

Pozzolan and Cementitious Byproducts as Mineral Admixtures for Concrete - A Critical Review

By P. Kumar Mehta

Synopsis: Granulated blast furnace slag and low-calcium fly ashes have long been used as portland cement additives or as mineral admixtures in concrete. With the addition of high-calcium fly ash, rice husk ash, and condensed silica fume to the list of traditional mineral admixtures, a scientific approach for characterization and evaluation of all industrial byproducts which are suitable for use as admixtures in concrete is needed. Since it is not the source of origin or the chemical composition of a mineral admixture but the mineralogical composition and particle characteristics which determine its contribution to concrete behavior, in this review the entire area is treated as a unified discipline. This approach seems to provide a better basis for explaining the similarities and differences in behavior between mineral admixtures originating from either the same or different sources. Mineralogical compositions, particle characteristics, current production rates, and utilization of major pozzolan and industrial byproducts available in the United States and Canada are included. Mechanisms by which the use of these byproducts in portland cement concrete can improve engineering properties are discussed, and examples of data from field and laboratory investigations are given.

Keywords: admixtures; alkali-aggregate reactions; blast furnace slag; compressive strength; concrete durability; fly ash; hydration; particle size distribution; permeability; pozzolans; rheological properties; rice; silica; sulfate resistance; thermal properties.

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INTRODUCTION

Power plants using coal or rice husks as fuel, and metallurgical furnaces producing pig iron, steel, copper, nickel, lead, silicon and ferrosilicon alloys are major sources of byproducts which amount to millions of tons every year. These byproducts are generally disposed by dumping into abandoned land, or in some instances used for low-value applications such as landfills, aggregates for concrete, and sub-base construction. There is currently great interest in exploiting the pozzolanic and cementitious properties of these materials by incorporating them as components of portland-cement concrete, either in the form of blended portland cements or directly as mineral admixtures in concrete. Since portland cement sells at about 60 to 80 U.S. dollars a ton and is produced at the expense of substantial amounts of energy, a partial substitution of portland cement by these byproducts which are generally available at substantially lower prices would clearly represent a high-value use of the materials. Furthermore, there is evidence that most of the mineral byproducts discussed in this paper are able to improve the ultimate strength and durability of portland cement concrete, especially when used partially to replace fine aggregate rather than cement.

Countries such as France, Germany, Italy, Japan, the Netherlands, and U.S.S.R. have had a longer history of interest in conservation of energy and virgin materials than the U.S. and Canada. These countries are already engaged in the production and use of large quantities of blended portland cements containing pozzolanic and cementitious additives. Due to various reasons, there is more interest in the U.S. and Canada in utilizing the byproduct materials in the form of mineral admixtures in concrete rather than as components of blended cements. It should be noted however, that the underlying mechanisms by which the combination of pozzolanic and cementitious materials with portland cement influences the engineering behavior of the product are not significantly affected by the way by which these byproducts are incorporated into concrete.

Typical chemical compositions of the industrial byproducts available in the United States which are discussed in this review

are shown in Table 1. For comparison purposes a typical chemical composition of portland cement is also included to show that both portland cement and the industrial byproducts being discussed are composed of similar elements. In specific cases, depending on the local raw materials, there may be large differences between the actual chemical compositions of the industrial byproduct used and the compositions shown in Table 1. However, this normally would have little or no influence on the pozzolanic and cementitious properties of the materials, which are controlled mainly by their mineralogical composition and granulometric characteristics.

Published literature contains many excellent papers including state-of-the-art reviews by numerous authors (1-9) which provide a wealth of information on composition and properties of the important mineral admixtures and on their influence on properties of concrete. The object of this paper, which is not intended to be a formal literature review, is to present a critical appraisal of the published data from the standpoint of providing scientific explanations for some of the phenomenological observations. This is needed for a clear understanding of the performance of these materials and to encourage their proper use by cement and concrete industries.

First, a brief review of the chemical reactions considered responsible for setting and hardening of portland cement will be given. This will be followed by defining pozzolans and pozzolanic reactions. The availability of major pozzolanic and cementitious byproduct types in the U.S. is discussed. Mineralogical and particle characteristics of major industrial byproducts suitable for use as admixtures in portland cement concrete are reviewed, especially in regard to relationships between physical-mineralogical properties of admixtures and performance characteristics of concrete. The latter include water demand, consistency, bleeding, workability, setting time, air entrainment, and temperature rise in fresh concrete; and strength, modulus of elasticity, creep, drying shrinkage, durability to sulfate attack, alkali-silica reaction, and corrosion of steel in hardened concrete. Finally, a brief discussion of costs and energy saving aspects is presented.

REVIEW OF CEMENTITIOUS AND POZZOLANIC REACTIONS

A brief review of the physics and chemistry of portland cement hydration process of the pozzolanic reactions will be helpful in understanding the mechanism by which mineral admixtures are able to modify the behavior of concrete.

Cementitious Reactions of Portland Cement

Portland cement consists essentially of crystalline compounds (minerals) of calcium combined with silica, alumina, iron oxide, and sulfate. Typically, the approximate composition and amounts



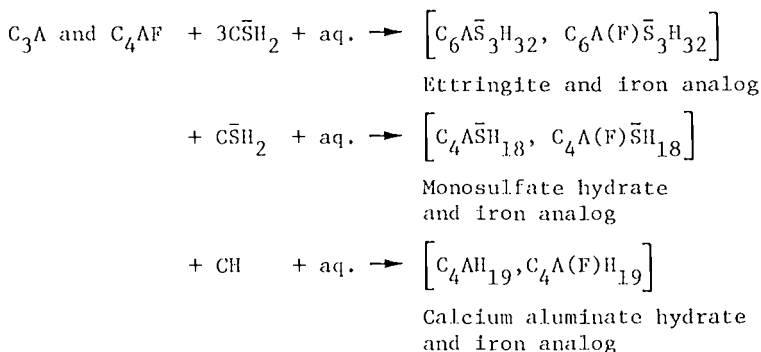
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of the principal minerals present are: $C_3S = 50\%$, $C_2S = 25\%$, $C_3A = 10\%$, $C_4AF = 8\%$, $C\bar{S}H_2 = 5\%$. These minerals are unstable in water and begin to undergo dissolution at various rates as soon as water is added to cement. In order to accelerate the hydration reactions, commercial portland cement is pulverized to about 90% passing 75 μm sieve or 300 to 400 m^2/kg Blaine surface area.

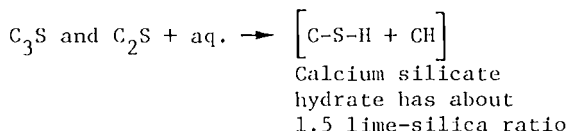
When water is added to portland cement the minerals begin to ionize, and the ionic species form hydrated products of low solubility which precipitate out of the solution. Due to the lower density of the hydration products as compared to the anhydrous minerals, the formation and deposition of these hydration products into previously water-filled space leads first to a progressive decrease in consistency, and after solidification (set) to progressive decrease in porosity. The process results in corresponding increases in strength and decreases in the permeability of the system, as illustrated in Fig. 1.

Although the chemical reactions of hydration of portland cement compounds are complex and do not proceed to completion, for the purposes of providing some idea of composition of the hydration products, a simplistic view of the chemistry of principal setting and hardening reactions may be presented as follows:

Hydration Reactions of Aluminates in the Presence of Gypsum and Lime



Hydration Reactions of Calcium Silicates in Portland Cement



The trisulfate hydrate ($C_6A\bar{S}_3H_{32}$), popularity known as ettringite, is usually the first product to precipitate out of the system, and is mostly responsible for the initial set and very early strength (up to 3 days) in portland cement. Subsequently,

depending on the content and reactivity of the sulfate, alkali, and aluminate bearing phases in the cement, either a monosulfate hydrate (C_4ASH_{18}) or a mixture of monosulfate and calcium aluminate hydrate (C_4AH_{19}) may also form. Hydration of the ferrite phase (C_4AF) in portland cement is somewhat slower than C_3A and produces iron analogs of ettringite, monosulfate, and calcium aluminate hydrate. It is important to note here that the reaction products of the aluminate-sulfate interaction, namely, ettringite, monosulfate hydrate, calcium aluminate hydrates and their iron analogs, are capable of contributing strength to hardened cement paste.

The main product of hydration of the silicate minerals in portland cement is a calcium silicate hydrate (C-S-H) of colloidal dimensions which, at early age, under a scanning electron microscope, usually shows up as an aggregation of acicular particles, or often as very fine equant grains partly intergrown together. It is highly cementitious and constitutes about 60 to 65 percent of the total solids in a fully hydrated portland cement. The other product of hydration of the silicate minerals is about 20 percent calcium hydroxide (CH), which usually occurs as large hexagonal crystals, and contributes little to the cementitious properties of the system. Also, being relatively more soluble and alkaline than the other hydration products, it is easily subjected to attack by water or acidic solutions, thus reducing the durability of portland cement systems to such environments.

Pozzolan Reactions

According to ASTM C 595, a pozzolan is defined as "a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties."

It is clear from the above definition of pozzolans, that portland cement minerals are not the only possible source of formation of the cementitious hydrates. There are many natural and industrial materials capable of providing components to form the calcium silicate hydrates, calcium sulfoaluminate hydrates, calcium aluminate hydrates, calcium aluminoferrite hydrates and calcium sulfo-aluminate-ferrite hydrates of the type discussed above. In fact, before the advent of the portland cement, mixtures of lime and volcanic ashes or calcined clays were routinely employed as hydraulic cements for making mortars and concretes. As defined earlier, such materials, which are mainly siliceous and aluminous, are called "pozzolans", and their reaction with lime, which is slow at ordinary temperature, is called "the pozzolan reaction".

Not all siliceous and aluminous materials are pozzolanic. It is known that crystalline minerals, for instance silica as quartz,

alumina as corundum, and aluminosilicates such as sillimanite ($\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$), and mullite ($3\text{SiO}_2 \cdot 2\text{Al}_2\text{O}_3$) do not react with lime solution at room temperature. It is only when the siliceous and aluminous materials are present in noncrystalline form and as small particles, that they can hydrate at a slow rate in alkaline solutions to furnish silica and alumina for reaction with lime which leads to formation of cementitious products. This is contrary to the hydration conditions in portland cement where the principal silicate (C_3S and $\beta\text{C}_2\text{S}$) and aluminate (C_3A) compounds are essentially crystalline but decompose rapidly in water to provide the desired silicate and aluminate ions for formation of the cementitious hydrates. Therefore for the purposes of evaluating the industrial byproducts for use in cement and concrete, it should be noted that the mineralogical composition and particle size rather than the chemical composition would determine whether or not, or how fast a material can provide silica and alumina for cementitious reactions with lime.

Again in portland cement hydration, the calcium ions needed for formation of the cementitious hydrates become available with the dissolution of the principal compounds present. In portland-pozzolan cements, the portland cement component becomes the source of calcium ions, because decomposition of C_3S and $\beta\text{C}_2\text{S}$ releases substantial amount of lime. Normally, the pozzolan component of the cement contains a little or no calcium. This is, however, not the case with many industrial ashes and slags, some of which contain 20 to 40 percent analytical CaO (Table 1). If a part or all of this calcium is available for the hydration reactions, the material may be self-cementitious like portland cement. This depends again on the mineralogical rather than the chemical composition of the material. Whereas crystalline C_3A , C_3S and $\beta\text{C}_2\text{S}$ present in portland cement hydrate readily at room temperature, many crystalline compounds of lime such as wallastonite (CS), gehlenite (C_2AS), anorthite (CAS_2), akermanite (C_2MS_2), etc. are not reactive. Like the aluminosilicates, when present in noncrystalline form, the materials corresponding to the latter compositions can hydrate in alkaline solutions, though at slow rate, to furnish calcium and other ionic species needed for formation of cementitious products. When this happens, the material can no longer be considered merely a pozzolan, in the classical sense of the term "pozzolan". It is more appropriate to consider these materials as "cementitious and pozzolanic," because they contain enough calcium to be self-cementing but need more of it from an external source in order to develop their full cementitious potential. However it should be obvious that due to their high calcium and lower silica and alumina content, when compared to normal pozzolans, larger proportions of these cementitious and pozzolanic materials may be used in a portland cement concrete for achieving a given level of mechanical strength at a specified age.

As a first approximation, the difference between the "pozzolanic reaction", (which as used here, is not limited to the lime-silica interaction but includes all cementitious reactions in the system $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$), and cementitious reactions in the hydration of portland cement, therefore, lies mainly in the reaction rates, and not in the character of the hydration products. The pozzolanic reaction, like other chemical reactions, can be accelerated by temperature and by chemical accelerators such as alkalis and sulfates.

