Part III

MICROSTRUCTURE
ABSTRACT

This study was conducted to evaluate the effects of inclusion of fly ash on concrete microstructure and its mechanical performance. Air entrained plain portland cement concrete was proportioned to obtain design strength of 6000 psi at the 28-day age. Concrete mixtures were also proportioned to have various cement replacements in the range of 15 - 70% with an ASTM Class C fly ash.

Microstructure of concrete specimens was studied by means of a computer simulation program as well as a scanning electron microscope. Mechanical properties of concrete such as compressive strength and splitting tensile strength were determined at various ages up to 91 days. The simulation results were compared to scanning electron microscopic investigations as well as strength properties of concrete.
INTRODUCTION

It is well established that the transition zone, the interfacial region between the coarse aggregate and the hydrated cement paste, is the weakest region in the concrete. Most of the concrete strength and durability properties are markedly influenced by the properties of the interfacial zone. As a result, the effects of properties of the interfacial region on concrete strength and durability of concrete have been the subject of many recent investigations.

Numerous investigations have been carried out to study microstructure of cement paste made with or without mineral admixtures (1-6). However, limited work has been directed toward studying the effect of mineral admixtures on microstructure of concrete, especially high-volume fly ash concrete systems.

This research was undertaken to investigate the effects of addition of Class C fly ash on concrete microstructure and strength properties. The microstructure of concrete was studied using a theoretical and electron microscopic techniques.

COMPUTER SIMULATION OF CONCRETE MICROSTRUCTURE

A three-dimensional digital image based model developed at the
National Institute of Standards (NIST) was selected to investigate microstructure of concrete containing high volumes of fly ash, especially the interface region of concrete \((1-2)\). The detailed description of the model is available in the literature \((1-2)\). A brief description of the model is presented in this paper. The model employs pixels, a series of discrete elements, to represent a volume. Each pixel is uniquely related to a specific phase of the cement hydrating system and is of 1 μm on a side. The phases considered in this simulation are coarse aggregate, porosity, \(C_3S\), \(C-S-H\), \(CH\), pozzolanic \(C-S-H\), and mineral admixtures.

In order to carry out the simulation, a starting microstructure is created. The various sizes of digitized spherical particles, representing cement and fly ash were added to the starting microstructure. A 3-D concrete model of 100 x 100 x 100 pixels was used in this work. First, a flat coarse aggregate (100x100x2 pixels) was placed in the middle of the system. The hydration process is modelled as an iterative process using discrete cycles as shown in Figure 1 for a two-dimensional system. Each hydration cycle involves three different processes: dissolution, diffusion and reaction. A fly ash reactivity factor of 1.04 was used in the model for this work. The present model considers that pozzolanic reaction involves only \(SiO_2\). The microstructure and data derived from the model concrete were obtained at a constant water-to-cementitious ratio.
of about 0.35±0.02 before and after completion of hydration process.

The computer model analyzes the microstructure for determination of volume fraction of the phases present in the concrete model as a function of distance from the aggregate surface. Images of two-dimensional slices from the middle of the concrete model were also obtained for visual inspection of the phases present.

EXPERIMENTAL PROGRAM

Air entrained concrete mixtures were proportioned to have 28-day strength of 6000 psi. The no-fly ash concrete mixture consisted of 661 lbs. cement, 2083 lbs. coarse aggregate (1" max size), and 1027 lbs. sand. The air content was maintained at about 6±1%. An ASTM Class C Fly ash (CaO ≈ 31%) was added to concrete mixture to have cement replacement in the range of 15-70% by weight of total cement used. The water-to-cementitious ratio was kept at about 0.35±0.02.

Cylindrical specimens (6x12 inch) for measurement of compressive strength and tensile strength, were prepared and tested using appropriate ASTM procedures.
Fractured concrete samples at 60-day age were sputter-coated with Au/Pd and examined with an Hitachi S-570 scanning electron microscope in order to assess the effect of fly ash on concrete microstructure.

In order to facilitate the investigation of the transition region, small blocks of concrete were fractured and both pieces mounted on the same stub so that the two complementary faces could be compared. This is particularly useful when the fracture plane passes through the transition region in that it permits examination of the aggregate "surface" in one fracture face and the corresponding "lift-out scar" on the complementary fracture face.

