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POZZOLANIC REACTIONS IN SYNTHETIC FLY ASHES

by

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INTRODUCTION

A primary goal of technological advancements has been to utilize

natural resources more efficiently and economically. Often such advances

tend to be self-limiting because of their associated negative influence

on the environment. An example is the introduction of the powdered-coal

or suspension-fired furnace in the 1920's as a means for improving the

efficiency of power generation (126). As the attendant problems of air

pollution rapidly became apparent, various methods were devised and

utilized to suppress obnoxious gases and to collect the flue ashes.

The demand for electrical power continues to increase and since such

fossil-fuel power plants are located within or adjacent to areas of high

population density, the associated environmental pollution problems have

generated considerable attention. An appreciation for the magnitude of

this problem can be gained by noting that in 1969 over 22 million tons of

solid waste material were collected from the flue gases of fossil-fuel

power plants (21). In the industry this material is termed "fly ash."

There is, of course, a cost factor involved not only in the removal of

fly ash from the flue gas but also in its disposal.

In the early 1930's, fly ash was found to possess various physical

and chemical properties characteristic of pozzolans (39). Pozzolans

are artificial and natural materials which of themselves are not

cementitious, but which react with hydrated lime and water to form

cementitious compounds, namely calcium silicate and aluminate hydrates of

low solubility. The pozzolanic nature of fly ash is largely responsible

for its present increasing usage in soil stabilization (1, 22, 35, 76, 117),

grouting (115) and as a component of concrete mixes (1, 37, 38, 103, 117, 140). Despite these and other applications only 6 to 8% of the fly ash produced in the United States is actually used; the remainder is simply disposed of at a cost ranging from $0.25 to $2.42 per ton (1, 20, 21, 27, 47, 132).

In spite of the increased use of fly ash as a pozzolan, and a recognition of pozzolanic cementation extending back to Roman times, there remains a lack of basic understanding of the role of fly ash as a pozzolanic material. This is partly due to its highly variable chemical and physical properties (116, 117, 136). Such variability arises not only from varying amounts of mineral matter in the coal from which fly ash originates, but also from the conditions of operation of the boiler, fineness of grinding of the coal prior to combustion, additives mixed with coal for pollution control, and methods of collection (20, 32, 82, 98, 132). As a result, it is not always possible to devise reliable specifications by which samples unsuitable for a particular application may be rejected. Nonetheless, some fly ash specifications have been established for particular applications and include limits on such parameters as particle size, percent loss on ignition, and other chemical constituents, e.g. SiO_2, Al_2O_3, Fe_2O_3, etc. The investigations which gave rise to these specifications for the most part study physical and chemical factors relating to the ash as a whole (88, 116). In view of the highly heterogeneous nature of commercial fly ashes, it is understandably difficult to unambiguously relate pozzolanic reactivity to such gross fly ash characteristics.

One approach to the study of pozzolanic reactions would be to separate

constituents of fly ash and allow them to react with lime separately.
Unfortunately practical difficulties in separation make this approach
impossible. Another approach is to synthesize fly ashes of known physical
and chemical properties in the laboratory and react them with lime. In a
unique approach to this problem Lees (73) and Watt and Thorn (137) passed
finely-ground natural minerals through a coal-gas-flame to produce
synthetic fly ashes of known chemical composition. Such studies to date
have been limited in scope and have not included a detailed investigation
of the lime-fly ash reaction mechanism.

The purpose of this investigation was to prepare synthetic fly ashes
from some common minerals associated with coal to characterize their
physical and chemical properties, and to study their pozzolanic activity.
Nine synthetic fly ashes of different chemical composition and nine others
of different particle size and crystallinity were investigated to represent
variations encountered in commercial fly ash and if possible relate to
pozzolanic reactivity. After the synthetic fly ash and lime samples were
allowed to react and tested for strength they were examined for reaction
production by means of x-ray diffraction and x-ray microelemental
analyses (XMA).

Since the pozzolanic strength in cured lime-fly ash mortars should
be a function of the reaction products, chemical tests were utilized to
determine the amount of reaction products and also the reactive constitu-
ents of the fly ashes. For the most part the pozzolanic activity was
investigated by strength gain.

REVIEW OF LITERATURE

Pozzolans can be divided into two categories: natural and artificial. The natural pozzolans include some volcanic ashes, diatomaceous earth and opaline chert. Natural pozzolans were used by the ancient Greeks and Romans to build structures, some of which stand in use today and thereby attest to the durability of lime-pozzolan cements. Artificial pozzolans include heat-treated clays and shales, Si-stoff (a waste by-product of the alum industry), blast furnace slags, and fly ashes (35). The pozzolanic activity of the above materials is believed due to their glassy or non-crystalline ionic structure derived from rapid quenching from high temperatures (72, 91, 127).

Production of Fly Ashes

The usefulness of fly ash as a pozzolanic material is significantly influenced and limited by its highly variable physical and chemical properties. The reasons for this great variability deserve attention. Broadly speaking, factors which influence fly ash properties are:

1. Origin and kind of mineral matter in coal (52, 53, 81, 98, 123);

2. Pollution control additives (93, 104);

3. Coal processing methods and furnace conditions (52, 70);

4. Methods of fly ash collection (20, 117, 123, 131).

Origin and kind of mineral matter in coal

Coals used in power plants may contain up to 25% incombustible mineral matter. Nelson (98) and Mackowsky (81) have classified such mineral matter as inherent (syngenetic) and extraneous (epigenetic).

Inherent mineral matter is that which was deposited during plant growth and was present in the plants themselves. Extraneous material includes minerals which were introduced into the coal beds subsequent to formation, as well as any mineral contamination deposited by wind and water into the joints and crevices of coal seams. As a result, the amount of mineral matter in coal varies not only horizontally with geographical location but also vertically within a coal mine from seam to seam.

Analyses for a number of United States coals for mineralogical composition has been summarized by Nelson (98). The data show that 95% of the mineral matter in coal is composed of kaolinite, pyrite, and calcite (10, 20, 98, 117). The general range of composition is indicated as follows: kaolinite 70-95%; pyrite 5-35%; calcite 0-20%. Higher percentages of pyrite and calcite are very rare in bituminous coals; however, lignites often have a high proportion of calcite (52). Other secondary or trace minerals seldom exceed 5% (98), and are believed to have little effect on the pozzolanic activity of the resulting fly ash (93, 136) but may be deleterious in specific applications such as use in portland cement concrete (ASTM C618). For example, the content of SO_3 is usually limited because of production of sulfuric acid: $SO_3 + H_2O = H_2SO_4$. The content of MgO is limited in artificial pozzolans and cements due to expansive hydration: $MgO + H_2O = Mg(OH)_2$, but the amount of MgO has not been limited in fly ashes, apparently because it has posed no problem (ASTM C618).

Recently powdered limestone or dolomite has been injected into bituminous coal burning furnaces to reduce the level of sulfur oxides emitted in the flue gases. Thus far this process is still considered to be in the experimental stage and has been partially successful. The

quantity and composition of fly ash collected from furnaces where the limestone process is employed obviously reflect such mineral additions. About twice the amount of stoicheometric requirement of dolomite powder is added to the pulverized coal to combine sulfur oxides. Although addition of dolomite to the coal is not in general use, where this practice is adopted the mineral matter in fly ash is approximately doubled by the amount of dolomite added (104).

Coal processing methods and furnace conditions

Detailed studies of combustion conditions in different types of furnaces have been made by Nelson (98), Gumz (52, 53), and Mackowsky (81). There is general agreement that the thermal changes which mineral matter undergoes during the combustion of coal in a furnace are influenced by the following factors (52, 78, 98, 126):

1. The size to which the coal is ground and its influence on the quantity and distribution of mineral matter;

2. The atmosphere in the furnace;

3. The temperatures to which the mineral matter is subjected, the rate of heating and quenching, and the residence time of mineral grains at those temperatures;

4. Boiler load conditions.

The main objective of pulverizing coal for use in suspension-fired furnaces is to increase the particle surface area. This reduces the burning time while increasing the rate of heat generated per unit volume (126). If coal is ground finer, there will be less waste, i.e. fewer particles will remain unburned (20). In grinding or pulverizing coal, the

mineral matter associated with the coal is also pulverized. It is generally believed that there is a direct relationship between the average size of fly ash particles and the degree to which the coal is pulverized. Pulverizer capacity, economic feasibility and other considerations place limits on the size to which coal is ground. Based on such factors, coal is usually pulverized so that 80 to 85% passes a 74 micron screen and 95% passes a 297 micron screen (20).

Littlejohn (77) studied the mineral characteristics in individual coal particles as a function of size. On the basis of pulverized coal "as fired" he was able to classify particles as

a) Clean coal particles containing only inherent mineral matter,

b) Mixed particles containing both clean coal and extraneous minerals and

c) Discrete mineral particles.

These observations were confirmed by Rekus and Haberkorn (107). Furthermore, Littlejohn found that as the coal particle size decreased, the proportion of clean coal decreased, and that the proportion of mixed particles and of discrete mineral fragments increased. Littlejohn also reported that finely ground coals yielded very fine fly ashes (77).

In suspension-fired furnaces, oxidizing conditions necessarily exist as contrasted to the reducing conditions found in stoker or cyclone furnaces. Since the majority of fly ash is obtained from suspension-fired furnaces, stoker or cyclone furnace conditions will not be discussed here.

Nelson (98) and Gumz (52) presented detailed descriptions of the atmosphere, temperature, and particle residence time in suspension-fired furnaces. The coal powder is fed with an air injector into the coal dust

flame. Air, 20 to 25% in excess of stoichiometric oxidation requirements, is injected into the system to achieve proper combustion and to keep the coal particles in suspension (20, 126). Oxidizing conditions therefore exist in the flame zone (53, 65, 98).

Flame temperatures vary between $1300^{\circ}C$ and $1700^{\circ}C$ (52, 98, 126, 139) and are always lower than temperatures in a stoker or cyclone furnace due to the cooling effect of the additional air fed into the suspension-fired furnace (98).

Air injection of pulverized coal forces the particles into the flame at a velocity of at least 60 feet per second (126). The particle residence time in the coal dust flame is believed to be a maximum of two seconds (24, 32). Injection of pulverized coal into the high temperature region of the furnace results in an extremely rapid increase in particle temperature with accompanying physical and chemical changes. With few exceptions, all mineral particles reach a fluid or plastic state (4, 52, 98). In the literature, such particles are referred to as "slagged" particles. Nelson (98) and Brackett (20) report that the flue gas temperature is much lower than the flame temperature, and therefore the slagged particles are quenched into glassy spheres which are exhausted in the stream of gases. Several investigations suggest that since the particles have limited opportunity to come in contact and agglomerate with other particles, the resulting ash particles are mainly glass spheres of one or at the most two mineral species (52, 53, 98, 136, 139). Watt and Thorn (125, 137) however, found brownish to reddish spongy particles which contained aluminum, silicon, iron, and calcium, suggesting intermixing of several mineral species in the hot zone.

Although complete combustion conditions exist in a suspension-fired furnace, the velocity of injected air is so high that 5 to 12% of the coal particles pass through the furnace unoxidized (32). Clendenning and Durie (32) found that the velocity of injected air varies with turbine loading conditions and consequently influences the carbon content of the fly ash. In their study of variable load conditions, they observed that a decrease in load, because of reduced velocity of primary air, resulted in an increase in carbon content and an accompanying increase in fineness of fly ash particles. The unburned coal particles are irregularly shaped and black in color. Microscopic studies by Watt and Thorn (136) and Procter and Taylor (106) and hydrometer analyses by Weinheimer (138) indicate that the size of such unburned coal particles varied from 20 to 200 microns as compared to 0.1 to 100 microns for spherical mineral particles.

The general change in fly ash properties mentioned above relates to changes in characteristics of individual minerals (52, 53, 81, 98, 138). For example, the clay mineral kaolinite first dehydrates and then undergoes thermal phase changes. Fly ash particles formed from kaolinite are white or colorless (73, 98, 136, 139). The majority are solid, spherical and glassy; some are hollow, termed cenospheres, and some are spongy in nature. On the basis of x-ray diffraction analysis, Watt and Thorn (125, 136) reported that the cenospheres and spongy particles contain more mullite and quartz than do solid glassy spheres.

Iron-containing minerals decompose to form hematite or magnetite. Pyrite, FeS_2, common in coal, oxidizes to iron oxides and gaseous sulfur oxides. The black or reddish iron oxide particles may be spherical or spongy, have a high specific gravity and are mostly crystalline (90, 125).

Lees (73) and Procter and Taylor (106) suggested that the reddish particles found in fly ash are a result of preheating of mixed minerals and subsequent heating to very high temperatures.

Nelson (98) and Whittingham (139) have suggested that calcite decomposes to form calcium oxide and calcium sulphate particles depending on the availability of sulfur from pyrites. Similar reactions with the loss of carbon dioxide take place in case of dolomite and other carbonates (104). Consequently, the weight of the resulting ash is 10 to 15% less than the original weight of the corresponding mineral matter in coal (20, 98, 139).

Methods of fly ash collection

Fly ash is collected from the flue gases either mechanically by cyclone separators or electrically by Cottrell precipitators (35). The electrical process is more efficient in collecting the fines (20, 35, 131). The effect of collection equipment on fly ash properties has been studied by Brackett (20) and Styron (123) who found that halloysite, which is a hydrated analogue of kaolinite, is a very effective electrical insulator. Although heat changes its form in a suspension-fired furnace, it does not change its insulating properties. The insulating properties prevent electrostatic collection by coating the plates with material have a high dielectric constant. As a result, halloysite ash cannot be collected by electrostatic precipitators. The best mechanical collection is about 90-95% efficient; electrical collection, about 97-99% (44, 102).

Properties of Fly Ashes

Substantial work has been done in an effort to relate pozzolanic activity of industrial fly ash to one or more physical and/or chemical parameters. Given below are some of the parameters investigated:

Physical properties

Specific surface area and fineness

Specific gravity

Crystallinity

Chemical composition

Silica and alumina

Iron oxide

Sulfur trioxide

Calcium and magnesium oxides

Carbon

Physical properties

Specific surface area and fineness   There is general agreement that the finer the fly ash, the higher the pozzolanic activity (1, 37, 39, 40, 60, 131). Snyder et al. (119) recently found that the pozzolanic strength of some industrial fly ashes increased with a decrease in the average particle size from >200 to 35 microns. However, any further decrease in average particle size was reported to result in a reduction of pozzolanic strength. Since fly ashes average 63 to 90% material passing a 325 mesh sieve (39, 91), fineness is usually expressed in terms of specific surface area determined by the Blaine air permeability method (1) and ranges from 2000 to 6000 cm^2/g (1, 39, 91, 138). However, high

specific surface area values may be due either to large amounts of fines in the inorganic particles or to a significant amount of porous carbon particles. Davis (37, 38) suggests that for optimum results in portland-pozzolan cement concretes the specific surface area of fly ash must not be less than 2500 cm^2/g. On the other hand, Vincent (131), Brink and Halstead (24), and Watt and Thorn (125) report that fly ash fineness measured by the air permeability method gives no indication of its pozzolanic activity, but that fineness of fly ash measured by the % passing 325 mesh sieve is a more reliable indicator. In a recent study Watt and Thorn (125, 137) determined fly ash particle size by a combination of light microscopy and sieving. The obtained values were then converted to specific surface area and were found to relate well with the pozzolanic activity measured by chemical methods. Jarrige (60), Venuat (130), Skaggs and Morrison (114) and others state that when fly ash is ground, pozzolanic activity increases significantly. This is a logical conse-quence, since most chemical reactions proceed faster with increased fine-ness (58, 70). Despite such general agreement relating size and pozzolanic activity, the desirable fineness and methods of measuring fineness are still matters of controversy (29). As a result, different organizations specify widely varying fineness limits of fly ashes for particular applica-tions (116).

Specific gravity   The influence of specific gravity on pozzolanic activity has not been studied as such but studies by Weinheimer (138), Minnick (90) and Watt and Thorn (125) indicate that specific gravity varies significantly for particles of different shape, color, and chemical composition. Irregularly-shaped black coal particles which contain few

mineral grains have a specific gravity between 1.3 to 1.6 (77). Such

particles are nonreactive and dilute the active pozzolanic material in

fly ash (1). The spherical and rounded light brown to black particles

contain 50 to 95% of the total iron in fly ash and have a specific gravity

between 3.6 and 4.8 (90, 136, 138). Minnick (90) reports that these high

iron particles, which he termed "ferro pozzolans", contain magnetic iron

oxide inclusions. Their reactivity is believed due primarily to the

presence of a high concentration of siliceous glass on the surface of each

of the particles. Removal of such particles tends to beneficiate the fly

ash (90, 125, 132); hence these are thought to be less reactive than the

glassy siliceous particles having a specific gravity between 2.2 to 2.6.

Watt and Thorn (125, 137), by use of strength tests, compared

pozzolanic activity of four different density fractions of fly ash

particles. They found that the reactivity passes through a maximum at an

intermediate density of the fly ash particles. The four density fractions

listed below have increasing order of reactivity:

$$1) \quad >2.74 g/cm^3$$

$$2) \quad <2.1 g/cm^3$$

$$3) \quad 2.1-2.5 g/cm^3$$

$$4) \quad 2.5-2.74 g/cm^3$$

The particles with a density greater than $2.74 g/cm^3$ are rich in iron and

are less reactive than those with a lower density. Particles having a

density between 2.5 and $2.74 g/cm^3$ are clear solid glassy spheres; and

those between 2.1 and $2.5 g/cm^3$ are glassy particles of low porosity.

Although these two types of particles have a similar chemical composition,

the former are more reactive than the latter. The fourth category of

particles with a density less than 2.1g/cm^3 is also glassy, but spongy and highly porous. The chemical composition of these was found to be essentially the same as that of other glassy particles; however, they are less reactive than particles having a density of 2.1 to 2.74g/cm^3, but more reactive than those of the highest density. Watt and Thorn also reported that the amount of mullite and quartz increases with a decrease in density. Since specific gravity and particle size are interrelated, air elutriation has been used to beneficiate certain fly ashes (20). Jarrige (60) and Venuat (130) have found that grinding the fly ash results in increasing not only the fineness but the apparent specific gravity as well, probably by crushing hollow or porous particles.

Crystallinity   Fly ashes contain 11 to 48% crystalline matter, the rest being amorphous material and carbon particles (112, 117, 136, 138). Quartz, mullite, hematite and magnetite form the major portion of the crystalline matter (84, 90, 117, 136). In addition, Mateos and Davidson (84) have also found corundum, calcium hydroxide, calcium carbonate and anhydrite. Since these are present in small quantities, they are not considered to significantly influence long-term pozzolanic activity (91, 93, 136). The amorphous portion consists of siliceous, aluminous and ferruginous glasses (60, 90, 106, 136). Davis (37), Minnick (91, 93) and others report that fly ashes which have a substantial portion of amorphous silica are more pozzolanic than those which have a crystalline form of silica. Simons and Jeffery (112) determined the amount of crystalline matter in some fly ashes by x-ray diffraction and estimated the glass content by subtraction. They report that, although there is no good correlation between glass content and pozzolanic strength, generally higher

strength is given by fly ashes containing higher glass content. From a similar study on 14 British fly ashes Watt and Thorn (125, 137) concluded that the pozzolanic activity of an ash resides mainly in the glassy and siliceous particles. No minimum amounts of glassy materials have been established.

Chemical composition

Investigations by Davis et al. (39), Watt and Thorn (136), Weinheimer (138), Jarrige (60) and others (37, 38, 40, 75, 131) show that variations in the chemical composition of fly ashes as a whole are mainly due to the carbon content and, to a lesser degree, other elements.

Chemical analyses of a large number of U.S. fly ashes show ranges in composition given in Table 1 (138). The chemical composition as shown in the table does not indicate the physical and/or chemical form in which the constituents are present. Jarrige (60) suggests that petrographic studies would be a useful source of information in this regard.

Table 1. Chemical composition of U.S. fly ashes (138)

Constituent	wt %
Silica, SiO_2	34 – 48
Alumina, Al_2O_3	17 – 31
Iron oxide, Fe_2O_3	6 – 26
Calcium oxide, CaO	1 – 10
Magnesium oxide, MgO	0.5 – 2
Sulfur trioxide, SO_3	0.2 – 4
Loss on ignition, carbon	1.5 – 20

Silica and alumina   The main constituents in fly ash are silica

and alumina and are present mainly in a glassy form (91, 93, 112, 125).

Leonard (74) and Minnick (91) have attempted to relate the chemical

composition of fly ashes to strength developed in lime-fly ash mixes; but

no definite correlation was found. However, Watt and Thorn (125) observed

that the amount of SiO_2 or $SiO_2 + Al_2O_3$ of a fly ash influences the

pozzolanic activity at long periods of cure; i.e., greater ultimate

strengths are obtained when the silica or silica plus alumina content is

high.

Iron oxide   Iron is found in fly ashes in both crystalline and

glassy forms; a substantial portion is magnetic in nature (90, 91, 136).

According to Minnick (90) the magnetic fraction in fly ash is made up in

part of extremely fine crystalloids of magnetite embedded in a siliceous

glass of high specific gravity. In addition to magnetite, iron is present

in this glass in several forms including dissolved iron oxides, together

with other amorphous and crystalline iron compounds. There is no evidence

of metallic iron in any of the fractions of fly ash (90). Jarrige (60),

Davis (37), and others (39, 117, 128) suggest that the amount of iron in

fly ash has some correlation with pozzolanic activity. Davis (37) states

that fly ashes which have moderate amounts of alumina and iron oxide are

superior to those containing a high amount of silica. On the other hand,

magnetic separation of iron is found to increase the pozzolanic activity

and fineness of the fly ash. Most specifications designate upper limits

of iron content in fly ash (88, 117).

Sulfur trioxide   All specifications limit the SO_3 content in fly

ash although studies by Chubbuck (31), Lea (70), and Minnick (91) indicate

that an increase in SO_3 content tends to increase the pozzolanic activity as measured in terms of strength developed in lime-fly ash mixes. However, the quantity of SO_3 in fly ash is so small that it cannot be taken as a decisive parameter for pozzolanic activity (4, 91).

Calcium and magnesium oxides   U.S. fly ashes contain less calcium and magnesium than European fly ashes. This may be due to the fact that most European fly ashes are produced from lignite (52). Fouilloux (45) states that high-lime fly ashes do not possess any pozzolanic qualities and suggests an addition to the definition of pozzolan incorporating the words "low in lime". Davis (37) maintains that up to 5% lime and magnesia are not harmful. Nelson (98) and Procter and Taylor (106) suggest CaO in fly ash as indicated in Table 1 may exist in the form of soluble CaO, $CaCl_2$ or $CaSO_4$. In a study of stabilization of sandy soils with fly ashes alone, Mateos (83) proposed that the amount of free lime and/or alkali in some fly ashes was sufficient to result in cementation and strength without addition of lime.

Carbon   Constituents other than silica, alumina, iron, lime and alkali sulphates have also been suspected to affect the pozzolanic reaction. Carbon represents the noncombustible portion of fly ash and varies essentially with the efficiency and load of power plant operations (32). Carbon tends to predominate in size fractions larger than 44 microns (77, 136, 138). Conflicting conclusions have been drawn about the effect of carbon on pozzolanic activity (1). Delbridge (40), Leonard and Davidson (75), Minnick (91, 93), and others have reported that relatively high percentages of carbon decrease the pozzolanic activity. Yet Fredrick (46), Davis et al. (39), and Clendenning and Durie (32) found that carbon

had no deleterious effect on strength of lime-fly ash mixes. Nevertheless, carbon which acts as a diluent of the active pozzolanic matter in fly ash is considered an undesirable constituent, and different organizations specifying the use of fly ash as a pozzolan limit the carbon or loss on ignition in fly ashes to from 5 to 12%.

