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Pozzolanic and Cementitious By-Products in Concrete—Another Look

by P.K. Mehta

<u>Synopsis</u>: This paper intends to update a previous (1983) critical review by the author on pozzolanic and cementitious by-products for use in concrete. The by-products included in this report are fly ash, granulated blast-furnace slag, and condensed silica fume. Recently available worldwide statistics on production and utilization rates of these mineral admixtures are given. As far as possible new and useful information is presented on their physical and chemical characteristics, structure and reactivity of the glassy phase present, mechanisms by which concrete properties are enhanced, and engineering properties of concrete containing siliceous by-products. A special emphasis is given to durability aspects of concretes incorporating fly ash, blast-furnace slag, or condensed silica fume. Finally, the status of standard specifications and test methods is reviewed, and the contribution of siliceous by-products to make concrete an environment-friendly material of construction is emphasized.

<u>Keywords</u>: admixtures; alkali-aggregate reactions; <u>blast furnace</u> <u>slag</u>; compressive strength; <u>concrete durability</u>; <u>fly ash</u>; glass; microstructure; particle size distribution; <u>reviews</u>; rheological properties; <u>silica fume</u>; specifications; workability

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INTRODUCTION

In 1983, at the First International Symposium on Fly Ash, Silica Fume, and Slag, the author presented a comprehensive report on pozzolanic and cementitious by-products used in concrete (1). During the last five years a relatively large number of publications dealing with the subject have appeared. For example, the proceedings of the Second Int'l Conference on Fly Ash, Slag, Silica Fume, and Natural Pozzolans (Madrid, 1986) contain 80 papers in a Special Publication of the ACI (SP-91), and the proceedings of the Eighth Int'l Congress on the Chemistry of Cements (Rio de Janeiro, 1986) contains 4 special reports and 43 supplementary reports on the subject. In addition to numerous research papers that are routinely published in scientific and technical journals, the author is aware of at least five books (2-5) and four committee reports (7-10) which attempt to cover the state of the art in a comprehensive manner.

This review is not intended to be a digest of the 1983-87 publications on pozzolanic and cementitious by-products used in concrete. Instead, it is the intention of the author to provide an update on the topics covered by the previous review (1) and highlight any new information which, in the author's view, represents a significant advancement to the state of the art.

First, a brief review of the more recent rates of production and utilization of pozzolanic and cementitious by-products in many countries of the world will be presented. This will be followed by new and useful information on their physical and chemical characteristics, influence on concrete properties, specifications and test methods, and contribution of siliceous by-products in making concrete an environment-friendly material of construction.

PRODUCTION AND UTILIZATION RATES

The 1984 production and utilization rates of fly ash, blast-furnace slag, and condensed silica fume for several countries of the world (Table 1) were compiled by the RILEM Technical Committee 73-SBC, Siliceous By-products in Concrete (10). A comparison between the 1984 and the 1980 statistics (1) shows that in some developed countries, whereas the annual rates of fly ash being produced and used in the cement and concrete industries have remained fairly stable, the corresponding rates for blast-furnace slag and condensed silica fume have dropped

steeply. For instance, during this period the U.S. production of blast-furnace slag has dropped from about 26 million tonnes to 13 million tonnes and condensed silica fume production from about 300,000 tonnes to 100,000 tonnes. This is because the production of these two by-products is related to the steel production which, in the recent years, has come down sharply in the United States.

Although the actual statistics from the U.S.S.R. are not available, it seems that the largest producers of fly ash in the world (with at least 10 million tonnes fly ash production per annum) are the U.S.S.R., U.S.A., China, India, U.K., and South Africa. The fly ash utilization rates by the cement and concrete industries vary from a high of about 20% for China to a low of about 1% for South Africa. In general, poor quality and lack of uniform composition are cited as the primary reasons for low utilization rates of fly ash as a pozzolan. With a better understanding of technical requirements for satisfactory performance of fly ash in concrete, followed by development of proper test methods and specifications, it seems that the utilization rate for fly ash can be much higher than at present.

Japan, China, Germany, USA, and France are among the largest producers of iron blast-furnace slag. Traditionally, a considerable proportion of the total available slag is air-cooled and, therefore, is not as cementitious as the quickly-cooled products (granulated or pelletized slags). The slag utilization rates shown in Table 1 are for the quickly-cooled slag, which is cementitious without excessive grinding. Unlike fly ash, the physical-chemical characteristics of iron blast-furnace slag from a given production facility do not show large variations from one day to another. The availability of a uniform-quality slag is one of the reasons why the rates of slag utilization are much higher than fly ash. For instance, the cement and concrete industries in many countries of the world consume approximately 1/3 to 2/3 of their total iron blast-furnace slag production.