CURRENT PRODUCTION RATES AND USES OF MAJOR POZZOLANIC AND CEMENTITIOUS BYPRODUCTS

Coal Ashes

During the combustion of powdered coal in modern power plants, as coal passes through the high-temperature zone in the furnace, the volatile matter and carbon are burned off whereas most of the mineral impurities deposited in coal during its formation, such as clays, shale, quartz and feldspar generally fuse and remain in suspension in the flue gas. The fused matter is quickly transported to lower temperature zones where it solidifies as spherical particles. Some of the mineral matter agglomerates to form bottom ash, but most of it flies out with the flue gas stream and hence is called "fly ash". This ash is subsequently removed from flue gas by mechanical separators, electrostatic precipitators, or bag filters.

In the U.S., according to Covey (10), total ash collection in 1980 reached 66.4 million tons which included 48.3 million tons of fly ash, 14.4 million tons of bottom ash, and 3.6 million tons of boiler slag. It is estimated that about a fifth of the 900 million tons of coal used annually is lignite and subbituminous, which is increasingly used by the power-generating stations in the West and Midwest. These coals generally produce high-calcium fly ash.

Due to their fine particle size and generally noncrystalline character, the fly ashes usually show satisfactory pozzolanic property, or in the case of high-calcium ashes, pozzolanic and cementitious properties. Yet only 6.4 million tons of the fly ash produced in the country was used in 1980, from which less than 6 percent (2.67 million tons) of the total found its way into cement and concrete products. In a report prepared for the Office of Recycled Materials, Frohnsdorff and Clifton (11) projected that about 18 million tons of fly ash could be consumed every year by the cement and concrete industry, provided there is adequate quality control and a better understanding of the technical requirements for satisfactory performance of the material. Therefore, in this paper, fly ash characterization and influence of fly ash on properties of concrete will be discussed in detail.

Rice Husk Ash

Rice husks, sometimes called rice hulls, are the shells produced during the dehulling operation of paddy rice. Since they are bulky, the husks present an enormous disposal problem for centralized rice mills. Each ton of paddy rice produces about 200 kg of husks, which on combustion produce about 40 kg of ash. The ash formed during open-field burning or uncontrolled combustion in industrial furnaces which use husks as fuel consists mainly of crystalline silica minerals such as cristobalite and tridymite, and must be ground to very fine particle size to develop pozzolanic property. On the other hand, the ash produced at low temperatures in a process developed by Mehta and Pitt (7) contains silica in a cellular, high surface area, noncrystalline form, and is therefore highly pozzolanic (8).

Although worldwide potential for production of this highly pozzolanic ash is high, about 80 million tons of husks per year, the economic feasibility is limited to areas of centralized paddy milling in large rice-growing countries. The U.S. potential is small (200,000 tons per year husk production) and is limited to the rice growing states of Arkansas, California, Louisiana, and Texas. In 1975, a furnace with a capacity to burn 7.5 tons of rice husks per hour to noncrystalline ash was installed in Arkansas (7), and plans to set up similar furnaces in Malaysia, India and Pakistan are reported to be in advanced stages.

Condensed Silica Fume

Condensed silica fume, sometimes known simply as silica fume or volatilized silica, is produced by electric arc furnaces as a byproduct of the production of metallic silicon or ferrosilicon alloys. In the reduction of quartz to silicon at temperatures up to 2000°C, a gaseous SiO is produced. It is transported to lower temperature zones where it oxidizes on coming in contact with air and condenses in the form of spheres consisting of noncrystalline silica. The material which is extremely fine is removed by filtering the outgoing gases in a bag-filter. Like rice husk ash, because it consists essentially of noncrystalline silica with a very high surface area (20-23 m²/g), condensed silica fume is highly pozzolanic.

The worldwide yearly production of condensed silica fume is estimated to be about 1.1 million tons, U.S.A., U.S.S.R., and Norway being the largest producers with 300,000 tons, 150,000 tons, and 120,000 tons production per year, respectively. Although there are reports of extensive laboratory research on the material, so far only limited field applications have been carried out.

Blast Furnace Slag

In the production of pig iron in a blast furnace, if the slag is cooled slowly in air, the chemical components of slag are usually present in the form of crystalline melilites ($C_2AS-C_2MS_2$ solid solution) which do not react with water at ordinary temperature. If ground to very fine particles, the material will be weakly cementitious and pozzolanic. However, when the liquid slag is rapidly quenched from high temperature (1400-1500°), either by water or a combination of water and air, most of the lime, magnesia, silica, and alumina can be held in a noncrystalline or glassy state. The water-quenched product is called granulated slag due to the sand-size particles, whereas the slag quenched by water and air is in the form of pellets, and is called pelletized slag. Normally the former contains more glass; however, both products when ground to 400 to 600 m²/kg Blaine surface area are capable of developing satisfactory cementitious and pozzolanic properties.

At present, the U.S. production of blast furnace slag amounts to 26 million tons. Most of the slag is slowly cooled in air, hence is poorly pozzolanic, and therefore is suitable only for use as aggregate for concrete or for subbase construction. Only 1.6 million tons of slag is available in the granulated form which is suitable as a cementitious and pozzolanic admixture. The Canadian blast furnace slag production is about 2.8 million tons per year from which up to 500,000 tons is pelletized. About 200,000 tons of the pelletized slag is used as a mineral admixture after fine grinding, the remaining being used as lightweight aggregate.

Steel Slags

Steel slags are a byproduct of the conversion of pig iron to steel. Basic oxygen furnace, open-hearth, and electric-arc furnace are used for this purpose. The slag is similar in chemical composition to iron blast furnace slag except that it usually contains a larger proportion of iron oxide and smaller amounts of silica and alumina. As may be expected, steel slag cooled slowly in air is virtually inert. However, reactive slag for use as a cementitious and pozzolanic admixture for concrete can be produced by water granulation.

In the U.S., about 9 million tons of steel slag are produced yearly. All of it is air-cooled, hence discarded or used for low-value applications. Similarly, nearly 3 million tons per year of the Canadian steel slag is generally discarded.

Non-Ferrous Slags

In the production of metallic copper, nickel, and lead, about 6 million tons of slag are produced by the various smelting furnaces. All these slags contain unusually large amounts of iron

oxide (40 to 60 percent). The copper and nickel slags are also characterized by low lime content. On water quenching and fine grinding, they show pozzolanic but not cementitious behavior. On the other hand, lead slags contain 10 to 20 percent CaO , and should be able to develop some cementitious character as well. However, at present, these slags are either being discarded or used for road construction.

Due to large variability in their composition as compared to blast furnace slags, it seems that granulated non-ferrous slags would be potentially less attractive for use as mineral admixtures in concrete; therefore they will not be discussed any further.

MINERALOGICAL COMPOSITION, PARTICLE CHARACTERISTICS, AND REACTIVITY

The rate at which cementitious products are formed as a result of interaction between a mineral admixture and portland cement hydration products depends on the composition of portland cement, mineralogical composition and particle characteristics of the admixture, reaction temperature, and ionic concentration of the solution phase in the system. In portland cement, a close relationship between chemical and mineralogical composition generally holds; however this is not the case with byproduct mineral admixtures which may contain large amounts of noncrystalline or glassy matter and are usually subject to greater variations in thermal history during the production process. Because no direct relationship exists between chemical and mineralogical composition (which controls the reactivity of these materials at room temperature) the standard specifications emphasizing chemical requirements do not serve much useful purpose. Therefore, closer attention needs to be paid to the mineralogical rather than to the chemical analysis of mineral admixtures.

On the basis of their cementitious and pozzolanic activity, which depends on mineralogical and particle characteristics, a classification of byproduct mineral admixtures suitable for use in concrete is suggested in Table 2. The mineralogical character of each of the important admixtures are discussed in detail below. Also discussed are particle size, morphology, and surface texture, which not only affect the reactivity of mineral admixtures in portland cement concrete but also exert an important influence on water demand, consistency, stability, and workability of concrete.

The Nature of Glass and Minerals in Fly Ash

From the standpoint of conspicuous differences in mineralogical composition and properties, fly ashes can be divided into two categories, which differ from each other mainly in their calcium content. The first category, containing usually less than 5 percent analytical CaO , is generally a product of combustion of anthracite and bituminous coals. The second category, containing

usually 15 to 35 percent analytical CaO generally happens to be the product of combustion of lignite and subbituminous coals. The ASTM Standard Specification for Mineral Admixtures (C 618) does not differentiate fly ashes on the basis of calcium content, although this objective is achieved indirectly by requiring a minimum of 70 percent of major non-calcium oxides (silica + alumina + iron oxide) for Class F fly ash, and 50 percent for Class C fly ash, since the latter is high in calcium.

The low-calcium fly ashes, due to the high proportions of silica and alumina, consist principally of aluminosilicate glass. In the furnace very large spheres of molten glass may not get cooled rapidly and uniformly, thus crystallization of aluminosilicates such as sillimanite ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) as slender needles, takes place in the interior of the glassy sphere. This partial devitrification of glass in low-lime fly ashes, therefore, would account for the presence of crystalline aluminosilicates which are relatively nonreactive. The microscopic evidence of the presence of the crystalline phases encapsulated within solid glassy spheres comes from many researchers including Diamond (12) who have examined fly ashes after chemical reactions in concrete or after etching to remove glass. Also, depending on the fineness to which coal has been ground before combustion, remnants of a quartz are likely to be present in the ash in the original (unaltered) crystalline state. Researchers, including Diamond (12) and Mortureux et al (13), have confirmed that the principal crystalline minerals in low-calcium fly ashes are α quartz, mullite, sillimanite, hematite, and magnetite. Since the crystalline minerals are nonreactive at ordinary temperature in the portland cement solution phase, their presence in large proportions, at the cost of the noncrystalline component or glass, reduces the reactivity of the ash. Also the assumption in the ASTM Specification C 618 that all silica, alumina, and iron oxide present in pozzolans is potentially reactive with lime (and therefore are in noncrystalline form) is incorrect since, in actual practice substantial amounts of these oxides occur as nonreactive crystalline minerals, such as SiO_2 as quartz, mullite, and sillimanite; alumina as mullite and sillimanite, and iron oxide as hematite and magnetite.

In regard to high-calcium fly ashes which may also contain significant amounts of magnesia, alkalis and sulfates, the situation is more complex than the low-calcium ashes from anthracite or bituminous coal. As will be discussed later, it appears that the chemical composition and reactivity of the noncrystalline or glassy phase is different from the glassy phase typically present in low-calcium fly ashes. Also, the principal crystalline mineral in high-calcium fly ash is generally C_3A , which is known to be the most reactive mineral present in portland cement. In some high-calcium fly ashes this writer as well as others have detected crystalline $\text{C}_4\text{A}_3\text{S}$, $\text{C}\bar{\text{S}}$ and free CaO (Fig. 2) which, in addition to C_3A , readily react to form cementitious calcium aluminates and sulfoaluminate hydrates. Alkali sulfates volatilize at high temperature and

later condense as crystalline sodium, potassium, or double-alkali sulfates on the external surfaces of fly ash spheres. Being highly soluble, they are available for fly ash and portland cement hydration reactions. Sometimes crystalline MgO (periclase) is detected, however, periclase formed at $> 1000^\circ\text{C}$ shows poor hydration characteristic at room temperature. As in low-calcium fly ashes, crystalline quartz, mullite, and iron oxide are also detected in high-calcium fly ash, however, their proportion is usually much smaller in the latter case. Thus, it should be immediately apparent that in general, the crystalline minerals in a low-calcium fly ash are nonreactive, whereas many of the crystalline minerals in a high-calcium fly ash are reactive, and capable of imparting cementitious characteristic to the ash. In fact, quick setting behavior of some ASTM Class C fly ashes due to rapid formation of C_4AH_{13} , $\text{C}_4\text{ASH}_{18}$, and ettringite has been observed by this writer as well as other researchers.