Pozzolanic Activity of Fly Ashes

The hydration reactions in lime-fly ash mortars progress with time and involve three basic constituents; lime, fly ash and water. It is, therefore, obvious that amount and/or type of each of the constituents will influence the pozzolanic reactions. The influence of various properties of fly ashes on their pozzolanic reactivity has already been discussed.

Lime factors

Type and grade of lime   Calcination of pure limestone yields calcium oxide, termed "quicklime", which on hydration converts to calcium hydroxide, termed "slaked or hydrated lime". Magnesium oxide is frequently found in lime due to the presence of the mineral dolomite in many limestones. The lime produced from carbonate rock containing magnesium and calcium in a molar ratio of one is termed dolomitic lime (35).

The calcination and hydration processes determine the grade of the lime. The limes in which magnesium oxide does not readily hydrate are called "normal hydrated" or "Monohydrated"; while those in which magnesium oxide also hydrates are called "Highly hydrated" or "Dihydrated". The slaking properties which are influenced by calcination temperature further subdivide the limes into slow, medium or rapid slaking (35). Unless otherwise noted, the term "lime" in this study refers specifically to

calcium hydroxide.

The pozzolanic reactions are highly sensitive to chemical class and type of the lime (35, 93). Laguros (68), from strength studies of soil-lime mixtures found that monohydrate dolomitic limes are more effective than the calcitic quicklimes which in turn are more effective than the calcitic hydrated limes. Lu (80) and Segal (111) studied the influence of synthetic limes of various calcium: magnesium ratios on the pozzolanic strength of soils and fly ash mortars respectively; and report little or no difference in the strength of mortars using pure $Ca(OH)_2$ and those using a 1:1 ratio of calcium: magnesium. In a similar study Wang (134) reported that dolomitic monohydrated lime imparts higher initial strengths to lime-soil mortars; however, high-calcium hydrated lime probably gives higher ultimate strength than the former. Of the different types of commercial lime, dolomitic monohydrated limes are the most effective in providing strength to fly ash mortars; high-calcium hydrated as well as dolomitic dihydrated are successively less effective (93). The mechanism and role of magnesium in lime has been explained in different ways by different investigators and the reactions may not be pozzolanic in nature (93, 134). It is for this reason that all specifications prescribe the type and grade of lime to be used to evaluate pozzolanic reactivity (116).

Lime-pozzolan ratio   The optimum weight ratio of lime to pozzolan in lime-pozzolan-aggregate mixtures depends heavily on the aggregate and reaction time (70). Various weight ratios of lime to fly ash have been investigated. Some workers suggest that a weight ratio of 1:10 may be optimum for lime-fly ash-soil mixtures while others report that increased strengths are obtained with an increase in the ratio up to

1:3 beyond which there is only minimal increase in strength (93).

According to Lea (71), at short curing periods the maximum strength is obtained using a lime pozzolan ratio of 1:4; for long curing periods the optimum ratio is approximately 1:2. Stoichiometric considerations cannot be used to determine optimum ratios of lime to pozzolan since very little information is available pertaining to the amounts and types of reactive ingredients in the pozzolans in general and fly ashes in particular (93). Turriziani (127), Watt and Thorn (125), Minnick (93), and various other investigators have used a lime to pozzolan ash ratio of 1:2 for studying pozzolanic reactivity in fly ash mortars. This possesses the advantages of making all such data comparable and reducing the possibility for reactions prematurely stopping due to depletion of lime.

Compaction moisture

From the definition of pozzolans it is amply clear that moisture plays a very important role in the pozzolanic reaction. No reaction or strength development would be achieved in the dry state (70). The amount of water combined with the pozzolans has been used to judge their quality (95). Minnick et al. (94) reported that the relative water requirement of a mortar containing fly ash can be used as a fair guide to predict the pozzolanic strength of an ash. In Germany, the pozzolan specifications prescribe a minimum limit for combined water, but Moran and Gilland (95) contend that the amount of combined water may not be significant even for the same type of pozzolan. Chu et al. (30) report that the optimum amount of water for lime-fly ash-soil mixtures is approximately the same as that required for maximum density. The results of work by

Mateos (82) indicate that the optimum moisture content for maximum pozzolanic strength is close to the plastic limit of the lime-fly ash mortars.

Time

Pozzolanic reactions are heavily time dependent but the rate and mechanism are not well known (93, 137). From results of short-term studies up to 45 days in lime-fly ash mortars, Wang (134) suggested that the pozzolanic reactions are second-order diffusion-controlled and that the diffusion constants vary with temperature and concentration of the reactants. Watt and Thorn (137) found that the time relationship between the amount of pozzolanic reaction as well as pozzolanic strength is almost linear up to 100 days. After 100 days the rate of strength gain is no longer constant and tends to level off. After 200 days the rate of strength gain is rather minimal. However, Lea (71) found that the pozzolanic reaction in some fly ashes was still in progress even after more than one year, albeit at a reduced rate.

Methods for Evaluating Pozzolans

Generally the test methods used to evaluate any product are of the performance type. However, in practically every application of pozzolans and related products, the long-range service performance is of critical importance. The years required to evaluate such products make it difficult if not impossible to rely on performance-type tests. Accordingly, these products are evaluated on the basis of readily measurable product charac-teristics and their correlation with the performance of the product. The test specifications for portland cement is an example (116).

Since strength development in lime-pozzolan mortars and cement mortars results from hydration reactions, the test methods used to evaluate portland cements have also been used to evaluate pozzolans (88, 116). Although most pozzolan evaluation tests have been developed from empirical correlations between pozzolan performance and characteristics established by extensive testing programs, others are based on arbitrary assumptions that certain characteristics are significant (116). The investigations of Davis et al. (37, 38), Minnick (91), and others (125) suggest that the presupposition of similarity between pozzolanic and cement hydration reactions is probably responsible for the similarity in pozzolan and cement characteristics selected for evaluation studies. Results indicate that the methods prescribed by various specifications either give misleading information or are unsatisfactory, especially when used alone (116). This is why evaluation methods specified by various organizations differ in several significant ways (Table 2). They differ in what is prescribed, in the limits placed on specified values, and in the methods used to measure the characteristics that are specified. Snyder (116) has presented an excellent historical and practical discussion on the methods and characteristics specified for fly ash evaluation by various organizations.

Despite the similarity of reaction products in pozzolans and from cement mortars the mechanism and rate of reaction are completely different (1, 35). The pozzolanic reaction is slow and predominantly physico-chemical; the cement hydration is fast and essentially chemical in nature. The testing of pozzolans is further complicated by the addition of lime and/or portland cement to develop cementation. Doubts have therefore been raised not only about the significance of some of the specified

Table 2. Typical specifications for fly ash for use in concrete (116)

Item specified	ASTM	Bureau of Reclamation	British standards	New York City	City of Chicago
Chemical specifications					
SiO_2, pct, minimum	70.0[a]	75.0[a]	—	35.0	42.0
Al_2O_3, pct, minimum	70.0[a]	75.0[a]	—	15.0	15.0
Fe_2O_3, pct, minimum	70.0[a]	75.0[a]	—	—	—
MgO, pct, maximum	5.0	5.0	—	3.0	3.0
SO_3, pct, maximum	3.0	4.0	2.5	3.0	6.0
Alkalies (Na_2O), pct, maximum	1.5	2.0	—	—	—
Mositure, pct, maximum	3.0	3.0	1.5	—	1.0
Loss on ignition, pct, maximum	12.0	5.0	7.0	12.0	6.0
Fineness requirements					
Surface area (Blaine), sq cm/g, minimum	—	3,000	Provides for 3 ranges	3,000	3,000
Avg particle size, microns, maximum	9.0	—	—	—	—
Pct retained on 325-mesh sieve, maximum	—	15.0	—	—	12.0
Activity or strength tests					
Strength mortar cubes, pct of control, minimum	100	85	—	—	—
Drying shrinkage, pct, maximum	+.03	+.04	—	—	—
Autoclave expansion, pct, maximum	.05	—	—	—	—
Cement pozzolanic activity, pct, of control, minimum	85	85	—	—	—
Lime pozzolanic activity, psi, minimum	800	900	—	—	—
Water requirement, pct of control, maximum	105	103	—	—	—

[a]Sum of SiO_2, Al_2O_3, and Fe_2O_3 should not be less than stated.

characteristics but also about the validity of some of the methods used to measure the pozzolan characteristics prescribed in the specifications (88, 116).

Several investigators in the field of fly ash research have generally adopted different methods to evaluate pozzolans, while others have attempted to devise new methods for reliable and quick evaluation of pozzolan performance (69, 94, 137). Test methods in general use fall into two categories: 1) direct methods which test performance, 2) indirect tests which measure certain other physical or chemical properties of the pozzolan which may in turn be related to long-term pozzolan performance. The evaluation tests are often described as physical and chemical tests in fly ash specifications.

Physical tests

Compressive strength tests   Unconfined compressive strength tests are the only direct tests commonly used to evaluate pozzolans. These tests have been carried out in a variety of ways by different investigators. The general procedure is to make samples of a certain size from a lime-pozzolan or lime-pozzolan-aggregate, cure them in a controlled environment, and then test the samples in compression after set periods of time. The choice of sample shape and size varies from 1/4 in. cubes to 1 1/2 in. cylindrical samples 3 in. in length. Variations in the type and weight ratio of lime, pozzolan and aggregates (particularly soils) influence the strength significantly and therefore must be specified to enable comparison of results with the results of other investigations. Standard sands are generally utilized when samples are made from

lime-pozzolan-aggregate mixtures (5, 125).

Compaction moisture and procedure affect the density and, therefore, the initial and ultimate strength of lime-pozzolan mortars (91, 131). Likewise, curing conditions influence the strength of lime-pozzolan mortars; e.g. samples cured by immersing in water or at higher temperatures develop higher strengths than those cured in air or at normal temperatures (37, 71, 108, 127, 137). Attempts have been made to predict ultimate pozzolan strength by autoclave curing; however, the literature indicates inconsistent correlations (2, 137). Possibly certain minerals that do not exhibit reactivity at ambient temperatures become pozzolanic at elevated temperatures; or initial reaction products formed at elevated temperatures do not allow formation of intermediate products (127). Despite the many variables and problems involved, compressive strength tests are considered to be the most reliable methods to evaluate pozzolans and the influence of various factors on the pozzolanic strength.

Petrographic analysis   Only a few attempts have been made to study pozzolanic reactions by petrographic examination of cured lime-pozzolan mixtures. The amorphous or poorly-crystallized nature of the reaction products and the high proportion of small fly ash particles (less than 2 microns) make study difficult and time-consuming (89, 137). Minnick (93), however, reports that petrographic studies can be successfully used to identify the morphology of reaction products in samples of lime-fly ash mortars cured for long periods of time. Light microscopy has been utilized by Watt and Thorn (125) to determine particle size distribution and particle morphology in fly ashes. They further report that the specific surface area of fly ashes as calculated from the data of light microscopic and

sieve analysis is representative of the surface characteristics of the fly ashes and has good correlation with pozzolanic activity.

<u>Electron microscopic observations</u>   Cement hydration products have been studied in great detail using the electron microscope (51). Pozzolanic reaction products in cured samples of lime-clay mixtures have also been studied morphologically (108); however, positive identification has not been possible. This is due partly to their amorphous nature and partly to the complex chemical and physical characteristics of the fly ashes. Nonetheless, the electron microscope has proved to be a valuable tool in determining the morphology and size distribution of particles which cannot be observed under a light microscope (61).

<u>X-ray diffraction analysis</u>   X-ray diffraction has been extensively used to identify reaction products in cement hydration. Identification of all cement hydration products has not been completed because of their small quantity in reacted samples, minute crystal size, and difficulty in their isolation (8, 14, 87). X-ray diffraction studies of cured lime-pozzolan mixtures pose similar problems (14, 93). However, it has been established that, although the rate of formation of reaction products in lime-pozzolan hydration is much slower than in cement hydration, the strength-giving compounds are almost the same (74, 75, 93). As described earlier, the ultimate pozzolanic strength of lime-pozzolan mortars varies with the curing temperature; x-ray studies indicate that the products vary similarly (74, 93). Various siliceous, aluminous, quaternary and secondary products have been reported to be found in lime-pozzolan hydration reactions (19, 72, 127).

Reaction products at normal room temperatures include gehlenite

hydrate $(C_2ASH_8)^1$ and hydrated calcium silicates of the tobermorite group, which have a variable C/S ratio, are found in varying proportions in reacted lime-burnt kaolinite mixes (127). However, at a temperature of about $50^{\circ}C$, gehlenite becomes unstable and gives rise to hydrogarnets with an approximate composition $C_3AS_{1/3}H_{3\ 1/2}$ (127, 134). From x-ray diffraction analyses of hydrated samples of lime and natural pozzolans Turriziani (127) concluded that the nature of reaction products containing Al_2O_3 are related to the composition of the vitreous phase in the pozzolan. When the vitreous phase is high in alumina, the nature of the reaction products is related to the lime concentration of the solution. He further suggests that mortars of natural pozzolans cured up to 6 months at room temperature gave tetracalcium aluminate hydrate (C_4AH_x), whereas lime-burnt kaolinite mortars contained unreacted calcium hydroxide and gehlenite (C_2ASH_8). Locher's (79) studies on the hydration of ternary synthetic glasses of the system $CaO-Al_2O_3-SiO_2$ indicate that the formation of gehlenite depends on the composition of the glass. The hydrated aluminate phase is mainly tetracalcium aluminate 8-hydrate if the glass is low in alumina. The study of pozzolanic reaction with burnt kaolinite by Brindley and Nakahira (23) suggests that the structure as well as the composition of the pozzolan reactive phase may be important (127).

The presence of up to 6% by weight gypsum $(CaSO_4 \cdot 2H_2O$ in a pozzolan also containing reactive alumina gives rise to quarternary aluminates such as ettringite $(C_3A \cdot 3CaSO_4 \cdot 32H_2O)$ which changes to the monosulphate form

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[1]Cement chemistry has its own peculiar shorthand for chemical compounds, thus; $C=CaO$, $S=SiO_2$, $A=Al_2O_3$, $H=H_2O$. C_3S would be read as tricalcium silicate.

($C_3A.CaSO_4.12H_2O$) when all $CaSO_4$ is consumed in cured lime-pozzolan

mortars. Tur iziani (127) reports that the formation of ettringite is

very rapid, and in mortars containing less than 6% gypsum the reaction

ceases after some weeks. The transformation of ettringite is, however,

very slow; even after 12 months the main quaternary aluminate is ettringite.

When the quantity of gypsum is low, the monosulphate and C_4AH_x coexist.

Turriziani suggests that the formation of ettringite needles is responsible

for the increased strength of lime-pozzolan mortars containing gypsum.

The literature provides very limited and questionable data regarding

lime-fly ash hydration products. The complex chemistry of individual fly

ashes offers the possibility of numerous reactions in mortars. Leonards

(74) suggests formation of calcium silicate hydrate and some other

transitional compounds not easily detectable in lime-fly ash mixtures. In

a recent study of hydration products of bituminous and lignite coal fly

ash mortars cured in sealed vials at $32^{\circ}C$, Minnick (93) found that

ettringite ($C_3A.3CaSO_4.32H_2O$) is generally found in all mortars along with

calcium-silicate hydrate (CSH (I) or CSH (II)) of the tobermorite group

and monosulphate ($C_3A.CaSO_412H_2O$). In samples cured by immersion in water,

tricalcium monocarboaluminate hydrate and tricalcium hemicarboaluminate

hydrate are also formed. It is possible that the curing temperature of

$32^{\circ}C$ might have been responsible for the ettringite in Minnick's samples

inasmuch as it has not been reported by other investigators. However,

Simons and Jeffery (112) suggest that ettringite may be responsible for the

self-hardening of moist fly ash stockpiles.

Chemical tests

Chemical tests are utilized to determine the chemical composition

of the pozzolans and the reaction products in the cured lime-pozzolan

mortars. Specifications prescribe certain tests and place limits on the

chemical constituents of the pozzolan (5, 116). As was already mentioned,

the reliability of such tests and limits is a matter of dispute (116).

Therefore, chemical tests to determine the amount of reaction that takes

place in hydrated lime-pozzolan mixtures have been used by many investi-

gators (118, 119, 137). Since fly ash reacts with and thereby decreases

the amount of calcium hydroxide in lime-pozzolan mortars, a quantitative

determination of either remaining free lime or the reaction products is

used to evaluate the amount of reaction which occurred.

Amount of free lime   Several methods have been devised to determine

the amount of free lime in reacted lime-pozzolan mortars, the extent of

lime depletion being a measure of pozzolanic activity. These methods of

measurement may be divided into two groups: extraction methods and

calorimetric methods.

Extraction methods are based on the assumption that the pozzolanic

reaction products are stable in various liquids, e.g. half-saturated lime

solution, aqueous sugar solution, ethylene glycol or phenol (15, 95, 105).

The extract is then titrated to determine the amount of free lime present.

Extraction methods, however, have two main sources of error: first,

fresh pozzolan surfaces may be exposed and react with lime during extrac-

tion; and second, the hydrated silicates and aluminates may be decomposed

by the extraction solutions (71, 105).

The calorimetric method is based on the fact that CaO, upon slaking,

gives off 276 calories of heat per gram. Samples are therefore heated to

$550^{\circ}C$ to dehydrate remaining $Ca(OH)_2$, and calorimetric methods are used to

measure the heat of hydration and thus the amount of free lime (16). A

possible source of error may occur during heating the lime-pozzolan mortars

to $550^{\circ}C$ since some of the lime may combine with pozzolan.

Amount of reaction product   Lea (71) states that the silicates

and aluminates in the reaction products are completely soluble in dilute

hydrochloric acid. Ruff (109) found that 0.2N HCl dissolves all the

cementitious compounds in reacted lime-clay mixtures. X-ray studies have

shown that silica and alumina enter the reaction to form reaction products;

therefore, quantitative analysis of alumina and silica in the HCl extract

of reacted lime-pozzolan samples gives a good indication of the extent of

pozzolanic activity (70, 108, 137). After comparing several methods, Watt

and Thorn (137) concluded that determination of silica and alumina of the

acid-soluble portion of the reacted lime-fly ash samples is a fairly good

test for evaluation of pozzolanic activity for curing periods up to 100

days.

Synthetic Fly Ashes

Studies with artificial fly ashes have been attempted in England with

some degree of success (73, 137). In one such study as reported by Lees

(73), Herington prepared fly ash-like particles from several natural

minerals finer than 76 microns by passing them through a coal gas-oxygen

flame. The particles were dropped into the flame which was directed down

a refractory tube. The heat-treated particles were collected by passing

the flue gases over a trough of water. Lees' (73) own arrangement consisted

of feeding natural mineral powders into a blow pipe flame which was positioned at the lower end of a vertical silica tube furnace. The silica tube was 2 inches in diameter and 6 feet long. The mineral powders were injected either into the center of the flame along with the gas or through a separate ceramic tube placed at different positions in the flame. Provisions were also made for the addition of oxygen. The fly-ash like particles were collected by impingement on a greased glass plate or by drawing some of the flue gases through filter paper. However, insufficient description of experimental detail makes it difficult to assess how closely industrial furnace conditions were approximated. From microscopic examination of these particles, Lees found that clay minerals are the source for colorless and white particles; and iron minerals, for black and red spheres. He also established that the character of the spherical particles depends on the condition of the substance prior to their spheroidization, and the temperature at which the spheres are formed. However, his laboratory set-up allowed production of only rather minute samples of ash (maximum 1 gram) which was insufficient to permit investigation of pozzolanic reactions.

Watt and Thorn (137) adopted a similar technique for production of fly ash-like particles from coal minerals utilizing an oxygen-gas flame. Analysis of the synthetic fly ashes from the natural mineral powders enabled them to identify the mineral origin of some main types of fly ash particles. Similar attempts at such correlation were also made by Schneider (110) and Gumz (53) in Germany.

In an effort to correlate pozzolanic activity with specific fly ash parameters, Watt and Thorn (125, 137) prepared fly ash-like particles from

synthetic glasses. These synthetic glasses were prepared by melting together chosen proportions of component oxides; the products were then ground and converted into fly ash-like particles. A criticism of the procedure used by Watt and Thorn is that the temperature history of industrial fly ash particles is completely different. Their technique of fusing oxides to a glass results in a more intimate chemical mixing than would ordinarily occur in a suspension-fired furnace. Nevertheless, the results from their study indicate that the underlying concept of investigating pozzolanic reactions by synthesizing fly ashes from natural minerals has merit.

OBJECTIVES OF THIS STUDY

Previous studies indicate that chemical composition, crystal structure and fineness of pozzolans influence their reactivity. However, because of the heterogeneity of pozzolans in general and industrial fly ashes in particular, the degree and nature of such influences are not known. The objective of this study was to produce synthetic fly ashes of variable physical and chemical properties from natural minerals associated with coal, and then to react these fly ashes with lime in an attempt to determine the influence of ash properties on their pozzolanic activity. The specific objectives were:

(1) to prepare, in sufficient quantities, synthetic fly ashes of controlled physical and chemical properties from minerals associated with the coal under conditions closely approximating those found in suspension-fired furnaces;

(2) to characterize the physical and chemical properties of these synthetic fly ashes;

(3) to react these ashes with lime for specified periods of time and to obtain the measure of the reaction by a) unconfined compressive strength, b) acid-soluble silica and alumina in the reaction products, c) x-ray diffraction, and d) electron microscopy;

(4) to relate the influence of certain basic fly ash parameters to their pozzolanic strength;

(5) to relate reaction product formation to pozzolanic reactivity and strength;

(6) by use of above procedures, to gain a more detailed view of the

pozzolanic reaction mechanism.

An obvious practical aspect of this research is to indicate those fly ash parameters which contribute significantly to pozzolanic strenth. Such information may serve as an aid in establishing and evaluating realistic use specifications and possibly even in the production of better quality industrial fly ashes.

PART I.   PRODUCTION AND CHARACTERIZATION OF

SYNTHETIC FLY ASHES

PRODUCTION OF SYNTHETIC FLY ASHES

The feasibility of producing synthetic fly ashes was successfully demonstrated in a study preliminary to the present investigation (61). The next question was what kind of fly ashes were to be made--specifically, what parameters should be varied and given emphasis. Two criteria were utilized:

(1) Fly ash parameters which appear significant in the typical fly ash use specifications of various agencies (see Table 2, page 23);

(2) Additional parameters suggested by investigations in the field of cement chemistry which might influence pozzolanic reactions. Basic to the above criteria was the concept that these synthetic fly ashes should be made as similar as possible to industrial ashes.

After considerable deliberation and experimentation, it was decided to investigate the following three parameters in detail:

(1) chemical composition

(2) fineness or particle size

(3) crystallinity

Furthermore, the attempt was made to vary each parameter while maintaining others constant, in order to isolate its influence on the pozzolanic reaction. Thus it was necessary to prepare three groups of synthetic fly ashes:

(1) those having identical fineness and crystallinity but with variable chemical composition;

(2) those having identical fineness and chemical composition but with variable crystallinity;

(3) those having identical chemical composition and crystallinity but with variable fineness.

Preliminary investigations indicated that it was possible to vary the parameter of chemical composition by varying the kinds and amounts of natural coal-associated minerals used. The size parameter could be varied by collection procedures and size fractionation of synthetic ashes. The crystallinity parameter was effectively varied by additional heat treatments of the synthetic ashes. All synthetic ashes were initially produced under conditions approximating those found in suspension-fired furnaces (61).

