Pozzolanic 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 concete 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 pozzolanic 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.

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INTRODUCTION

Power plants using coal or rice husks as fuel, and metallur-
gical 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 in-
stances used for low-value applications such as landfills, aggre-
gates for concrete, and sub-base construction. There is currently
great interest in exploiting the pozzolanic and cementitious prop-
erties 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 port-
land cement sells at about 60 to 80 U.S. dollars a ton and is pro-
duced at the expense of substantial amounts of energy, a partial
substitution of portland cement by these byproducts which are gen-
erally available at substantially lower prices would clearly rep-
resent 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 re-
place fine aggregate rather than cement.

Countries such as France, Germany, Italy, Japan, the Nether-
lands, and U.S.S.R. have had a longer history of interest in con-
servation 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 mate-
rials 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 con-
crete.

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 impor-
tant 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 ex-
planations for some of the phenomenological observations. This is
needed for a clear understanding of the performance of these mate-
rials and to encourage their proper use by cement and concrete in-
dustries.

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 par-
ticle characteristics of major industrial byproducts suitable for
use as admixtures in portland cement concrete are reviewed, es-
pecially in regard to relationships between physical-mineralogical
properties of admixtures and performance characteristics of con-
crete. The latter include water demand, consistency, bleeding,
workability, setting time, air entrainment, and temperature rise
in fresh concrete; and strength, modulus of elasticity, creep, dry-
ing shrinkage, durability to sulfate attack, alkali-silica reac-
tion, 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 ce-
ment 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,
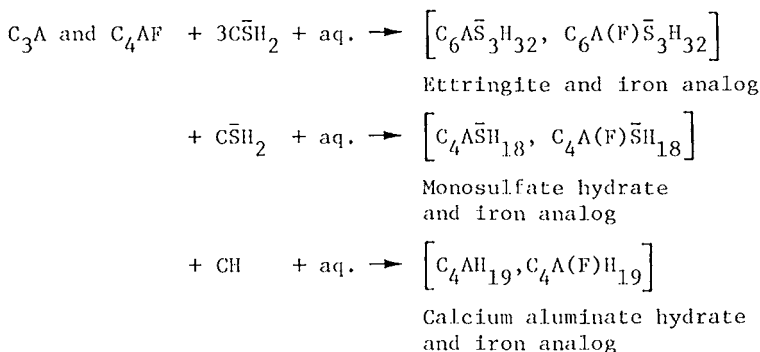and sulfate. Typically, the approximate composition and amounts

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.
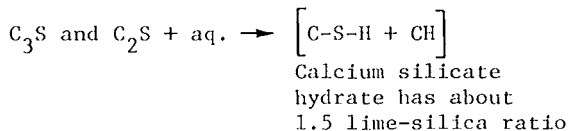
When water is added to portland cement the minerals begin to ionize, and the ionic species form hydrated products of low solubility which precipitate out of the solution. Due to the lower density of the hydration products as compared to the anhydrous minerals, the formation and deposition of these hydration 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

$$C_3A \text{ and } C_4AF + 3C\bar{S}H_2 + aq. \rightarrow \left[C_6A\bar{S}_3H_{32}, \ C_6A(F)\bar{S}_3H_{32} \right]$$

Ettringite and iron analog

$$+ C\bar{S}H_2 + aq. \rightarrow \left[C_4A\bar{S}H_{18}, \ C_4A(F)\bar{S}H_{18} \right]$$

Monosulfate hydrate
and iron analog

$$+ CH + aq. \rightarrow \left[C_4AH_{19}, C_4A(F)H_{19} \right]$$

Calcium aluminate hydrate
and iron analog

Hydration Reactions of Calcium Silicates in Portland Cement

$$C_3S \text{ and } C_2S + aq. \rightarrow \left[C-S-H + CH \right]$$

Calcium silicate
hydrate has about
1.5 lime-silica ratio

The trisulfate hydrate ($C_6A\bar{S}_3H_{32}$), popularly 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 $(C_4A\bar{S}H_{18})$ 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 soluable 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.

Pozzolanic 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 pozzolanic 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 ($SiO_2 \cdot Al_2O_3$), and mullite ($3SiO_2 \cdot 2Al_2O_3$) 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 βC_2S) 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 βC_2S 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 βC_2S 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 $CaO-SiO_2-Al_2O_3-Fe_2O_3-SO_3-H_2O$), 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 pro-
duced during the dehusking operation of paddy rice. Since they are
bulky, the husks present an enormous disposal problem for central-
ized 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 in-
dustrial furnaces which use husks as fuel consists mainly of crys-
talline 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 fil-
tering 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 m^2/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 m^2/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