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SEM Investigation of Microstructure in high performance concrete with binary and ternary mixes

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ABSTRACT

HPC mixes may be made with Silica fume for cement and binary and ternary mixes involving Industrial By-products of Bottom ash and steel slag aggregate for the replacement of Fine aggregate and Coarse aggregate. Binary mixes involved combinations of silica fume and bottom ash, silica fume and steel slag aggregate, bottom ash and steel slag aggregate and ternary mixes involved combination both of three materials in concrete consumes CH leads to development of a different morphology in ITZ. This paper presents SEM for the three phases and an evaluation of the ITZ in the three cases for making HPC.

Introduction

Concrete made from raw materials of cement, fine aggregates, coarse aggregates, chemical admixtures, mineral admixtures and water. Conventional concrete as only the binding materials are common for attaining compressive strengths upto 60 MPa at an age of 28 days. Based on SHRP (The Strategic Highway Research Programme) high performance concrete has been defined in terms of certain target strengths and durability criteria. A High performance concrete is a concrete in which certain characteristics are developed for a particular application and environment, so that it will give excellent performance in the structure (1). A study of the morphology of concrete surfaces involves observation of the form, shape and size of the individual particles, particularly through high resolution electron microscopes. Many of the properties of concrete particles are determined by its chemical nature and microstructure. Microstructure constitutes the nature of the solid portion and nonsolid portion. Some factors of micro structural features are physical and chemical nature of the cement, type and amount of admixture etc. The solid portion of the microstructure involves size and shape of the bonding structures, surface area and density in morphology concept. Also the non solid portion involves porosity, pore shape and size of the distribution analysis in microstructure. The term microstructure can be used for the microscopically magnified portion of a macrostructure. Most of the properties of concrete are evaluated according to standard procedures of SEM. The application of SEM techniques has made it possible to resolve the structure of materials to a fraction of a micrometer. Also concrete strength is heterogeneous and highly complex. At the macroscopic level the concrete may be considered to be a two phase material, consisting of aggregate particles dispersed in a matrix of the cement paste. Several specimens of high performance concrete containing the same amount of water but different amounts of cement are examined at various time intervals. The volume of capillary voids in the hydrated cement paste would decrease with decreasing w/c ratio or with increasing age of hydration. The homogeneous distribution of solids and voids are alone for a well hydrated cement paste. However, micro structural studies have shown that this cannot be done for the hydrated cement paste present in concrete. The structure of hydrated cement paste in the nearness of large aggregate particles is very different from the structure of bulk paste while presence of aggregate. The transition zone which represents the interfacial region between the particles of coarse aggregate and the hydrated cement paste [2].

When OPC is dissolved in water, the calcium sulphate and the high temperature compounds of calcium tend to go into solution. As a result of combinations between calcium, sulphate, aluminate and hydroxyl ions within a few minutes of cement hydration can be created. The needle shaped crystals of a calcium sulfoaluminate hydrate called ettringite. The characteristics of calcium aluminate hydrate which are formed in the hydrated pastes of under sulphated Portland cements. A scanning electron micrograph illustrating the typical morphology of phases prepared by mixing a calcium aluminate solution with calcium sulphate solution can be determined. The calcium silicate hydrate phase makes up to 50 to 60 % of the volume of solids in a completely hydrated Portland cement paste. The morphology of calcium silicate hydrate also varies from poorly crystalline fibers to reticular network. Calcium hydroxide crystals constitute 20 to 25% of the volume of solids in the hydrated paste. Due to distinctive hexagonal prism morphology, calcium hydroxide tends to form large crystals. When compared to Calcium silicate hydrate, the calcium hydroxide can be dissolved highly due to chemical durability of acidic solutions in hydrated Portland cement with the presence of considerable amount of calcium hydroxide. Calcium sulfoaluminate compounds occupy 15 to 20% of the solids volume in the hydrated paste (3). It can form a needle shaped prismatic crystals of ettringite.

In the present study, samples of high performance concrete made with control mix, control mix with combination

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of silica fume, bottom ash and steel slag act as a binary mixes, combination of three materials act as a ternary mixes.

Experimental Investigation

Material characterization

A 43 grade ordinary Portland cement were used for this investigation. The fine aggregate used in the experiment were clean natural sand with specific gravity of 2.61 and fineness modulus of 2.76, maximum size not more than 35mm. While coarse aggregate was used as (10-5) mm crushed granite stone with specific gravity of 2.66. Silica Fume used was Elkem Micro Silica Grade 920-D in dry state and packed in 20 kg bags, obtained from thermal power plant, Neyveli Lignite Corporation Ltd., Neyveli, Tamil Nadu, India was used in this investigation.