Production Equipment and Procedures

In the first phase of this project, a laboratory-model furnace and collection system for the production of synthetic fly ash from the mineral kaolinite was designed and successfully operated (61). With minor modifications this same basic system was used in the production of all ashes in the present study.

Basically, apparatus requirements included some means of suitably introducing mineral powders into a flame for a specified duration and of collecting these heat-treated particles. The specific prerequisites were as follows:

(1) injection of mineral powders directly into the flame;

(2) flame temperatures between 1300-1700°C (98, 139);

(3) maximum particle residence time of 2 sec in the flame (125, 126);

(4) oxidizing conditions (52, 98, 126);

(5) collection of heat-treated particles from the flue gases.

In addition, despite the pilot-plant nature of the equipment, its design

was such that fairly large quantities of minerals could be treated within a reasonable period of time.

A burner was designed and constructed which utilized combustible laboratory gases to give the desired temperature, allowed for reasonable powder feed rates, and did not present any unusual problems in collection. The burner consists of three 9 in. long concentric tubes of 0.250, 0.5625, and 1.250 in. internal diameters mounted flush at the exit end. When using natural gas and air, the burner produced a flame over 60 cm long. The mineral powders were fed into the innermost tube along with primary air; gas was carried in the middle tube; and secondary air was carried in the outermost tube. Flows were adjusted to a velocity of 31 cm/sec so that the maximum residence time for particles in hot zone was 2 sec.

A Plasma Dyne Corporation "powder hopper" mounted on a vibrator was utilized for injecting powders into the burner. The burner was installed at one end of a horizontal furnace which was constructed of three layers of high-temperature insulating firebricks laid on edge and supported by a steel angle iron frame as shown in Figure 1. A 2 3/4 in. internal diameter mullite liner was inserted into a 3 in. diameter hole drilled in the central layer of brick. A 4 in. ID x 6 ft stainless steel flue pipe was placed at the collection end of the furnace, and a tapered pipe was connected to the exit end of the flue pipe and carried the gases and particles to the cyclone separator. Extra air was injected through this tapered pipe into the cyclone separator to cool the hot gases and increase efficiency of collection in the cyclone separator.

The efficiency of the cyclone separator was only 50-60%, and initially particles escaping with the exhaust gases were collected with the aid of
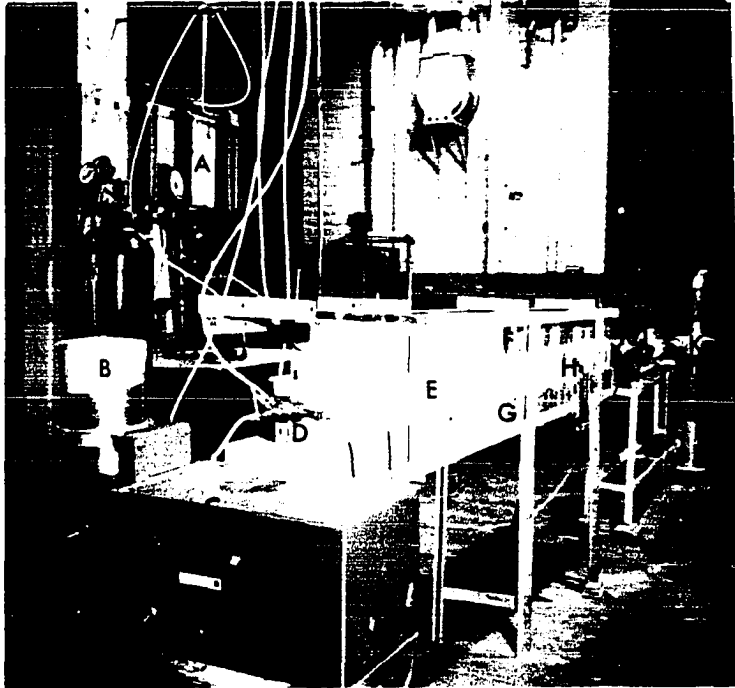
A. Gas control panel
B. Powder hopper
C. Hopper vitrator unit
D. Burner
E. Fire brick encasing mullite liner tube
F. Fire brick for insulation
G. Fire brick for insulation
H. Fire brick for insulation
I. Cooling pipe
J. Reducer section
K. Cyclone separator

Figure 1. Apparatus used for producing and collecting synthetic fly ashes

a shop-type vacuum cleaner. These have been characterized elsewhere (61). Due to the high temperature of the flue gases and possible damage to the vacuum unit, these fine particles were not collected in this phase of the research. Some particles were trapped in the mullite tube and formed a porous coating which slowly restricted the opening to about 1 1/2 in. after three to four hours of continuous operation. The spheroidization process was stopped at this time and the system allowed to cool so that the coating could be removed. The furnace liner deposits were substantial when firing certain mineral mixtures; however, the feed, combustion, and collection conditions could be reproduced with reasonable accuracy. The heat-treated mineral powders recovered from the furnace liner and cyclone separator are termed "furnace fly ash" and "cyclone separator fly ash", respectively; and were not mixed together inasmuch as they were subjected to completely different environments. The equipment was capable of producing about 200g of synthetic fly ash per day. Specific design and operational details are presented elsewhere (61).

Selection of Minerals

Simple reaction equations given by Whittingham (139), Gumz (52, 53), and Mackowsky (81) were utilized to calculate the molar weights of minerals required to give the desired compositional ranges in synthetic fly ashes. For example, the thermal reaction equation for the clay mineral kaolinite is the following:

$$[Al_2(OH)_4(Si_2O_5)]_2 \rightarrow [Al_2O_2(Si_2O_5)]_2 + 4H_2O \uparrow \qquad (1)$$
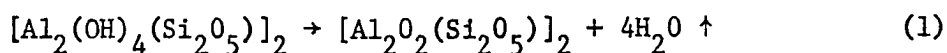
Accordingly, one mole or 516·303g of kaolinite yields 72.052g of water and

444·251g of solids. Therefore, 117g of kaolinite is required to produce

100g of alumino-siliceous material. The simultaneous decomposition and

oxidation reactions of pyrite and calcite were assumed to be as follows:

$$6FeS_2 + 15O_2 \rightarrow Fe_3O_4 + 2Fe_2O_3 + 10SO_2 \uparrow \qquad (2)$$

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow \qquad (3)$$
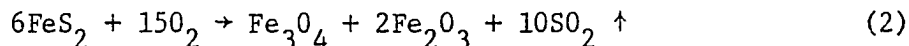
Calculations indicated that 153g of pyrite were necessary to produce 100g

of Fe_2O_3 and Fe_3O_4 in equal amounts. Similarly, 179g of calcite yielded

100g of calcium oxide. From such calculations it was a simple arithmetic

manipulation to determine the proportions of various minerals necessary

for production of fly ashes of known chemical composition.

It was decided to prepare a synthetic fly ash from pure kaolinite in

order to determine the pozzolanic reactivity of an alumino-siliceous

material. Fly ashes were also prepared from various mixtures of kaolinite-

pyrite, kaolinite-calcite, and kaolinite-pyrite-calcite. Table 3

presents the calculated or attempted chemical composition of the synthetic

fly ashes prepared. Fly ash notations given refer to oxides derived from

the added minerals.

The K+P fly ashes are representative of industrial fly ashes which are

produced from bituminous coals containing only trace amounts of calcite,

while K+P+C fly ashes cover the general range of industrial fly ashes and

compare fairly well with the chemical composition of industrial fly ashes

produced from bituminous coals in this country.

Although there are hardly any coals which contain only kaolinite and

calcite yet the K+C fly ashes can be said to be representative of some

Table 3. Predicted chemical compositions of synthetic fly ashes prepared

Fly ash notation	% silica and alumina	% iron oxide	% calcium oxide
K-Cyc	100	--	--
K+10P	90	10	--
K+20P	80	20	--
K+30P	70	30	--
K+40P	60	40	--
K+50P	50	50	--
K+5C	95	--	5
K+10C	90	--	10
K+15C	85	--	15
K+10P+5C	85	10	5
K+10P+10C	80	10	10

lignite coal fly ashes containing up to 15% calcite and trace amounts of pyrite. However, the aim of producing these bi- and trimineralic fly ashes was to investigate effect of pyrite and calcite separately on the pozzolanic properties of the fly ash. The chemical analyses of the synthetic fly ashes presented later indicate that although the predicted proportions of various oxides were not precisely achieved, the differences were of the order of 1 to 5%, and the samples cover the desired range of chemical composition of industrial fly ashes.

Pulverization of Minerals

The fineness to which the minerals were ground prior to spheroidization was decided after investigating the fineness of coal powder and associated minerals as well as the fineness of industrial fly ashes. Commercial coal pulverizers are designed to produce powder containing 80

to 85% passing a 74 micron sieve and 98% passing a 250 micron sieve (20).

Although no analysis is made of the size fraction passing 74 micron for

industrial control of coal fineness (77), Littlejohn (78) and Kurtzrock

et al. (67) found that the majority of particles passing a 74 micron sieve

are actually less than 50 microns. It is also evident from their data

that the fly ash produced from a certain coal powder is always much finer

than the coal powder itself. Littlejohn reasoned that when the carbona-

ceous portion of the "mixed" particle burns, it leaves behind a much

smaller mineral particle, and therefore the resultant fly ash is finer than

the coal powder (78).

The particle size of industrial fly ashes ranges from 0.1 micron to

100 microns; the majority are less than 50 microns (67). Since particle

size analysis of fly ash is usually reported in terms of weight percent

passing certain sieves (5), and since most fly ashes are much finer than

the finest sieve, i.e. 325 mesh (44 microns), no information is readily

available on the particle size distribution below 44 microns. Other

investigators have attempted particle size analysis of industrial fly

ashes by the hydrometer method (74, 138); however the method errs in

assuming an average specific gravity of 2.65. Nonetheless, median sizes

of 28 to 38 microns have been reported by Leonards (74).

With such data in mind, it appeared reasonable to grind the minerals

to pass a 200 mesh sieve (74 microns). The kaolinite[1] selected was already

in a powdered form. Best-grade crystalline pyrite from Colorado and

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[1]The properties of this material are given in Appendix A.

first-grade, nonoptical cleavages of Mexican Iceland Spar were obtained

from Ward's Natural Science Establishment. The pyrite was first passed

through a laboratory jaw crusher; the calcite was hand-crushed in a mortar

and pestle. Pyrite was charged into a steel ball mill; and calcite, into

a porcelain ball mill for further grinding. The mineral powders were then

passed through a 200 mesh sieve (74 microns) on a Ro-Tap sieve shaker.

The mineral mixtures indicated in Table 3, page 42, were prepared by

weighing out the appropriate amount of each mineral, combining and then

dry-blending them in a V-blender for 8 hours to ensure homogeneity.

Fly Ash Size Separation

The synthetic fly ash produced from pure kaolinite was separated

into various size fractions so that quantitative information could be

obtained concerning size and pozzolanic reactivity.

A rising-current elutriator[1] was used to obtain the following size

fractions: <5, 5-10, 10-20, and >20 microns. It was not readily possible

to separate the synthetic fly ash prepared from mineral mixtures into

various size fractions inasmuch as all fractionation methods based on

sedimentation include a specific gravity term. Synthetic fly ashes

prepared from more than one mineral would necessarily have a substantial

range in specific gravity which would result in mixed sizes. Use of

micromesh sieving proved too difficult and time-consuming.

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[1]Design details of the elutriator and fractionation procedure are
given in Appendix B.

Modification of Fly Ash Crystallinity

During the production of synthetic fly ash from kaolinite, Joshi
(61) observed and investigated particles deposited in the furnace. This
layer of particles could be easily removed with the help of a brush.
Light and electron microscopic observations of these particles indicated
that a large number were either spherical or rounded and the majority
were anisotropic or crystalline. X-ray studies indicated that the mullite
peaks had sharpened and the amorphous hump had been considerably suppressed,
probably as a result of the longer residence time in the furnace. It was
therefore decided to heat-treat some cyclone fly ash in an attempt to
produce synthetic fly ashes of identical composition but varying crystal-
linity.

Alumina crucibles containing 500g of cyclone fly ash were placed in a
small "globar furnace" heated by a silicon carbide heating element. The
samples were heated to $1500^{\circ}C$ for 24 hours and cooled at a rate of $100^{\circ}C/$
hour. The synthetic fly ash soaked at elevated temperatures tended to form
a porous mass which easily crumbled under finger pressure.

Three synthetic fly ashes of different crystallinity but with similar
chemical composition could thus be obtained: cyclone separator fly ash
with a very small fraction of crystalline material, furnace fly ash which
was partly crystalline, and the recrystallized ash. These three fly ashes
were also fractionated into the same size fractions of <5, 5-10, 10-20,
and >20 microns. Thus fly ashes of the same chemical composition and
fineness but of varying degrees of crystallinity were obtained.

CHARACTERIZATION OF SYNTHETIC FLY ASHES

All of the synthetic fly ashes were analyzed to determine their physical and chemical properties prior to reacting them with lime. Such analyses were also helpful in understanding some of the basic properties of fly ashes and reasons for their variability.

Physical Methods of Analyses

Microscopic observations

Light microscopy   Representative samples of fly ashes were dispersed in liquids of various refractive indices and observed under a Zeiss Ultraphot II petrographic microscope. Studies included measurement of refractive index, description of particle shape, and isotropy. Becke lines were used to measure refractive indices, using immersion oils in increments of 0.002. Photographs of typical particles were recorded on Polaroid type 52 film.

Electron microscopy   Samples were prepared by evaporation of a water-ash suspension on a carbon coated grid. A Siemens Elmiskop I electron microscope was operated at 80 KV and images were recorded on a Dupont Cronar film. (Ortho-S-Litho)

Magnetic separation

Magnetic separation of synthetic fly ashes in the dry state could not be achieved satisfactorily since magnetic and nonmagnetic particles tended to agglomerate. Therefore, 100g of synthetic fly ash were dispersed in 500 ml of water in a separatory funnel which was placed between the poles of a strong horseshoe magnet. The magnetic particles were attracted

to the funnel walls adjacent to the poles of the magnet, and the suspension containing nonmagnetic particles was drained into a large beaker. The magnetic particles were then washed down into a separate beaker. The two fractions were repeatedly subjected to this process until visual observation indicated that no more separation occurred. The water from the two beakers was removed by decantation and evaporation and the two fractions were weighed separately.

Specific gravity determination

A slightly modified version of the liquid displacement method described in ASTM Designation C-135-66 (6) was used to determine the specific gravity of the various size fractions of the kaolinite fly ash as well as other synthetic ashes. When water was used as the liquid, fine particles of fly ash floated due to surface tension effects. In addition, the water solubility of calcium compounds present in some of the fly ashes prohibited the use of water as a displacement agent. Among various other liquids attempted, amyl acetate was found to be most suited because of its low specific gravity. Its low boiling point, however, necessitated use of a vacuum-jacketed, covered specific gravity bottle[1].

Particle size determination

Mechanical sieving   Attempts were made to perform standard dry sieving with precision sieves and the Allen Bradley Sonic Sifter, Model L 3P. The static charge on the particles, however, caused balling, particularly in the size fraction less than 45 microns. Samples weighing about

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[1]The vacuum-jacketed specific gravity bottles were procured from Sargent-Welch Scientific Co., Skokie, Illinois.

2g were dry-sieved through 250, 150, 75, and 45 micron sieves. The
fraction passing 45 microns was wet sieved through 30, 20, and 10 micron
sieves.

Electron microscope particle count method   A small sample of fly
ash dispersed in Formvar ethylene dichloride solution was spread over a
glass microscope slide and the ethylene dichloride allowed to evaporate.
The thin film was scored into 2 mm^2 segments which were floated onto a
water surface and then caught on copper specimen grids.

A Siemens' Elmiskop I was used with 80 KV electrons at a magnifica-
tion of 1250 X on the fluorescent screen. A Siemens' TV camera viewed
this screen and projected the particle images onto a 525 lines/frame
television screen at a magnification of 5000 X. One centimeter on this
screen was equivalent to one micron; the accuracy in size determination
was 0.2 micron. Maximum observable size was limited by screen diameter to
18 microns. Five specimen grids were prepared from each fly ash sample,
and 500-1000 particles/grid were measured and grouped into different sizes.
Mean diameters representing length, volume, and surface of all the
measured and counted particles were evaluated by writing a computer program
to solve the following five equations devised by Perrot and Kinney (101).

$$\text{Mean diameter (length)} = d_1 = \frac{\Sigma nd^2}{\Sigma nd} \tag{4}$$

$$\text{Mean volume diameter} = d_v = \sqrt[3]{\frac{\Sigma nd^3}{\Sigma n}} \tag{5}$$

$$\text{Mean surface diameter} = d_s = \sqrt{\frac{\Sigma nd^2}{\Sigma n}} \tag{6}$$

$$\text{Mean volume surface diameter} = d_{vs} = \frac{\Sigma nd^3}{\Sigma nd^2} \tag{7}$$

$$\text{Weight mean diameter} = d_w = \frac{\Sigma nd^4}{\Sigma nd^3} \qquad (8)$$

where n is the number of particles of diameter d. An "Olivetti Underwood Programma 101" model computer was used for this purpose. The electron microscope was found to be helpful in determination of particle size distribution of the fly ashes since a major fraction of the fly ashes is composed of particles smaller than 20 microns.

Specific surface area determination

The fineness of fly ash is frequently described in terms of specific surface area determined by the Blaine air permeability method since the particles are too fine to be fractionated by ordinary sieving procedures. The fineness then is reported in cm^2/gram of fly ash. Generally, the higher the measured specific surface area of a given material, the finer it is (36). The procedure employed is described in ASTM Designation C-204-55 (5).

Specific surface areas of various synthetic fly ashes were also determined by calculation from the electron microscopic size analysis. The number of particles per gram of sample could be obtained from the specific gravity of the sample as indicated below.

$$\text{Volume of particles per gram} = \frac{1}{\text{Sp gr}} \qquad (9)$$

$$\text{Since weight of one particle} = \text{volume x Sp gr} = \frac{\pi \, d_{vs}^3}{6} \times \text{Sp gr} \qquad (10)$$

$$\text{Number of particles per gram} = \frac{1}{\text{Sp gr}} \times \frac{6}{\pi \, d_{vs}^3} \qquad (11)$$

Specific surface area of the particles per gram

$$= \frac{6}{\text{Sp gr } \pi d_{vs}^{3}} \quad \times \pi d_{vs}^{2} \tag{12}$$

$$= \frac{6}{\text{Sp gr } \times d_{vs}} \tag{13}$$

If d_{s} and d_{v} are substituted for d_{vs} in Equation 12 above, in the surface area and volume terms respectively, Equation 13 becomes

$$= \frac{6 d_{s}^{2}}{\text{Sp gr } d_{v}^{3}} \tag{14}$$

It will be recognized that substitution of the values of d_{s} and d_{v} from Equation 5 and 6 in Equation 14 will become Equation 13.

X-ray diffraction analysis

A General Electric XRD-5 diffractometer was employed with filtered molybdenum or copper radiation. A 1° beam slit, MR Soller slit, and a 0.2° detector slit were used. Samples were packed in 2 in. specimen holders and scanned at a rate of 2°/min. The diffraction pattern for each sample was recorded on a strip chart using a full scale of 500 counts/sec, a time constant of 3 sec, and a chart speed of 1 in./min. Identification of diffraction maxima was aided by the use of the ASTM Powder Diffraction File for inorganic compounds (7).

Chemical Methods of Analysis

Elemental analysis

Fly ashes were analyzed by analytical chemistry methods to determine

the amount of total silica, alumina, and iron. Standard methods as

prescribed by the Official Association of Agricultural Chemists were

adopted (9). The results of chemical analysis on four separate samples

were averaged and recorded with the maximum variations given as tolerances.

Total calcium was determined by the EDTA method using calcein indicator

as described by Diehl (42). Some magnetic and nonmagnetic fractions of

synthetic fly ashes prepared from kaolinite-pyrite mixtures were also

analyzed to find the amount of silica and alumina integrally attached to

magnetic particles.

Acid-soluble content

Various European authors have reported that hydrofluoric acid causes

preferential solubility of glass as compared to crystalline silica and

mullite. Konopicky and Kohler (66) reported that up to 40% ice-cold (0°C)

hydrofluoric acid does not dissolve a significant amount of mullite,

quartz and other similar crystalline substances associated with fired

ceramic glasses and glazes. They concluded that even after several hours

of extraction with ice-cold 2% hydrofluoric acid, only the glass phase is

removed. They recommend, however, an optimum period of 2 hours.

McGee (85, 86) heat-treated kaolinite for 3 hours at various tempera-

tures ranging from 1250-1500°C and subsequently rapid-quenched the materials.

He analyzed these materials by x-ray diffraction using the internal

standard method to determine the various crystalline phases present. The

glassy phase was obtained by subtraction. McGee's heat-treated materials
were available and adopted as standards against which the validity of
HF-solution treatment suggested by Konopucky and Kohler could be tested.
Treatment of McGee's materials with ice-cold 40% HF solution for 2 hours
gave values for the glassy phase which were within 2% of McGee's data.

Accordingly, 1/2g samples of various synthetic fly ashes were
allowed to stand with 200 ml ice-cold 40% HF in polypropylene beakers
which were in turn placed in an ice-water bath. The contents of the
beakers were stirred every 15 min for 2 hours, after which the residue
was filtered and washed with 0.1N sulfuric acid. After ashing the filter
paper and residue at 700°C, the weight was noted and converted to percent.
The results could be reproduced with an accuracy of $\pm$2%.

However, the method as described so far does not take into account
other non-glassy but acid-soluble phases present in the ashes. Separate
1/2g ash samples were therefore treated with 200 ml of 0.2N HCl at room
temperature for 1/2 hour on the assumption that only calcium and iron
compound would be soluble. The loss in weight after treatment was
recorded as percent HCl-soluble material. This percent value was subtracted
from the corresponding HF-treatment value to give the HF-soluble percent
corresponding to the percent glassy phase.

X-ray elemental microanalysis (XMA)

The x-ray microanalysis spectrometer attachment to the Siemens'
electron microscope was used to gain some insight into the distribution of
various elements in the particles comprising several of the synthetic
ashes. Specimens were prepared as for normal microscopy; however, it

was found necessary to vacuum deposit a thin layer of carbon for particle

stability in the electron beam. Elements analyzed for were aluminum,

silicon, calcium and iron.

FLY ASH NOTATIONS

It was found convenient throughout the course of this research to refer to specific samples with the aid of a personalized type of abbreviation or notation. These notations are listed below and will be used throughout this dissertation.

FA = Synthetic fly ash

K = Synthetic fly ash prepared solely from kaolinite

K+P = Synthetic fly ash prepared from a mixture of kaolinite and pyrite

K+C = Synthetic fly ash prepared from a mixture of kaolinite and calcite

K+P+C = Synthetic fly ash prepared from a mixture of kaolinite, pyrite and calcite

Cyc FA = Synthetic fly ash collected in the cyclone separator

Furn FA = Synthetic fly ash deposited in and collected from the furnace liner

Recrys FA = Synthetic fly ash prepared by reheating and slowly cooling cyclone fly ash

If numbers precede the letter K, these refer to the particle size, e.g. 5-10 K refers to kaolinite fly ash 5-10 microns in size.

If numbers precede the letter P or C, these refer to the wt % of iron or calcium oxide in the fly ash, e.g. K+10P refers to a synthetic fly ash containing 10% iron oxide, K+10P+5C refers to fly ash containing 10% iron oxide and 5% calcium oxide, the remainder being composed of oxides of silica and alumina derived from the kaolinite.