Compared to approximately 1 million tonnes production in 1980 (1), the current world production of condensed silica fume appears to be of the order of 500,000 tonnes, which is considerably less than the total available quantities of fly ash or blast-furnace slag. Due to the highly-pozzolanic characteristics of the material, it is relatively more expensive and therefore its use is limited to special applications, such as for making high strength or high durability concrete mixtures. Specially processed rice husk ash is also highly pozzolanic (1), however at present it is not being produced or used in any significant quantity.

CLASSIFICATION

It is generally accepted now that the cementitious and pozzolanic properties of siliceous by-products used as cement additions depend on their particle characteristics and mineralogical composition, and not on their chemical composition and source of origin. Therefore, in the previous paper (1) the author made an attempt to classify these products on the basis of their cementitious or pozzolanic activity when used in combination with portland cement. Since this classification transcends the traditional barriers according to which the materials are classified by source, a benefit from this approach is the possible development of a single, performance-based, standard specification covering all mineral admixtures. Table 2 shows the revised version of the original classification (1),

which has recently been approved by the RILEM Technical Committee on the use of siliceous By-products in Concrete (10). According to the classification proposed in Table 2, all siliceous by-products used by the cement and concrete industries can be divided into five categories, which are briefly described as follows:

The Cementitious mineral admixtures consist of fine particles of essentially a silicate glass, which has been considerably modified by the presence of large amounts of calcium, magnesium, and aluminum ions. Relatively small amounts of portland cement or other activators (e.g., alkalies or gypsum) are needed to accelerate the hydration and the rate of strength development from this class of mineral admixtures, to which rapidly-cooled blastfurnace slag and some high-calcium fly ashes (> 20% CaO) belong.

As will be discussed later, the composition of the silicate glass in some industrial by-products may not be uniform. It is possible that a part of the glass is essentially an aluminosilicate glass whereas the remainder is a silicate glass containing large amounts of calcium and magnesium. In such a case, the product will be partly cementitious and partly pozzolanic. The high-calcium fly ashes, with 10 to 20% CaO, are categorized as **cementitious and pozzolanic** mineral admixtures.

By-product materials which consists mostly of a silicate glass, modified with aluminum and iron, are categorized as normal pozzolans. Compared to the calcium-magnesium substituted silicate glass, the aluminum-iron substituted glass appears to be less reactive. The low-calcium fly ashes containing this type of glass are categorized as normal pozzolans.

By-products, which consist essentially of silica in a non-crystalline and high surface-area form, exhibit great pozzolanic activity and are therefore categorized as highly pozzolanic. Condensed silica fume and specially processed rice husk ash belong to this category.

The last category contains mineral admixtures of low reactivity, such as slowly-cooled blastfurnace slag and bottom ash, which must be pulverized to very fine particle size in order to develop acceptable levels of strength in combination with portland cement.

PHYSICAL AND CHEMICAL CHARACTERISTICS

A summary of typical physical and chemical characteristics of the principal by-products used as mineral admixtures in concrete is presented in Table 2. It is the particle shape and size distribution as well as the mineralogical composition of a mineral admixture, including the types and amounts of both crystalline and non-crystalline (amorphous or glassy) phases present, which affect concrete behavior. It would therefore be useful here to compare the similarities and differences in physical and chemical characteristics of fly ash, granulated blast-furnace slag, and condensed silica fume. Particular attention should be paid to the nature of glass in fly ash because, since the previous review (1), some valuable information has recently become available on this subject.

Particle Characteristics

Fly ash is a condensation product from droplets of molten coal ash, and is therefore mostly spheroidal, with individual particles ranging from less than 1 μ m to greater than 1 mm. Condensed silica fume is formed by condensation of silicon oxide vapor, and the particles are also spheroidal. However it is a much finer material than other mineral admixtures, with grain size distribution in the 0.02 to 0.3 μ m range. The most commonly used method of rapid cooling of slag is by water granulation. The molten slag is broken up by high-pressure water jets to sand-size grains, which are subsequently dried and mechanically pulverized to < 45 μ m particles (passing No. 325 mesh sieve).