RESULTS AND DISCUSSION

Simulation Model Results

Some sample micrographs of the concrete models at various cement replacement levels generated by the simulation model are shown in Figure 2. Analysis of the model results revealed that up to a certain level, addition of fly ash increased total amounts of C-S-H crystals and decreased porosity in the interfacial region of concrete. The best results were obtained at 30% cement replacement with the fly ash with respect to improvement in concrete microstructure.
In general, amounts of pozzolanic C-S-H crystals increased with fly ash content within the range investigated. However, total amounts of C-S-H crystals, resulting from cement hydration and pozzolanic reaction of fly ash, decreased when fly ash content was increased to replace 50% or more cement (Figure 2). Therefore, in order to obtain high-strength of concrete, cement replacement with fly ash should not exceed 30%, although it can vary to some extent with type and source of fly ash.

**SEM Investigations**

Fly ash particles are shown in Figure 3. In the plain portland cement concrete specimen, the bulk cement paste between aggregates is characterized by the presence of large CH crystals. While the calcium hydroxide is generally in the form of solid blocks, stacks of CH plates interleaved with C-S-H (Fig. 4A) have also been observed. In addition, calcium hydroxide in the form of single large plates and stacks of smaller, thinner plates has partially filled in some of the large pores in the paste (Fig. 4B). Ettringite crystals are occasionally observed in association with the CH.

Addition of 15 - 30% fly ash to the concrete mixture has minimal effect on the microstructure of the bulk cement paste. At higher concentrations, there is a profound effect on the appearance of calcium hydroxide in the bulk cement paste, with both the size and
number of CH crystals decreasing markedly at fly ash concentrations of 50 - 70%. At these levels, the massive euhedral CH crystals have been largely replaced by thinner hexagonal plates arranged singly and/or in small stacks which are separated by fly ash, C-S-H and ettringite (Fig. 4C). The ability of fly ash to reduce the amount of calcium hydroxide in the paste has been documented previously (4,5).

The extent to which the fly ash particles have reacted with the cementitious components can be derived from observations of the particle surface. Etching of the glassy component of the fly ash shell is evidence of pozzolanic reaction (5). Varying degrees of etching (Fig. 5A) have been observed, although a number of fly ash particles appear to be unreacted. Fly ash particles are often ensheathed by a duplex film (Fig. 5B). As a similar film lines many of the sockets formed when fly ash particles are pulled out during fracture, it can be assumed that most of the "naked" fly ash particles were actually covered by duplex films in the intact concrete. The presence of a duplex film does not preclude further reaction of the particle (6).

It is generally held that the micromorphology of the transition region, a band 40 to 50 μm wide surrounding aggregates in concrete differs from that of the bulk concrete paste (4). As was found for
the bulk pastes, addition of fly ash reduces the size and amount of calcium hydroxide in the transition region. Since fly ash particles fill in the spaces between the clinker particles and the aggregates, there is less room for the calcium hydroxide crystals to grow. This was particularly striking when the microstructure of
the aggregate scars of the control and fly ash containing samples were compared.

Figure 6 illustrates complementary fracture faces through the transition region in a no-fly ash control sample. The aggregate surface (Fig. 6A) is covered by of Type II C-S-H with some ettringite and parallel CH plates adhering to it. The complementary lift-out scar shows extensive regions of calcium hydroxide plates parallel to the surface (Fig. 6B) as well as some plates which are oriented perpendicular to the surface. C-S-H and clusters of ettringite occupy the spaces between the CH plates.

A fracture through the transition zone of the 50% fly ash sample is shown in Figure 7. The material adhering to the aggregate surface consists of fly ash, C-S-H, ettringite and some calcium hydroxide (Fig. 7A). The corresponding lift-out scar (Fig. 7B) reveals that the areas covered by CH are less extensive, and there is considerably more ettringite relative to the control samples.

**Strength Properties and Their Relation to Microstructure**

Strength properties of concrete such as compressive strength and splitting tensile strength were measured. Both compressive and tensile strength of concrete increased with age. Compressive
strength increased with inclusion of fly ash up to 30% cement
replacement. Tensile strength of concrete was maximum at a cement replacement of 15% with fly ash.