RESULTS AND DISCUSSIONS

General Observations

An immediately apparent observation of the synthetic fly ashes was

their variety of color, usually white to very dark gray. The color of

fly ash collected in the furnace always differed from the fly ash collected

in the cyclone separator. Where possible, fly ash colors are designated

by means of the Munsell Color Notation System (96) and are given in

Table 4.

The K-Cyc FA was very slightly gritty to the touch and white to very

light gray in color. The white color of this fly ash appeared to have a

lower value than the color of kaolinite mineral powder, suggesting that

the spheroidized fly ash particles have a different reflectivity than the

platy kaolinite. The various size fractions of this ash appeared identical

in color.

The K-Furn FA occurred as colored banded deposits, appeared sintered,

and felt very gritty to the touch. Material was usually white adjacent t >

the furnace liner, and a color sequence of white to gray to yellow was

found which varied with different firings. The material from all three

layers was mixed together, yielding a white powder with a standard

notation of 1.5 Y/8/1.5 on the Munsell color chart.

The K-Recrys FA was white and much more gritty than the other two

monomineralic fly ashes. Although prepared from the cyclone fly ashes,

its color was not at all similar to K-Cyc FA or to the natural kaolinite

mineral. A possible reason for the change in color appears to be the

development of larger and more numerous crystal planes and faces capable

Table 4. Munsell color notations of synthetic fly ash samples

Type of fly ash	Color notation	
	Color name	Hue/croma/value
K-Cyc FA	white	N 9.5
K-Furn FA	white	1.5Y/8/1.5
K-Recrys FA	white	N 10
K+10P whole sample	light gray	2.5Y/7.5/1
K+20P whole sample	light gray	7.5YR/7/1
K+30P whole sample	gray	7.5YR/5.5/1
K+40P whole sample	dark gray	7.5YR/4.5/1
K+50P whole sample	very dark gray	7.5YR/3.5/1
K+10P nonmagnetic fraction	white	5Y/8/1
K+20P nonmagnetic fraction	white	10YR/8/1
K+30P nonmagnetic fraction	light gray	10YR/7/1
K+40P nonmagnetic fraction	light gray	10YR/7/1
K+50P nonmagnetic fraction	light gray	10YR/7/1.5
K+10P magnetic fraction	very dark gray	7.5YR/3/1
K+20P magnetic fraction	very dark gray	7.5YR/3/1
K+30P magnetic fraction	very dark gray	7.5YR/3/1
K+40P magnetic fraction	very dark gray	7.5YR/3/1
K+50P magnetic fraction	very dark gray	7.5YR/3/1
K+5C	white	N 9.5
K+10C	white	N 9.75
K+15C	white	N 10
K+10P+5C whole sample	light gray	10YR/6.5/1
K+10P+10C whole sample	light gray	2.5Y/7/1

of reflecting more light than the spherical or platy particles. The various fractions of this fly ash were identical in color and to the touch.

The color of bimineralic and trimineralic fly ashes seemed to be controlled by the proportion of the minerals. The bimineralic K+C ashes were lighter and the K+P ashes much darker gray than the monomineralic K-Cyc FA. The possible compounds of calcium produced by heat treatment and quenching would include the oxide, hydroxide and silicate forms, all of which are white (102). The compounds of iron, on the other hand, are black, brown or red in color and impart a darker shade to the fly ash. The color of the K+P fly ashes darkened with increasing amount of pyrite, ranging in color from gray (7.5YR/7.5/1) to very dark gray (7.5YR/3.5/1). Industrial fly ashes also fall within this range. The dark gray color of industrial fly ashes may be attributed to the iron compounds as well as unburnt carbon particles. Although magnetic separation of K+P fly ashes removed the dark iron oxide particles, the nonmagnetic fractions of these ashes were much darker than the monomineralic K-Cyc FA. The magnetic fractions of different fly ashes of K+P series were much darker than the whole fly ash sample but did not differ in color from each other as is observed from the similarity of the Munsell notation of 7.5YR/3/1 for all of them (Table 4). Although all K+P fly ashes collected in the cyclone were equally gritty, the magnetic fractions were more gritty.

The trimineralic fly ashes in the K+P+C series also showed variation in color with the proportion of different minerals, an increase in calcium in part tending to compensate for darkness due to the increase in iron.

Microscopic Examinations

The most conspicuous property of industrial fly ash particles when observed under the light microscope is their heterogeneity with respect to shape which ranges from angular to irregularly-rounded to spherical (118, 119, 125, 138). Furthermore, the particles may be clear to red-colored to opaque. Light microscope observations of synthetic fly ash particles from the cyclone separator revealed a similar heterogeneity in particle morphology and color.

Watt and Thorn (125) adopted a system of classification for industrial fly ash particles based on the criteria of shape, color, crystallinity and texture. This system of classification was used in the present investigation (Table 5). Although no sharp distinction was seen between the types indicated, the combination of criteria was found suitable to unambiguously classify particles under one of the types given in Table 5.

Monomineralic fly ash particle types

K-Cyc FA   Although size was not used as a criterion for classifying particles, examination of separate size fractions of K-Cyc FA (Figure 2 through 6) indicated that certain types of particles dominate in particular size fractions. Approximate limits are shown in Table 5.

All of K-Cyc FA was made up of spherical and sausage-shaped particles of Types 1 and 3 (Figure 2). An occasional colored or opaque particle was observed. The particles of K-Cyc FA <20 microns in diameter did not differ significantly with respect to distribution of particle type and shape (Figures 3, 4, and 5), but particles >20 microns were frequently curved and sausage-shaped and of Type 3 (Figure 6). Their shape suggests

Table 5. Types of synthetic fly ash particles observed in the light microscope

Type	Shape	Color		Crystallinity and texture	Size range microns	Remarks
1	Spherical and rounded	colorless	a	clear, solid, isotropic	0-20	Typical of K-Cyc FA
			b	dark periphery and bright center but isotropic, probably cenospheres	5-50	
			c	isotropic, with small inclusions of birefringent particles	0-20	The term "speckled" is applied to these particles
			d	solid, predominantly birefringent		
2	Spherical and rounded	light brown to black	a	light colored, solid isotropic	0-20	Deepening color probably reflects increasing iron content
			b	light colored, isotropic but quite grainy, probably due to bubbles	5-200	
			c	opaque, rough surface	0-200	Mostly magnetite
3	Curved, sausage-shaped, rounded and elongated		a	isotropic, clear	10-200	
			b	isotropic, with inclusions of circular shape having dark periphery and bright center		The term "grainy" is applied to these particles. Several small & large gaseous bubble, inclusions possibly cenospheres and

Table 5. (Continued)

Type	Shape	Color	Crystallinity and texture	Size range microns	Remarks
					curved grainy particles. Predominant in fraction larger than 20 microns.
			c isotropic and aggregated (small particles loosely attached)		
4	Rounded and cylindrical	part brown to opaque, part colorless	colorless portion is isotropic	5-200	Mixed particles of glass and magnetite
5	Irregular to rounded	colorless	solid, sintered inclusions, birefringent particles	10-200	Probably particles in which mullite crystals have grown and glass composition has changed
6	Rhombic and/or irregular	varicolored	birefringent	5-200	Calcite particles
7	Needles	colorless	birefringent	0-200	Acicular habit suggest they are mullite
8	Angular	colorless	crystalline, solid	5-200	Probably cristobalite
9	Angular	red	crystalline, solid	5-200	Hematite or other compound containing iron

that they are collapsed cenospheres. Perhaps the rounded and elongated particles also formed from these cenospheres. As the air or gas trapped inside the cenosphere expands, the thin film of molten material ruptured. Temperatures may have been sufficiently high enough to heal the rupture and form a curved cylindrical or elongated particle. It is also possible that some bubbles may have been trapped in this process giving rise to curved and sausage-shaped particles of Type 3b. Observation of partially collapsed spheres lends support to this hypothesis. The circular inclusions having a dark periphery and bright center imparting grainy appearance to the particles may be due either to gas bubbles in the particles or to small particles attached to their surface. However, electron microscopic observations (Figure 3 and 6) indicated that almost all the particles in K-Cyc FA had smooth outer surfaces, while under light microscope many of the particles >10 microns showed presence of air bubbles readily identifiable from very low refractive index and high relief. Therefore, the grainy appearance of particles such as in Figure 6(a) is probably due to gaseous inclusions. Watt and Thorn (125) report the presence of numerous particles with gas inclusions in industrial fly ashes.

Some small particles occurred loosely aggregated to bigger particles in the fraction >20 microns, as shown in Figure 6; these particles, however, disagglomerated when rubbed between the glass slide and cover slip. Some spherical, rounded and curved sausage-shaped particles of Type 1 and Type 3 in K-Cyc FA contained anistropic needles suggesting mullite. Such particles appeared speckled and the specks showed high birefringence (Figure 2). The abundance of needle-shaped crystals in particles of Types 1, 3, and 5 (especially Type 5) indicated substantial crystallization

Type 1c

Type 1a

Type 3b

Type 3a
(bottom-center)

Type 1d

(a)

10 μ

(b)
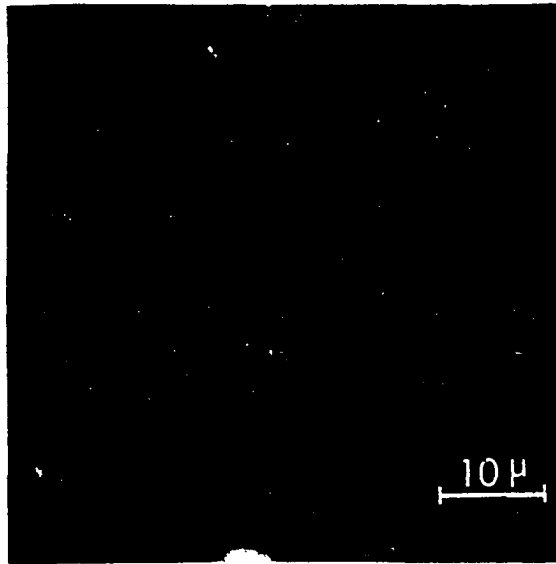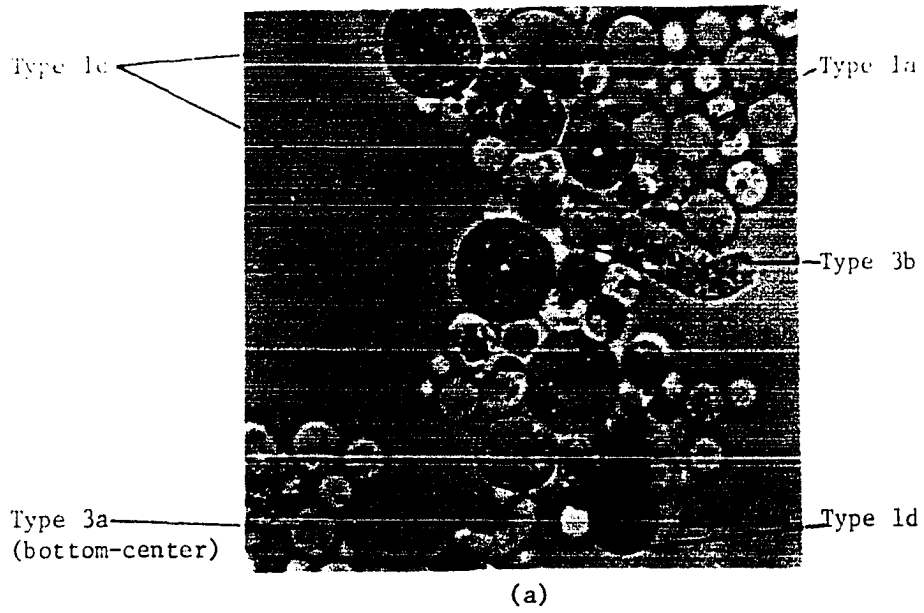
Figure 2. Photomicrographs of typical Types 1 and 3 particles in
K-Cvc FA: (a) under transmitted light, (b) under crossed
Nicols
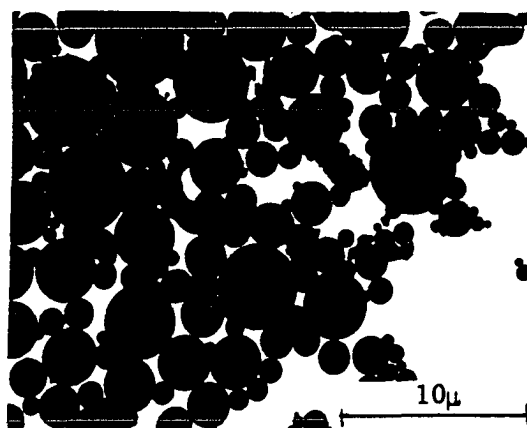
(a)
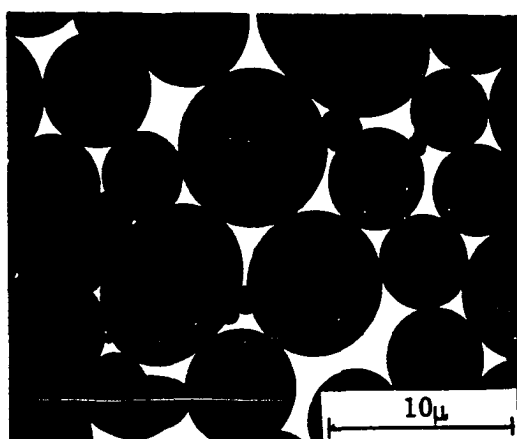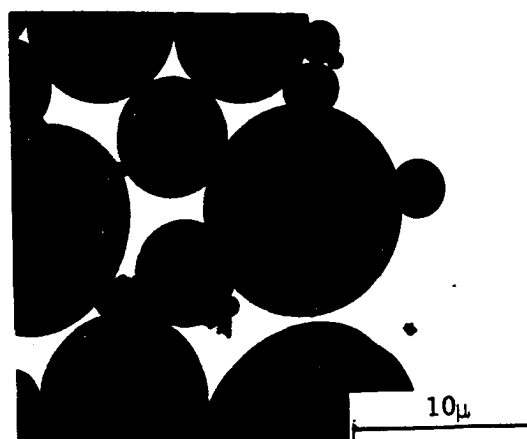
(b)   (c)

Figure 3.   Electron micrographs of different size fractions of
            K-Cyc FA: (a) <5 K-Cyc FA, (b) 5-10 K-Cyc FA, (c) 10-20
            K-Cyc FA
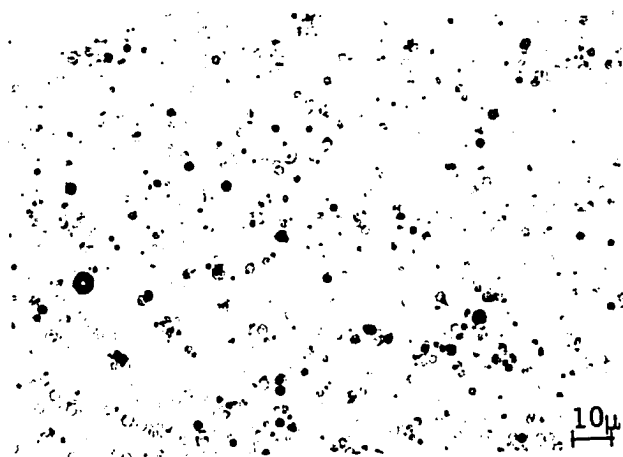
(a)
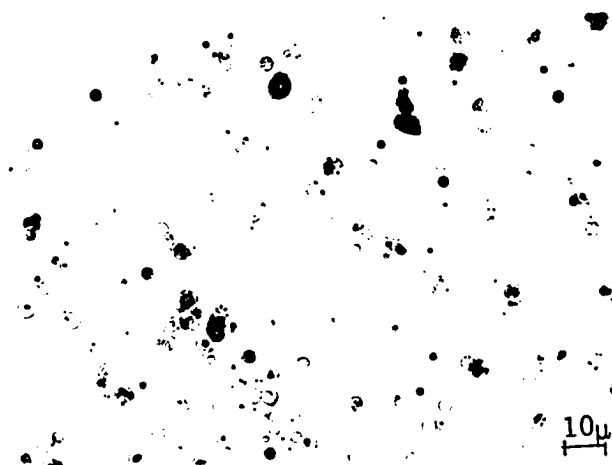
(b)

Figure 4. Photomicrographs of K-Cyc FA fractions under transmitted light: (a) <5 K-Cyc FA, (b) 5-10 K-Cyc FA
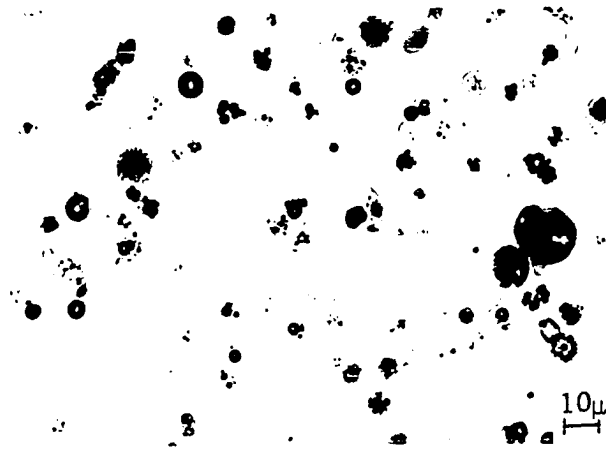
(a)

(b)

Figure 5. Photomicrographs of 10-20 K-Cyc FA particles: (a) under
transmitted light, (b) under crossed Nicols

Type 5

10μ

(a)

10μ
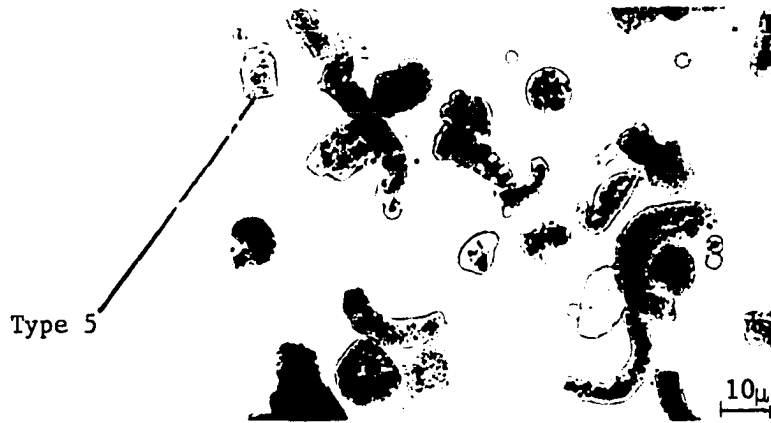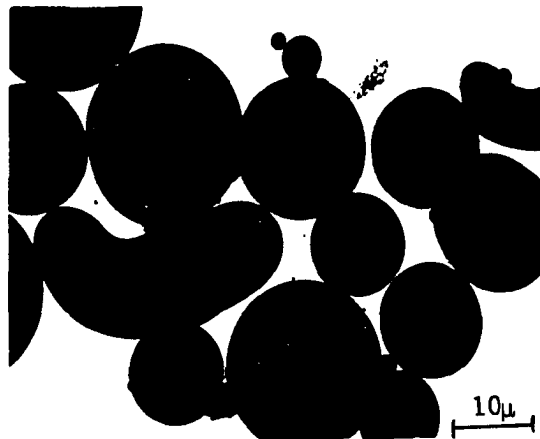
(b)

Figure 6. >20 K-Cyc FA sample containing an abundant number of
sausage-shaped Type 3b particles: (a) micrograph under
transmitted light, (b) electron micrograph of Type 3b
particles

(Figure 7). An insignificant number of such particles exist in K-Cyc FA.

The existence of crystals within the glassy matrix in such particles must

alter the glass composition of the particle and therefore possibly the

pozzolanic activity (125).

Table 6. Refractive indices of isotropic particles and matrix in various
synthetic fly ashes

Fly ash notation	Refractive index
K-Cyc FA	1.552 ± .002
K-Furn FA	1.570 ± .002
K-Recrys FA	1.588 ± .002
K+10P (nonmagnetic)	1.556 ± .002
K+20P (nonmagnetic)	1.558 ± .002
K+30P (nonmagnetic)	1.560 ± .002
K+5C	1.556 ± .002
K+10C	1.556 ± .002
K+15C	1.556 ± .002
K+10P+5C	1.560 ± .002
K+10P+10C	1.558 ± .002

The majority of the clear spheres observed in the K-Cyc FA were

isotropic (Figure 2 and 5) and had a refractive index of 1.552 ± .002.

The isotropic nature of the particles indicates that these are glassy or

amorphous. Other types of particles occurred in lesser amounts in K-Cyc FA.

K-Furn FA   The K-Furn FA contained a higher proportion of Type 5

birefringent particles, many of which seem to be sintered or aggregated

(Figure 8a, 8b and 9a). The proportion of clear, spherical and

isotropic particles of Type 1 in K-Furn FA is much less than in the

K-Cyc FA. Close examination of Figure 8(b) indicates that the particle

surfaces of K-Furn FA have greater crystalline inclusions than the interior

as evidenced by brighter birefringent spots on particle perphery. The

matrix glass of K-Furn FA particles has a refractive index of 1.570 + .002.

K-Recrys FA   The majority of the particles in the K-Recrys FA are

sintered and birefringent of Type 5 and 7 and are more irregularly shaped

than the particles of the other two monomineralic fly ashes previously

described (Figure 9(b) and 10). In addition, angular particles of Type 8,

which were practically nonexistent in the K-Cyc and K-Furn fly ashes, are

present in abundance in this fly ash. These particles have been formed at

the cost of solid, smooth, spherical and isotropic particles of Type 1 in

the K-Cyc FA from which this ash had been prepared. Type 1 particles were

not observed in the K-Recrys FA. With the exception of needle-shaped and

angular particles of Type 7 and 8 respectively, all others exhibit a

light brown color in transmitted light and appear to be grainy and frac-

tured. They also show more and larger birefringent crystalline particles

embedded in them as compared to the particles in the other two monomineralic

fly ashes (Figure 10). The increased amount and size of crystalline inclu-

sions and/or surface aggregates seem to be responsible for the irregularity

of the surface as seen in the electron micrographs (Figure 10(b)). This

may also explain the fractured appearance and increased birefringence of

the K-Recrys FA particles in general and particle surfaces in particular

observed under light microscope (Figure 7 and 10). The refractive index of

the matrix glass of most Type 5 particles in this fly ash increased to

1.588 + .002 (Table 6), implying a definite change in the composition and

possibly also stress conditions in the glass.