Definitions

A structure is the type, amount, size, shape and distribution of phases present in solid constituents in concrete. The term macrostructure is generally used for the gross structure, visible to the human eye. The limit of resolution of the unaided human eye is approximately one-fifth of a millimeter. Whereas microstructure is a term which is used for the microscopically magnified portion of a macrostructure and the magnified capability of modern electron microscopes of the order of 10^5 times. A microscope is a device that reveals details of an object finer than what can be seen by the naked eye. The microstructure of concrete is described as an integrated system consisting of hydrated cement paste (HCP), coarse and fine aggregates and the interface between aggregate and hydrated cement paste (HCP), also known as hydrates (C-S-H) and calcium hydroxide crystals and few is occupied by calcium sulpho-aluminate hydrates. The C-S-H phase plays a vital role in concrete and most important component in concrete for enhancing the binding property. Transition zone which represents the interfacial region between the particles of coarse aggregate and the hydrated cement paste. The hydrated the interfacial transition zone (ITZ) or paste-aggregate interface. In normal concrete the hydrated cement paste consists of cement hydration products include calcium silicate cement paste and the transition zone generally contain a heterogeneous distribution of different types and amounts of solid phases, pores and micro cracks. A calcium hydroxide crystal appears in different size and shapes with distinctive hexagonal prism morphology, the interface between paste and aggregate can develop the calcium hydroxide crystals. The Scanning electron microscopes identifies the two morphology of calcium sulpho-aluminate hydrates of ettringite and monosulphate in concrete.

Structure of the Aggregate Phase

Natural aggregate has a rounded shape and smooth surface texture. Crushed rocks have a rough texture depending on the rock type and the choice of crushing equipment. The crushed aggregate may contain a considerable proportion of fault or elongated particles which adversely affect many properties of concrete. The aggregate phase is predominantly responsible for some properties such as unit weight; elastic modulus and dimensional stability of concrete depend to a large extent on the bulk density and strength of the aggregate. The physical characteristics of volume, size and distribution of pores are more important than the chemical and mineralogical composition of the solid phases in aggregate. The properties of concrete can also affect the porosity, the shape and texture of the coarse aggregate.

Structure of Hydrated Cement Paste

The term hydrated cement paste is a paste made from Portland cement and it develops as a result of chemical reaction between the Portland cement minerals and water. The size range 1 to 50µm of an anhydrous Portland cement is produced by pulverizing a clinker with a small amount of calcium sulfate, the clinker being a heterogeneous mixture of several minerals produced by high temperature reactions between calcium oxide and silica, alumina and iron oxide. The solution between calcium sulfate and the high temperature compounds of calcium may create when cement is dispersed in water. So due to this combination reaction between calcium, sulfate, aluminate and hydroxyl ions within a few minutes of cement hydration, ettringite like needle shaped crystals of a calcium sulpho-aluminate hydrate can create. After some few hours the pores can fill the empty spaces by the combination of prismatic crystals of calcium hydroxide and very small fibrous crystals of calcium hydrates are occupied by water and the dissolving cement particles.

Calcium Silicate Hydrated (C-S-H) is the most important in properties of the aggregate paste and makes up 50 to 60 % of the volume of solids in a completely hydrated Portland cement paste. The exact structure of C-S-H crystals could not be able to known due to usage of different types and properties of materials. Calcium hydroxide crystals contains 20 to 25% of the volume of the solids in hydrated cement paste and can form large crystals with a distinctive hexagonal prism morphology. Compared with C-S-H the acidic solutions can affect on chemical durability because of high solubility of calcium hydroxide with the presence of considerable amount of calcium hydroxide in hydrated Portland cement.

Calcium sulpho-aluminate compounds can occupy 15 to 20 % of the solids volume in the hydrated paste. Calcium sulpho-aluminate plays a vital role in minor role in the structure property relationship.

Properties of Hydrated Cement paste

Hydrated cement paste contains several types of voids which have important influences on their properties. Capillary voids represent the space not filled by the solid components of the hydrated cement paste. The total volume of a cement water mixture remains essentially unchanged during the hydration process. A method of calculating the total volume of capillary voids is known as porosity. The total capillary porosity can evaluate the characteristics of a hydrated cement paste capillary voids larger than 50 nm as macro-pores. The air voids may appear to be empty in hydrated cement paste under SEM microscopy due to specimen drying under high vacuum. Depends on the environmental humidity and the porosity of the paste the untreated cement paste is capable of holding a large amount of water can exists in hydrated cement paste because of addition to vapor in empty or partially water-filled voids.