Using X-ray sedimentation technique, particle size distribution data for several U.S. fly ashes was reported by Mehta (11). In general, probably due to the presence of larger amounts of alkali sulfates, the high-calcium fly ashes tend to be finer than the low-calcium fly ashes. This study showed the possibility of a relationship between the amount of < 10 μ m particles in fly ash and the 7 or 28-d compressive strength of blended cements containing fly ash. Similarly, using electron microscopy, particle size distribution plots for several types of condensed silica fume are reported by Aitcin et. al (12). Condensed silica fume from silicon metal manufacture is usually finer because of the higher furnace temperature. With ferrosilicon alloy furnaces, as the amount of iron increases in the alloy, the temperature of the furnace decreases and the grain size distribution of the condensed silica fume tends to shift toward coarser particles. Like fly ash, the observed difference in the reactivity of different types of silica fume can, to some extent, be related to the size distribution of particles (6).

Typical nitrogen adsorption surface areas for fly ash, ground granulated blast-furnace slag, and condensed silica fume are on the order of 300 to 500 m^2/kg , 400 to 600 m^2/kg , and 17,000 to 20,000 m^2/kg , respectively.

The physical characteristics of siliceous by-products account for their water-reducing ability in portland cement concrete mixtures. The vitreous (glass), smooth, and non-absorbing surface texture of these admixtures is in part responsible for better workability and lower water requirement of pastes, mortars, and concretes containing siliceous by-products as cement replacement. Another reason seems to be the reduction in the volume of voids that is made possible by a denser packing, when fine spherical particles are present in a concrete mixture. Helmuth (13) believes that the water reduction in portland cement-fly ash mixtures is the result of a better dispersion of cement particles. Very small fly ash particles get adsorbed on the surface of electrically charged cement grains, causing dispersion of the system in a manner similar to conventional (organic) water-reducing admixtures.

Chemical Characteristics

From numerous publications including the previous review (1), the wide variations in the oxide analyses of siliceous by- products become readily apparent. In the U.S. typical chemical analyses for low-calcium fly ashes (< 10% CaO), usually formed by combustion of bituminous coal, show 45-65% SiO₂, 20-30% Al_2O_3 , 4-20% Fe₂O₃, 1-2% MgO, up to 3% alkalies, and up to 5% loss on ignition (9,11). The high-calcium fly ashes (> 10% CaO) formed by combustion of

subbituminous and lignite coal, typically contain 20-50% SiO₂, 15-20% Al₂O₃, 15-30% CaO, 5-10% Fe₂O₃, 3-5% MgO, up to 8% alkalies, and less than 1% loss on ignition. The chemical composition range for iron blast-furnace slag produced in the U.S. and Canada (5,8) corresponds to 32-40% SiO₂, 7-17% Al₂O₃, 29-42% CaO, 8-19% MgO, and up to 2% each sulfur and iron oxide. The condensed silica fume from Si and FeSi-75% industries shows a relatively narrow chemical composition range (6,7,12) which, typically, corresponds to 90-95 SiO₂, 0.3 to 0.7% Al₂O₃, 0.1 to 3% Fe₂O₃, 0.1 to 0.5% MgO, 0.1 to 1% CaO, up to 1% alkalies, and up to 4% loss on ignition.

It is generally accepted that there is little correlation between the oxide analysis of a mineral admixture and its performance in concrete. From the standpoint of concrete behavior, the chemical composition is important only to the extent that it influences the mineralogical characteristics of the mineral admixture, including the glass content and type. In addition to chemical composition, the processing conditions also influence the mineralogical characteristics of the product. Therefore, variations in processing parameters in industrial furnaces make it possible that two samples of fly ash, with a similar chemical analysis, would give entirely different mineralogical compositions and performance characteristics in concrete.

Although the crystalline components present in some mineral admixtures have the ability to affect properties of concrete, it should be noted that most of them are inert or poorly reactive to water. The predominant constituent in fly ash, granulated blast-furnace slag, and condensed silica fume is the, non-crystalline (amorphous), silicate glass. There is a growing realization among the researchers now that the key to differences in reactivity (for instance, between two fly ashes or two slags, or between a fly ash and a slag) has to be sought in the characteristics of the glass present.

