PART I

Fly Ash Characterization

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Gregory J. McCarthy and Robert J. Lauf
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CHARACTERIZATION OF FLY ASH AND ITS REACTIONS IN CONCRETE

DELLA M. ROY*, KAREN LUKE**, AND SIDNEY DIAMOND***
*Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA
**Department of Chemistry, University of Aberdeen, Old Aberdeen AB9 2UE, Scotland
***School of Civil Engineering, Purdue University, Lafayette, IN 47906, USA

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ABSTRACT

Fly ashes are currently being produced that are much more widely different from each other in composition and other characteristics than had been previously experienced, owing to the widespread use of low rank subbituminous and lignitic coals. The current ASTM classifications into Class F and Class C pozzolan categories are not adequate to describe all their important properties. Current characterization methods are reviewed, including physical characterization by particle size distribution, shape, apparent specific gravity, content of hollow grains and of residual coal fragments, etc., chemical procedures of various kinds, and SEM, EDXA, XRD, and other methods for the determination of mineralogical content and glass character. Etching and chemical dissolution procedures are particularly important. The state of these various methods, current results of their use in fly ash characterizations, and the relations of these to reactivity and performance of fly ashes in cement and concrete are discussed.

INTRODUCTION

Fly ash is a material whose characteristics reflect its origin from incombustible mineral matter in powdered coal burned in large electrical power plant boilers. Because of extensive variability both in the coals and in the operation of the boilers and collection of the fly ash, fly ashes differ from each other in important characteristics. Moreover, the chemical composition and other characteristics of different fly ash particles in a given ash may be extremely different from each other, reflecting the particular bits of mineral matter giving rise to that particle. These complications render the appropriate characterization of fly ashes for use in concrete and elsewhere difficult and intricate [1a].

By definition, all particles of fly ash are 'fine'--at least fine enough to have been swept along in the air stream and delivered to the electrostatic precipitator or baghouse collection system. Actual sizes may vary from several hundred micrometers to several tenths of a micrometer.

The particles are primarily spherical, although incompletely rounded spheres, rough, vacuole-containing massy agglomerates, and unburned coal fragments are also found. The spheres are primarily solid, although hollow spheres occur to a small extent in many fly ashes. The spheres are mostly glassy, although crystals are usually found within them, and deposits of crystalline powders of several kinds on the spherical surfaces are not infrequently found.

The relative proportions of spherical and other particles, the size distributions, the kind of crystals present, the nature of the glass, the type of surface deposit, if any, the nature and proportion of unburned coal, and many other parameters vary among different fly ashes. These variations, and accompanying variations in overall chemical composition result in

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variations in behavior when fly ash is used in concrete, and in other uses as well.

Use of fly ash as a cementitious substitute or mineral admixture in concrete is a major application of the material, although only about 6% of the total produced in the U.S. is currently used in the concrete industry [1b]. A major factor limiting more extensive use is the intrinsic variability of the material, coupled with the complexity of its characterization. Characterization and specification methods currently prescribed are generally not adequate to insure optimum selection of fly ash for use in concrete, nor to insure adequate quality control on a continuing basis.

The purpose of the present paper is to review the current status of fly ash characterization, especially with regard to parameters that may influence behavior and suitability of fly ash for use in concrete, specifically:

Methodologies for characterization,
Morphology, composition, and mineralogy,
Chemical composition and physical properties,
Classification, and
Reactions with cement and concrete components.

Table I. Methodology for Characterization.

