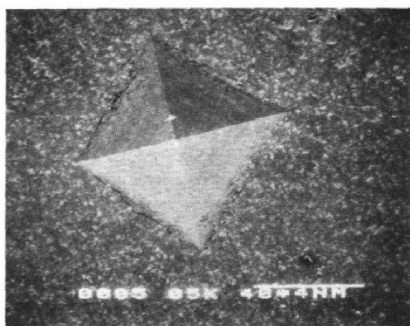


FIG. 10(a)

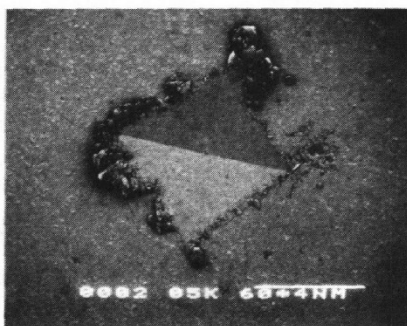


FIG. 10(b)



FIG. 10(c)

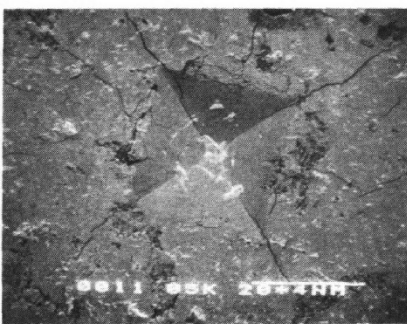


FIG. 10(d)

Concluding Remarks

In ordinary portland cement concrete, the transition zone between the hydrated cement paste and the particles of coarse aggregate is characterized by a highly heterogeneous microstructure, containing numerous areas of large pores and preferentially oriented and large crystals of calcium hydroxide. These characteristics of the transition zone microstructure seem to be the primary sites of weakness, at which microcracks originate, when concrete is subjected to any internal or external stresses.

By reducing the sites of weakness in the microstructure of the transition zone,

the hydrated cement paste matrix in concrete can be made more homogeneous and, therefore, less prone to microcracking. This study shows how the differences in the aggregate type, cement, and mineral admixtures can influence the microstructure of the transition zone. For instance, it is shown that fine particles of pozzolanic and cementitious admixtures are helpful in improving the transition zone characteristics through processes of pore refinement and grain refinement. To cause the beneficial change in the microstructure of the transition zone, several mechanisms may be simultaneously at work, such as reduction in the permeability of fresh cement concrete (therefore less internal bleeding), presence of numerous nucleation sites for crystallization of hydration products, (therefore formation of small crystals of calcium hydroxide, with less tendency for preferred orientation), and slow pozzolanic reaction (therefore causing a further reduction in calcium hydroxide, with concurrent densification of the system by the products of the reaction).

For meaningful relationship between the microstructure of the cement paste in the transition zone and its mechanical properties, it is essential to develop micro-level testing techniques. Hardness using a Vickers Indentation Pyramid can be used for preliminary evaluation of the mechanical strength of the interfacial film.

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