(a)

(b)

Figure 7. Photomicrographs of Type 5 particles in synthetic fly ashes:
(a) under transmitted light, (b) under crossed-Nicols
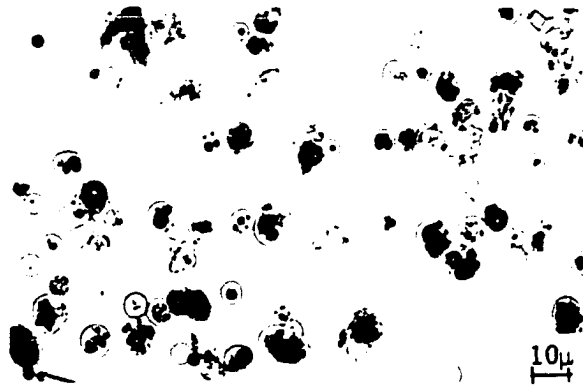
(a)

(b)

Figure 8. Photomicrographs of 10-20 K-Furn FA: (a) under transmitted light, (b) under crossed-Nicols
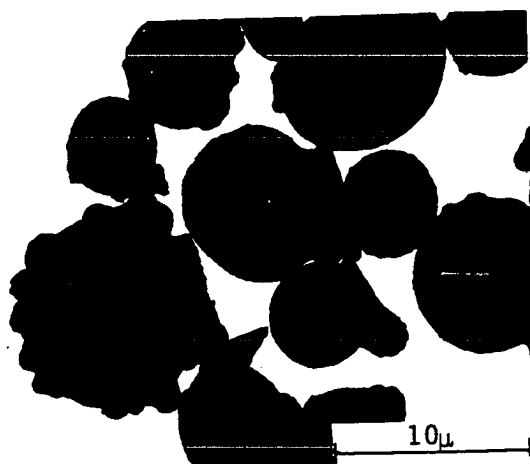
(a)
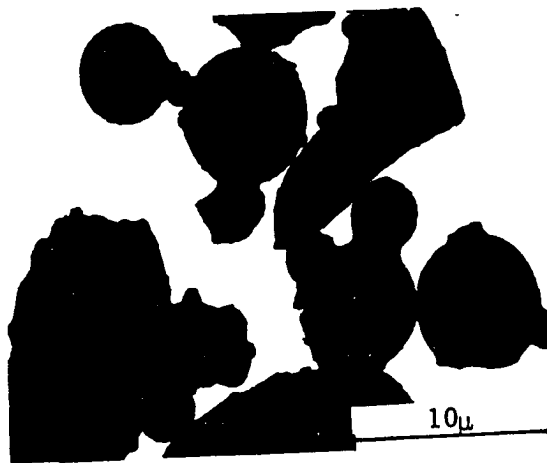
(b)

Figure 9. Electron micrographs of (a) K-Furn FA and (b) K-Recrys FA

Type 8

(a)

(b)

Figure 10. Photomicrographs of 10-20 K-Recrys FA: (a) under transmitted
light, (b) under crossed-Nicols

<u>Differences</u> <u>in</u> <u>particles</u> <u>of</u> <u>three</u> <u>monomineralic</u> <u>ashes</u>   With regard

to composition and stress conditions of glasses and crystals Kingery (64)

states:

> In general,...the ionic polarizability will increase with
> the size of the ion and with negative charge on iso-
> electric ions. Since the index of refraction increases
> along with the polarizability...we obtain high refractive
> indices with large ions. However, immediate surroundings
> also affect the refractive index; only in glasses and in
> cubic crystals is the index independent of crystallographic
> direction. In other crystal systems the index of refrac-
> tion is high in directions that are close-packed in the
> structure. Similarly, the more open structures of high-
> temperature polymorphic forms have lower refractive
> indices than the low-temperature forms, and glasses have
> lower indices than crystals of the same composition. For
> SiO_2, for example, $n_{glass} = 1.46$, $n_{tridymite} = 1.47$,
> $n_{cristobalite} = 1.49$, $n_{quartz} = 1.55$.
>
> In the same way that densely packed directions in crys-
> tals have the highest refractive index, the application
> of a tensile stress to an isometric material such as a
> glass increases the index normal to the direction of the
> stress and decreases the index along the stressed direc-
> tion. Uniaxial compression has the reverse effect.
> Since the incremental changes in light velocity (refrac-
> tive index) are directly proportional to the applied
> stress, the birefringence (difference in indices in
> different directions) can be used as a method of
> measuring stress.

The K-Cyc FA may be considered a glassy form of the kaolinite from

which it was prepared. This is suggested by the lowering of the index of

refraction from 1.566 (Kerr <u>et</u> <u>al.</u> report a range of 1.558 to 1.571) for

kaolinite (18, 63) to 1.552 for the K-Cyc FA. The K-Furn and K-Recrys fly

ashes, however, have higher refractive indices than the kaolinite which

indicates that these have a crystalline phase different and possibly denser

than the kaolinite from which these have also been prepared. The reason

for the difference in glassy and crystalline phases of these ashes lies in their temperature history. McGee (86) reported that the glass composition as well as crystalline phase in heat-treated kaolinite samples differ with the temperature of treatment and method of quenching. Furthermore, the glassy particles of the K-Cyc FA produced from rapid quenching of the liquid phase are probably under a high stress condition. The glasses of the K-Furn and K-Recrys FA particles on the other hand have been formed under respectively slower rate of cooling and should therefore be relieved of stresses. In addition, the particles in these two fly ashes are devitrified as evidenced by the presence of crystalline inclusions in them; such particles should contain glass of different composition and structure. Evidence for these is the increased refractive index of the K-Furn and K-Recrys FA particles.

Bimineralic fly ash particle types

K+P fly ashes   The K+P ashes contained numerous brown, red, and opaque particles; the majority of which were spherical (Types 2, 4, and 6). Type 9 particles of hematite were also observed which increased with increasing amounts of iron in these fly ashes. Efforts to count the number of brown, red, and opaque particles proved futile because of the limit on resolution of the light microscope.

The magnetic fraction of the K+P fly ashes had more opaque and mixed particles of Type 2c and 4 respectively. Electron microscopic observations showed that these particles had a good deal of surface roughness and this increased with increasing amounts of iron (Figure 12). Clear spherical particles of Type 2a and 2b predominated in the nonmagnetic fraction

(Figure 11). Electron microscopic observations indicated that the surfaces in the nonmagnetic fraction of K+P fly ashes of particles were characteristically smooth. This was true regardless of the iron content. It should, however, be pointed out that most of the nonmagnetic particles appeared to be grainy under the light microscope. These observations once again suggest that the grainy appearance of particles is, in all probability, due to the presence of submicroscopic bubbles in them rather than to minute particles adhering on the surface of larger particles.

It would not be out of place to mention that the K+P ashes felt grittier to the touch than the K-Cyc FA; and the magnetic fractions felt grittier than the whole sample of the K+P ashes. This grittiness may be related to the rough surface morphology of magnetic particles of K+P ashes observed in the electron microscope.

Light microscopic examination of particles in the magnetic fraction revealed that these were probably covered with a thin layer of glassy material (Figure 11b). This supports the suggestion made by Minnick (90) that a thin layer of glassy material exists on the surface of magnetic particles in industrial fly ashes.

Although the proportion of clear spherical particles decreased with an increase in the amount of iron in the fly ash, the color of these particles did not change appreciably but the refractive index increased (Table 6). This is probably a reflection of the change in glass composition rather than stress conditions of the glass since these fly ashes were prepared in a similar manner as the K-Cyc FA.

K+C fly ashes   The bimineralic fly ashes of K+C series did not appear different from the K-Cyc FA except that they contained some

(a)

(b)
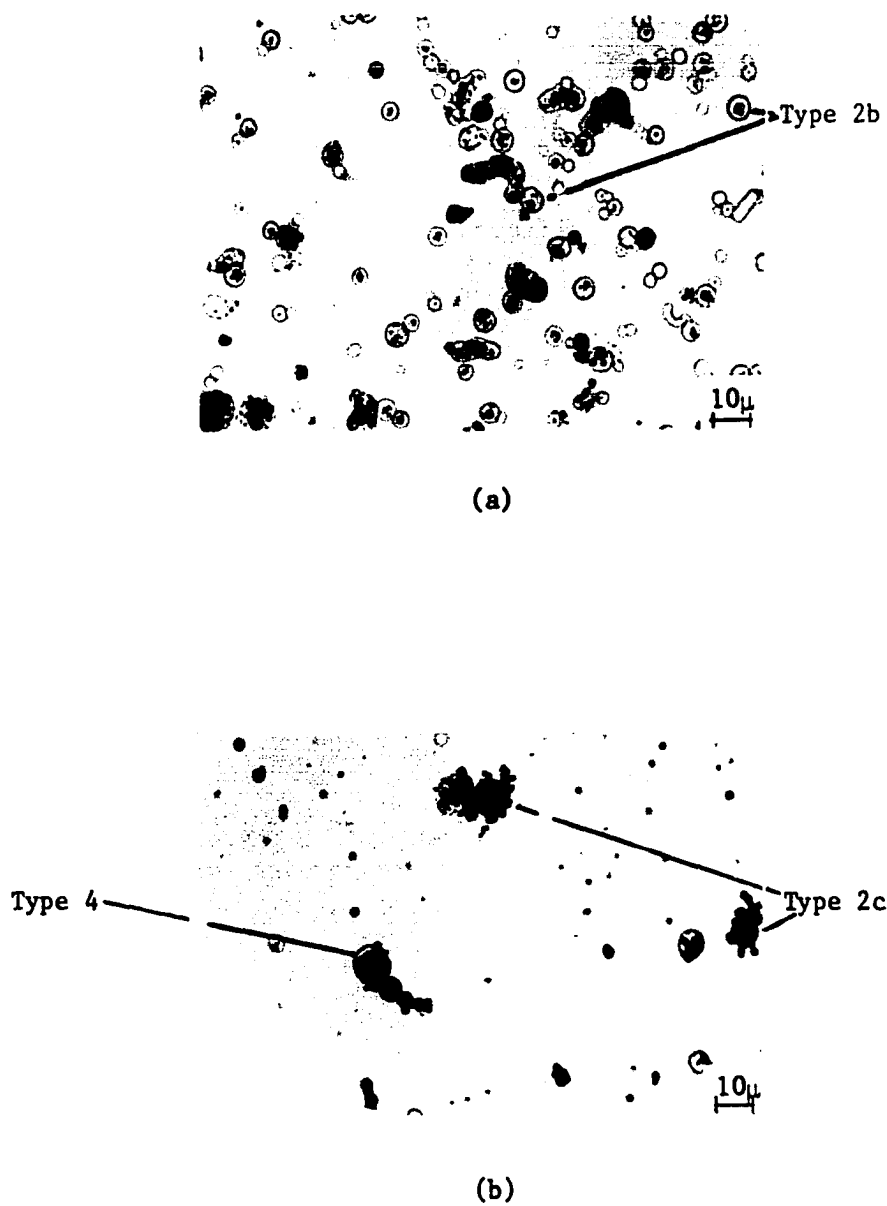
Figure 11. Photomicrographs of particles typical in the K+P fly ashes:
(a) nonmagnetic particles under transmitted light,
(b) magnetic particles under transmitted light
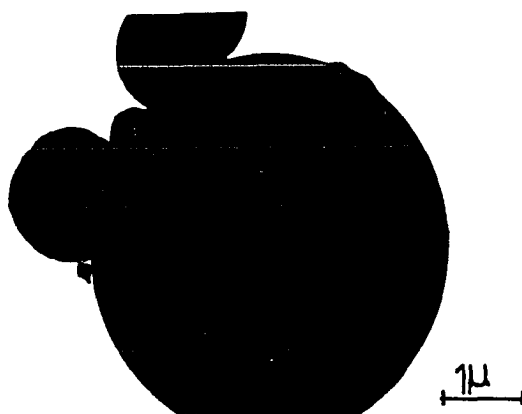
(a)
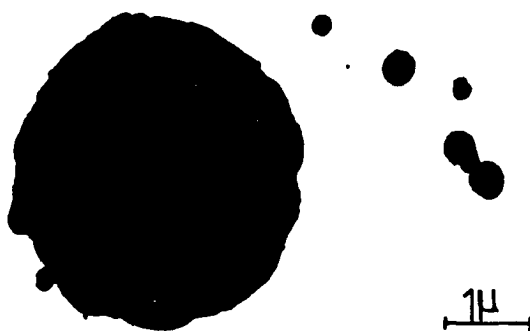
(b)

Figure 12. Electron micrographs of nonmagnetic and magnetic particles
in K+P fly ashes: (a) nonmagnetic particles, (b) magnetic
particles

rhombohedral particles of calcite (Type 6) which were easily recognizable due to their high birefringence. However, the index of refraction of glasses in K+C fly ashes does not vary with increasing calcium in the fly ashes. It is possible that only a limited amount of calcium can be incorporated into kaolinite glass at ambient furnace conditions.

Trimineralic fly ash particle types

As might be expected, light microscopic observations of the two trimineralic fly ashes in K+P+C series were a conglomerate of the observations made on the mono- and bimineralic fly ashes. The refractive index of the glassy phase in these fly ashes differed only slightly. Simons and Jeffery (112) reported that glassy particles of complex chemical composition are abundant in industrial fly ashes which implies intermixing of more than two minerals in suspension-fired furnaces. Such particles would have different indices of refraction; the present study bears this out.

Magnetic Separation

The data presented in Table 7 indicates that the amount of magnetic fraction is a function of the pyrite added. However, the magnetic fraction is composed of more than just magnetite or iron containing particles susceptible to magnetic separation. This is indicated by the consistently lower Fe_2O_3 values in the whole ashes. In industrial fly ashes the magnetic fraction is always higher than the amount of reported Fe_2O_3 (90, 125). The most likely reason for this is the predominance of mixed particles of Type 4 (Figure 11) in the magnetic fraction as well as the observed surface coating of glassy material around opaque presumably magnetite particles. Chemical analyses of the magnetic fraction of some

Table 7. Distribution of iron in synthetic fly ashes

		Wt %		
Fly ash notation	Magnetic fraction in the fly ash	Iron (as Fe_2O_3) in whole sample of fly ash[a]	Iron (as Fe_2O_3) in the magnetic fraction of fly ash[a]	Iron (as Fe_2O_3) of whole ash present in magnetic fraction
K+10P	10.2	7.08[a]	--[b]	--[b]
K+20P	16.8	14.11[a]	80.64	96.0[c]
K+30P	30.5	24.91[a]	76.73	93.9[c]
K+40P	37.1	--[b]	--[b]	--[b]
K+50P	44.8	--[b]	--[b]	--[b]
K+10P+5C	11.8	8.97[a]	--[b]	--[b]
K+10P+10C	11.7	9.48[a]	--[b]	--[b]

[a]Determined by chemical analysis.

[b]Not determined.

[c]Calculated from total chemical composition of ash in Table 17.

fly ashes further indicate that constituents other than Fe_2O_3 are essentially associated with them.

Results of chemical analyses of K+20P and K+30P fly ashes point out that more than 90% of the iron (as Fe_2O_3) resides in the magnetic fraction. Watt and Thorn (125) report a comparable value of 51 to 73% for industrial fly ashes. The difference in the values may be due to the method of separation in this research, and possibly also to the greater complexity of industrial ashes.

The presence of iron in the nonmagnetic fraction may be due to either

incomplete separation or to iron compounds not susceptible to magnetic

separation. There seems to be a greater possibility of the latter as

suggested by the increased refractive index of the glassy matrix in the

nonmagnetic fraction of K+P fly ashes. It is, however, possible that a

small fraction of iron may be present in a crystalline form not susceptible

to magnetic separation. Industrial fly ashes also contain a substantial

amount of iron which cannot be removed magnetically (90, 125).

Specific Gravity

The specific gravity of various synthetic fly ashes is presented in

Table 8. The data for the different size groups of the K-Cyc FA indicate

that the finer the size fraction the higher the specific gravity. The

reason for this may be that grainy appearing particles containing gas

inclusions predominate in the coarser fractions and thus reduce the specific

gravity. The presence of cenospheres would have the same effect.

As expected, the specific gravity of K+P fly ashes is higher than

that of the K-Cyc FA, and appears to be a function of the iron content.

Undoubtedly, a portion of the added pyrite was converted to magnetite,

hematite or wüstite which have specific gravities ranging from 5.18 to 5.7

(102). Additionally, some iron may have been incorporated in the glassy

phase as was indicated by increased refractive index of the glasses of K+P

fly ashes. The specific gravities of ferruginous glasses range from 2.5

to 4.8 (72, 99).

The specific gravities of the nonmagnetic fractions of the K+P ashes

are lower than those of the corresponding whole ash samples, but higher

Table 8. Specific gravity of synthetic fly ashes

Fly ash notation	Specific gravity, g/cc
K-Cyc (whole sample)	2.4495
<5K-Cyc	2.5956
5-10K-Cyc	2.4845
10-20K-Cyc	2.4774
>20K-Cyc	2.2038
K+10P (whole sample)	2.6427
K+20P " "	2.8305
K+30P " "	3.1246
K+40P " "	3.3946
K+50P " "	3.6647
K+10P (nonmagnetic)	2.5704
K+20P "	2.6166
K+30P "	2.6326
K+40P "	2.7627
K+50P "	2.7656
K+5C (whole sample)	2.4767
K+10C " "	2.5024
K+15C " "	2.5512

than the K-Cyc FA. This may be a reflection of incomplete magnetic separation due to limitations imposed by the method itself or to the possibility that ferruginous glass or crystalline particles were not sufficiently susceptible to magnetic separation.

The K+C fly ashes also have higher specific gravity values than the K-Cyc FA. This may be attributed to the fact that the majority of calcium compounds, which are formed during the spheroidization process, have specific gravities above 2.9 (102). Further support for this interpretation is evidenced by the fact that the specific gravity increases with an increase in calcium.

The specific gravity values of the synthetic fly ashes are well within the range of 1.88-2.84 reported for industrial fly ashes (1). The values for the K+P fly ashes containing 30 or more percent added pyrite are higher than the range for industrial ashes not only because of the abnormal amount of iron but also because of the lack of unburnt carbonaceous particles which would tend to lower the average specific gravity of the fly ash.

<div align="center">Particle Size Analysis</div>

Sieve analysis

The sieve analysis data for the synthetic fly ashes collected are presented in Table 9.

An interesting feature is that all synthetic fly ashes have particles larger than the maximum size particle present in the parent mineral powder, e.g., the K-Cyc FA has 11 wt % particles larger than 20 microns, whereas the kaolinite mineral powder contained only 2 wt % (Appendix A). As particles pass into the hot zone of the furnace, at least two processes are active. Initially, particles such as kaolinite lose their structural water and perhaps even some SiO_2 as suggested by the investigations of Schneider published by Mackowsky (81). Similarly, pyrite thermally

Table 9. Sieve analysis of synthetic fly ashes (wt % passing)

| | Sieve opening microns | Monomineralic | | | Bimineralic | | | |
| | | Whole sample | | | | | | |
		K-Cyc	K-Furn	K-Recrys	K+10P	K+20P	K+30P	K+50P
	250	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	210	99.99	99.35	99.05	96.24	00.06	95.50	96.73
Dry	105	99.92	98.23	98.31	91.70	95.52	89.52	89.27
	75	99.82	96.40	97.61	88.07	90.93	83.73	85.95
	45	98.43	92.28	89.26	84.30	84.14	77.47	82.41
	30	95.16	73.36	68.65	77.58	78.26	68.38	76.63
Wet	20	89.05	52.00	36.36	60.42	66.40	54.66	62.72
	10	35.30	13.11	3.15	14.38	16.53	19.36	8.16

Bimineralic						Trimineralic	
Nonmagnetic fraction			Whole sample				
K+10P	K+20P	K+30P	K+5C	K+10C	K+15C	K+10P+ 5C	K+10P+ 10C
100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
97.32	96.92	98.22	95.10	96.52	98.36	98.49	99.80
95.49	94.54	96.39	91.00	93.73	93.55	97.42	99.27
92.08	91.67	92.81	87.80	91.34	90.78	96.27	98.74
88.39	88.57	88.99	82.85	86.88	85.22	94.32	92.09
85.35	85.81	86.77	78.90	83.51	81.77	91.84	81.11
74.69	77.45	79.30	70.22	76.20	76.23	84.41	73.72
5.62	13.02	16.66	5.66	17.17	24.13	22.83	13.25

dissociates releasing sulfur, and calcite loses carbon dioxide. Such thermal dissociation processes lead to the formation of much finer particles which probably are characterized by highly reactive surfaces. The other process, which may occur simultaneously, involves intimate particle contact leading to agglomeration and/or sintering. The net result may be particles which are larger than the particles originally entering the hot zone. This appears to be the case with the synthetic fly ashes produced, and very probably occurs in industrial suspension-fired furnaces as well. The presence of partly opaque partly transparent particles in the K+P and K+P+C fly ashes lends further support to this conclusion. This intermixing is probably responsible for the large proportion of brown and red colored particles in some industrial fly ashes described by Watt and Thorn (137) as having a complex chemical composition. Simons and Jeffery (112) and Rekus and Haberkorn (107) have also reported that x-ray analysis of individual particles indicates intermixing of minerals in fly ashes.

Fineness comparison with industrial fly ashes   In an attempt to compare the size distribution of synthetic and industrial ashes, four industrial fly ashes which were readily available in the laboratory were also dry sieved through 150, 105, 75, 60, 45, 30, 20, and 10 micron sieves. The data given in Table 10 indicates the variations which can be expected of typical industrial fly ashes in the midwestern United States. This data agrees with the published data for industrial fly ashes which indicate that the wt % passing the 45 micron sieve ranges from 50 to 98% (4, 91, 125, 131, 138). On this basis all of the synthetic fly ashes may be considered as representing very fine industrial ashes.

Table 10. Sieve analyses of some industrial fly ashes[a]

Sieve opening microns	wt % passing					
	Fly ash #1	Fly ash #2	Fly ash #3	Fly ash #4	Fly ash #5	Fly ash #6
150	92.13	97.65	97.89	96.56	Not done	Not done
105	86.10	93.64	94.17	92.39	"	"
75	78.76	88.06	90.06	86.73	"	"
60	71.55	81.46	85.02	80.28	"	"
Dry 45	62.38	70.39	78.39	71.71	"	"
30	50.98	57.54	65.57	61.42	"	"
20	37.57	42.38	51.88	48.65	"	"
10	13.72	16.57	21.69	12.66	"	"
Wet 45	86.05	Not done	90.76	88.79	83.76	93.73

[a]These industrial fly ashes were selected at random from various ashes readily available in the Soils Research Laboratory. Sources of these fly ashes are

#1 - Sixth Street Power Station, Cedar Rapids, Iowa, Iowa Electric Light and Power Co.

#2 - Grand Avenue Power Station, Kansas City, Kansas City Power and Light Co.

#3 - St. Clair Power Station, Detroit Edison Co., Detroit, Michigan.

#4 - Montrose Power Station, Kansas City, Kansas City Power and Light Co.

#5 - Maryville Power Plant, Detroit Edison Co.

#6 - Paddy's Run Power Station, Luisvill Gas And Electric Co., Louisville, Kentucky.

Fineness based on wt % passing 45 microns   Since some organizations

(Bureau of Reclamation, ASTM, and City of Chicago) prescribe minimum limits

on the fraction finer than 45 microns, the results will first be discussed

from this aspect.

The K-Cyc FA is the finest of all the synthetic fly ashes produced. The fact that the K-Furn and K-Recrys fly ashes are increasingly coarser is a reflection of their different thermal history.

On the basis of wt % passing 45 micron sieve the K+P fly ashes are coarser than the K-Cyc FA which may be due to addition of iron. However, no correlation between the amount of iron present in the fly ash and the wt % <45 microns is observable. The nonmagnetic fractions of the K+P fly ashes are consistently finer than their whole sample counterparts indicating that the magnetic portion of these ashes is relatively coarser. This is in agreement with Minnick's observations that magnetic removal of iron increases fineness of the fly ashes.

The fineness of the K+C ashes, based on the fraction finer than 45 microns, is comparable to the K+P ashes. Again, no trend in the wt % <45 micron is noticed with increasing calcium content. Although it might be expected that addition of iron and calcium, as for example, in K+P+C ashes, would also result in coarser fly ashes, these ashes are unusually fine with regard to the amount passing 45 micron. Both the ashes of K+P+C series are only slightly coarser than K-Cyc FA.