The crystalline minerals in low-calcium fly ashes generally comprise of quartz, mullite, and magnetite or ferrite spinel. In addition to quartz, the crystalline phases in subbituminous fly ashes are known to include C_3A , $C_4A_3\bar{S}$, calcium sulfate, and alkali sulfates. The calcium compounds and alkali sulfates are reactive. In fact, some fly ashes with large proportions of C_3A or free CaO are known to cause quick setting and high heat of hydration, but such fly ashes are exceptions rather than the rule. The crystalline compounds identified in devitrified blast-furnace slags (1,5) are mainly the melilite solid solution series with end members gehlinite (C_2AS) and akermanite (C_2MS), and lesser amounts of monticellite (CMS), diopside (MCS₂), and merwinite (C_3MS_2).

Typically, fly ashes contain 60 to 90% glass, granulated slags contain 85-95% glass, and condensed silica fume consists essentially of vitrified silica (100% glass). The characteristics of the glassy phase in siliceous by-products, which range from simple (condensed silica fume) to highly complex (fly ashes), are discussed next. It will also be helpful here to include a brief description about the structure of glass, which is based on a review by Hemmings and Berry (14).

Structure of Glass

Solid materials lacking long-range interatomic order are generally non-crystalline. Among these, glasses form a special group that can best be

described as, "the product of fusion of inorganic materials, which have cooled to a rigid condition without crystallizing". The degree of disorder in a glass can be inferred by observations of the way in which it diffracts X-rays to form a diffraction pattern. Fig. 1 illustrates diffraction patterns of: (a) ordered, crystalline SiO₂ (cristobalite); and (b) non-crystalline SiO₂. In the non-crystalline state, diffraction of X-rays results in a broad diffuse halo rather than sharp diffraction peaks.

Further, according to Hemmings and Berry (14), a feature of simple glass-forming oxides, such as pure SiO_2 , is that although the integral structure lacks long-range order, there is continuity in the chains of constituent atoms (Fig. 2a). The disorder results from randomness in the size of the rings into which these chains are linked to form a structural network. When more complex glasses are formed, for example by introducing sodium ions into the silicate structure, a greater level of disorder results. Not only are the rings of the glass-forming component disordered, but also many are broken to form non-bridging oxygen atoms (Fig. 2b). As more constituents are introduced into a glass, further levels of disorder result, e.g., random chemical disorder may be caused by the replacement of Si by Al or Fe (Fig. 2c). Most of the glasses of practical interest to the cement industry are disordered both by chain breaking through the presence of modifier cations such as Na, K, and Ca, and by chemical disordering of the chains (Al, Fe).

<u>Glass in condensed silica fume</u>--X-ray diffractograms of samples of different types of condensed silica fume shown in Fig. 3a (6) reveal that the material is essentially vitreous silica with a diffuse halo peak at about 4.4Å (21.9° $2\theta_{max}$, Cu K α). This happens to be the strongest peak for cristobalite. In fact, when heated to 1100°C and subsequently cooled slowly, condensed silica fume will form crystalline cristobalite (Fig. 1a).

<u>Glass in rapidly cooled blast-furnace slag</u>--X-ray diffractograms of three quenched blast-furnace slag samples are shown in Fig. 3b (14). The predominant halo with $2\theta_{max}$ at about 32°, clearly indicates their essentially noncrystalline composition, with minor amounts of crystalline components present (melilite, merwinite, and quartz). It should be noted that in the previous review the author (1), on the basis of the diffuse halo peaks on diffractograms, was able to point out the similarity in the composition of glass between a granulated blast-furnace slag and a high-calcium fly ash.

<u>Glass in fly ash</u>--Since glass is the major component of fly ashes, the impetus for research on composition of glass in fly ash came from the general observation that low-calcium fly ash is less reactive than high-calcium fly ash. On the basis of the position of the diffraction halo produced by X-ray scattering, Diamond and Lopez-Flores (15) as well as this author (1) pointed out that the composition of glass is different in low-calcium and high-calcium fly ashes. Typically, low-calcium fly ashes show a diffuse halo maxima at $21-25^{\circ} 2\theta$ (Cu K α), and high-calcium fly ashes at $30-34^{\circ} 2\theta$.

From similarities in the X-ray diffraction diffuse halo maxima between high-calcium fly ash and granulated blast-furnace slag, this author (1) speculated that the composition of the glass in high-calcium fly ash is essentially melilitic, i.e. a silicate glass modified with calcium and aluminum. On the other hand,

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Diamond (16) attributed the $32^{\circ} 2\theta$ diffraction halo from glass in high-calcium fly ashes (> 20% CaO) to a calcium aluminate type glass, similar to $C_{12}A_7$. Recent reports of work by Roode (17) and Hemmings and Berry (18), as will be discussed next, support the conclusion reached by this author (1).