Since the noncrystalline phase or glass is the major component of fly ashes (sometimes 90 percent or even more), it seems that the reasons for high reactivity of high-calcium fly ashes may partially lie in the chemical composition of the glass which is different than the glass in low-calcium fly ashes. Diamond and Lopez-Flores (14) have made an important contribution to the state-of-the-art by pointing out that the position of the diffraction halo (diffuse-band) produced by X-ray scattering can provide some indication of the glass composition. This is consistent with the findings of the writer as shown in Fig. 2. It can be seen that the maximum intensity of the diffuse-band due to glass in the low-calcium fly ash is between 21 to $25^\circ 2\theta$ (Cu radiation), whereas the diffuse-band due to glass in the high-calcium fly ash shows high intensity between 30 to $34^\circ 2\theta$. It is interesting that the writer (Fig. 2) and Regourd et al (15) found a similar diffuse-band with highest intensity between 31 to $35^\circ 2\theta$ in a granulated blast furnace slag containing 42.5% CaO , 33.6% SiO_2 , 12.2% Al_2O_3 , and 8.4% MgO . It can be deduced therefore that, as a first approximation, the chemical composition and reactivity of glass in rapidly cooled high-calcium fly ashes may be similar to the glass in granulated blast furnace slag. The slag portion in portland cement granulated blast furnace slag mixtures normally starts hydrating 3 days after adding water, and the fly ash portion of low-calcium fly ashes in portland cement-fly ash mixtures does not show any significant degree of hydration until about two weeks after adding water. Therefore, it appears that the calcium aluminosilicate glass in high-calcium fly ash, which is similar in composition to the glass in granulated blast furnace slag, would be more reactive than the aluminosilicate glass in low-calcium fly ashes. Although small amounts of alkalis and iron oxide may be present in the glass of low-calcium fly ash, and some MgO may be present in high-calcium fly ash, the deduction that a more reactive glass is present in the latter appears reasonable to the writer.

Another difference between the low-calcium and high-calcium fly ash, which is commonly reported by many observers, is that in

the latter there is usually a little ($< 1\%$) or no unburned carbon. In the former case complete removal of carbon is rare and the presence of 2 to 10 percent carbon, which can be easily determined by the loss on ignition test, is quite common in industrial products. Some of this carbon may be encapsulated in glass, but a major portion appears to occur as cellular, or lacy particles which have a high internal surface, and are therefore capable of adsorbing large amount of water and chemical admixtures from an aqueous solution. If the proportion of cellular or lacy particles of carbon which are usually larger than $45\text{ }\mu\text{m}$ is high in a fly ash, the use of such fly ash as a mineral admixture in concrete increases water requirement and consumption of air-entraining admixtures. It may be noted however that the relationship between $+45\text{ }\mu\text{m}$ fraction and the carbon content in fly ash need not be direct since a portion of the coarse particles may consist of quartz; furthermore some of the unburned carbon may be present within glass.

Particle Characteristics of Fly Ash

Scanning electron micrographs of typical fly ashes, both low-calcium and high-calcium, are shown in Fig. 3. In general fly ash consists of glassy spheres of sizes varying from under $1\text{ }\mu\text{m}$ to as large as $100\text{ }\mu\text{m}$, although typical particle size distribution (Fig. 4) shows that most of the material is under $20\text{ }\mu\text{m}$. Due to the lower proportion of surface deposits consisting of alkali sulfate crystals, low-calcium fly ashes tend to show a cleaner appearance under the microscope. On the basis of optical and scanning electron microscope observations, Fisher et al (16) and Lauf (17) have proposed several morphological categories of fly ash which may be summarized as follows:

- (i) Most of the fly ash particles occur as solid glass spheres, which are mostly transparent but may be partially devitrified.
- (ii) Irregular masses of large size may exist either as agglomerates of small silicate glass spheres or porous particles of incompletely burnt carbonaceous matter.
- (iii) Magnetite and hematite occur as opaque spheres in high-iron fly ashes.
- (iv) Sometimes low-calcium fly ashes may contain a small amount (up to 5% by weight) of hollow spheres which are either completely empty (cenospheres) or packed inside with smaller spheres (plerospheres). A scanning electron micrograph of a broken plerosphere is shown in Fig. 3C.

It appears that differences in particle size distribution, morphology, and surface characteristics of fly ash would influence water demand and reactivity. Fly ashes consisting of clean, glassy, spherical particles (Fig. 3A), by virtue of being good void-fillers in concrete, should be able to reduce water requirement, especially in lean concretes or when the proportion of fines in aggregate is lacking. Rough-textured and porous glass spheres

(Fig. 3B) which are sometimes seen in high-calcium fly ashes possess larger surface area for reactivity than smooth spheres, hence particle size distribution alone may not reflect the potential reactivity of a fly ash.

Granulated Blast Furnace Slag

Although high-calcium fly ashes are relatively of recent origin, and the production and use of granulated blast furnace slag is more than one hundred years old, there are many striking similarities in the mineralogical character and properties of the two products. Not only are both essentially glassy (usually 90 percent noncrystalline), but also the composition and reactivity of the glass appears to be similar. The chemical composition of the glass in granulated blast furnace slag corresponds to melilite phase which is a solid solution phase between gehlenite (C_2AS) and akermanite (C_2MS_2). It should be noted that gehlenite, akermanite, and melilites are nonreactive when crystalline; however when they are in noncrystalline state Akatsu et al (18) and Regourd et al (15) found that the reactivity of slag generally goes up with increasing ratio of gehlenite to akermanite composition in the glass. In addition to crystalline gehlenite and akermanite, the presence of diopside (CMS_2) and merwinite (C_3MS_2) have been detected in the devitrified particles of granulated blast furnace slag. All of these crystalline minerals are nonreactive at room temperature.

Therefore, one difference between some high-calcium fly ash and granulated blast furnace slag, is in the types of crystalline phases that may be present. The former may contain reactive crystalline compounds such as free CaO , C_3A , $C_4A_3\bar{S}$, $C\bar{S}$, and alkali sulfates; whereas all the crystalline compounds in the latter are essentially nonreactive. This makes some high-calcium fly ashes very reactive, so that hydration reactions may begin to take place almost immediately after addition of water. On the other hand, the hydration of granulated blast furnace slag in a portland cement-slag mixture must await the hydration of the portland cement which provides alkalies and sulfate for "activating" the slag component, i.e., for initiating the hydration of glass and formation of cementitious products. Data from the work of Sadatsune (19), and Hogan and Meusel (6) shows that under normal conditions it takes about 3 days before the contribution of the cementitious properties of the granulated slag to the composite system becomes noticeable.

Although the glass content of granulated slag is the most valuable parameter in characterizing the value of the material for use in cement and concrete industry, there is evidence that the reactivity of a glass may depend not only on its composition but also on the degree of disorder and content of flaws which are affected by the overall thermal history of slag. Obviously, slags cooled from higher temperature and at a faster rate are likely to

contain more reactive glass. There is also some evidence that in the range of 80 to 100 percent glass content, the slags with a lower glass content sometimes show reactivity similar to the slags with higher glass content. However, Akatsu et al (18) found that such differences in reactivity play a role only in the early stages of hydration up to 7 days; the strengths at later ages (28 days and after) of portland cement-slag mixtures are primarily related to the total glass content.

In the pig iron manufacturing process, the thermal history affecting the glass content and reactivity of slag can not be easily altered because the slag is only a byproduct. However, the slag obtained even after granulation is too coarse for use as a mineral admixture. For example, Hogan and Meusel (6) reported that 50% particles were larger than No. 20 mesh. This presents an opportunity to improve the reactivity of the material by controlling the fineness of grinding. Wada and Ikawa (20) found that slag particles less than 10 μm contributed to early strength development in concrete (until 28 days), whereas 10 to 40 μm particles continued to hydrate thereafter. In short, the ground slag for use as mineral admixture in concrete should not only be glassy, but also should contain few particles above 45 μm and a considerable proportion of particles below 10 μm .

A major difference between fly ash and ground granulated blast furnace slag is in the shape and texture of the particles. The fly ash particles are mostly spherical and have generally a smooth surface texture. In contrast, slag is angular and has rough surface texture. Due to their glassy nature both are often able to reduce the water requirement for standard flow of pastes or mortars. However, in a given concrete mixture the workability and finish should be superior with fly ash additions than with granulated slag additions.

Condensed Silica Fume and Rice Husk Ash

As stated earlier, both condensed silica fume, and rice husk ash produced by controlled combustion consist essentially of silica in noncrystalline form. They belong to a superior class of pozzolans because they do not suffer the variability in composition and heterogeneity in mineralogical character typical of fly ashes. Also, both materials possess exceedingly high surface area which is an important reason for their highly active pozzolanic behavior. There are however significant differences between the two in regard to particle characteristics.

Condensed silica fume particles are mostly spherical like fly ash, although they are about 100 times smaller in size (0.1 μm average diameter). Typical scanning electron micrographs are shown in Fig. 5A and 5B and particle size distribution is plotted in Fig. 4. Rice husks ash from the controlled burning process developed by Mehta and Pitt (7) is very soft and is easily pulverized to < 45 μm size. Unlike condensed silica fume, the particles

of rice husk ash are angular yet highly cellular, hence the reactive surface is not reflected by the particle size distribution but by the internal porosity of the individual particles. A typical scanning electron micrograph of the rice husk ash is shown in Fig. 50.

Surface areas of the order of 20 to 23 m²/g for condensed silica fume and 50 to 60 m²/g for rice husk ash are reported in the published literature. At a given water-cement ratio small additions (2 to 3% by weight of cement) of these byproducts may be useful for improving the stability and workability of concrete by reducing the tendency towards bleeding and segregation. However large additions would produce dry or unworkable mixtures unless water-reducing admixtures are used.

In regard to reactivity of condensed silica fume or rice husk ash when used as mineral admixture in portland cement mortar and concrete, the writer observed (8) that the rice husk ash showed significant reactivity even at ages 1, 3, and 7 days. For instance, at a constant water-cementing materials ratio in ASTM C 109 mortars, portland cement-rice husk ash mixtures containing as high as 70 percent ash by weight of the total cementing material exceeded the strength of the reference portland cement even at 3 days after casting. Due perhaps to the lower surface area and denser surface texture, the condensed silica fume reacts somewhat at a slower rate than the rice husk ash. Carrette and Malhotra (21) have reported that concretes containing condensed silica fume show considerably lower strength than the control specimens at age 1 day but begin to show a significant improvement in strength from about 3 days after casting. Due to the adsorptive character of rice husk ash particles, concretes containing rice husk ash require more water for a given consistency. However, there is evidence that this does not lead to lower strengths of the same order as would be expected in portland cement concretes.

MECHANISMS BY WHICH MINERAL ADMIXTURES IMPROVE CONCRETE PROPERTIES

By adding mineral admixtures, many aspects of concrete can be favorably influenced, some by physical effects associated with small particles which have generally a finer particle size distribution than does portland cement, and others by pozzolanic and cementitious reactions resulting in certain desirable physical effects which will be discussed later. Concrete mix proportions, rheological behavior of plastic concrete, and degree of hydration of portland cement are among the physical effects associated with the particle size of mineral admixtures. Strength and permeability of hardened concrete; resistance to thermal cracking, alkali-silica expansion, and sulfate attack are the main effects associated with the pozzolanic and cementitious reactions.

Compared to the portland cements of fifty years ago, cements produced by modern plants are more reactive because they are finer,

contain more C_3S and at times more alkali sulfates. Therefore durability of concrete structures built today is likely to suffer due to causes mentioned above unless adequate precautions are taken. The use of mineral admixtures in modern concrete makes sense, since they should cause considerable improvement in durability. However, experience shows that the potential benefits from application of admixtures are not always realized. Therefore, a discussion on the mechanisms by which improvement in properties of concrete takes place is given below in the hope that this will lead to proper selection and use of mineral admixtures.

Concrete Mix Proportions

For a given consistency of concrete, reduction in the water requirement can lead to an overall improvement in many engineering properties. Granulometric characteristics of the coarse aggregate, fine aggregate, and cement particles influence the volume of voids and water requirement of a concrete mixture. Addition of fine particles of a mineral admixture, typically of the order of 1 to 20 μm size, would supplement the effect of portland cement grains in further reducing the volume of voids in the concrete mixture, thus requiring less water to produce a concrete of given consistency. Berry and Malhotra (2) cite two cases in which 30 percent fly ash substitution for cement was found to reduce the water requirement by about 7 percent at constant slump. Using three fly ashes of different particle size, Lane and Best (5) reported 5 to 10 percent reduction in mortars of equal consistency when 33, 67, or 133 percent fly ash by weight of cement was added. Similarly, investigations by Hogan and Meusel (6) on a granulated blast furnace slag, ground to various particle sizes corresponding to 508 to 608 m^2/kg Blaine surface area, showed that about 6.4 percent reduction in water required for standard flow (ASTM C 109) was possible for a large number of portland-cement slag mixtures containing 40 to 65 percent cement replacement by slag.

Not all mineral admixtures will reduce the water demand. For instance, many investigators have observed that the use of a coarse fly ash, or a fly ash with high loss-on-ignition (usually 10 percent or more) caused an increase in the water requirement instead of reducing it. It is now known that this would happen only when a considerable amount of cellular particles of coke, which are usually large in size (100 μm), are present in the fly ash. Again, some high-calcium fly ashes may contain significantly large amounts of C_3A which tend to increase the water requirement due to loss of consistency caused by the rapid formation of calcium aluminate hydrates or sulfoaluminate hydrates. Mineral admixtures having extremely fine particle size or very high surface area, such as condensed silica fume or rice husk ash, are generally known to increase the water required for normal consistency in almost direct proportion to their amount present by weight of cement.