Chemical

Chemical Analysis - Bulk (including LOI)
Available Alkalies

Physical

Pozzolanic Reactivity - Lime (7 days)
Cement (28 days)
Specific Gravity
Autoclave Expansion
Fineness
- Sieve %
- Blaine
- BET (N_2)
- Sedigraph (Liquid), Coulter
- SEM

Other

Mineralogical Analysis - (Qualitative, Quantitative)
- X-ray Diffraction Phase Analysis
- Microscopic (Optical and Scanning [SEM])
- TEM (rarely)

IR, Raman Spectroscopy
SEM, EDS - Morphology/Chemistry
Selective Dissolution
Soluble Components

METHODOLOGIES FOR CHARACTERIZATION

Insight into the behavior of fly ash in concrete can be achieved most suitably by a broad, multi-method approach to characterization, although not all methods are equally valuable. Table I contains a list of methodologies which may be important. The list includes the chemical and physical procedures specified in ASTM C 618 and C 311, but is certainly not limited to these relatively simple standard procedures. It is commonly found that the results of the standard procedures are by themselves inadequate to explain behavior, and in view of the complexity and variability of fly ashes this is not surprising. It is thus necessary to consider a significantly longer list of methodologies which may serve in due course as a source for upgrading standard procedures. The state of the art at this stage is probably not yet ready for the proposal of a new comprehensive characterization scheme, but this paper, along with others in the symposium, may help to provide the needed input.

Morphology, Composition, and Mineralogy

Spherical fly ash particles get their shape as a result of cooling and solidifying from molten droplets of inorganic coal residue. The surfaces are often quite smooth and 'glassy' in character, but in some ashes they tend to be rough and pebbly on a micro scale, and in others may be partly covered with a deposit of powder condensed from the vapor phase after the spheres have solidified (Fig. 1). The material deposited is often alkali sulfate [1] and as such it is readily soluble.

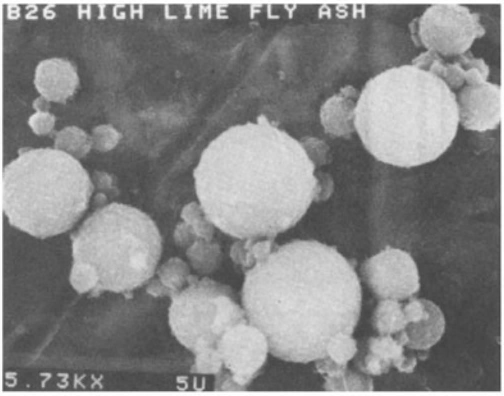

Fig. 1. High-Calcium Fly Ash Spherical Particles, Showing Adherence of Finer Particles to the Surface (bar = 5 μm) [2].

Some particles solidify around a trapped gas bubble and are thus hollow spheres, frequently thin-walled. Additionally, hollow spheres containing smaller incorporated fly ash spheres are found on occasion, with the incorporated spheres being mostly solid, but themselves occasionally hollow. Curiously, a third level of incorporated spheres can sometimes be seen within hollow spheres incorporated in larger hollow spheres, but these are rare.

Empty hollow spheres are usually called cenospheres; those containing included spheres, plerospheres. Factors involved in their formation are not as yet fully understood. Cenospheres can be readily segregated from other fly ash particles by flotation methods, and are used in several industrial applications.

Cenospheres and plerospheres are often recognized in scanning electron microscope (SEM) study of fly ashes by the fact that shells may be incomplete or broken in spots. Completely unbroken hollow spheres cannot be recognized as such, but may be detected in optical microscopy or if cut through in special mounting or sectioning procedures.

The hollow spheres are ordinarily completely glassy; solid spheres may be so, but usually contain incorporated crystals of various kinds embedded within the glass matrix.

The nature of the glass present in fly ashes is coming under serious study, since glass is usually the predominating phase, constituting about 60 to 90 percent of most fly ashes. It has been determined [1–7] that differences exist in the structure of the glass in low-calcium ('Class F') and in high-calcium ('Class C') fly ashes. Glasses give rise to an amorphous scattering 'hump' in x-ray diffraction, and the differences are reflected in the position of the maximum of this broad hump (Fig. 2). The glass structure of the low calcium fly ashes is of a siliceous type [2,5,6], and it is likely that the structure, suitably modified, can accommodate increasing CaO contents found in high-calcium fly ashes of up to perhaps 20% total CaO content (a significant proportion of which is incorporated in