From the theoretical and experimental microstructure investigations, it was found that at a 15% cement replacement with fly ash, not much pozzolanic reaction occurred because a large number of CH crystals were present in the interface region. These investigations further revealed that number of CH crystals decreased with increasing fly ash content. In this work, total amount of C-S-H crystals increased with addition of fly ash up to 30% cement replacement. Also, volume fraction of porosity of the system was also diminished up to this level of cement replacement. Probably, increase in strength due to addition of fly ash up to 30% cement replacement was primarily attributed to increase in hydration products as well as decrease in porosity resulting from pore filling and grain refinement effects.

The rate of increase in strength for fly ash mixtures was much higher than that for no-fly ash concrete mixture (Figures 8 and 9). This was probably due to increase in C-S-H contributions resulting from fly ash reactions with CH. The maximum strength should depend upon the amounts of C-S-H produced from cement hydration and pozzolanic reactions. However, not only the amount of C-S-H influences concrete properties, but also microstructure and porosity of the system affect
the strength of concrete. Therefore, up to certain levels of fly ash addition, concrete strength can increase due to the increase in the hydration products and/or improved grain structure, and decrease in porosity of the concrete systems.

CONCLUSIONS

1. Both theoretical and SEM investigations revealed that homogeneity of the interface microstructure is greatly improved due to addition of fly ash. This was primarily attributed to the pore filling effects as well as pozzolanic reaction of the fly ash.

2. The microstructure analyses of concrete showed that presence of fly ash in concrete mixtures reduces the amount of calcium hydroxide that formed during early stages of hydration process.

3. In general, the rate of pozzolanic reaction increased with fly ash content in concrete. However, total C-S-H increased with fly ash addition up to 30% cement replacements. The concrete mixture with 70% cement replacement showed the highest rate of increase in concrete strength with age.
4. The maximum compressive strength and tensile strength were obtained at respective cement replacements of 30% and 15% with the Class C fly ash. However, the fly ash mixtures up to 50% cement replacements showed adequate strengths at 28 days for structural applications.

REFERENCES


Figure 8-1  Schematic of the Rules of Hydration for the Simulation Model
(a) 15% cement replacement  
(b) 30% cement replacement  

(c) 50% cement replacement  
(d) 70% cement replacement  

Figure 8-2 Composite Image of Middle Slice of the Concrete Model Generated by the Simulation Model after Hydration: Red represents cement particles, Yellow represents C-S-H, Blue represents CH, Magenta represents
aggregate, Brown represents pozzolani C-S-H and fly ash, and Black represents porosity
Figure 8-3  Scanning Electron Micrograph of the Type C Fly Ash Used in this Study.

Figure 8-4  (A) Stacks of CH Plates Interspersed with CSH in the Bulk Concrete Paste; Control.  (B) Large and Small CH
Plates Fill in a Void in the Bulk Concrete; Control.
(C) Individual Plates and Small Stacks Interspersed with CSH and Fly Ash (Arrowheads); 70% Fly Ash Sample.
Figure 8-5  The Pozzolanic Reaction of Fly Ash Results in Etching of the Glassy Surface to Reveal Underlying Crystalline Features, Unreacted Particles (*) are also Present; 70% Fly Ash Sample.

Figure 8-6  Complementary Fracture Faces through the Transition Region of the No Fly Ash Control. (A) Material
Adhering to the Aggregate Surface Consists of CSH, Ettringite and Thin CH Plates. (B) Lift Out Scar is Characterized by Extensive Regions of CH Plates, CSH Fills in the Areas Between the Plates.
Figure 8-7  Complementary Fracture Faces through the Transition Region of the 50% Fly Ash Sample. (A) Fly Ash, Ettringite, CH and Small Areas of CSH Cover the Aggregate Surface. (B) Lift Out Scar is Characterized by Fly Ash and Ettringite, along with some CH and CSH.
Figure 8-8  Compressive Strength Gain of Concrete as a Function of Age.
Figure 8-9   Tensile Strength of Concrete as a Function of Age.