Rheological Behavior of Plastic Concrete

The mechanism by which bleeding may be reduced or eliminated by addition of very fine particles of silica fume in a cement paste is illustrated in Fig. 6. In the same manner, the presence of fly ash or ground blast furnace slag between the aggregate particles helps to reduce bleeding. A substantial reduction in the size of bleed-water channels in concrete would evidently decrease the tendency for segregation, and improve finishability characteristics. It should be apparent that lean concretes or those made with aggregates deficient in fine-size fraction would benefit more from fly ash addition. Non-bleeding concrete containing condensed silica fume or rice husk ash additions must be suitably protected when conditions for plastic shrinkage cracking prevail.

Workability is another important property of plastic concrete; it depends mainly on cohesiveness. Cohesiveness is largely controlled by the volume of the paste in concrete. An advantage from replacement of cement in concrete by an equal weight of lower-density mineral admixtures lies in the resulting increase in the paste content. For instance, Lane and Best (5) calculated that on equal weight basis the volume of fly ash with 2.4 Mg/m^3 density will exceed the volume of portland cement by approximately 30 percent. Proportioning fly ash concrete on an equal 28-day strength basis would require a cement replacement ratio greater than 1:1 by weight (the additional fly ash replacing a portion of the fine aggregate), thereby producing even a greater increase in the paste (cement + fly ash + water) to aggregate ratio. It is due to the superior cohesiveness that the pumpability of fly ash concrete is generally excellent.

In regard to setting time, Davis et al had concluded as early as 1937 (1) that fly ash-cement mixtures set more slowly than corresponding cements but the setting times were within the usual specification limits. Experience of Lane and Best (5) with modern fly ashes generally confirms this, especially for high-carbon fly ashes which increase the water requirement for normal consistency, and thus the setting time. By replacing the cement with 60 percent fly ash by weight, the blend with the high-carbon ash (12% carbon) produced an increase of 200 percent in the time of final set of the control mixture, without exceeding the ASTM C 150 maximum limit of 8 hours. Such concretes must be protected against freezing in cold weather. It may be pointed out, however that the observations of both Davis et al, and Lane and Best pertain to low-calcium fly ashes. The high-calcium fly ashes which are generally low in carbon and high in reactive constituents (both crystalline and non-crystalline) sometimes exhibit opposite behavior. Calling such ashes "reactive", Covey (10) states, "When you add water to the reactive materials, you had better be prepared to get to the job site in about 30 minutes". Obviously, this refers to the quick setting tendency of concretes containing certain high-calcium fly ashes. Not all high-calcium fly ashes would cause quick setting. Diamond and Lopez-Flores (14, 34) studied three high-calcium and

two low-calcium fly ashes, all of which retarded the initial set by 2 hours or more, and final set by at least 5 hours. Therefore, it seems that before using an unknown fly ash, the influence of the fly ash on setting time of concrete should be investigated and suitably controlled when necessary by application of set-modifiers.

Ground blast furnace slag when added as mineral admixture to concrete is likely to improve resistance to bleeding and segregation but due to its angular texture may not improve finishability and workability to the same extent as fly ash addition. Hogan and Meusel (6) reported that both the initial and final time of set of portland-blast furnace slag mixtures containing 40, 50, or 65 percent slag by weight increased by about one hour when compared to the reference portland cement.

Acceleration of Cement Hydration

Kobayashi and Sato (22) showed that by helping to separate or disperse the flocculated structure of particles of portland cement more efficiently, the presence of fine particles of any material increases the early hydration of cement. Thus strength of concretes at a given cement content to which a fly ash or limestone powder was added (as fine aggregate replacement) was equally enhanced at 7 and 28 days. Only at 91 days or more, did the fly ash concrete show higher strength, which was attributed to the pozzolanic reaction.

Strength and Impermeability of Concrete

The two factors which adversely affect both strength and impermeability of concrete are: (i) the presence of large voids in the hydrated cement paste, and (ii) the microcracks at the aggregate-cement paste transition zone. Since it is the view of this writer that improvements in strength and durability of concrete associated with the use of mineral admixtures are possible only through transformation of large pores into fine pores, and reduction of microcracking in the transition zone, a detailed discussion of these mechanisms follows.

From an investigation on the rate of strength development in blended portland cements containing a natural pozzolan, the writer (23) found that at various stages during the curing process the volume of large voids (> 100 nm), not the total porosity of the hydrated paste, was inversely correlated to strength. This suggests that strength improvement as a result of pozzolanic reaction is accompanied by and partly results from reduction in the volume of large pores. Manmohan and Mehta (24) showed that additions of pozzolanic and cementitious admixtures such as rice husk ash, fly ash, and granulated blast furnace slag to portland cement were instrumental in causing pore refinement or transformation of large pores into fine pores—a process which had a far reaching influence on the permeability of the hardened cement pastes. Typical

pore size distribution plots for various levels of additions of the three mineral admixtures in 28 days old cement pastes are shown in Fig. 7.

The exact mechanism by which pore refinement occurs in hydrated pozzolan cements is not fully understood. However, Regourd et al (25) observed that compared to the C-S-H phase in hydrated portland cements, a less compact C-S-H is found in well-hydrated portland-pozzolan cements. Evidently, if such a product forms as a result of chemical reaction between pozzolanic silica and lime, it would have the effect of filling up large empty spaces. This mechanism is illustrated by the writer (26) in Fig. 8. Thus conversion of high density phases and large voids in a portland cement paste system to low density products and small voids, as a result of pozzolanic reaction, appears to be the most logical explanation for increase in strength and impermeability, which is generally observed in well hydrated portland-pozzolan cement pastes. Among others, Feldman (27) using a fly ash and a slag as admixtures, and Sellevold et al (28) using silica fume as admixture have confirmed the process of pore refinement and its significance to strength and impermeability.

In concrete it is now known that the transition phase between the aggregate and hydrated cement paste plays a very important part in determining the mechanical properties and long-term durability characteristics. In normal portland cement concretes the transition zone is generally less dense than the bulk paste and contains a larger amount of plate-like crystals of calcium hydroxide, with c-axis perpendicular to the aggregate surface. It is consequently more prone to microcracking by tensile stresses induced by normal thermal and humidity changes. The structure of the transition phase, therefore, explains why it is the weakest phase in concrete, and would thus exercise a great influence on the properties of the material.

There is not much information on the effect of mineral admixtures on the structure and properties of the transition phase in concrete. Carles-Gilbergues et al (29) investigated the influence of water-to-cement ratio and pozzolanic admixtures on the two important parameters of the transition phase, namely its thickness and the degree of orientation of calcium hydroxide crystals in it. With increasing water-to-cement ratio, both the thickness of the transition phase and the degree of orientation of calcium hydroxide increased, which is expected from the corresponding increase in the bleeding characteristics of the mortars. Compared to the reference mortar containing only portland cement, the thickness of the transition phase decreased with the addition of a condensed silica fume. The latter, due to very high surface area ($23 \text{ m}^2/\text{g}$), had the effect of reducing the consistency and setting time of the reference mortar. The presence of silica fume or a lignite fly ash reduced the degree of orientation of calcium hydroxide crystals in the transition phase; on the other hand the addition of a bituminous coal fly ash (which exerted little influence on the

consistency and setting characteristics of the reference mortar) increased both the thickness of the transition phase and the degree of orientation of calcium hydroxide at the same hydration age (28 days). Therefore at this age, mortars and concretes containing the silica fume or the lignite fly ash would be expected to show better mechanical properties than corresponding products containing the bituminous ash.

In the context that mineral admixtures are capable of altering the water requirement, consistency, bleeding characteristics or time of setting of portland cement pastes, it is apparent that they can be made to exercise a beneficial effect on the structure and mechanical strength of the transition phase. This, together with their ability for pore refinement in hydrated portland cement pastes as discussed above, holds the promise that concretes containing mineral admixtures can be stronger and more durable than concretes without them. From an understanding of the mechanism by which mineral admixture can improve the properties of portland cement concrete it may be concluded that the use of admixtures which would reduce water demand and bleeding in fresh concrete, decrease the size and number of large voids in hydrated cement paste, lower the amount and degree of orientation of crystalline calcium hydroxide as well as microcracking in the transition phase, should improve the ultimate strength and impermeability of a portland cement concrete. This clearly underscores the importance of proper curing of concretes containing mineral admixtures, since without sufficient progress in the pozzolanic and cementitious reactions associated with the mineral admixtures, significant improvements in strength and durability of concrete can not be expected.

EXPERIENCE FROM FIELD AND LABORATORY INVESTIGATIONS

In the light of the above mechanisms by which mineral admixtures are able to improve the properties of concrete, it would be interesting to examine the results of some selected cases of field and laboratory experience from the standpoint of durability of concrete to thermal cracking, sulfate attack, alkali-silica expansion, and corrosion of reinforcing steel in concrete. Strength development and other properties such as modulus of elasticity, creep, and drying shrinkage are also discussed below.

Durability to Thermal Cracking

In thin sections of structural concrete, heat produced by cement hydration is quickly lost to the environment, and the temperature rise is usually not large enough to cause serious thermal stress on cooling. However in mass concrete even in sections as small as 600 mm, depending on the cement type and content, thickness and type of formwork, and concrete placement temperature, the temperature rise at times may amount to 20°C to 50°C. This is too great to ignore. Assuming that maximum temperature in structural

concrete is reached within 2 to 5 days after placement, mineral admixtures such as fly ash and blast furnace slag have the potential of reducing the temperature rise almost in proportion to the amount used as cement replacement since generally they do not react to any significant degree for several days. Thus Berry and Malhotra (2) cite MacInnis who found that 30 percent substitution of portland cement with a fly ash reduced the maximum temperature rise in concrete (which occurred 4 days after the placement) from 47°C for plain concrete to 33°C for fly ash concrete. However in a field test Bamforth (30) found the reduction in temperature rise in concrete sections, 2.5 m and 4.75 m deep, was about 15 percent at 30 percent cement replacement level. From the standpoint of thermal stress on cooling, cement replacement by fly ash offers an obvious advantage and has long been exploited in mass concrete construction where low cement contents and high fly ash portions (60 to 100 percent by weight of cement) are often used to counteract thermal cracking. Since after long-term curing the ratio of flexural strength to compressive strength in fly ash concrete is higher than the plain concrete because of the superior aggregate-cement paste bond, many investigators including Kobayashi (31) also recommend the use of fly ash for normal reinforced cement structures and highway pavements.

The disadvantages of temperature rise in massive concrete containing only portland cement, and the advantage of replacing a part of the cement by a mineral admixture are clearly shown by Bamforth (30) who found that the early age heat cycle reduced the in-situ 28-days strength of portland cement concrete up to 30 percent, when compared to laboratory-cured specimens. This was probably due to less microcracking at a lower thermal gradient in the laboratory. However, this was not the case in portland-fly ash concretes where thermal gradient is lower and healing of microcracks by the products of fly ash-cement interaction, which is accelerated at higher than normal temperature, is possible. Thus when concrete is exposed to high temperatures at early age, a marriage between portland cement and fly ash or other mineral admixtures is mutually advantageous. The mineral admixtures which react slowly at normal temperature can benefit from the heat of hydration of portland cement, which otherwise goes to waste. Another example was given by Kobayashi (31) for the intake pressure tunnel of Kurobegawa Power Station in Japan which was located in hot base rock (100-160°C). In this case the use of 25 percent fly ash as cement replacement showed favorable effect on concrete strength.

Since high-calcium fly ash is generally more reactive, there is some concern that it may not be as effective as low-calcium ash in reducing the heat of hydration. For instance, Vance and Roberts (32) found that the total heat of solution by the method described in ASTM C 186 was 422 to 507 cal/g for a number of high-calcium ashes, whereas the heat of solution values for several low-calcium ashes were less than 405 cal/g. Using the same method, Cook (33) reported an 11 percent reduction of the heat of hydration at 7 days with 20 percent cement replacement by a high-calcium fly ash, 25 percent reduction with 30 percent ash, and only an 18 percent

reduction with 40 percent ash. Diamond and Lopez-Flores (34) also found that high-calcium fly ashes contributed substantially to early heat evolution.

Mehta and Pirtz (35) successfully used 30 percent by weight replacement of Type I portland cement by rice husk ash in a high-strength mass concrete (6000 psi designed strength at 28 days) which on adiabatic curing showed 12°C less temperature rise at 28 days than the reference concrete without the admixture. Since the 7 and 28 day compressive strength of the rice husk ash concrete were higher, it was concluded that cement-pozzolan combinations produce more strength per unit of temperature rise than portland cement alone.