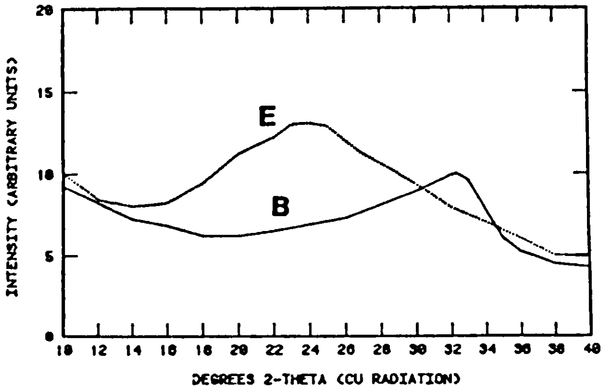

Fig. 2. Typical Traces of X-Ray Background Scattering 'Humps' for Fly Ash B (High Calcium) and Fly Ash E (Low Calcium), with the Crystalline Phase Subtracted [4].

crystalline components in most such fly ashes). Fly ashes with overall CaO contents above 20% likely will form glass with a calcium aluminate type structure, a melilite (= pyrosilicate, Si_2O_7 or $SiAlO_7$ structure) type silicate glass, or sometimes a mixture of glass types. Calcium aluminate glasses are believed to be more reactive in concrete.

Table II. Common Crystalline Phases in Class F Fly Ashes.

mullite	$Al_6Si_2O_{13}$
quartz	SiO_2
magnetite-ferrite	$Fe_3O_4-(Mg,Fe)(Fe,Mg)_2O_4$
hematite	Fe_2O_3
anhydrite	$CaSO_4$

In addition to the glass, there are a large number of crystalline phases present in most fly ashes. With few exceptions the individual crystalline phases occur only in small amounts, usually only a few percent at most of each type being present. As indicated in Table II, the common suite found in most low-calcium fly ashes and others as well includes —quartz, mullite, hematite, and magnetite (although the last-named phase is better described as a spinel). Anhydrite is found in some higher CaO content Class F fly ashes, and in many Class C fly ashes as well.

Many fly ashes contain alkali sulfates, ordinarily as surface deposits. The crystalline species present include potassium sulfate (α-K_2SO_4), sodium sulfate (thenardite), and mixed sulfates, principally aphthitalite [$(Na,K)_2SO_4$] and potassium-calcium sulfates.

A further group of crystalline components are calcium compounds primarily associated with high-calcium fly ashes, as listed in Table III [8] and Fig. 3. Several of these can become involved in various hydration reactions, so that they are of particular interest in concrete applications.

In many of these fly ashes a portion of the overall analytical CaO content is present as crystalline CaO, typically amounting to between 2% and 5% CaO. Individual crystalline particles are not ordinarily detected, and the crystalline material is either embedded within the glass or deposited as a film on its surface [7–13]. From its ready availability to solution, the latter seems more likely. The dissolved CaO is capable of reacting with the glass phase in a 'self-pozzolanic' reaction, but this is relatively slow. When crystalline CaO is not reactive upon first contact with solutions, it can remain to cause unsoundness problems because of the reactive lime to portlandite reaction [14].

Table III. Class C Fly Ash Primary Crystalline Phases.

melilite (gehlenite-akermanite)	Ca,Mg,Al(Si_2O_7)
ferrite spinel	(Mg,Fe)(Fe,Mg)$_2$O$_4$
merwinite	$Ca_3Mg(SiO_4)_2$
bredigite, larnite	Ca_2SiO_4
lime	CaO
periclase	MgO
nepheline, carnegieite	$NaAlSiO_4$
feldspar	(Na,Ca,Al,Silicate)
pyroxene	(Mg,Fe,Ca,Al,Silicate)
cristobalite/quartz	SiO_2
C_3S	Ca_3SiO_5 [C_3S]*
C_3A	$Ca_3Al_2O_6$ [C_3A]
anhydrite	$CaSO_4$
Al-hauyne (sodalite structure)	$C_4A_3\bar{S}$
$12CaO \cdot 7Al_2O_3$	$C_{12}A_7$

*Cement nomenclature: C = CaO, A = Al_2O_3, S = SiO_2, $\bar{S}$ = SO_3.