There is no doubt that the value of $2\theta_{max}$ on a typical XRD pattern for fly ash indicates the extent of glass modification. Diamond (16) concluded that with increasing calcium content of fly ash in the zero to 20% analytical CaO range, the value of $2\theta_{max}$ increased gradually from about 22° to 28° 2 θ ; however with highcalcium ashes (20-30% CaO) the $2\theta_{max}$ shifted to 32° 2 θ (Fig. 4). Diamond attributed 32° $2\theta_{max}$ to a calcium aluminate type glass similar in composition to C₁₂A₇. Other researchers including McCarthy et. al (19), Roode and Hemmings (17), and Mehta (20), working with a broad base of fly ashes, confirmed the general trend of increase in the $2\theta_{max}$ value with increasing CaO in fly ash but could not confirm the discontinuity in the CaO vs $2\theta_{max}$ plot as reported by Diamond (Fig. 4). Whereas the interpretation vis-a-vis C₁₂A₇ glass remains in doubt, there is little doubt from the XRD data of fly ashes that the composition of the silicate glass is modified by substitution with other ions, such as Al, Ca, Mg, Fe, Na, and K.

Hemmings and Berry (18) have presented an excellent overview of the state-of-the-art on the nature of glass in fly ash. The authors attempted to resolve two important issues which have a direct bearing on the relationship between the composition of fly ash and its reactivity. To address the question: is the value of $2\theta_{max}$ an indication of the extent of glass modification, the work of Roode and Hemmings (17) is cited. The authors examined sodium silicate model glasses in which sodium content varied from zero to 50% (Table 3). In these systems, the ratios between non-bridging oxygens to silicon ranged from zero to 2, with structures that became progressively more depolymerized (i.e. network > sheets > chains > monomer). From the corresponding XRD patterns (Fig. 5), it can be observed that there is a marked shift in the halo to the higher $2\theta_{max}$ with increasing Na₂0 content. It should be noted that the halo shows at least two maxima of varying intensity: a low-angle composition at $22-24^{\circ} 2\theta_{max}$ and a high-angle composition at $30-34^{\circ} 2\theta_{max}$. Therefore, Roode and Hemmings (17) concluded that, even in simple systems, different glass types can co-exist over a wide range of compositions (i.e. they are phase separated, and are distinguishable by their XRD patterns). Hemmings and Berry (18) point out the significance of this investigation to fly ash systems. The implications are that if the fly ash halo is asymmetric and shifts in position, it may be attributable to any or all of the following: (a) different glass with different modifier levels in different particles (inter-particle speciation), (b) different glasses in the same particle (intra-particle speciation), or (c) phase separation.

Hemmings and Berry (18) investigated the extent of inter-particle differences in fly ash glass by examining ash fractions separated by density. Density-separated fly ash fractions exhibited not only dramatic changes in bulk chemical composition but also in their XRD patterns. It was shown that the $2\theta_{max}$ values of the diffuse halos of these fractions correlated strongly with the total network modifier cation contents of the glasses. Thus, the authors concluded that **different glass types co-existed within samples of fly ash from a single source**, and therefore the asymmetry of the glass halo in the bulk ash is caused by an overlap in the XRD patterns of the constituent glasses. The authors also concluded

that the shift in the XRD halo to higher $2\theta_{max}$ values for different size fractions of a fly ash is the result of an increasing content of cation modifiers in essentially the same aluminosilicate matrix (and not due to formation of a new type of glass, viz, $C_{12}A_7$ glass).

REACTIVITY

In solids, a close relationship exists between the microstructure of a material and its properties. The microstructure of hydraulic cement products is influenced by the hydration reactions of various constituent phases, both crystalline and noncrystalline, under given curing conditions. The previous paper (1) contains a comprehensive review of the physical-chemical changes associated with the hydration of portland cement minerals, and relative rates of reactivity of various siliceous by-products when used in combination with portland cement. Briefly, it was shown that portland cement consists essentially of highly reactive crystalline minerals, which hydrate under ambient curing conditions to form a relatively porous solid with a heterogeneous structure composed mainly of calcium silicate hydrates (CaO/SiO₂ ratio, approximately 1.5), calcium hydroxide, and calcium sulfoaluminate hydrates.