Durability of Concrete to Sulfate Attack

Davis et al (1) investigated five low-calcium fly ashes at 20 percent cement replacement level for their effectiveness in improving the sulfate resistance of cement. Before immersion into a 10 percent sodium sulfate solution, the 3 by 6 inch concrete cylinders were normally cured for 28 days. Compressive strengths of the specimens were determined after 5 months of immersion. On the basis of the ratio of compressive strengths of fly ash concrete to the corresponding plain concrete specimens, all fly ash concretes were found to be superior to the corresponding plain concrete specimens. The fly ash containing low-carbon and the lowest alumina content (16.4%) exhibited a slight increase rather than decrease in the compressive strength during the 5-month sulfate immersion period. Similarly, using an accelerated test procedure for evaluation of sulfate resistance, Mehta (36) found that a hydrated cement paste containing 20 percent fly ash of low alumina content (15% Al_2O_3) showed 8 percent strength gain, whereas the cement paste containing high alumina (30% Al_2O_3) fly ash showed 23 percent strength loss.

Many researchers have found a similar correlation between the alumina content of blast furnace slag and sulfate resistance of portland cement products containing the slag. The European slags are relatively high in alumina (13-15%) as compared to the American slags (8 to 10%). Whereas 70 percent or more Type I cement replacement by slag is recommended for sulfate resistance in Europe, investigation by Hooten et al (37) on a Canadian slag confirmed that 50 percent Type I cement (12% C_3A content) replacement by slag provided as good sulfate resistance as shown by that of a Type V sulfate resisting portland cement. It was once believed that the improvement in sulfate resistance of portland pozzolan and portland slag cements was caused primarily by reduction in free lime and reactive alumina content due to pozzolanic reaction. The writer (26), however, has shown that reduction in permeability as a result of pore refinement associated with the pozzolanic reaction is equally important, which again underscores the importance of proper curing of concretes containing mineral admixtures

if potential benefits from their use are to be realized.

Permeability and Corrosion of Steel in Concrete

Reduction of alkalinity of the cement paste by carbonation from atmospheric CO_2 is generally the first step in the process of corrosion of steel in concrete. In a hydrated portland cement paste, about 20 percent Ca(OH)_2 is present to provide the reserve basicity for steel protection. Since pozzolanic reaction consumes Ca(OH)_2 , theoretically about 25 percent reactive silica present in a portland-pozzolan mixture is enough to consume all the available Ca(OH)_2 from portland cement hydration. This has caused some concern among construction engineers who feel that due to the reduced alkalinity of concrete, the addition of pozzolans to reinforced and prestressed concrete would present a danger for corrosion of steel.

According to Massazza (38), the resistance to the carbonation of concrete does not appear to be related to the amount of calcium hydroxide in the pore solution since many researchers including Diamond (39) have reported that the pore solutions in mature portland cement pastes contain little or no calcium. Like sulfate resistance therefore, causes of resistance to carbonation must be sought mainly in physical factors such as permeability of the cement paste.

Mannohan and Mehta (24) found that 10, 20, or 30 percent rice husk ash by weight of cement, and 30 or 70 percent blast furnace slag effectively reduced the size of large pores in 28-days curing, yielding cement pastes of very low permeability. In the case of cements containing 10, 20, or 30 percent fly ash, the pore-size refinement and a drastic drop in permeability of the cement paste (from $11\text{--}13 \times 10^{-11}$ to 1×10^{-11} cm/sec.) occurred during the 28 to 90 days curing period. This is consistent with the results of Davis, cited by Berry and Malhotra (2) on permeability of concrete pipe containing fly ash, which was higher than plain concrete at 28 days, but substantially lower after 6 months of curing. Again, the importance of differences between the reactivity of various mineral admixtures and the significance of prolonged curing are obvious if the benefits from the use of such materials are to be realized.

In conclusion, the pozzolanic and cementitious reactions associated with byproduct mineral admixtures while reducing the free lime present in the cement paste on one hand, decrease the permeability of the system on the other hand, thus improving the overall resistance to CO_2 attack. Suggesting that enough hydroxyl ion concentration and free calcium hydroxide is always present in the portland-pozzolan cement pastes, even when very active SiO_2 -rich pozzolans are used, Massazza (38) feels that the danger

due to carbonation should be of less concern in concretes containing pozzolans.

Expansion Due to Alkali-Silica Reactions

A slow reaction between the alkaline solution from a high-alkali portland cement ($> 0.6\% \text{ Na}_2\text{O}$ eq.) and certain forms of silica in aggregate is known to cause expansion and cracking in concrete. In numerous laboratory investigations, a partial replacement of the high-alkali cement by a mineral admixture has been found to be effective in reducing the expansion due to the alkali-silica reaction. The exact mechanism by which this reaction causes expansion, and the mechanism by which mineral admixtures are able to reduce expansion are still imperfectly understood. It appears that in some silica or silicate structures highly alkaline solutions (pH 13 to 14) are able to destroy bonding and the products thus formed can swell by imbibition of water. When a part of the portland cement is replaced by a mineral admixture, the available alkali in the system is reduced by the amount of the admixture present, provided the latter does not contain "soluble alkali". A further reduction in alkalinity may also occur with the progress of the pozzolanic reactions.

Berry and Malhotra (2) reported that 75 percent reduction in expansion according to the ASTM Standard C 441 test was achieved by numerous investigators when 36 to 48 percent of the volume of high-alkali portland cement was replaced by fly ash. The authors question whether the early strength losses caused by such high cement substitutions by fly ash would be tolerable for more than a limited number of applications. However, Mehta and Polivka (40) reported that only 10 percent rice husk ash by weight of cement was sufficient for effectively reducing the alkali-silica expansion in ASTM C 441 test, and there was no loss of early strength.

It should be noted that similar to high-alkali portland cements, the addition of some high-calcium fly ashes containing large amounts of soluble alkali sulfates might increase rather than decrease the alkali-silica activity. Such a phenomenon has been reported by the writer (36), and also by Diamond (41). Both investigators have pointed out that it is the soluble alkali and not the total alkali present in a fly ash which plays a role in increasing the alkali-silica reactivity.

Compared to fly ash, it seems that blast furnace slag additions would be less sensitive to the amount and variation in slag composition from the standpoint of combating alkali-silica reaction. Hogan and Meusel (6) showed that portland cement replacement by 40, 50, or 65 percent granulated slag in ASTM Test C 227, with pyrex glass as reactive aggregate, reduced the expansion of the control mortar bar specimens from about 0.3 percent to 0.07 percent or less.

Effect of Mineral Admixture on Concrete Strength

It is not easy to summarize the large volume of published data on the effect of mineral admixtures on concrete strength. Both the strength development rate and the ultimate strength, which are important to the construction engineer, are controlled by the kinetics of hydration reaction of compounds of portland cement and mineralogical phases of the admixture. This is because strength development is a function of the pore-filling process which takes place with the formation of hydration products. Therefore, subject to variations in the mineralogical composition and particle characteristics of the mineral admixture, composition of the portland cement, curing temperature and humidity, and concrete mix proportions, the following general observations can be made in regard to the effect of mineral admixtures on: (i) rate of strength development, and (ii) ultimate strength of concrete.

(i) With highly active pozzolans, such as rice husk ash and condensed silica fume, the pozzolanic reaction may start as soon as calcium and hydroxyl ions are available from the hydration of portland cement compounds. In the presence of rice husk ash with the high internal porosity of its particles, significant effects of the pozzolanic reaction on the mechanical properties of mortars and concretes were observed by the writer at all ages, even at 1-day after hydration at 20°C. In the case of condensed silica fume, Sellevold et al (28) found considerable pozzolanic reaction and improvements in properties associated with it during 2 to 14 days curing at 20°C.

For a typical low-calcium fly ash, Owens and Butler (42) reported that the pozzolanic reaction commenced at 11 days after hydration at 20°C, and significant effect of the reaction on crushing strength was noticed in the 28-day test. Similarly the low calcium fly ashes used by Diamond and Lopez-Flores (34), at 30 percent cement replacement by weight showed no contribution to the strength of ASTM C 109 mortars tested at 1, 3, and 7 days. However, thereafter significant contribution of the pozzolanic reaction was observed to the 28-day strength; by 90 days the strengths of the cement-fly ash mortars were of the same order as the reference portland cement. As expected, with high-calcium fly ashes the authors found significant contribution to strength at 3 days, and strengths similar to those of the reference mortar at 7 days.

In conclusion, whereas the highly active pozzolans start their contribution to strength almost from the beginning of portland cement hydration, the low-calcium fly ash does not show large enough pozzolanic activity to affect strength until about two weeks after hydration; the high-calcium fly ash may start its cementitious and pozzolanic activity as early as 3 days after hydration. It seems that availability of hydroxyl, sulfate and calcium ions in the surrounding solution triggers the hydration of high-calcium fly ash relatively quickly, and the process is self-sustaining due to the supply of these ions from the hydration of fly ash itself.

In regard to ground granulated blast furnace slag, cementitious and pozzolanic behavior is essentially similar to high-calcium fly ashes. At 40, 50, or 65 percent cement replacement by weight, Hogan and Meusel (6) found that generally through 3 days of age, strength contribution of slag to ASTM C 109 mortars was low, however strengths similar to the reference portland cement were achieved at 7 days, and higher strengths thereafter. From the standpoint of contribution to strength, the relative rates of reactivity of various byproduct mineral admixtures in the presence of portland cement and moisture are illustrated in Fig. 9. It is worth pointing out here that blending low-calcium fly ash with silica as suggested by Mehta and Gjorv (43) or a high-calcium fly ash or granulated blast furnace slag offers an interesting approach for reducing the early strength loss resulting from cement replacement by a low-calcium fly ash alone.

(ii) The ultimate compressive strength of products containing mineral admixtures depends on cement content, water-to-(cement + admixture) ratio, and degree of hydration. It is well known that plain portland cement mortars or concretes, even at very high cement content (1000 lb/yd^3 or 600 kg/m^3) do not show more than about 50 MPa ultimate strength. This maybe because the presence of large amounts of crystalline calcium hydroxide within the bulk hydrated cement paste, and at the aggregate-cement paste transition phase, creates zones of weakness. The pozzolanic reactions associated with the mineral admixtures in concrete are able to consume calcium hydroxide and thereby strengthen the material, principally through pore refinement during the early stage of hydration and later by improving the strength of the transition phase.

According to Berry and Malhotra (2), high-strength concrete mixtures containing 850 lbs/yd^3 portland cement, 100 lbs/yd^3 low-calcium fly ash (ASTM Type F), and a water-reducing agent (ratio of water-to-cementitious material = 0.33) developed for use in the Water Tower Place and River Plaza in Chicago, showed about 70 MPa compressive strengths at 50 days. For application in Texas, similar strengths were obtained by Cook (33) from concrete mixtures containing only 667 lbs/yd^3 (400 kg/m^3) portland cement, 167 lbs/yd^3 (100 kg/m^3) high-calcium fly ash (ASTM Type C) and a water-reducing admixture (ratio of water-to-cementitious material = 0.33).

Hogan and Meusel (6) reported that cements containing 40 or 50 percent granulated blast furnace slag of $608 \text{ m}^2/\text{kg}$ Blaine surface area gave about 60 MPa compressive strength at 60 days in ASTM C 109 mortars whereas, at the same age, the reference mortar had only 47 MPa compressive strength. At a water-to-(slag + cement) ratio of 0.38, concretes made with cements containing 40 or 50 percent slag gave about 55 MPa strength at 28 days, when compared to 48 MPa for the reference concrete. The striking similarity in behavior between granulated blast furnace slag and high-calcium

fly ash is again demonstrated by the data of Dodson and Roberts (32) which show that a high-calcium fly ash replacing 70 percent cement by weight when incorporated into concrete at 0.3 water-to-(cement + ash) ratio gave 53 MPa compressive strength at 90 days.

In regard to rice husk ash, the writer (8) found that 30 percent cement replacement by rice husk ash gave 40 percent strength increase over the control mortars at ages 3, 7, and 28 days in ASTM C 109 test. The 90-day strength of rice husk ash cement mortars was 63 MPa, when compared to 47 MPa for the control portland cement. It should be noted that no water-reducing agent was used in this test. In a concrete containing the same proportion of rice husk ash and a water-reducing agent about 80 MPa compressive strength was achieved at one year (ratio of water to cement + ash = 0.4). Similar results are reported from the use of condensed silica fume in concrete mixtures. Many researchers have claimed that the silica fume addition to concrete yields an efficiency factor of 3 to 4, which means that within certain limits of cement replacement 1 pound of silica fume can replace 3 to 4 pounds of portland cement at a given compressive strength. Using special aggregates of controlled particle size distribution and a high range water-reducing agent, Bache (44) was able to produce concretes with less than 0.2 water-to-(cement + silica fume) ratio which gave over 200 MPa compressive strengths after curing.