Structure of the Transition Zone

Micro-morphological investigations have demonstrated the presence of a thin layer of hydration product on the aggregate surface. A layer of duplex film consisting of calcium hydroxide crystals with their c-axis oriented perpendicular to the aggregate surface, surrounded by a layer of C-S-H. Beyond this thin film of hydration is the main transition zone, about 50 mm thick with pronounced high porosity, which makes the interface the weakest zone in concrete. First, in freshly compacted concrete, water films from around the large aggregate particles.

This may be for a higher w/c ratio closer to the larger aggregate than away from it. Next, as in the bulk paste calcium, sulfate, hydroxyl and aluminate ions, produced by the dissolution of calcium sulfate and calcium aluminate compounds, combine to form ettringite and calcium hydroxide. Strength of the Transition Zone

The strength of the transition zone at any point depends on the volume and size of the voids presents in the hydrated cement paste due to the cause of adhesion between the hydration products and the aggregate particle. The characteristics of the transition zone also influence the durability of concrete. At earlier ages of concrete the volume and size of voids in the transition zone will be larger than in the bulk mortar even for low w/c ratio concrete. With increasing age of the concrete strength of transition zone may become equal to or even greater than the strength of the bulk mortar. It gives the result of crystallization of new products in the voids of the transition zone by slow chemical reactions between the cement paste constitutes and the aggregate, formation of calcium silicate hydrated in the case of siliceous aggregates. The transition zone of the concrete will become poor strength due to the presence of micro cracks. The amount of micro cracks depends on numerous factors including aggregate size and grading, cement content, w/c ratio, degree of consolidation of fresh concrete, curing conditions, environmental humidity of concrete. Generally the transition zone of weakest link of the chain is considered the strength limiting phase in concrete. The structure of the transition zone, especially the volume of voids and micro cracks presents have a great influence on the stiffness and the elastic modulus of concrete. The Interfacial transition zone serves as a bridge between the two components the mortar matrix and the coarse aggregate particles in case of usage of composite materials.

SEM Investigations

High performance Concrete samples were derived from the specimens after testing the cubes for compressive strength at 28 days age. The samples were immediately washed with acetone and before undergoing scanning electron microscope, a thin gold coating was applied on the samples to enable proper conduction. A Leo model scanning electron microscope was used to investigate the transition zone in the three types of HPC concrete exhibiting similar compressive strength at 28 days age. SEM observations on the concrete mixes with 28 day cube strength have been reported in the study presented here. Whereas the capillary voids are irregular in shape, the air voids are generally spherical. Air can be entrapped in the fresh cement paste during the mixing operation. Entrapped air voids may be as large as 3 nm and entrained air voids usually range from 50 to 200 µm.

HPC with CC

Figure 1(a) shows a typical SEM micrograph obtained with binding material as conventional mixes alone. It shows presence of a large quantity of calcium hydroxide crystals and voids presents in the Interfacial transition zone. The hydrated cement paste in a conventional concrete consists of cement hydration products that include calcium silicate hydrate (CSH). Figure 1(b) shows occupied by calcium sulfoaluminate hydrates incompletely hydrated cement particles and paste porosity presence in solid CSH.

HPC with Binary Mix

i) Silica fume & Bottom ash

Figure 2(a) shows a typical SEM obtained in a binary mix concrete of silica fume and bottom ash with conventional concrete mix, where the silica fume percentage used was 5% of volume of cement and bottom ash percentage used was 10% of volume of fine aggregate. CSH and hydrated cement paste is seen in abundance in Figure (a).

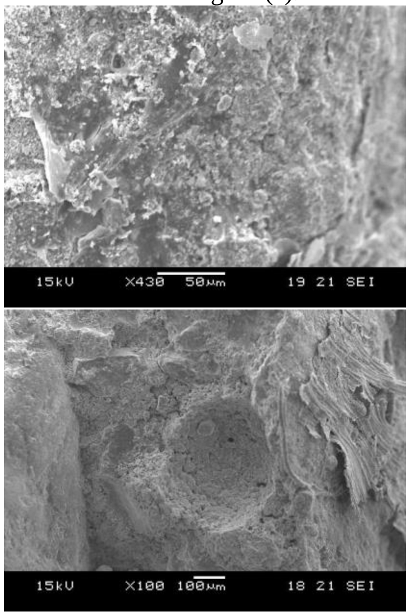

Figure 1a & 1b. Conventional concrete mix with extensive CH.