The pozzolanic and cementitious by-products consist essentially of non-crystalline matter,* which, under ambient conditions hydrates slowly even in the presence of the alkaline solution that is formed by the dissolution of portland cement minerals. The reason for the slow reactivity is the mechanism of hydration according to which the particles of mineral admixtures hydrate essentially in situ by diffusion controlled reactions, as will be discussed. This is why particle size or surface area plays a dominant role in determining the relative rates of reactivity. For instance, it was stated that condensed silica fume which, typically, has extremely fine particle size $(0.1 - 0.3 \,\mu\text{m})$ compared to the average particles in slag or fly ash $(10-20 \,\mu\text{m})$, begins to contribute to the strength of portland cement mortar or concrete after 1-d curing, whereas slags take more than 3 days, and fly ashes more than 7 to 14 days (1).

The relative rates of hydration of pozzolanic and cementitious materials depend, in general, on their particle size and composition of the non-crystalline phase, both of which control the activation energy available for the hydration reactions. The concept of activation energy involves chemical energy from the chemical reactants (i.e., chemical composition of the non- crystalline phase and the solution chemistry of the contact fluid), mechanical energy from fine grinding, and thermal energy from heat of hydration or an outside heat source (21). Important findings on reactivity, hydration reactions, and microstructure of blended portland cements containing various pozzolanic and cementitious admixtures are summarized next.

^{*}exception to this, as discussed earlier, are some high-calcium fly ashes containing crystalline minerals, such as C_3A and $C_4A_3\bar{S}$, which are reactive.

According to Hooton (22), factors affecting the <u>slag reactivity (hydraulicity)</u> are the degree of vitrification (glass content), the chemical composition, the fineness of grinding, and the activation of slag glasses by chemical or thermal means. Although increasing glass devitrification (crystallization) reduces the reactivity of a slag, the relationship between the glass content of slag and the strength development in a blended portland cement containing the slag is not linear. In fact Demoulian et al. (23), and more recently Frearson and Uren (24), have reported that the presence of some crystalline merwinite in certain slag glasses made them more reactive.

Although the non-crystalline structure (glassy state) is essential to the slag reactivity, the chemical composition of slag is also a factor. For instance, it is generally known that commercial high SiO₂ glasses are not readily attacked by water or alkaline solutions, but their reactivity increases with increasing content of CaO, MgO, and Al₂O₃. In fact a basicity factor, $(C+M+A)/S \ge 1.0$, is used in Germany to evaluate the quality of slag for use in blended cements. Also, in his review Hooton (22) cites Kondo's work showing that iron blast-furnace slag is both cementitious and pozzolanic. For instance, to develop high levels of strength, some Japanese slags require more calcium hydroxide than is needed for glass activation alone.

Compared to hydrated portland cement, a similar slag-cement paste (with identical water/cement ratio and curing conditions) will have a denser microstructure and a relatively lower calcium hydroxide content. Many investigators including this author (1), have reported that in normally-cured cement pastes the inclusion of slag shifts the pore size distribution from coarser to finer pores. Since the presence of large capillary pores is believed to be responsible for high permeability and low strength of a hardened cement paste, this physical modification of the microstructure rather than any chemical modification seems to play a more important role in improving the strength and durability of slag-cement products.

Recently, Harrison et al. (25) reported the microstructure of hydrated cement pastes containing 40% slag. Reaction rims around slag particles and relics of fully reacted slag particles demonstrated that the slag hydration reactions were diffusion-controlled. Qualitatively, the microstructure resembled neat portland cement pastes of similar ages except that less $Ca(OH)_2$ was present, and the composition of the C-S-H in fully reacted slag particles corresponded to a Si/Ca ratio of 0.62.

As with iron blast-furnace slag, the reactivity of fly ash in portland cement-fly ash mixture depends largely on dissolution of the glassy structure by the hydroxide ions present as a result of the portland cement hydration. Again, many researchers including this author (20), have shown that the reactivity of fly ash is greatly influenced by the curing temperature and the fineness of fly ash. Portland cement-fly ash mixtures made with several U.S., low-calcium or high-calcium fly ashes, when cured at 50°C, produced similar levels of strength in 7 days as normally cured (20°C) mixtures in 28 days. Under most ambient conditions, massive concrete members can easily attain temperatures of the orer of 50°C due to the heat evolved during the hydration of portland cement. Also, from the data on the particle size distribution of fly ashes, the author (20) concluded that fly ash particles smaller than 10 μ m have a positive influence on