Modulus of Elasticity, Creep, and Drying Shrinkage

Although individual studies have shown contradicting data, there is general agreement that modulus of elasticity, creep and drying shrinkage characteristics of concrete are greatly influenced by strength of concrete and stiffness of the aggregate. For instance, Lane and Best (5) found that compared with plain concrete, the compressive strength and modulus of elasticity of fly ash concrete were lower at early ages but slightly higher at 90 days. Since creep is influenced by compressive strength and modulus of elasticity of concrete, higher creep strains were found in fly ash concrete at early age loading when strength was low; however the rate of creep decreased at later ages. In general up to 25 percent cement replacement showed no significant difference in creep for up to 100 days; beyond this age concrete containing fly ash produced less creep.

In regard to drying shrinkage Lane and Best (5) quoted a TVA study which showed that the drying shrinkage of plain and fly ash concrete prisms was essentially the same after 400 days. Earlier Davis et al (1) arrived at a similar conclusion. They found for concrete masses of ordinary thickness, such as highway slabs and walls and frames of buildings, the drying shrinkage at the exposed surfaces of fly ash concretes, as compared to that of plain concrete was similar up to the age of one year and somewhat lower for the fly ash concretes. At a short distance from the exposed surface, the drying shrinkage of the fly ash concretes was substantially less.

Hogan and Meusel (6) found that concrete containing 40, 50, or 65 percent blast furnace slag by weight of total cementitious material exhibited somewhat greater drying shrinkage than plain portland cement concrete. However, research in Japan has shown that this can be remedied by correcting the optimum sulfate content of the total cementitious material. For highest strength and lowest drying shrinkage, most portland cement-slag combinations were found to require 2 to 2.5 percent SO_3 content. Not much data are available on creep and drying shrinkage properties of concretes containing condensed silica fume and rice husks ash; however, due to their ability to contribute high early strength, they are likely to reduce rather than increase the drying shrinkage and creep. Carette and Malhotra (21) reported that up to 84 days of test period the drying shrinkage of concretes containing 5, 10, 15, and 20% silica fume by weight of portland cement was less than the control concrete.

ECOLOGICAL, ECONOMIC, AND ENERGY CONSIDERATIONS

Ecological problems associated with the current disposal practices of the industrial byproducts discussed in this report are well known. For instance, stockpiling on land causes air pollution, whereas dumping into ponds or streams would release toxic metals which are usually present in small amounts. Tashiro and Oba (45) have shown that many toxic metal ions can be chemically bonded in the calcium aluminate and sulfoaluminate hydrates in concrete.

In regard to energy savings, the manufacture of 1 ton of portland cement in the United States requires fossil fuel input of the order of 7.4 million Btu (48). Since fly ash, condensed silica fume, and rice husk ash normally do not need additional energy input before use, it is clear that the energy saving from cement replacement by such admixtures in concrete will be in direct proportion to the amount used. Blast furnace slag needs to be dried and ground before use. Spellman (46) has estimated that the total energy input for this purpose is about 1/5 of that required for portland cement production, thus offering a substantial potential for energy savings. Using bleeded cements containing portland cement, plaster of Paris, and large proportions of fly ash, rice husk ash, or condensed silica fume, the writer (47) showed that up to 75 percent energy in cement production can be saved, while the strength and water-resisting qualities of the products remain suitable for many applications in the construction industry.

Several authors including Lane and Best (5) have convincingly demonstrated the economic benefits from use of fly ash as a mineral admixture in concrete. For instance, for 94,000 yd³ (72,000 m³) of concrete placed at Normandy Dam, 10,000 tons of fly ash were required, resulting in a cement reduction of 6600 tons and a

cost saving of \$225,000. Again according to the authors, at the Watts Bar Nuclear Plant scheduled for completion in 1984, an estimated 320,000 yd³ of structural and mass concrete containing fly ash would require \$825,000 less cost, since about \$1.75/yd³ for structural concrete and \$2.0/yd³ for mass concrete will be saved by the use of fly ash.

Given the potential engineering benefits from the use of many industrial byproducts as supplementary materials in cement and concrete in addition to ecological, economic, and energy benefits pointed out by numerous authors including the writer (48), it is surprising that the U.S. cement and concrete industry shows no visible signs of making rapid progress toward utilization of available quantities of these byproducts. For certain materials such as fly ash there is some concern about variability and quality control of the material. However similar problems have existed in the cement manufacturing process which are resolved satisfactorily by proper blending or homogenization of materials. Problems of specifications and accelerated tests for evaluating the suitability of mineral admixtures for use in concrete are difficult but not insurmountable. This is proven by the approach taken by fly ash marketing agencies in the United Kingdom and some other countries (49).

CONCLUDING REMARKS

1. Ecological, economic, energy, and engineering considerations require that the use of those industrial byproducts which are pozzolanic and cementitious should be increased in the cement and concrete industry. Both as cement additions and as mineral admixtures, the use of granulated blast furnace slag and low-calcium fly ash is widely practiced by many countries outside the U.S. Due to historic reasons, the science and technology associated with these materials have developed along separate lines. However, with the advent of many additional byproducts, such as high-calcium fly ash, rice husk ash, condensed silica fume, and granulated non-ferrous slags, there is a need to treat the entire subject as a unified discipline. A review of the mineralogical composition of these materials and their reactions in the presence of portland cement and water shows that this is not only possible but highly desirable.

2. The engineering benefits from the use of mineral admixtures in concrete result partly from their granulometric characteristics, such as particle size and texture, and partly from the pozzolanic and cementitious reactions. The latter cannot be taken for granted because curing conditions (for instance, environmental humidity and temperature) and concentration of ions in the surrounding medium play a very important role in the hydration of mineral admixtures.

3. The slower hydration characteristic of most mineral admixtures, when compared to portland cement, requires that the user should pay special attention to concrete curing temperature and humidity. He should also be cautioned that in general mineral admixtures tend to slow down the time of set and rate of strength development at early age. Some of the problems can easily be solved by proper mix proportioning (increase of cement content or addition of some highly pozzolanic material) and application of water-reducing or set-accelerating admixtures. Similarly, due to the high surface area of mineral admixtures (especially in the presence of cellular carbon particles), more air-entraining agent may be needed for proper air-entrainment in a concrete which needs to be protected against frost action.

4. Since it is the mineralogical composition, and not the chemical composition, which would govern the pozzolanic and cementitious behavior of a mineral admixture, classifications and specifications emphasizing the chemical composition are more of a hindrance than help in promoting the use of mineral admixtures in cement and concrete industries. New classifications, specifications, and accelerated tests such as the one reported by the writer (50) that are capable of relating the desired performance criteria to the microstructure of the hydrated cement paste containing the admixture are urgently needed.

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TABLE 1. Analytical Oxide Content of Typical Portland
Cement and Industrial Byproducts

Oxide Analysis [*] , %	S	A	F	C	M	$\bar{S}$	LOI ^{**}
Portland Cement:	22	6	3	63	3	2	1
<u>Ash from the Combustion of:</u>							
Anthracite or Bituminous Coals	48	28	9	4	2	1	5
Lignite or Subbituminous Coals	38	22	4	24	5	3	1
Rice Husks (Uncontrolled Temperature)	96	-	-	-	-	-	1
Rice Husks (Mehta-Pitt Furnace)	85	-	-	-	-	-	12
<u>Condensed Silica Fume from:</u>							
Metallic Silicon Furnace	94	-	1	-	-	-	3
Ferrosilicon Alloy Furnace	90	-	2	1	1	-	4
<u>Slag from Metallurgical Furnaces:</u>							
Iron Blast Furnace	36	9	1	40	11	-	-
Steel (Open Hearth)	33	7	10	37	10	-	-
Copper	35	3	52	2	1	-	-
Nickel	38	6	50	3	3	-	-
Lead	22	8	40	17	2	-	-

* Abbreviations used by cement chemists are as follows:

$\text{SiO}_2 = \text{S}$; $\text{Al}_2\text{O}_3 = \text{A}$; $\text{Fe}_2\text{O}_3 = \text{F}$; $\text{CaO} = \text{C}$; $\text{MgO} = \text{M}$; $\text{SO}_3 = \bar{\text{S}}$;
 $\text{H}_2\text{O} = \text{H}$; Loss of ignition = LOI.

** In portland cement, LOI is generally due to combined water in gypsum. In industrial byproducts, it is generally due to the presence of carbonaceous matter.

TABLE 2. Classification, Composition, and Particle Characteristics
of Cementitious and Pozzolanic Byproducts for Concrete

Classification	Chemical and Mineralogical Composition	Particle Characteristics
I. Cementitious and Pozzolanic		
Granulated Blast Furnace Slag:	Mostly silicate glass containing mainly calcium, magnesium, aluminum, and silica. Crystalline compounds of melilite group may be present in small quantity.	Unprocessed material is of sand size and contains 10 to 15% moisture. Before use it is dried and ground to particles less than 45 μm (usually about 500 m^2/kg Blaine). Particles have rough texture.
High-calcium fly ash:	Mostly silicate glass containing mainly calcium, magnesium, aluminum, and alkalis. The small quantity of crystalline matter present generally consists of quartz and C_3A ; free lime and periclase may be present; C_2S and $\text{C}_4\text{A}_3\text{S}$ may be present in the case of high-sulfur coals. Unburnt carbon is usually less than 2%.	Powder corresponding to 10-15% particles larger than 45 μm (usually 300-400 m^2/kg Blaine). Most particles are solid spheres of less than 20 μm diameter. Particle surface is generally smooth but not as clean as in low-calcium fly ashes.
II. Highly Active Pozzolans		
Condensed Silica Fume:	Consists essentially of pure silica in noncrystalline form.	Extremely fine powder consisting of solid spheres of 0.1 μm average diameter (about 20 m^2/g surface area by nitrogen adsorption).
Rice Husk Ash: (Mehta-Pitt process)	Consists essentially of pure silica in noncrystalline form.	Particles are generally less than 45 μm but they are highly cellular (about 60 m^2/g surface area by nitrogen adsorption).
III. Normal Pozzolans		
Low-calcium Fly Ash:	Mostly silicate glass containing aluminum, iron, and alkalis. The small quantity of crystalline matter present consists generally of quartz, mullite, sillimanite, hematite, and magnetite. Unburnt carbon is usually less than 5%, but may be as high as 10%.	Powder corresponding to 15-30% particles larger than 45 μm (usually 200-300 m^2/kg Blaine). Most particles are solid spheres of average 20 μm diameter. Cenospheres and plerospheres may also be present. Particles have a smooth texture.
IV. Weak Pozzolans		
Slowly-cooled blast furnace slag, bottom ash, boiler slag, field-burnt rice husk ash.	Consists essentially of crystalline silicate minerals, and only a small amount of noncrystalline matter.	The materials must be pulverized to very fine particle size in order to develop some pozzolanic activity. Ground particles are rough in texture.