The amount of hydrated cement paste depends on cement and silica fume fineness, w/c ratio and degree of cement hydration. It is observed that the homogeneity has increased in the 40 to 50 µm region near the aggregate face due to the addition of silica fume. Figure 2(b) shows a silica fume particles in close nearness of the crack seem to be the small size of the silica fume particles and it is observed that the size of the silica fume particles was 0.9 to 1.2 µm. The CSH phase in this concrete produced at normal temperature is represented by gel structure ad it can range from poorly crystalline to crystalline.

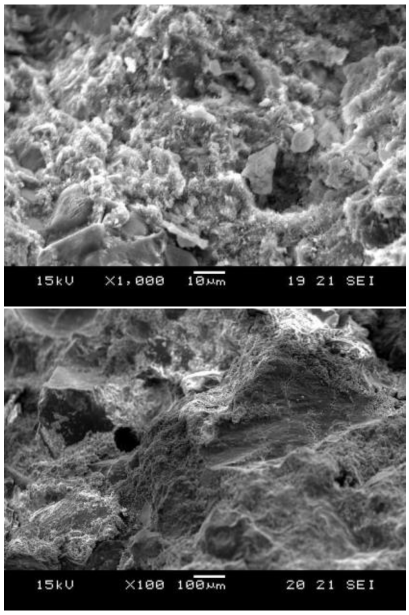

Figure 2 a & 2 b. ITZ in Binary Mix of SF + BA

ii) Silica fume and Steel slag aggregate

Figure 3 (a) shows that the presence of small crystals of CSH, calcium sulfoaluminate hydrates and the hexagonal calcium aluminates possesses enormous surface areas and adhesive capability. These hydration products of Portland cement with silica fume tends to adhere strongly not only to each other, but also to low surface area solids such as calcium hydroxide, anhydrous clinker grains an fine and coarse aggregate particles. Figure 3 (b) shows a typical SEM obtained in the amount of microcracks depends on numerous parameters, including steel slag aggregate size and grading, cement content, environmental humidity, curing conditions of concrete.

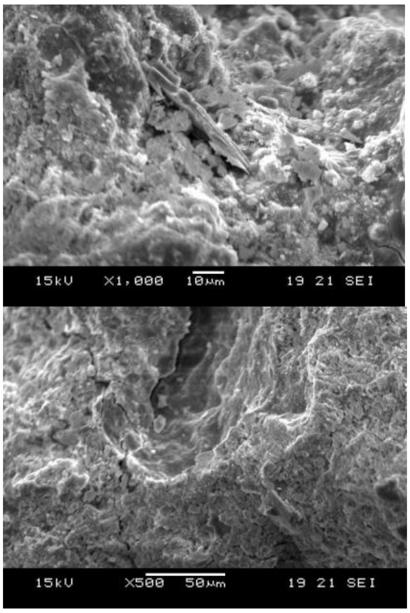

Figure 3 (a) & 3 (b). ITZ in Binary Mix of SF + SSA.

iii) Bottom Ash and Steel slag aggregate

Figure 4 (a) shows that the calcium hydroxide crystals appear in many different shapes and sizes, starting from massive, platy crystals often tens of microns across with distinctive hexagonal prism morphology, large thin elongated crystals, and blocky masses to finely disseminated crystals. A thin micro cracks are formed due to the combination of bottom ash and steel slag materials. Figure 4 (b) shows that the hydrated cement paste contains small capillary pores representing areas which were originally occupied by water in between the unhydrated cement grains and slag aggregate, but now appear as vacant spaces between the hydrated CSH gels.

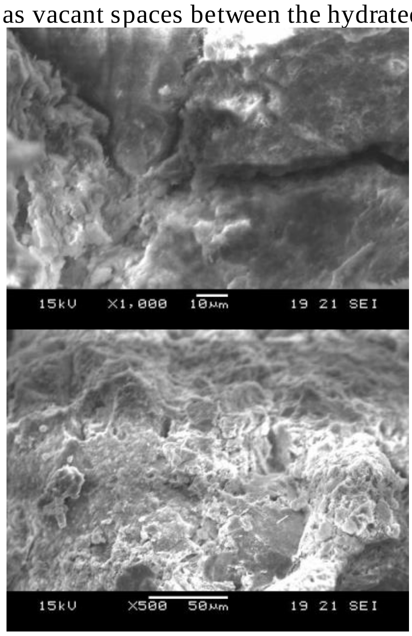

Figure 4 a & 4 b . ITZ in Binary Mix of BA plus SSA

iv) Silica fume, Bottom ash & steel slag aggregate

HPC with Ternary Mix of Combination of Silica fume, Bottom ash & Steel slag Figure 5 (a)& (b) shows a typical SEM obtained in a ternary mix concrete containing silica fume, bottom ash and steel slag. The silica fume content used was 5% of the volume of the cement weight, the bottom ash & slag content used was 10% of the volume of fine and coarse aggregate. In this type of concrete large areas are presents calcium hydroxide due to the present of three different by-products. A higher degree of densification is observed in the nearness of the aggregate phase. It illustrates that the presence of silica fume facilitates further dispersion of silica fume and bottom ash particles leading to the packing of the zone adjacent to the aggregate face. When compared to conventional concrete, the ternary mix of concrete having higher packing density of the particles.