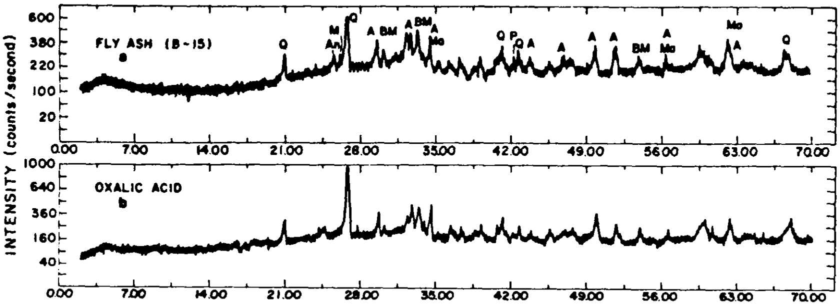

Fig. 3. X-ray Diffractogram of High-Calcium Fly Ash (B-15) Similar to that in Fig. 1. (a) Before etching, (b) after 45 minutes oxalic acid, etch. (Q = quartz, m = mullite, A = alite, BM = brownmillerite, Ma = magnetite, P = periclase) [2].

Another common component of high calcium fly ashes, present frequently in fairly substantial amounts, is C_3A. This compound can react rapidly with any anhydrite present to generate ettringite, and self-setting high calcium fly ashes are known where the setting is clearly due to rapid production of ettringite rods that link and bind adjacent spheres.

C_2S and even C_3S are detected occasionally in high-calcium fly ashes, but only in small amounts; their eventual hydration probably contributes slightly to the formation of cementitious products.

Periclase (crystalline MgO) is reported in some fly ashes, in small amounts. ASTM C 618 limits the analytical MgO content of fly ash to be used in concrete to 5% or less, based on experience with portland cement where $Mg(OH)_2$ formation may lead to unsoundness. However, high-calcium fly ashes having up to 6% analytical MgO (present as periclase, merwinite, and in glass) routinely show no unusual expansion in the ASTM autoclave expansion test, so this requirement appears not to be appropriate for fly ash (O. Manz and T. Demirel, private communication).

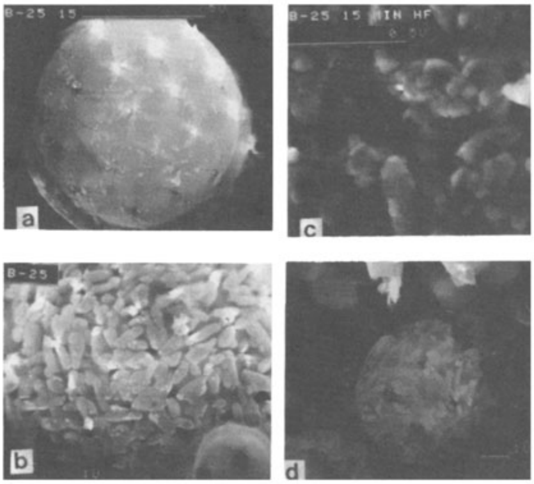

Fig. 4. SEM Photomicrographs of a Low-Ca Fly Ash (B-25) Etched in HF for 15 Minutes. (a) Sphere with a layer of noncrystalline solid (NCS) partially etched away, (b,c) iron oxide crystals on the surface of sphere, (d) mullite crystals [12]. Scale (a) 1 cm = 5µm, (b) 1 cm = 1µm, (c) 1 cm = 0.5µm, (d) 0.5 cm = 1µm.

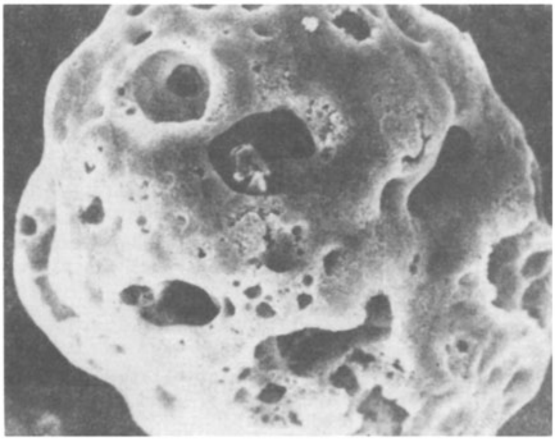

Fig. 5. Scanning Electron Micrograph of Vesicular Spherical Particle After HF Treatment, X370, Believed to be Largely or all Mullite [11].