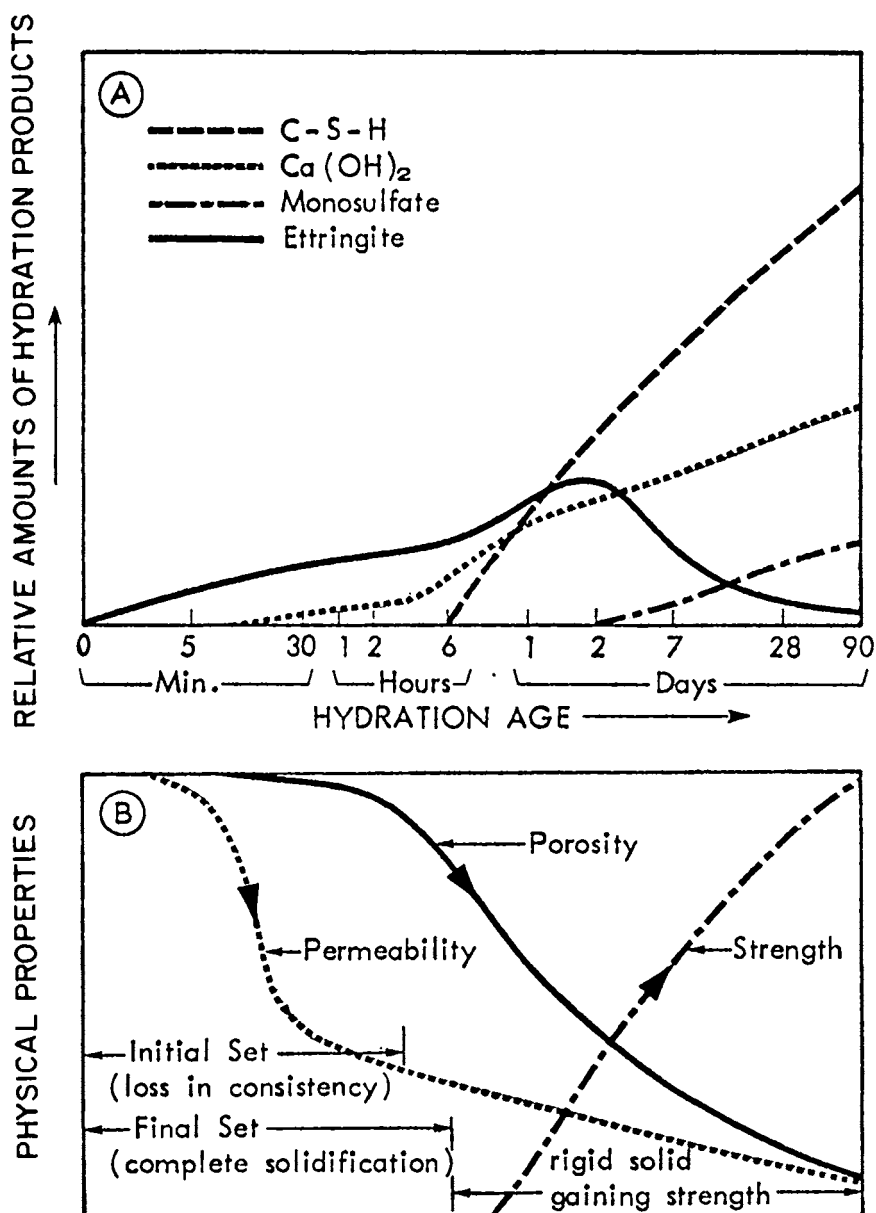


Fig. 1--Changes in a portland cement paste with hydration

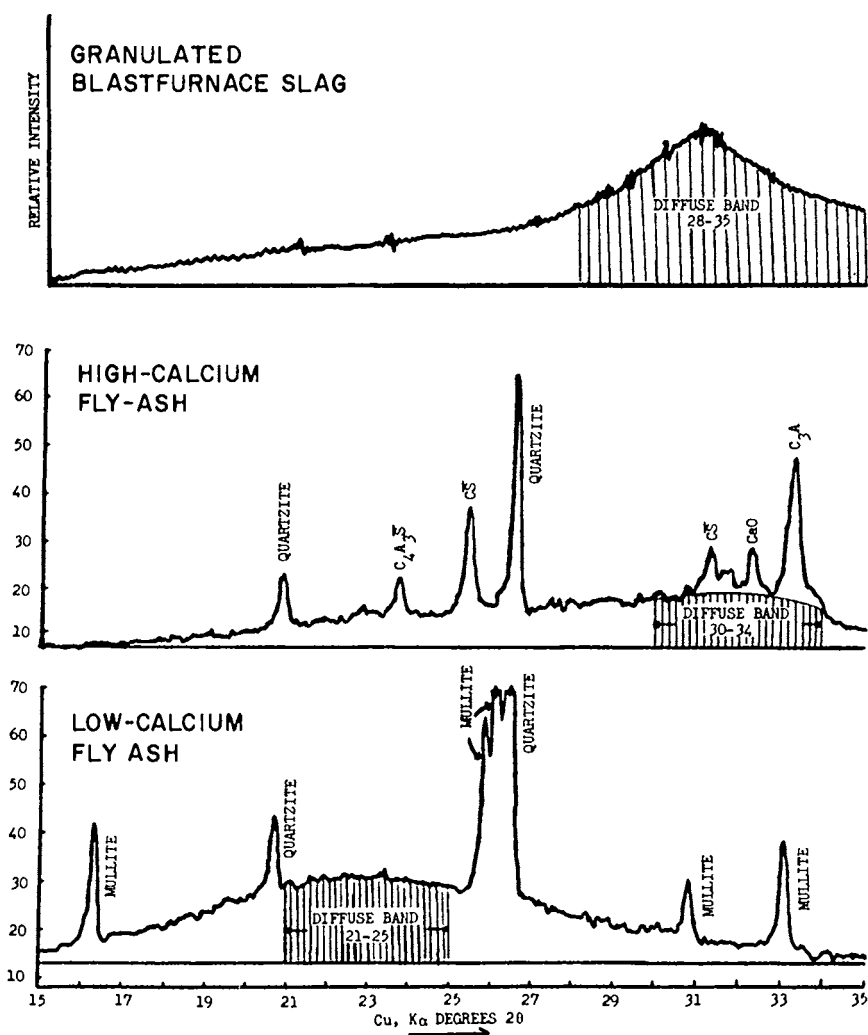


Fig. 2--X-ray diffraction patterns of fly ashes and granulated blast furnace slag

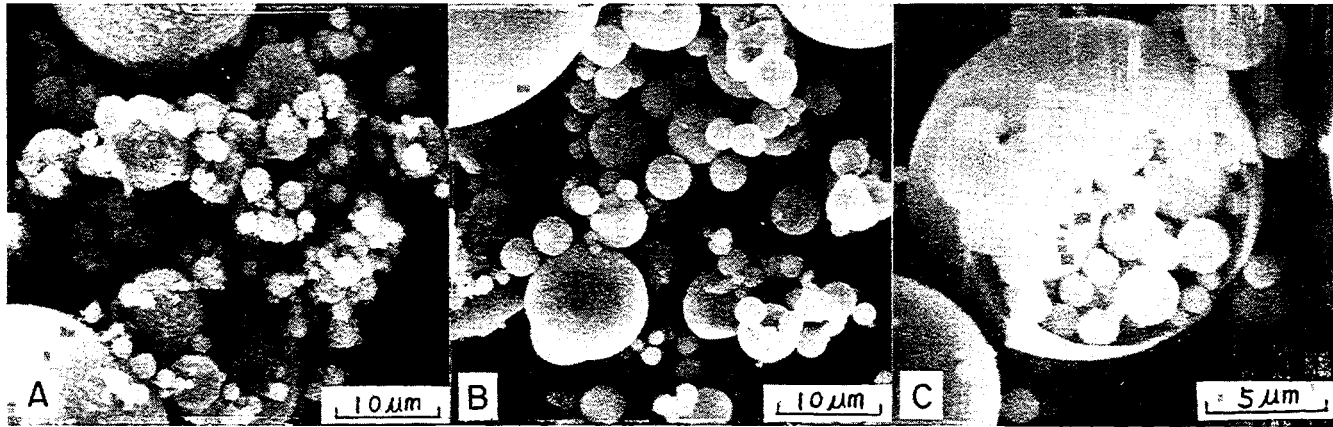


Fig. 3--Scanning electron micrographs of a: (A) low-calcium fly ash, (B) high-calcium fly ash; (C) broken plerosphere in a low-calcium fly ash

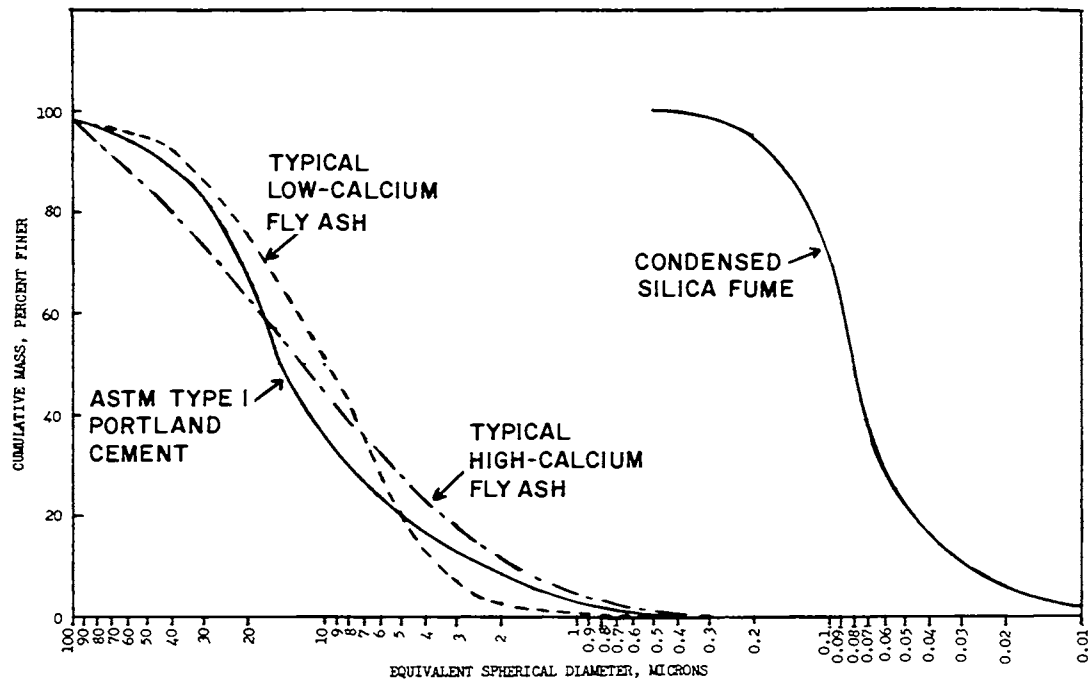


Fig. 4--Particle size distribution of typical materials

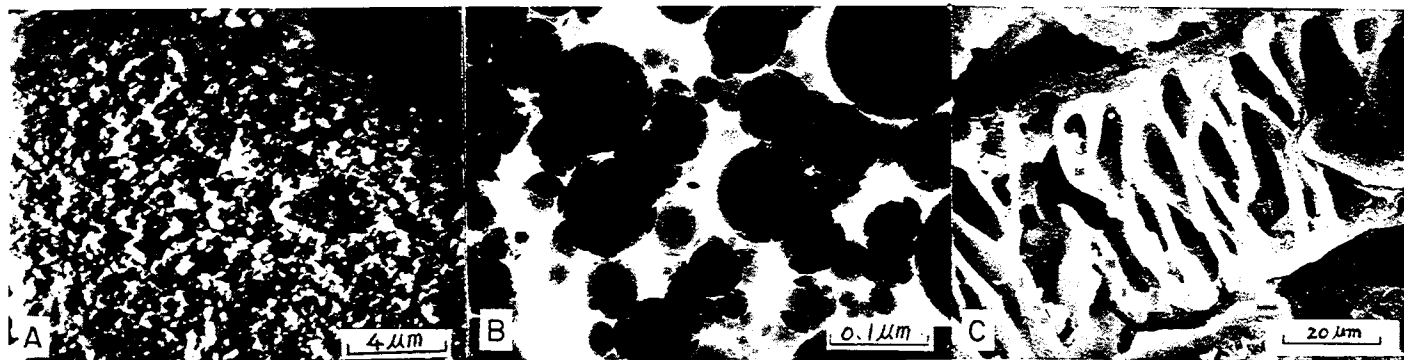


Fig. 5--Scanning electron micrographs of: (A) condensed silica fume, (B) condensed silica fume at high magnification (courtesy of P. Aitcin, Univ. of Sherbrooke, Canada), (C) rice husk ash