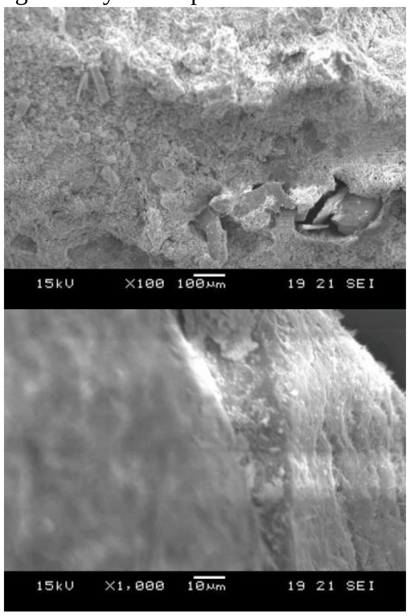

Figure 5 a & 5 b. ITZ in Binary Mix of SF + BA + SSA

Discussions on SEM Observations

The various differences in the ITZ features as observed for high performance concrete with the three types of different by-products reported in this paper, compared to the ITZ of conventional concrete are enumerated below:

1. A foreknowledge of the basic microstructure of concrete, which can be obtained from examination of a normal concrete under the SEM, is essential for understanding its mechanistic behaviour and long term performance.
2. Presence of calcium hydroxide layer at the aggregate surfaces as reported extensively for conventional concrete is not seen in high performance concrete because of use of ternary mix of combination of silica fume, bottom ash and slag by-products.
3. Presence of partially hydrated cement grains in conventional concrete matrix and the ITZ of binary and ternary mixes. At the age of 28 days curing, the silica fume and bottom ash are seen in abundance. It is widely reported that the permeability of concrete reduces drastically with inclusion of silica fume. So there may be a very little chance of moisture ingress in mature concrete in case of binary or ternary mixes of HPC concrete.
4. In conventional concrete in case of moisture finds entry into concrete, it may lead to the initiation of hydration reaction of the partially hydrated cement grains presents in control mix of concrete.
5. When the growth of the micro crack in the matrix is confronted with these particles, the micro cracks are observed to be unable to pass through these micro aggregates. Consequently, the cracks encircle the spherical particles of silica fume before moving forward.

6. Steel slag aggregate mix of concrete shows that the presence of ettringite in direct contact with aggregate of calcium hydroxide film in the ITZ of normal concrete.

Concluding Remarks

The present paper had presented results of the experimental study to evaluate the feasibility of utilizing industrial by-products as raw materials in high performance concrete with mechanical properties. The foregoing discussion on the influence of structure and properties of the transition zone on concrete in terms of the effect of the w/c ratio on the concrete mixtures as a whole.

- ✓ A foreknowledge of the basic microstructure of concrete, which can be obtained from examination of a normal concrete under the SEM, is essential for understanding its mechanistic behavior and long-term performance.
- ✓ The features of the interfacial transition zone are quite different from those reported in normal concrete. The calcium hydroxide film adjacent to the aggregate surface is not seen in binary or ternary mixes at all. The presence of ettringite is also not observed in the binary and ternary mixes when investigated at 28 days age.
- ✓ In ternary mix of large amounts of un-reacted silica fume micro-aggregates at 28 days which make the path of the micro-cracks not straighten or tortuous.
- ✓ The pozzolanic reaction continues in both binary and ternary mixes beyond 28 days age.
- ✓ The porous zone of the transition zone as observed in the case of binary mixes is replaced by a C-S-H rich transition zone in the case of ternary mix concrete.
- ✓ SEM obtained in a binary mix concrete of silica fume and bottom ash with the replacement ratio of 5% and 10% used by the volume of cement and fine aggregate has observed about the micro crack investigates that the silica fume particles in close vicinity of the crack seem to have no effect on its propagation path.
- ✓ The presence of silica fume, bottom ash and steel slag aggregates provides an impetus or moving force to the dispersion of particles and densification of the matrix is enhanced due to the presence of three ranges of particles.

The pozzolanic reaction of binary mix of concrete and the hydration reaction of ternary mix of concrete are still continuing at this age. These pozzolanic and hydration reactions are expected to consume more calcium hydroxide which is present at this age.

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