Finally, gehlenite ($Ca_2Al_2SiO_7$) or melilite solid solutions (Ca, Mg, Al pyrosilicates) are sometimes observed in high calcium fly ashes: these are not ordinarily very reactive.

Because the crystalline phases of fly ashes are ordinarily embedded within the glassy spheres, their morphologies are not usually recognizable in the untreated fly ash. They are made visible by deliberate etching treatments to dissolve away some of the glass, or after the glass has reacted in concrete [2,5,7–11].

The x-ray diffraction pattern of a typical high-calcium fly ash is shown in Fig. 3(a). Here the broad amorphous glass maximum occurs at ~32°2θ (Cu radiation), and several crystalline phases are present as evident from the sharp diffraction peaks.

Selective dissolution techniques are often used to attempt to separate individual phases for analysis. Figure 3(b) shows the result of oxalic acid dissolution, which has removed much of the glass in a high-calcium fly ash [2]. Hydrofluoric acid (HF) dissolution of the glass in low-calcium fly ashes has been used quite successfully to separate a residue of crystalline components including mullite, quartz, and sometimes iron oxides from low-calcium fly ashes [2,7]. The SEM images of ashes resulting from one such treatment are shown in Fig. 4. A view of an individual residual mullite skeleton left after HF treatment of a low-calcium fly ash is shown in Fig. 5. Occasionally, fly ashes show spheres with substantial crystals of insoluble substances (as distinguished from soluble powders condensed from the vapor phase) on their surfaces, evident even without etching. Figure 6 shows such crystals, thought to be hematite, on the surface of spheres of an iron rich low-calcium fly ash. Lauf [7c] has further shown the detail which can be revealed through ion beam etching for TEM studies.

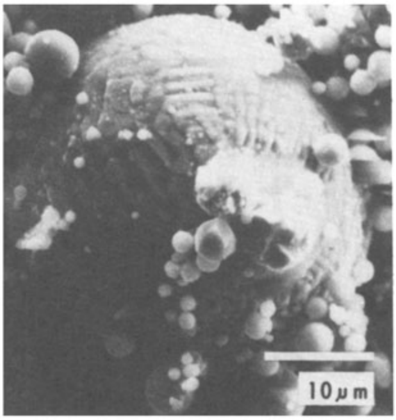

Fig. 6. Surface Deposition of Hexagonal (Hematite) Crystals on a Sphere in an Iron-Rich Low-Ca Fly Ash.

Particles of unburned coal residue occur in many fly ashes, and are common in those formed under poor burning conditions [13]. They occur in various morphologies, some of which are illustrated in Fig. 7 [11]. Unburned coal particles constitute a major fraction of the coarsest fraction of many fly ashes, although they are found in fine sizes as well. Irregular oversized particles composed mostly of vesicular glass are also common, and may not immediately be distinguishable from coarse unburned coal fragments. Many carbonaceous fragments, both oversize and fine, contain voids in which fine mineral fly ash spheres have been formed, apparently by melting and resolidification of the finely-divided clay and other mineral matter within the ground coal fragment.

It would be extremely desirable to have a procedure available for the quantitative determination of the amounts glass and of each of the crystalline components of a given fly ash. This is an extremely difficult undertaking, and a general procedure satisfactory for all fly ashes has not yet been developed. However, considerable success has been recently reported for such quantitative mineralogical analysis of certain low-calcium fly ashes [10].