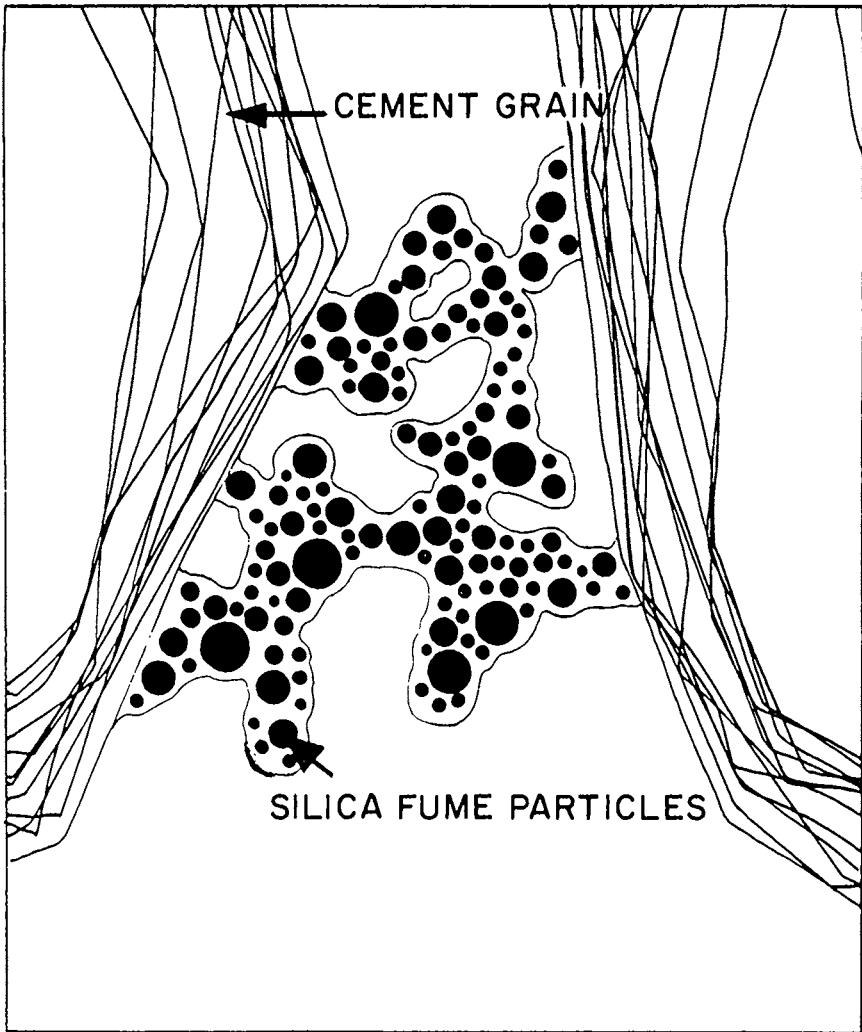
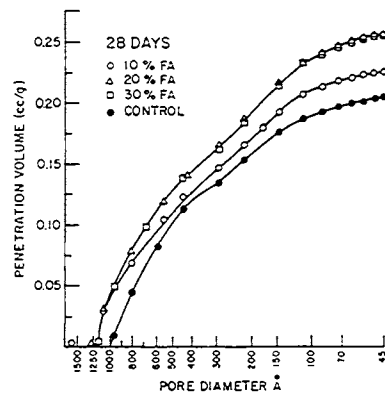
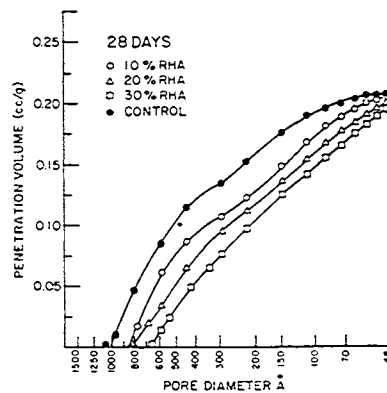


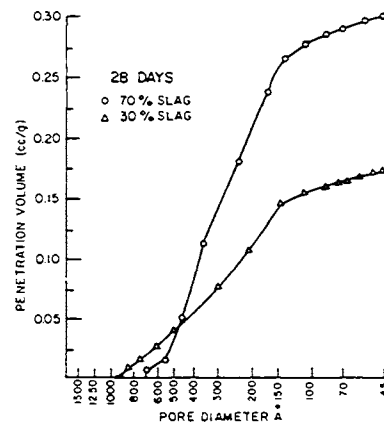
Fig. 6--Mechanism of bleeding reduction in cement paste by silica fume addition (Courtesy of L. Hjørth, Aalborg Cement Co., Denmark)



FLY ASH



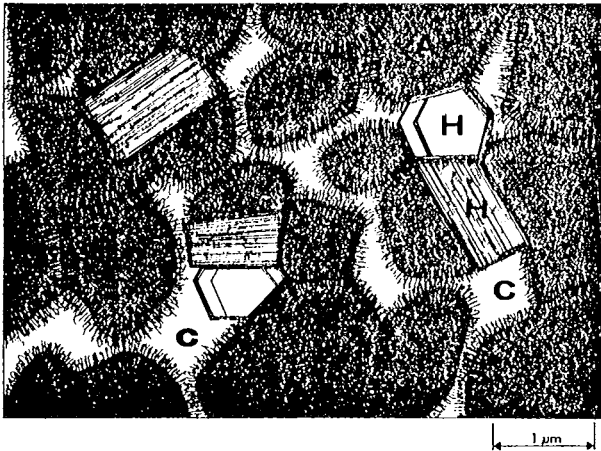
RICE HUSK ASH



SLAG

Fig. 7--Effect of fly ash, rice husk ash or slag additions on pore size distribution of hydrated cement pastes

PORTLAND

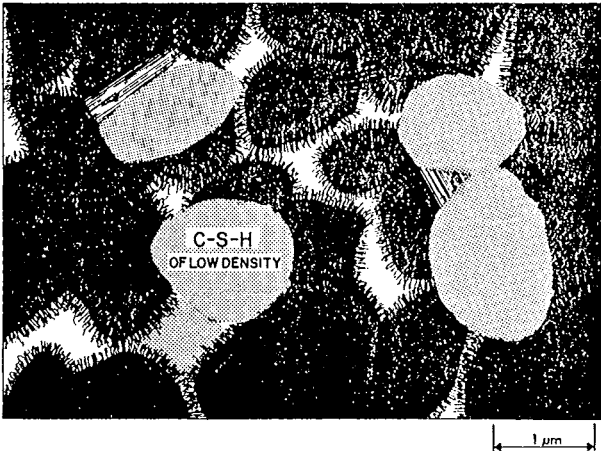


A represents aggregation of poorly crystalline C-S-H particles which have at least one colloidal dimension (1 to 100nm). Inter-particle spacing within an aggregation is 0.5 to 3.0nm (avg. 1.5nm).

H represents hexagonal crystalline products such as CH , $\text{C}_4\text{A}\cdot\text{H}_{10}$, C_4AH_{13} . They form large crystals, typically 1μm wide.

C represents capillary cavities or voids which exist when the spaces originally occupied with water do not get completely filled with the hydration products of cement. The size of capillary voids ranges from 10nm to 1μm, but in well-hydrated, low water-cement ratio pastes, they are <100nm.

PORTLAND POZZOLAN



$\text{CH} + \text{S} \rightarrow \text{C-S-H of low density}$
Pozzolanic reaction converts the denser CH phase and larger pores in to less dense C-S-H and smaller pores.

Fig. 8--Model of well-hydrated pastes of portland or portland-pozzolan cement

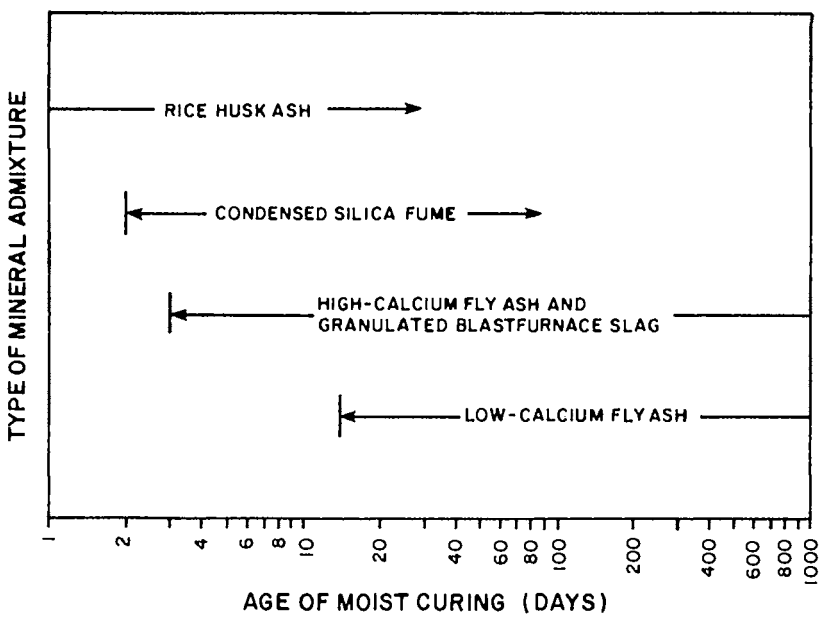


Fig. 9--Effective period of strength contribution from various mineral admixtures

Twenty-Five Years' Experience Using Fly Ash in Concrete

By Joseph F. Lamond

Synopsis: The U.S. Army Corps of Engineers has used fly ash as a material that partially replaces portland cement in concrete for twenty-five years. Initially research was performed on use of fly on concrete properties for bleeding, permeability, heat rise, resistance to freezing and thawing, elasticity, and compressive and flexural strength development. Those properties affected by partial replacement of portland cement with fly ash were heat rise in mass concrete, resistance to freezing and thawing and strength development. The concrete materials properties of three massive concrete gravity dams are reported. Since construction, these dams have been periodically inspected. Although these structures have some minor cracking, spalling, and erosion, their performance has been similar to other concrete gravity dams constructed using concrete without fly ash. Cost savings per cubic yard of concrete has been the benefit derived from using fly ash as a partial cement replacement material in massive concrete structures. Fly ash is specified to conform to ASTM C618, Class C or Class F with modifications to this specification as needed based on location or type of structure. Fly ash may replace portland cement up to 35 percent by absolute volume in interior mass concrete and 25 percent by absolute volume in exterior mass concrete and in structural concrete. Fly ash concrete has performed satisfactorily on Corps of Engineers projects over the last twenty-five years.

Keywords: bleeding (concrete); compressive strength; concrete durability; flexural strength; fly ash; freeze-thaw durability; fresh concrete; hardened concrete; gravity dams; mix proportioning; permeability; pozzolans; temperature rise (in concrete); water content; workability.

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INTRODUCTION

In 1958 fly ash was first used in concrete construction in Sutton Dam by the U.S. Army Corps of Engineers. This project was part of the Corps Civil Works program and, since that time, fly ash has been used in approximately 50 projects. The Corps Military program used fly ash concrete for rehabilitation of the U.S. Army Base wharf in Boston, Massachusetts in the 1950's but it has not been used on many other military projects.

An investigation of pozzolan as a cement replacement material was performed by the U.S. Army Waterways Experiment Station. This investigation, authorized by the Office Chief of Engineers, started in 1950 and was completed in 1966. This investigation was directed toward large size aggregate concrete used in massive structures. The investigation studied the properties of both fresh and hardened concrete. Acceptance testing procedures for fly ash were standardized during this investigation.

The Office Chief of Engineers authorized a study on the use of fly ash concrete in airfield pavement at the U.S. Army Corps of Engineers, Rigid Pavement Laboratory, in 1956.

Field experience on three Corps of Engineers Civil Works projects was reported by Waugh in American Concrete Institute SP-6(1). Economy was the major benefit derived from the use of

fly ash as a cement replacement material. The fly ash concrete usually required less water and more air-entraining admixture per cubic yard than similar concrete made without fly ash. With equal slump fly ash concrete was reported to be more workable. Periodically the three projects reported by Vaugh (1) have been inspected. The twenty-five year performance of fly ash concrete is satisfactory.

The original design guidance on use of fly ash has changed little over the twenty five years since the Corps first adopted its use. The term "cement replacement material" was first used in 1953 design guidance to describe fly ash and other mineral admixtures. The present design guidance defines fly ash as either Class F or Class C pozzolan conforming to ASTM C618(2).

LABORATORY INVESTIGATIONS

In 1950 an investigation was authorized to study materials that could be used in concrete to replace a portion of portland cement. This investigation was performed by the U.S. Army Waterways Experiment Station in Vicksburg, Mississippi. Five types of portland cement were investigated in combination with sixteen cement replacement materials. Fly ashes from four different sources were among the sixteen replacement materials. Among the properties that were studied were bleeding, permeability, heat rise, resistance to freezing and thawing, elasticity, compressive strength to an age of ten years and flexural strength. Sixteen reports were published between April 1955 and November 1967 (3-17).

In 1966 another investigation was authorized to study use of fly ash in airfield pavements. This investigation was performed by the U.S. Army Corps of Engineers, Rigid Pavements Laboratory,

Cincinnati, Ohio. A report (18) published in January 1960, investigated three sources of fly ash in combination with one type of portland cement. Among the properties studied were flexural strength and resistance to freezing and thawing. The physical and chemical properties of the fly ashes used in the two investigations are shown in Table 1. The fly ash sources designated I and V are from Illinois, II and VII from Michigan, III from Pennsylvania, IV from Maryland and VI from Kentucky.

EFFECTS OF FLY ASH ON PROPERTIES OF FRESH CONCRETE

For each investigation fine and coarse aggregates were from one source. The slump and air contents were controlled to very close limits. The workability of the mass concrete study was controlled by a remolding test. The remolding test determined the mechanical effort required to remold samples of freshly mixed concrete from a molded form of a frustum of a cone to a cylindrical disk. This method is CRD-C6 (19).

The water requirements per cubic yard of concrete were usually reduced when fly ash replaced cement. This amount of reduction varied with each source of fly ash. Essentially no reduction was experienced with two fly ash sources. Factors influencing water requirements are discussed in ACI 212.2R (21).

The air content of freshly mixed concrete was maintained at 6.0 ± 0.5 percent. As the percentage of fly ash increased in the mixture, the amount of air-entraining admixture had to be increased to maintain the air content. The quantity of air-entraining admixture needed when the percentage of fly ash remained constant varied considerably for different sources of fly ash. Factors influencing air-entraining admixture requirements are discussed in ACI 212.2R (21).