The synthetic ashes of different chemical composition may be arranged in order of increasing coarseness as indicated by the wt % <45 micron:

1. K-Cyc FA

2. K+P+C ashes

3. K+P (nonmagnetic fraction)

4. K+C

5. K+P (whole sample)

6. K-Furn

7. K-Recrys

Fineness based on fractions smaller than 30 micron   Although

analysis of the data for the wt % passing the 30, 20, and 10 micron sieves

leads to the same general conclusions, certain trends in fineness of

synthetic fly ashes are conspicuously identifiable.

The influence of prolonged and different thermal treatment of the

pure kaolinite fly ashes is very clearly noticeable in the particles <10

microns. The K+P whole ash samples are equally coarser as compared to the

K-Cyc. However the nonmagnetic fractions of K+P ashes and whole samples

of the K+C ashes show an interesting trend. With the increasing amounts

of iron and calcium the wt % passing 10 microns markedly increases.

Possible interpretations for this observation are that during the spheroidi-

zation process: a) the pyrite and calcite particles themselves decompose

yielding finer particles and/or b) the presence of pyrite and calcite

influences the kaolinite to yield finer particles.

The sieve analysis data in Tables 9 and 10 for fraction <30 microns

can be utilized as such to show certain other trends, however, the

histograms plotted for representative synthetic and industrial fly ashes

in Figure 13 from this data give a better picture of their size distribu-

tion. It is observed that, irrespective of the fly ash composition, the

mode in each of the histograms is in the size range 10 to 20 microns.

Furthermore all the histograms show a right-handed skewness exhibiting

almost similar size distribution.

The increasing devitrification imparted by successively slower rate

of quenching or cooling tends to produce a larger proportion of coarser
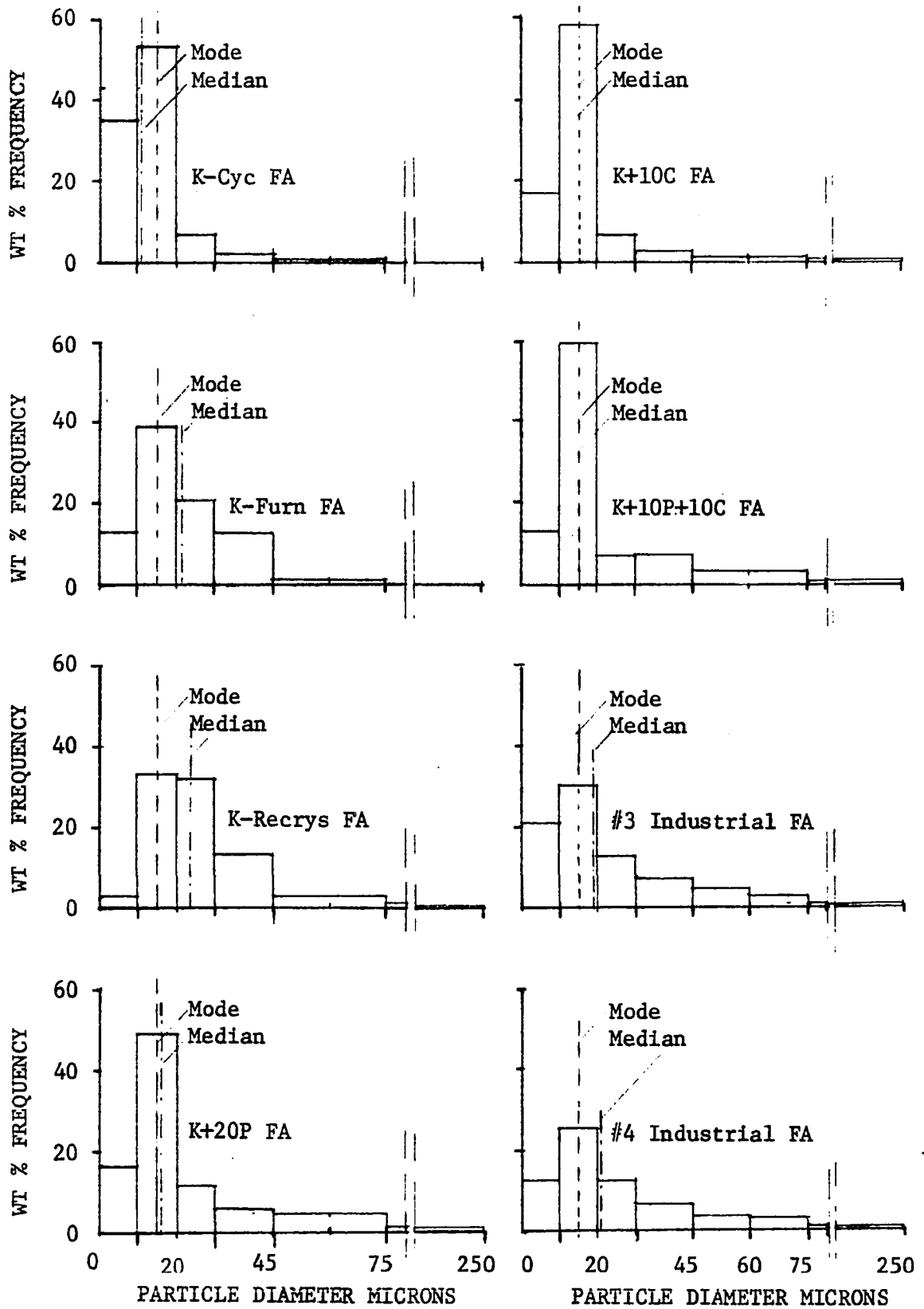
Figure 13. Histograms of particle size distribution of some synthetic and industrial fly ashes

particles as is evidenced by the reduced frequency of the mode and the increased right-handed skewness of the histograms of K-Furn and K-Recrys fly ashes as compared to K-Cyc FA. The composition of the synthetic fly ashes also influences their size distribution but not as much as their temperature history since the frequency of the mode in these fly ashes is not too different from that of K-Cyc FA. The close similarity in the degree of skewness of the histograms of various bi- and trimineralic fly ashes suggests similar size distribution of these ashes.

Close examination of Figure 13 reveals that the industrial fly ashes do not differ significantly in size distribution from the bi- and trimineralic as well as devitrified monomineralic synthetic ashes. Data in Table 10 for wet sieving of industrial fly ashes through 45 micron sieve suggests that had these ashes been wet-sieved through 30, 20, and 10 micron sieves like synthetic ashes, the size distribution of the fraction <30 microns of the former would have been almost exactly similar to the latter.

The sieve analyses further indicate that practically all of the synthetic fly ashes would meet the ASTM, City of Chicago, and Bureau of Reclamation specifications with regard to the maximum amount retained on the 45 micron sieve. Such specifications which limit the amount retained on the 45 micron sieve to 12 or 15% by weight are designed to limit the amount of carbon and are not reliable as an indicator of possible pozzolanic activity. Placing a limit on the amount retained on a certain sieve size says nothing about the size distribution of particles passing that sieve.

Fineness in terms of median weight diameter   The sieve analyses data from Table 9 were plotted on log-probability paper in an attempt to

obtain median weight diameters and compare the fineness of these ashes. The plots resulted in two straight lines meeting at the 30 micron value. The change in distribution at 30 microns may be due to the fact that dry-sieving of the whole ash sample was employed for sieves 45 microns and larger; whereas fraction passing 45 micron sieve was wet-sieved through 30, 20, and 10 micron sieves. Had the whole ash sample been wet-sieved through all sieves, it is suspected that the data obtained would have yielded a single straight line relationship indicating a Gaussian distribution. Wet-sieving, however, has its own limitations including the agglomeration of particles as well as a decrease in sieve openings due to water films.

Since the wet-sieve data for the synthetic fly ashes show that the majority of the particles is less than 30 microns, the straight line relationship for the data below 30 microns may be utilized with greater confidence to obtain median diameters. The K-Cyc FA has a 11.0 microns; the median diameters for all bi- and trimineralic fly ashes range between 14.0 and 17.5 microns (Table 15). This suggests that these latter ashes do not appreciably differ from each other with respect to median particle diameter.

Dry-sieve data obtained from four industrial fly ashes show median diameters ranging between 19 and 29 microns (Table 15). As explained earlier, the increase in median particle diameter may be due to the fact that these ashes were dry-sieved. The results of wet-sieving of four industrial fly ashes through 45 micron supports this contention (Table 10).

Electron microscope particle count method

Since the previous data indicated a range of median diameters roughly between 10 to 20 microns, it appeared desirable to obtain more specific

values. In addition, use of an entirely different method would offer

possibility of method accuracy.

Table 11 presents the data obtained for all synthetic ashes by counting

and measuring particles observed in the electron microscope. Electron

microscope specimens were prepared from the fraction finer than 45 microns

in the industrial fly ashes and from whole samples of the synthetic ashes.

The data in Table 11, however, are limited to sizes less than 20 microns.

One reason for this limitation may be seen from the sieve analysis data

which indicate that the majority weight percentage of particles in almost

all fly ashes is less than 20 microns in size. The numerical percentage

of particles coarser than 20 microns is still less. Therefore, the

probability of observing such particles was considerably reduced. In

addition, at the time these analyses were being performed, it was thought

that utilization of the high resolving power of the electron microscope to

observe particles down to 0.2 micron in diameter would yield potentially

significant information. This, however, automatically placed a limit on

the number of particles larger than 20 microns which could be observed

within the total number of particles counted. In fact, out of 3000

observed particles, never were more than 5 found which were larger than

20 microns. These few particles were included in the 18-20 micron range

in the data in Table 11.

The microscope count data indicate that addition of pyrite and calcite

tend to produce a larger numerical proportion of finer particles, i.e., less

than 4 microns. Although this observation is in conformity with the

conclusions drawn from the sieve analysis, the numerical count data as

such does not give true indication of the size distribution in terms of

Table 11. Numerical particle size distribution of synthetic fly ashes determined by electron microscopic particle count method

Particle size range, micron	Average particle size, micron	Numerical % particles									
		Whole sample						Nonmagnetic fractions			
		K-Cyc	K+10P	K+20P	K+30P	K+40P	K+50P	K+10P	K+20P	K+30P	K+40P
0.00-0.20	0.1	3.06	13.45	9.54	11.04	9.27	12.54	4.76	5.02	7.23	6.36
0.21-0.40	0.3	7.75	10.09	8.63	10.54	10.68	16.62	6.92	7.93	12.41	9.66
0.41-0.60	0.5	8.05	9.30	6.18	7.80	5.97	8.81	7.60	8.89	7.23	7.07
0.61-0.80	0.7	4.20	4.71	3.72	3.95	3.69	4.80	4.76	4.43	4.34	4.71
0.81-1.00	0.9	4.38	2.91	3.45	2.74	5.54	3.58	2.72	4.32	2.05	4.12
1.00-2.00	1.5	7.63	7.29	5.63	7.70	9.27	9.46	5.56	5.60	3.86	8.83
2.10-4.00	3.0	14.53	10.31	14.35	14.29	16.03	16.05	12.81	16.22	14.94	13.78
4.10-6.00	5.0	20.30	13.45	15.35	16.21	16.03	12.39	21.88	17.97	16.63	13.66
6.10-8.00	7.0	15.68	11.55	12.26	11.35	10.68	8.17	16.44	12.14	13.98	13.19
8.10-10.00	9.0	8.17	7.40	6.90	5.47	6.44	3.87	9.75	5.83	6.99	7.30
10.10-14.00	12.0	5.41	6.84	7.90	5.88	6.13	2.44	5.22	6.42	5.66	7.77
14.00-18.00	16.0	.66	1.01	3.81	1.52	1.81	1.00	1.36	2.45	2.41	2.47
18.00-20.00	19.0	.18	1.46	2.27	1.52	2.04	.29	.23	2.68	2.29	1.18

Table 11. (Continued)

Particle size range, micron	Average particle size, micron	Numerical % particles										
		Whole sample						Industrial fly ashes (fraction <45 micron)[a]				
		K+50P	K+5C	K+10C	K+15C	K+10P+5C	K+10P+10C	#1	#3	#4	#5	#6
0.00-0.20	0.1	5.44	48.77	22.78	43.50	13.41	40.80	0.61	12.75	0.00	0.56	0.00
0.21-0.40	0.3	7.21	10.68	30.50	15.56	11.11	20.57	7.88	19.80	5.13	4.21	6.42
0.41-0.60	0.5	4.48	4.61	1.41	4.07	6.51	9.43	5.76	8.05	4.81	4.49	10.40
0.61-0.80	0.7	2.56	2.04	1.41	1.26	5.36	3.48	8.79	5.37	6.09	4.77	7.03
0.81-1.00	0.9	2.64	2.18	3.04	3.22	2.30	1.81	4.55	4.36	9.93	4.49	6.73
1.00-2.00	1.5	5.76	5.41	11.07	8.81	8.81	7.32	7.57	14.76	27.56	12.08	21.10
2.10-4.00	3.0	14.57	7.17	12.94	11.36	16.86	5.75	12.12	18.76	25.64	26.12	19.88
4.10-6.00	5.0	16.81	7.93	6.32	4.77	17.24	3.75	18.18	5.37	10.90	16.01	15.29
6.10-8.00	7.0	17.05	4.75	3.16	2.52	7.09	2.14	13.64	5.37	2.56	8.71	5.20
8.10-10.00	9.0	9.37	2.71	1.87	1.07	4.60	2.07	8.18	3.02	2.88	5.34	2.45
10.10-14.00	12.0	8.97	2.42	.76	1.12	4.60	1.77	4.54	1.34	1.92	8.15	3.75
14.00-18.00	16.0	3.28	.71	.47	.19	1.15	.40	5.45	1.01	1.28	1.97	1.83
18.00-20.00	19.0	1.52	.62	.23	.28	.96	.70	2.72	.33	1.28	2.09	.92

[a]Sources of these fly ashes are given in Table 10.

wt %. Because the volume of weight of one particle having a diameter of

1 micron is equivalent to the volume or weight of 1000 particles of 0.1

micron in diameter. As a result, the size distribution or median diameter

are practically unaffected by the presence of numerous fine particles.

This will be explained further when the numerical data in Table 11 is

converted into weight fractions.

The data in Table 11 were interpreted to give various parameters in

Table 12 with the help of equations given by Perrot and Kinney (101).

According to them, similarity in various parameters of a powder indicates

uniform particle size, and successive increases from $d_1 \rightarrow d_s \rightarrow d_v \rightarrow d_{vs} \rightarrow d_w$

suggests a uniform distribution of particles in all the sizes. In case of

powders having Gaussian distribution, the mean diameter (length) is about

one-third less than the weight mean diameter. Furthermore, the mean

surface diameter is always the smallest since the surface area per unit

weight or volume increases with inverse square of the diameter.

A close examination of Table 12 reveals some interesting features

about the size distribution of synthetic as well as industrial fly ashes

and the validity of the electron microscope particle count data. In the

fractionation process a significantly large proportion of the K-Cyc FA

particles was found to lie in the two fractions of 5-10 and 10-20 micron

fractions; the particles in the fractions less than 5 micron as well as in

larger than 20 micron fraction accounted for a very small portion of the

ash. This suggests that various mean diameters should lie between 5-20

microns. The values in Table 12 are in agreement with the previous

observations. This indicates that the size distribution as well as mean

diameters determined by the electron microscope count method are fairly

Table 12. Mean diameters (in microns) of synthetic fly ashes obtained
from particle count data

Fly ash notation	Mean diameter (length) d_1	Mean surface diameter d_s	Mean volume diameter d_v	Mean volume surface diameter d_{vs}	Weight mean diameter d_w
<5K-Cyc fraction	3.89	3.06	3.13	4.45	4.69
5-10K-Cyc "	7.84	7.78	7.83	7.96	8.09
10-20K-Cyc "	12.65	12.59	12.91	12.81	13.01
>20K-Cyc[a] "	23.20	22.73	23.39	24.87	27.78
K-Cyc FA whole sample	7.18	5.57	6.18	8.87	10.29
K+10P " "	8.52	5.82	6.88	11.00	12.96
K+20P " "	9.48	6.80	7.92	12.19	14.09
K+30P " "	8.32	5.78	6.86	11.11	13.30
K+40P " "	8.62	6.03	7.15	11.57	13.79
K+50P " "	7.77	5.01	6.50	11.06	13.07
K+10P nonmagnetic fraction	7.52	5.88	6.57	9.25	10.79
K+20P " "	9.02	6.48	7.65	12.04	14.27
K+30P " "	8.90	6.38	7.42	11.71	13.92
K+40P " "	8.68	6.24	7.20	11.15	12.98
K+50P " "	8.76	6.68	7.90	11.09	12.92
K+5C whole sample	7.70	3.85	5.25	10.86	13.14
K+10C " "	8.05	4.52	5.82	10.76	11.99
K+15C " "	5.58	2.78	4.00	9.33	12.35
K+10P+5C " "	7.59	3.24	6.18	10.50	12.83
K+10P+10C " "	7.49	3.88	4.94	11.79	14.18
Industrial fly ashes[b]					
#1 <45 micron fraction	9.74	7.12	8.68	12.89	15.12
#3 " " "	6.33	3.79	5.24	10.02	12.86
#4 " " "	6.78	4.53	6.21	11.66	15.15
#5 " " "	9.11	6.66	8.27	12.72	15.23
#6 " " "	7.10	4.80	6.36	11.14	14.15

[a]The sieve analysis data was converted to numerical data and the various diameters calculated.

[b]The sources of these fly ashes are given in Table 10.

accurate. The mean diameter values for the three size fractions of K-Cyc

FA, i.e. <5, 5-10 and 10-20 microns confirm the separation and lend

support to the accuracy of the electron microscope method. Therefore, the

values in Table 12 for other synthetic fly ashes as well as industrial fly

ashes are believed fairly representative of various parameters.

It is noticed that values of various mean diameters for different fly ashes with the exception of K+C and K+P+C ashes in Table 12 lie in a very narrow range suggesting that most of the synthetic fly ashes prepared in this study are not different from each other or from industrial fly ashes in their size distribution or average mean particle size. The K+P+C fly ashes have smaller mean particle, surface and volume diameters; however they have mean length, volume-surface and weight diameters in the range of other fly ashes, i.e. 9 to 12 and 11 to 14 respectively. The differences in surface and volume diameters is probably the reflection of very high proportion of particles <0.4 microns in diameter.

It should be pointed out that the particles >20 microns were included in 18-20 micron range and therefore various parameters calculated from such data may be slightly on the lower side for all fly ashes. The industrial ashes had a larger wt % of such particles than the synthetic ashes, and to compensate for this, the 18-20 micron size fraction was assumed to have an average size of 20 microns in place of an average size of 19 microns in calculating various diameters. Therefore, various parameters calculated for the synthetic and industrial fly ashes can be assumed to be comparable at least for the size fraction up to 20 microns. It should also be pointed out that even a 30 to 50 wt % of particles >20 microns accounts for a very insignificant numerical percent of the total number of particles in a fly ash sample. In addition the weight mean diameters of industrial fly ashes obtained from dry-sieve analysis data were found to lie between 19 and 29 microns which suggests that particles >20 microns would form a very insignificant numerical percent of the total sample of the industrial ashes investigated. Therefore, the actual weight mean diameters of these ashes

would not be significantly different from those obtained by electron microscope particle count method. It should however be realized that the electron microscope particle count method would not yield reliable results for the industrial fly ashes if they contain few fine particles and a significant amount of particles >20 microns. Since this is not uncommon, such ash particles may be counted and measured by using a lower magnification for accurate determination of the desired parameter.

Combination of sieve and microscopic analysis

In order to utilize the numerical data from the microscope in giving added information regarding the distribution of particles less than 20 microns, it was necessary first to convert the numerical values into wt % values. Assuming an average size value for each fraction and a spherical particle shape for all particles, the numerical data was converted to volumetric units. The volumetric distribution thus obtained represented the size distribution by weight provided the further assumption of uniform specific gravity was made. This latter assumption was known to be faulty; however, practical expediency prompted the assumption nonetheless. Any resulting error was considered to be insignificant with respect to the K-Cyc FA and to be minimal with other bi- and trimineralic ashes.

The size distributions determined by sieve analysis and the electron microscope particle count method were combined by proportionally weighting the numerical count data for fractions finer than 20 microns. That is, the size distribution obtained from electron microscope particle count data was considered to be only for the fraction passing 20 micron sieve.

Table 13 shows the incremental percentage; Table 14 the cumulative

percentages obtained. As pointed out earlier, the data in Tables 11, 13,

and 14 indicate that although finer particles are much more numerous than

the coarse particles, they contribute much less to the weight. For

example, more than 50 to 80% of the particles in synthetic as well as

industrial fly ashes, numerically, have diameters <4 microns, but these

particles account for less than 5 wt % of the ashes. It is because of

this in appreciable volume and weight contribution that the corresponding

mean diameters of the fly ashes having significantly different proportions

of such particles are almost the same.

The cumulative data in Table 14 for all the fly ashes were plotted on

log-probality paper to determine the median diameter. Although these

plots appeared similar to those obtained from the sieve analysis data,

the distribution above and below the 20 micron point were described by two

straight lines. The fact that a kink exists is a reflection of the size

limitations of the two methods employed. One source of methodological

error may be the use of dry-sieving for fractions larger than 45 microns

and wet-sieving for fractions less than 45 microns. Another error, already

mentioned, involves the reduced probability of observing particles larger

than 20 microns in the electron microscope. The location of the kink in

the plots between 18 and 20 microns for all ashes suggests a methodology

error rather than a size distribution characteristic. The mean weight

diameters, however, have been obtained from the combined data by reading

the diameter size corresponding to 50 wt % passing and are presented in

Table 15. For comparison the values for mean diameters obtained from sieve

Table 13. Particle size distribution of synthetic fly ashes obtained
by combining data from the electron microscope particle
count method and sieve analysis

Particle size size range	Wt % in the size range[a] Whole sample				
	K-Cyc	K+10P	K+20P	K+30P	K+50P
0.01- 0.2	.00	.00	.00	.00	.00
0.21- 0.4	.00	.00	.00	.00	.00
0.41- 0.6	.00	.00	.00	.00	.00
0.61- 0.8	.00	.00	.00	.00	.00
0.81- 1.0	.01	.00	.00	.00	.00
1.1 - 2.0	.08	.03	.02	.03	.11
2.1 - 4.0	1.26	.44	.45	.56	1.51
4.1 - 6.0	8.19	2.71	2.25	2.98	5.01
6.1 - 8.0	17.36	6.39	4.95	5.73	9.79
8.1 - 10.0	19.22	8.71	5.92	5.86	9.76
10.1 - 14.0	30.18	19.09	16.07	14.95	14.73
14.1 - 18.0	8.72	6.68	18.38	9.16	14.31
18.1 - 20.0	3.98	16.17	18.33	15.34	6.95
20.1 - 30.0	6.11	17.29	11.86	10.28	13.91
30.1 - 45.0	3.27	6.73	5.87	6.91	5.78
45.1 - 75.0	1.38	3.77	6.79	8.00	3.54
75.1 -105.0	0.10	3.62	4.58	7.96	3.32
105.1 -210.0	0.07	4.54	3.54	6.86	7.46
210.1 -250.0	0.00	3.75	0.93	5.32	3.25

[a]Values reported only up to two decimal places and therefore the
wt % in size ranges up to 1 micron in most ashes is 0.00%.