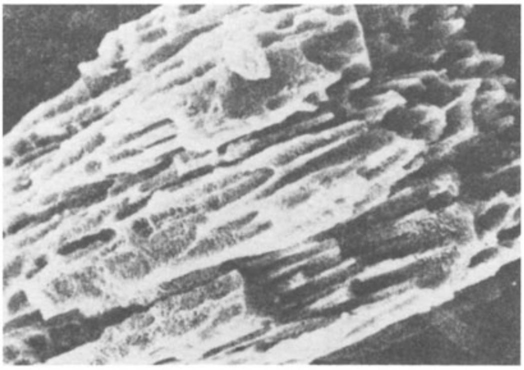

Fig. 7. Scnning Electron Micrograph of an Opaque Particle of Vesicular Carbon from High Lime Ash, X250 [11].

Chemical Composition and Physical Properties

The variability of the chemical composition of fly ash is illustrated

Table IV. Fly Ash Chemical Composition, wt% Range.

Oxide	Class F	Class C
SiO_2	38 - 65	33 - 61
Al_2O_3	11 - 33	8 - 26
Fe_2O_3	3 - 31	4 - 10
CaO	0.6 - 13.3	14 - 37
MgO	0 - 5.0	1.0 - 7.0
Na_2O_3	0 - 3.1	0.4 - 6.4
K_2O	0.7 - 5.6	0.3 - 2.0
TiO_2	0.7 - 5.6	0.9 - 2.8
SO_3	0 - 4.0	0.5 - 7.3
LOI	0.1 - 12.0	0.2 - 1.4

in Table IV, which is derived from analyses reported throughout the literature. In almost all cases these are represented in United States fly ashes. Naturally, such variations in composition cause concern over performance of fly ashes in cement and concrete [15]. For example, reaction of the sulfates with hydrating aluminates can result in delayed setting and lower the resulting concrete strength. Thus, while ASTM C 618 limits the SO_3 content of both types of fly ash to 5%, some ashes have contents in excess of this limit (Table IV).

The variations in element distribution in sub-bituminous and bituminous coal ashes found within six different generating stations are shown in Fig. 8. Electrostatic precipitator ashes from air and boiler aside, and bottom ash are contrasted from the same power plant and coal source. There were no consistent trends, except for iron-rich ashes which showed a marked concentration of Fe in the bottom ash.

Unburned carbon particles are relatively inert in cement hydration reactions [1], acting mostly as a diluent to the system. However, if present in substantial quantity, they can adversely affect the workability, and lead to lower concrete strength [23]. Usually the high-calcium fly ashes have low carbon contents, while the carbon contents of low-calcium fly ash are somewhat more variable and higher. Carbon content is reflected in the loss on ignition (LOI) values, with typical ranges given in Table IV.

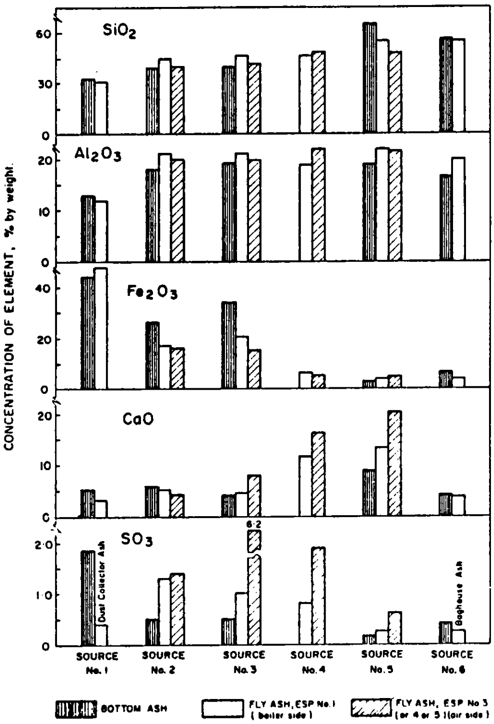

Fig. 8. Variation in SiO_2, Al_2O_3, Fe_2O_3, CaO and SO_3 in Different Thermal Regimes [23].

Specific gravity and fineness are usual physical properties reported. The specific gravity of fly ash varies considerably ranging from 1.6 to 2.8, related partly to its chemical