Nonmagnetic faction				Whole sample			
K+10P	K+20P	K+30P	K+5C	K+10C	K+15C	K+10P+5C	K+10P+10C
.00	.00	.00	.00	.000	.00	.00	.00
.00	.00	.00	.00	.007	.00	.00	.00
.00	.00	.00	.00	.001	.00	.00	.00
.00	.00	.00	.00	.00	.00	.00	.00
.00	.00	.00	.00	.02	.02	.00	.00
.04	.02	.02	.07	.33	.31	.09	.14
.37	.67	.67	.84	3.15	3.24	1.38	.92
6.41	3.43	3.45	4.30	7.13	6.30	6.57	2.78
13.23	6.37	7.96	7.08	9.78	9.13	7.41	4.36
16.67	6.50	8.46	8.58	12.30	8.24	10.22	8.97
21.16	16.97	16.24	18.18	11.85	20.45	24.24	18.19
13.07	15.35	16.39	12.64	17.37	8.22	14.36	9.74
3.70	28.11	26.08	18.48	14.23	20.29	20.08	28.55
10.66	8.36	7.4?	8.67	7.30	5.54	7.44	7.38
3.04	2.75	2.21	3.95	3.37	3.45	2.48	10.98
3.96	3.09	3.82	4.95	4.45	5.55	1.95	5.65
3.41	2.87	3.54	3.20	2.38	2.77	1.15	1.53
1.83	2.37	1.86	4.09	2.79	4.80	1.07	0.53
2.66	3.07	1.77	4.88	3.46	1.62	1.50	0.19

Table 14. Cumulative size distribution of synthetic fly ashes obtained
by combining data from the electron microscope count method
and sieve analysis

Particle size	Cumulative wt % finer[a] Whole sample				
	K-Cyc	K+10P	K+20P	K+30P	K+50P
0.2	.00	.00	.00	.00	.00
0.4	.00	.00	.00	.00	.00
0.6	.00	.00	.00	.00	.00
0.8	.00	.00	.00	.00	.01
1.0	.01	.00	.00	.00	.02
2.0	.10	.04	.02	.04	.13
4.0	1.36	.49	.48	.61	1.64
6.0	9.56	3.21	2.74	3.59	7.05
8.0	4.92	9.61	7.69	9.32	16.85
10.0	46.15	18.32	13.61	15.19	26.71
14.0	76.33	37.42	29.69	30.15	41.45
18.0	85.06	44.10	48.07	39.31	55.76
20.0	89.05	60.28	66.41	54.66	62.72
30.0	95.16	77.58	78.26	64.94	76.63
45.0	98.43	84.30	84.14	71.85	82.41
75.0	99.82	88.07	90.93	79.85	85.95
105.0	99.92	91.70	95.92	87.82	89.27
210.0	99.99	96.24	99.06	99.67	96.73
250.0	100.00	100.00	100.00	100.00	100.00

[a]Values reported only up to two decimal places and therefore the
wt % finer than 1 micron in most fly ashes is 0.00%.

Non-magnetic faction			Whole sample				
K+10P	K+20P	K+30P	K+5C	K+10C	K+15C	K+10P+5C	K+10P+10C
.00	.00	.00	.00	.00	.00	.00	.00
.00	.00	.00	.00	.00	.00	.00	.00
.00	.00	.00	.00	.00	.01	.00	.01
.00	.00	.00	.00	.01	.01	.00	.01
.01	.00	.00	.01	.03	.03	.01	.02
.05	.03	.02	.09	.37	.35	.10	.17
.42	.70	.69	.93	3.52	3.59	1.49	1.09
6.84	4.14	4.15	5.24	10.65	9.86	8.06	3.88
20.07	10.51	12.11	12.32	20.43	19.02	15.48	8.25
36.75	17.01	20.57	20.91	32.74	27.27	25.71	17.22
57.92	33.98	36.82	39.09	44.59	47.72	49.95	35.42
70.99	49.34	53.21	51.74	61.97	55.94	64.32	45.17
74.70	77.46	79.30	70.23	76.21	76.24	84.81	73.73
85.35	85.81	86.77	78.90	83.51	81.77	91.84	81.11
88.39	88.57	88.99	82.85	86.88	85.22	94.32	92.09
92.08	91.67	92.81	87.80	91.34	90.78	96.27	97.74
95.49	94.54	96.36	91.00	93.73	93.55	97.42	99.27
97.32	96.92	98.22	95.10	96.52	98.36	98.49	99.80
100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

analysis and electron microscope particle count data are also given in this table.

A study of the data in Table 15 indicates that the median diameters obtained from combined data are slightly but consistently larger than the values obtained from the particle count method alone; nonetheless, they all lie in a range between 10 to 18 microns. Although median diameters obtained by sieve analysis are also greater than those obtained by particle count method and also lie within the same range of 10 to 18 microns, these do not show any trend with the median diameters obtained from combined data. The differences in the values of median diameters obtained by the three methods are due to errors inherent to a particular method. The third method hopefully minimizes the errors of the other two methods and data are therefore believed more representative of the synthetic fly ashes. Median weight diameters of several United States fly ashes determined by the hydrometer method have been reported to range from 26 to 38 microns. As mentioned, in selection of the size analysis method, such analyses always give larger median sizes than the actual and hence cannot be relied upon. Watt and Thorn's (136) data from sieve analysis and light microscopy shows a median particle diameter range of 7 to 46 microns for five British fly ashes, which range encloses the present value of 10 to 18 microns. The present study includes size distribution of particles from 0.1 to 3 micron, which was ignored by Watt and Thorn.

The size distribution data and the calculated median diameters for the synthetic fly ashes lead to some important conclusions: 1) the percent passing the 45 micron sieve is not a reliable indication of the fineness of a fly ash, 2) all of these ashes have a similar size distribution since

Table 15. Mean diameters obtained from sieve analysis data, electron
microscope count data, and from combining the two data

Fly ash notation		Weight mean or median diameter d_w in microns		
		From sieve analysis data	From particle count data	From combined data of sieve analysis and particle count
K-Cyc	whole sample	11.0	10.3	10.6
K+10P	" "	17.0	13.0	15.0
K+20P	" "	16.0	14.1	17.5
K+30P	" "	17.5	13.3	18.0
K+50P	" "	17.5	13.1	16.0
K+10P	nonmagnetic fraction	17.5	10.8	12.5
K+20P	" "	15.0	14.3	17.5
K+30P	" "	14.5	14.0	17.0
K+5C	whole sample	17.0	13.1	15.0
K+10C	" "	15.0	12.0	15.0
K+15C	" "	14.0	12.4	15.0
K+10P+5C	" "	15.0	12.8	17.0
K+10P+10C	" "	15.0	14.2	16.0
Industrial fly ashes[a]				
#1		28.9[b]	15.12	18.5
#2		25.0[b]	Not determined	Not determined
#3		19.0[b]	12.86	16.0
#4		21.0[b]	15.15	17.5
#5		Not determined	15.23	Not determined
#6		Not determined	14.16	Not determined

[a]Source of these industrial ashes given in footnote of Table 10.

[b]Obtained from dry-sieve analysis data.

the major fraction of these fly ashes is composed of particles between 10-18 microns, 3) the median weight diameter of these fly ashes does not differ too much indicating that they have a similar size distribution, 4) the fly ashes contain larger particles than the parent mineral powder suggesting agglomeration and intermixing of two or more mineral grains in the furnace, 5) the added amounts of pyrite and calcite increase the proportion by weight of coarse particles in fly ashes, 6) the magnetic particles are invariably larger than most particles since median diameters of nonmagnetic fractions of corresponding K+P fly ashes are smaller than the median diameter of the whole sample, 7) although only 6 industrial fly ashes were investigated, it seems likely that the industrial fly ashes also have average mean weight diameters between 10 and 20 microns or just slightly larger.

It should be pointed out that only 50 to 60% of the synthesized fly ash could be collected in the cyclone separator, and the remaining was either deposited in the furnace liner or escaped with the flue gases. The size distribution and mean particle diameters were, therefore, obtained from the samples collected in the cyclone separator. However, the fly ash fractions which deposited in the furnace and escaped with the flue gases were very much coarser and finer respectively as compared to the fraction collected in the cyclone separator (61). It is, therefore, expected that the size distributions and the mean diameters of the combined three fractions of the synthetic fly ashes would not have been too different from those already obtained.

Specific Surface Area

The specific surfaces of the synthetic fly ashes were calculated on a unit weight basis using the mean volume surface diameters in Table 12. The data are presented in Table 16 along with values obtained from the Blaine air permeability method. The latter values are an average of four separate analyses with a precision of ± 300 cm^2/g.

As expected, both sets of surface area values for the K-Cyc FA generally decrease with increasing particle size. Good agreement exists between the sets of values on the two size fractions less than 10 microns; there is poorer agreement for the two size fractions larger than 10 microns. It is to be pointed out that the calculation method assumes a perfectly spherical particle shape and does not take into account any surface irregularities as does the air permeability method. Furthermore, the calculation method utilizes size data obtained in the electron microscope which is initially recorded as equivalent diameters for different size ranges as well as particle shapes. The equivalent diameters of irregularly shaped particles, which comprise the majority of the fractions larger than 10 microns, will invariably yield smaller surface areas than exist in reality. Therefore, the increased amount of irregularly shaped particles as well as speckled particles in the fractions larger than 10 microns will result in higher surface areas when measured by the air permeability method than obtained from microscope analyses.

The close agreement in surface area values of the whole sample of K-Cyc FA obtained by calculation and from the permeability method is a reflection of the fact that 35 wt % of the particles in the K-Cyc FA pass the 10 micron sieve.

Table 16. Specific surface areas of synthetic fly ashes

Fly ash notation	Specific surface area, cm^2/g	
	Calculated from mean volume surface diameter	Determined by air permeability method
<5 K-Cyc	5445	5180
5-10 K-Cyc	3111	2960
10-20 K-Cyc	1956	2545
>20 K-Cyc	1140	1830
K-Cyc whole sample	2672	2550
K+10P nonmagnetic fraction	2651	3280
K+20P " "	1964	3220
K+30P " "	1767	3320
K+40P " "	1959	3280
K+50P " "	1961	3335
K+5C whole sample	2618	3645
K+10C " "	2314	4270
K+15C " "	2103	5252

The specific surface areas of the bimineralic fly ashes determined by the two methods, however, differ greatly. All bimineralic fly ashes had a higher percentage of particles coarser than 20 microns. These fly ashes also had more irregularly shaped particles than the K-Cyc FA. It is possibly for this reason that the specific surface area values as measured by the air permeability method are higher than the values obtained by calculation method. It should be noted that the surface areas of the

different K+P fly ashes are consistent and dependent on the method used.

The surface area values of ashes for the K+C series present a slightly different picture. The calculated values for the K+C ashes are by and large higher than comparable values for the nonmagnetic fraction of the K+P ashes. This may be caused by the fact that particles less than 0.4 microns comprise 50% (numerically) of the K+C ashes, whereas the K+P ashes have a much smaller number of particles in this size range. The air permeability method measures much more accurately the large number of particles less than 2 microns in the K+C ashes. In fact, the number of particles less than 2 microns increases with increasing calcite content and the air permeability values increase correspondingly.

At present, problems are encountered in satisfactorily interpreting the decrease in calculated surface area values with an increase in calcite content.

Both methods utilized to determine specific areas have their limitations. For example, the surface in regularities are either ignored or not observable in the electron microscope particle count method. Furthermore, an assumption has to be made that all the particles are spherical. Although this was dictated by practical expediency, it was a knowledgeable error.

On the other hand, the air permeability test is strongly influenced by sample packing. It does possess the advantage of internal comparison of various ashes and also makes the obtained data comparable with data reported in the literature. Probably any of the recently available commercial instruments which provide for automatic microscopic particle measurement and computations for tremendous number of particles would

result in more accurate data and reduce the time necessary to obtain

such data.

X-ray Diffraction Analysis

The diffractometer traces presented in Figure 14 through 16 for

various synthetic fly ashes show that the samples contain variable amounts

of crystalline and amorphous material.

The crystalline phase in the K-Cyc and K-Furn fly ashes was identified

as mullite ($3Al_2O_3 \cdot 2Si\ O_2$). Similar intensities of various peaks and

the broad maxima in the diffraction traces of these two fly ashes indi-

cates that they have almost equal amounts of crystalline and amorphous

phases. However, close examination of Figure 14 points out that a weak

and broad peak has partially replaced the maxima representative of amorphous

material in the x-ray trace of K-Furn FA, indicating presence of either

small amounts of crystalline material other than mullite or minute

crystallites associated with the amorphous material in this ash. The

K-Recrys fly ash on the other hand has very little amorphous material as

indicated by the suppression of broad maxima in Figure 15. It is noticed

that K-Recrys FA also contains significant amounts of β-cristobalite

in addition to mullite as indicated by an intense peak at 9.8° 2θ. It

is interesting to note that the β-cristobalite peaks have developed at

the cost of broad maxima in the K-Recrys FA. This suggests that the

amorphous material probably is highly siliceous and on crystallization

gives rise to high temperature form β-cristobalite.

According to Schneider (110), kaolinite should give rise only to

mullite and glass under conditions of rapid heat treatment and subsequent

quenching. The K-Cyc FA has been prepared in this manner and hence the presence of only one crystalline phase is justified.

The increase in intensities of mullite in K-Furn and of mullite and β-crystobalite in K-Recrys fly ashes can be attributed to the prolonged heat treatment and relatively slow rate of cooling of the two fly ashes. Perhaps it is possible to ascribe an increase in cristobalite size as being partly responsible for the increase in the intensities of various maxima in K-Furn and K-Recrys fly ashes. McGee (86) found that equilibrium treatment of kaolinite to 1350-1550°C results in the formation of cristo-balite, liquid and mullite. Obviously the thermal treatment of K-Furn and K-Recrys fly ash samples approaches McGee's results.

The diffraction traces suggest that there is little mullite and no cristobalite in the K-Cyc FA and that the major portion of this fly ash is x-ray amorphous. This confirms the light microscopic studies presented earlier. On the other hand, the K-Furn and K-Recrys fly ashes contain more crystalline matter. Various fractions of different K- fly ashes appear to differ in the proportion of crystalline and liquid phases as observed from the two x-ray traces of four size fractions of K-Cyc FA fractions. It is difficult to estimate the exact quantities from such traces; however qualitatively, there appears to be a trend of increasing crystalline matter with the increase of particle size.

The K+P fly ashes contain hematite and magnetite in addition to mullite (Figure 16). With increasing amounts of iron in the fly ash, the intensity of hematite and magnetite peaks increases while intensity of mullite peaks decreases. Figure 16 indicates that the amorphous material
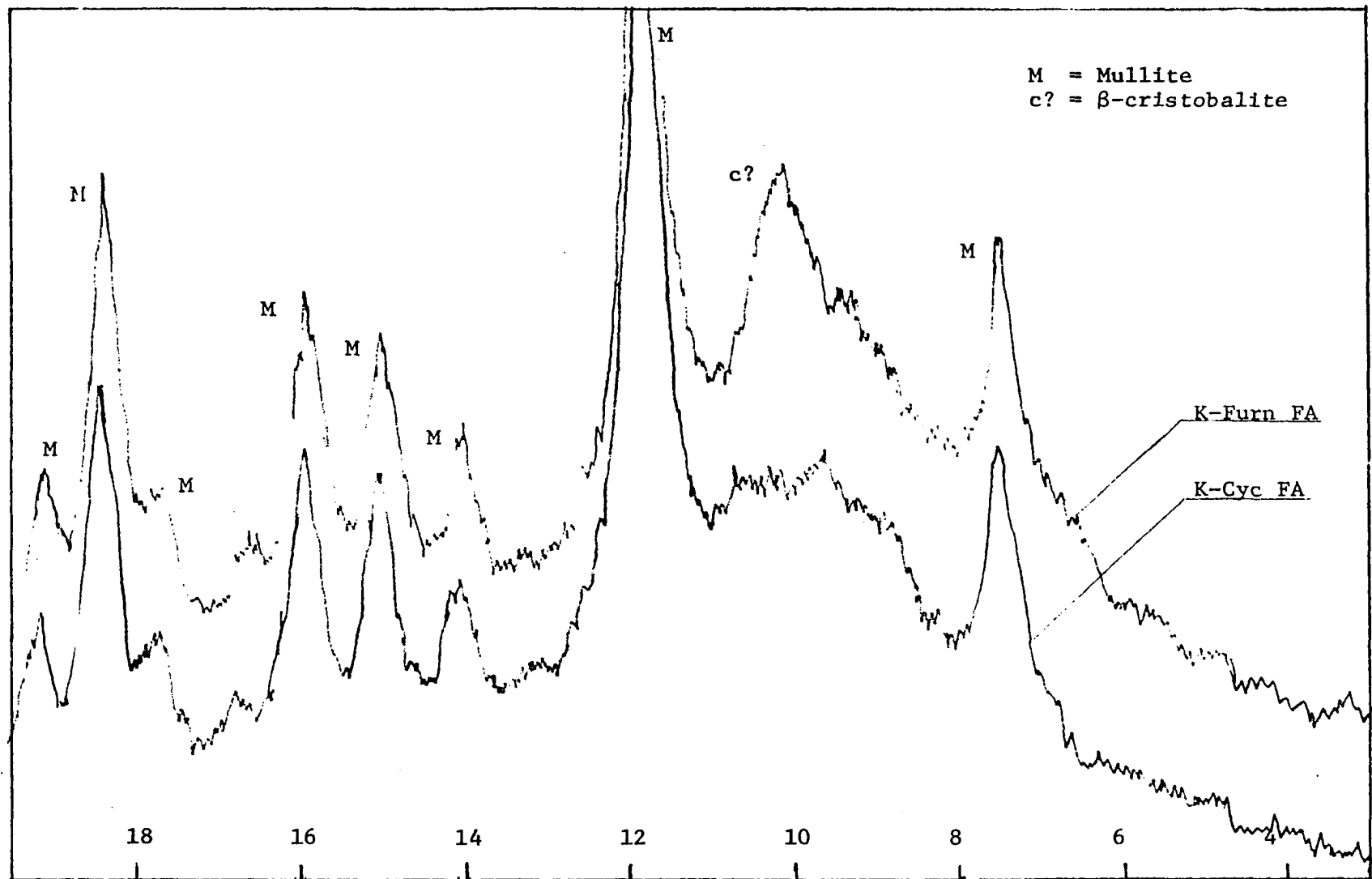
Figure 14. X-ray diffraction patterns of K-Cyc and K-Furn fly ashes

M = Mullite
c = β-cristobalite
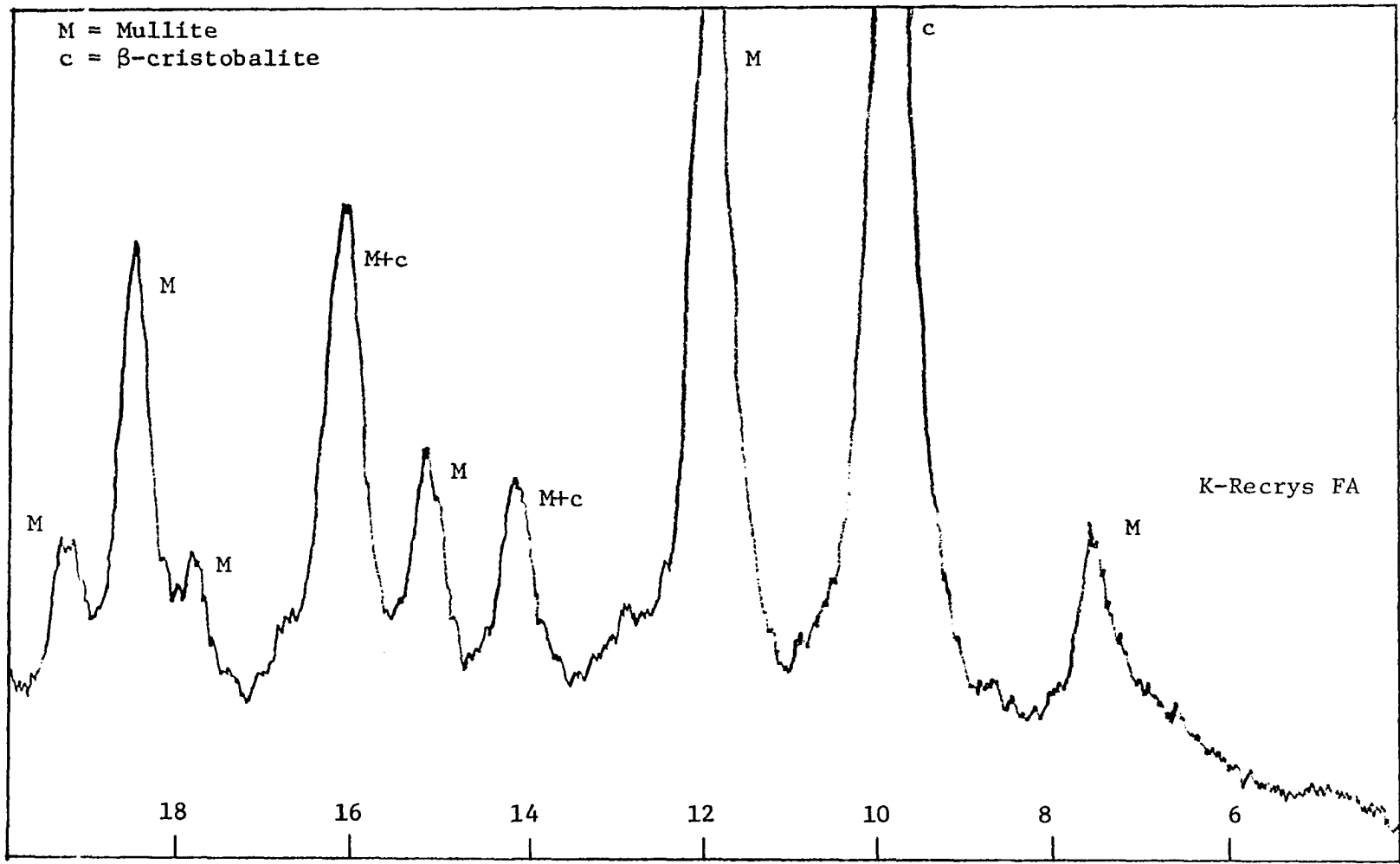
K-Recrys FA

18   16   14   12   10   8   6

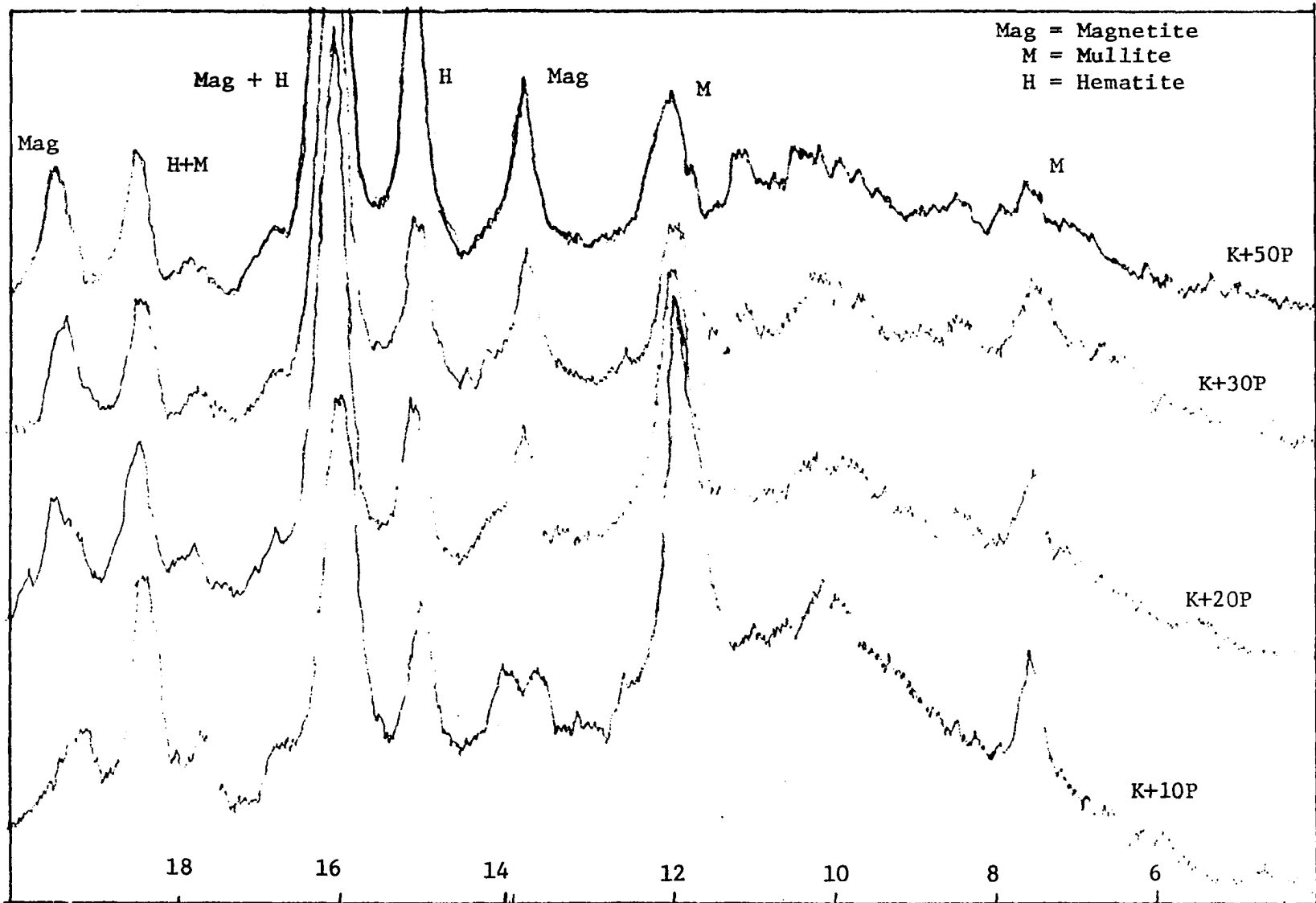Figure 15. X-ray diffraction pattern of K-Recrys FA

Figure 16. X-ray diffraction patterns of whole samples of K+P fly ashes

also reduces simultaneously with the increasing amounts of iron in the fly

ashes as evidenced by the proportionate suppression of the broad maxima.

The reduction in mullite and amorphous material may be explained by the

reduction in kaolinite in the raw material as increasing pyrite is added.

The reduction in amorphous or liquid phase with increasing amount of pyrite

added indicates that little iron goes to glassy phase; and this is also

born out by the presence of increasing amounts of magnetite and hematite

in the resultant fly ashes. However, it should be noted that despite

50 wt % iron in K+50P fly ash, the amorphous material still exceeds that

in K-Recrys FA (Compare Figure 15 and 16).

The x-ray traces of K+C fly ashes showed that they contained $Ca(OH)_2$,

calcite and some other unidentified compounds, the diffraction intensities

for calcite and $Ca(OH)_2$ increasing with increasing amounts of calcium in

the ashes. In all probability, the unidentified compounds are some

silicate, aluminate or alumino-silicates of calcium. The diffraction

patterns also indicated that amorphous material in K+C fly ashes decreases

with increasing amounts of added calcite.

The presence of $Ca(OH)_2$ as a major crystalline phase in the K+C ashes

suggests that most of the CaO produced from calcination of calcite is

hydrated, and the remainder becomes carbonated to again give rise to

calcite. Alternately, in the spheroidization process, not all of the

calcite may be decomposed to CaO; that which is hydrated under ambient

moisture conditions to $Ca(OH)_2$. The presence of increasing amounts of

calcite phase with increasing calcium in fly ashes was also observed in

light microscopic examinations.

The two trimineralic fly ashes do not have all the crystalline

substances found in K+P and K+C ashes, but have some other additional crystalline phases present, e.g. calcium sulfate. No calcium hydroxide was found. There are a few other peaks with weak intensities which cannot be attributed to any of the compounds found in K+P or K+C fly ashes. It appears some compounds of complex chemical composition are formed. The calcite in coal minerals gives rise to calcium sulphate by combining with the sulfur released from pyrite (139). These observations are, therefore, in agreement with published data.

Summary of Physical Analyses

Light and electron microscopic observations of pure kaolinite fly ash particles indicate that the shape and texture of particles varies with size. Smooth, solid, spherical and isotropic particles are predominant in size fractions below 10 microns, whereas the curved sausage-shaped particles with gaseous and crystalline inclusions are predominant in size fractions coarser than 20 microns. The 10-20 micron size fraction is a combination of the two. The presence of inclusions also reflected in the specific gravity values of various size fractions with increasing size, specific gravity decreased. Devitrification makes the pure kaolinite fly ash coarser and increases the index of refraction.

Devitrification makes the pure kaolinite fly ash coarser and increases crystalline inclusions and refractive index of particles. The devitrification is probably more on the particle surfaces as evidenced by increased peripheral birefringence.

Microscopic observations further indicate that in iron containing fly ashes, the number of opaque particles and surface roughness of such

particles increases with increase in iron content. This must be attributed to iron since it does not occur in ashes synthesized from pure kaolinite or kaolinite plus calcite. The K+P ashes also show evidence of intermixing of minerals. Magnetic separation of K+P ashes not only removes most of the opaque iron containing particles but also increases proportion of fine particles.

Chemical analysis and refractive index measurements of bimineralic fly ash particles suggest that iron and possibly calcium enter into solid solution with the alumino siliceous glassy particles. Furthermore, the specific gravity values increase with an increase in iron or calcium.

Specific surface area values obtained from air permeability method and calculated from size analyses exhibit some trends, but problems are encountered in meaningful interpretation.

X-ray studies confirm the presence of crystalline iron and calcium compounds in K+P and K+C ashes respectively. The presence of calcium sulphate in K+P+C ashes probably results from a reaction between sulfur oxides from pyrite and calcium oxide released from decomposition of calcite.

Quantitative Chemical Analysis

The results in terms of wt % of various oxides are presented in Table 17. The percent of Fe_2O_3 in the K+P whole ash samples is slightly less than that indicated by the abbreviation symbols which, it may be remembered, represented the amount of iron desired. This discrepancy may be due to preferential deposition of iron-containing particles in the furnace during firing.

Table 17. Chemical analyses of synthetic fly ashes

Fly ash notation	Constituents wt %				
	SiO_2	Al_2O_3	CaO	Fe_2O_3	Total
K-Cyc whole sample	52.67	46.69	0.31	0.37	100.04
K+10P " "	49.20	43.27	0.99	7.08	100.54
K+20P " "	44.72	41.78	1.03	14.11	101.64
K+20 nonmagnetic fraction	51.77	47.75	0.28	1.39	101.19
K+20P magnetic fraction	11.38	10.44	0.29	80.64	102.75
K+30P whole sample	39.50	34.24	1.58	24.91	100.23
K+30P nonmagnetic fraction	49.98	46.89	0.30	2.37	99.54
K+30P magnetic fraction	13.06	14.76	0.30	72.81	100.93
K+5C	48.18	–	5.88	<0.01	–
K+10C	45.06	–	10.38	<0.01	–
K+15C .	40.96	–	15.17	–	–
K+10P+5C	44.91	41.08	4.70	8.97	99.66
K+10P+10C	42.23	37.83	10.35	9.42	99.83
Tolerance	+0.77	+1.69	+0.32	+0.54	–

The alumina and silica in the bi- and trimineralic fly ashes are present in almost the same ratio as in the monomineralic ashes, but their combined proportion decreases with increasing iron or calcium oxides. Additions of pyrite and calcite dilute the alumina and silica content in these bi- and trimineralic fly ashes.

Most of the iron in the K+20P and K+30P fly ashes resides in their

magnetic fractions. However, the magnetic particles also contain some silica and alumina. This is in agreement with the light microscopic examinations. Results of chemical analyses obviously do not indicate the form of chemical constituents existing in fly ash.

Table 18. Chemical analyses of monomineralic fly ashes

Fly ash notation	Constituents wt %				
	SiO_2	Al_2O_3	CaO	Fe_2O_3	Total
K-Cyc whole sample	52.67	46.69	0.31[a]	0.37	100.04
K-Furn " "	52.46	45.32	0.37	0.49	98.64
K-Recrys " "	51.84	47.46[b]	0.30[a]	.40	100.00
<5 K-Cyc	50.99[c]	45.79[c]	0.17	.51	97.46
>20 K-Cyc	52.11	47.06[b]	0.30[a]	.53	100.00
Tolerance	+0.63	+0.33	+0.08	+.08	

[a]Values approximate since tolerance exceeded.

[b]Values obtained by subtraction.

[c]Tolerance limit +1.09.

The data for chemical analyses of various monomineralic fly ashes are given separately in Table 18. In addition to silica and alumina, which account for about 99 wt %, these fly ashes also contain very small amounts of iron and calcium oxides. Such elements are normal impurities in natural kaolinite (Appendix A).

The data in Table 18 indicate that chemical composition of the ashes remained constant regardless of thermal treatment or size fractionation.

Acid-Soluble Content

HCl-soluble content

Table 19 presents the acid-soluble amounts of the various synthetic fly ashes. Although the amount varies, a portion of each of the fly ashes is soluble in HCl, the bimineralic fly ashes of the K+C series and the two trimineralic fly ashes having a major amount of HCl-soluble material.

Previous data presented show that the monomineralic fly ashes contain an alumino-siliceous glassy phase and some crystalline phase (mullite and cristobalite) which have little or no solubility in dilute HCl. Chemical analyses show the presence of some calcium and iron in these fly ashes which may account for the HCl soluble amounts obtained.

The data in Table 19 suggests a trend of increasing HCl-soluble amount with decreasing size and with decreasing crystallinity. The particle size or increasing concentration of calcium and iron compounds in finer size fractions might possibly be responsible for the former. The latter trend of increasing HCl-soluble amount with decreasing crystallinity is difficult to explain at the moment.

The K+C fly ashes have a higher HCl-soluble content than the wt % calcium oxide as found by chemical analyses of these ashes. The reason for this is also possibly the same as explained earlier. X-ray analyses of these fly ashes also revealed that the calcium in these ashes is present as hydroxide, carbonate and possibly aluminate and silicate forms.

Table 19. Acid soluble content of various synthetic fly ashes

Fly ash notation	wt %		
	Soluble in 40% HF ice cold	Soluble in 0.2N HCl at room temperature	Glass content (% HF sol.- % HCl sol.)
K-Cyc whole sample	89.603	2.718	86.885
K-Furn " "	78.896	1.678	77.218
K-Recrys " "	41.815	0.816	40.999
<5 K-Cyc	92.596	3.636	88.960
5-10 K-Cyc	87.257	2.462	85.795
10-20 K-Cyc	87.923	1.819	86.104
>20 K-Cyc	88.416	1.695	86.721
K+5C whole sample	91.426	8.008	83.318
K+10C " "	89.649	14.851	74.798
K+15C " "	89.445	17.132	72.313
K+20P " "	Not determined	0.999	Not determined
K+50P " "	Not determined	3.496	Not determined
K+10P nonmagnetic fraction	91.040	1.743	89.297
K+20P " "	90.729	1.837	88.892
K+30P " "	88.968	1.486	87.482
K+10P+5C whole sample	88.932	8.004	80.928
K+10P+10C " "	87.767	14.875	72.892
Tolerance		±0.500	±2.000

The iron in fly ashes seems to play a very different role since the HCl-soluble amount in all iron-containing synthetic fly ashes is much less than in any of the other bi- and trimineralic fly ashes. Most of the iron in fly ashes is present as ferroso-ferric oxide which is soluble in HCl. However, even the magnetic fraction of these ashes has a very insignificant amount soluble in HCl. This is probably because of the thin coating of glassy material as was found to exist by light microscopic examinations. Minnick also reports the presence of some type of alumino-siliceous or ferruginous glassy surface layer on the magnetic particles. The increasing refractive index of glassy matrix in K+P fly ashes also indicated the possibility of iron going into solid solution.

The HCl-soluble fractions of the trimineralic fly ashes are comparable to the amounts found in the bimineralic K+C ashes. It is possible that the HCl-soluble matter in these fly ashes is also composed of calcium compounds, but the K+P+C ashes had very different crystalline phases of calcium than did the K+C ashes. Therefore, the similarity in HCl-soluble amounts of the two types of ashes is probably coincidental. The magnetic fraction of the K+P+C ashes was, however, insoluble in HCl as the magnetic fraction of K+P ashes. These observations further confirm the coating of magnetic particles by glassy material.

HF-soluble content

Table 19 presents the wt % of various synthetic fly ashes soluble in HF as a measure of the glass content. This may be confirmed by comparing HF-soluble amounts from the K-Cyc, K-Furn and K-Recrys fly ashes which were prepared under different conditions to vary the degree of

crystallinity. The difference in crystallinity of these three mono-
mineralic fly ashes is reflected in their HF-soluble amount from which
it can be concluded that K-Cyc FA contains the most amorphous material
while the K-Furn and K-Recrys ashes have successively less amorphous
material. This is in complete agreement with x-ray and light microscopic
observations.

The various size fractions of K-Cyc FA do not appear to differ much in
crystallinity since they contain HF-soluble amounts within the limits of
reproducibility of the test, i.e. $\pm2\%$.

The nonmagnetic fractions of K+P fly ashes were treated with HF to
determine if there is any difference in the solubility of the glass formed
from heat treatment of kaolinite with increasing amounts of pyrite. The
HF-soluble amount of these K+P fly ashes seems to lie in too close a range
to detect any variations between their solubility or glass content as a
consequence of increased iron content. However, it is observed that the
HF-soluble amount of the nonmagnetic fraction of the various K+P fly ashes
is the same as that of K-Cyc FA. This suggests that addition of iron does
not change the solubility of their glass in HF.

The bimineralic fly ashes of K+C series and trimineralic fly ashes
of K+P+C series, however, have decreasing HF-soluble amounts with increasing
calcite in the parent mineral mixture from which these ashes were prepared.
This decrease in HF-soluble amount is compensated for by increased HCl-
soluble amounts. The total acid soluble amount of these ashes is the same
as that of the K-Cyc FA. Despite this, the test seems to be fairly valid
in predicting glass content of the monomineralic fly ashes.

X-ray Elemental Microanalysis (XMA)

Particles of all shapes in different fly ashes were analyzed by use of the electron microscope with a fluorescent analyzer to study the particle composition. This did not prove very useful since none of the spheres less than 20 microns in any of the bi- and trimineralic fly ashes showed any characteristic peaks. Only a few of the particles larger than 20 microns showed the presence of silicon and aluminum. All of the particles in K-Recrys FA (Figure 9), irrespective of size or shape, showed characteristic peaks for silicon and/or aluminum. The presence of calcium in rhombohedral particles in K+C and K+P+C fly ashes and iron in K+P ashes could be detected only in very few spheres larger than 20 microns.

It is difficult to explain why all particles in the more crystalline K-Recrys FA showed the presence of silicon and aluminum, whereas most of the particles in the K-Cyc, K-Furn and other fly ashes having less crystallinity failed to show the presence of any elements. Crystallinity should not be a factor in such an analysis.

PART II. POZZOLANIC REACTIONS STUDIES IN

SYNTHETIC FLY ASHES

METHODS AND EQUIPMENT FOR STRENGTH AND REACTION STUDIES

General

A review of the literature indicates that data obtained from compressive strength tests are a reliable indicator of pozzolanic activity. In fact, specifications almost always include some requirement in terms of strength. A serious drawback to this type of test, particularly for commercial usage of industrial fly ashes, is that the method is time-consuming. Therefore, several investigators have suggested other methods which might be used to predict pozzolanic behavior of a given fly ash. The lime-depletion test (69, 71, 95, 125, 134) and acid-soluble reaction product test (95, 125) are examples. In this research several approaches were used.

For compressive strength tests, use was made of the miniature molding apparatus described by Roderick (108) in order to find the most suitable ratio of lime to fly ash and the optimum moisture content for molding. Six ratios of lime to fly ash ranging from 1:1 to 1:3 were investigated in this series by means of compressive strength tests up to 8 weeks. The optimum ratio was found to be 1:2. This ratio has also been suggested by various workers using commercial fly ashes, and has been adopted in many of their investigations (93, 136). Since different CaO/SiO_2 (C/S) ratios produce different reaction products and hence different strengths (14, 70, 71, 122, 127), it was considered desirable to adopt a single lime-fly ash ratio in this study. In addition, the C/S ratio of this mixture is approximately 1.0, which was considered appropriate in terms of expected reaction products.

The compaction moisture amount was determined which gave maximum strength to the lime-fly ash mortars and was found to vary with the physical and chemical properties of the synthetic ashes. An increase in crystallinity and iron content reduced the optimum moisture content of the lime-fly ash mortars, while increased amounts of calcium had the opposite effect. It was observed that even slight variations in the compaction moisture caused a substantial reduction in the initial and ultimate pozzolanic strength of the fly ash mortars. The molding device itself provided a good control on the optimum moisture content since slightly dry or wet mixtures could not be molded into samples of desired density. Apparently the compaction moisture that provided maximum dry density also provided maximum pozzolanic strength.

The lime used in this study was chemical reagent grade $Ca(OH)_2$ to avoid any influence due to impurities[1].

Concurrent to preparation of samples for strength tests, another parallel series of lime-fly ash mortars were prepared with an excess amount of water. These were analyzed by x-ray diffraction for the presence of reaction products at regular time intervals.

The techniques used for various tests are presented in the following paragraphs.

Physical Methods of Strength and Reaction Studies

Specimen molding

In view of the large number of fly ashes involved in this study a sample size of 1 in. in height and 1/2 in. in diameter was adopted. This

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[1]The type and amount of impurities in the chemical grade lime used in this study are given in Appendix C.

resulted in considerable savings of time and material, and the data obtained provided a good comparison within the series tested. The unconfined compressive strength of lime-fly ash samples is mainly a function of the cohesive strength developed due to formation of reaction products and are sufficiently valid for comparative studies.

Weighed amounts of lime and fly ash were first dry-mixed by hand in a glove box into which nitrogen was continuously fed. This precaution minimized the carbonation of lime. After five minutes of dry-mixing, a measured amount of water was added and the mortar was further mixed for at least a period of ten minutes. The lime-fly ash-water mixture was spooned into a cylindrical mold and compressed to a predetermined height by means of a lever arrangement. This assured uniform density and moisture content in each sample. The samples were then immediately transferred to a curing compartment.

Specimen curing

The curing compartment[1] described by Nakayama and Handy (97) was modified to provide 100% R.H. and a carbon dioxide-free atmosphere. The cylindrical test specimens were placed on plastic discs which were perforated to avoid accumulation of water. In addition, the perforations allowed free flow of moist nitrogen all around the specimens.

The specimens could be inserted or removed from the curing compartment by opening only one Plexiglas door, since the shelves could be rotated in the desired direction. The Plexiglas permitted complete visual examination

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[1]Details of curing compartment are given in Appendix D.

of the conditions inside the cabinet. Whenever the compartment door was opened, the nitrogen flow was increased to ensure that no air got into the sample compartment. Also after closing the door the compartment was flushed with nitrogen as a further precaution.

Specimen strength testing

After specified curing periods ranging from 2 weeks to over 6 months, the specimens were tested by means of a proving-ring type compression testing machine with an accuracy of ± 1 lb. The rate of strain was maintained at 0.1 in. per minute. Early strength tests, i.e. 1 to 7 days, were performed on an "Instron Precision Testing Machine" with an accuracy of ± 0.01 lb.

Any specific compressive strength value given represents an average of three to six separate strength measurements.

X-ray diffraction studies of reacted specimens

Three types of specimens were prepared for x-ray examination. These were selected to show the rate of formation and changes in the reaction products under different curing conditions. In one series, pastes made of lime-fly ash were placed in Bakelite powder diffraction mounts which were then wrapped in "Saran Wrap". These were cured for specified periods in a constant temperature-humidity room (20°C and 100% R.H.) after which they were scanned in the x-ray diffraction unit. Mateos (82) found that "Saran Wrap" was suitable for long term storage of such specimens. In another series, lime-fly ash mixtures were cured in plastic bottles filled with water to provide excess moisture conditions during curing. The bottles were shaken every third day. Some of the suspension was removed after

shaking the bottles and placed on a porous porcelain plate to absorb water

and provide a smooth surface for x-ray examination. In a third series,

for detailed investigation, specimens from the strength tests were dried

in a desiccator over magnesium perchlorate and Ascarite for at least 48

hours and then ground to pass No. 325 mesh sieve. The powder was mounted

in a brass ring powder holder by compressing under a load of 1000 psi.

All of these specimens made from the three different series of lime-

fly ash mixtures were x-rayed under a carbon dioxide-free atmosphere.

This was achieved by placing a cylindrical Plexiglas chamber over the

specimen during x-ray analysis. The chamber has a Mylar-covered window

for free passage of x-rays. Moist nitrogen was continuously fed into the

chamber to minimize specimen carbonation.

Chemical Methods of Reaction Studies

Chemical analyses for pozzolanic reactivity

In a very comprehensive study Ruff (109) devised tests to determine

quantitative amounts of silica and alumina in the pozzolanic reaction

products of lime-clay mixtures. His procedures, which were modifications

of standard tests for quantitative analyses of silica and alumina described

by Vogel (133) and Govett (50),were used in this research.

Another approach adopted by various investigators is to quantitatively

determine the lime used up in the pozzolanic reaction. The literature

indicates that all solvents used for dissolving lime also dissolve the

reaction products to some extent, so no reliable test is yet available for

this purpose. A test modified after the one adopted by Lea (71) was used

to determine free lime left in the reacted samples. A one-gram sample of

reacted powder was allowed to stand for 2 hours in 500 ml of water maintained at $0^{\circ}C$. Neither fly ash nor the reaction products are believed soluble to any extent in ice-cold water, while calcium hydroxide has a solubility of 0.185 g/100cc at $0^{\circ}C$ (102). The soluble lime was titrated by the EDTA method described by Diehl (42).

X-ray elemental microanalyses

The specimens were prepared in the normal manner for the electron microscope. A gypsum crystal was used in the spectrometer. All particle forms, unreacted spheres and partly reacted spheres, were examined for silicon, aluminum, calcium and iron.

RESULTS AND DISCUSSION

Influence of Fineness on Compressive Strength

The influence of the basic parameter fineness on the pozzolanic

strength developed in fly ashes was investigated by utilizing four size

fractions of K-Cyc FA. As previously shown, various physical and chemical

tests indicated that in spite of differences in their fineness, the

fractions were similar in chemical composition and crystallinity.

Figure 17 shows that the smaller the particle size of a fly ash, the

higher the ultimate strength. The lower strength trend of <5 K-Cyc FA for

a 10 day curing time was not observed for any other fly ash and may be

erroneous. It is observed that the relationship between ultimate as well

as initial strength and particle size is probably described either by two

straight lines (one from ≃4 microns to ≃13 microns and another from ≃13

microns to 27 microns and possibly onwards) or by a straight line from

≃4 microns to ≃13 microns and an asymptotic curve thereafter. The increase

in strength with decrease in particle size from 27 microns to ≃13 microns

is much less than the corresponding increase in strength for decreases in

particle size below ≃13 microns, and the pozzolanic strength of a fly ash

is inversely proportional to its average particle size below ≃13 microns.

Furthermore, the fly ashes with average particle size larger than ≃13

microns develop strengths less than 500 psi even after 2 weeks of curing

period. This may be the reason why some industrial fly ashes, even after

meeting various ASTM requirements (4) for fineness, fail to meet the

strength requirements.

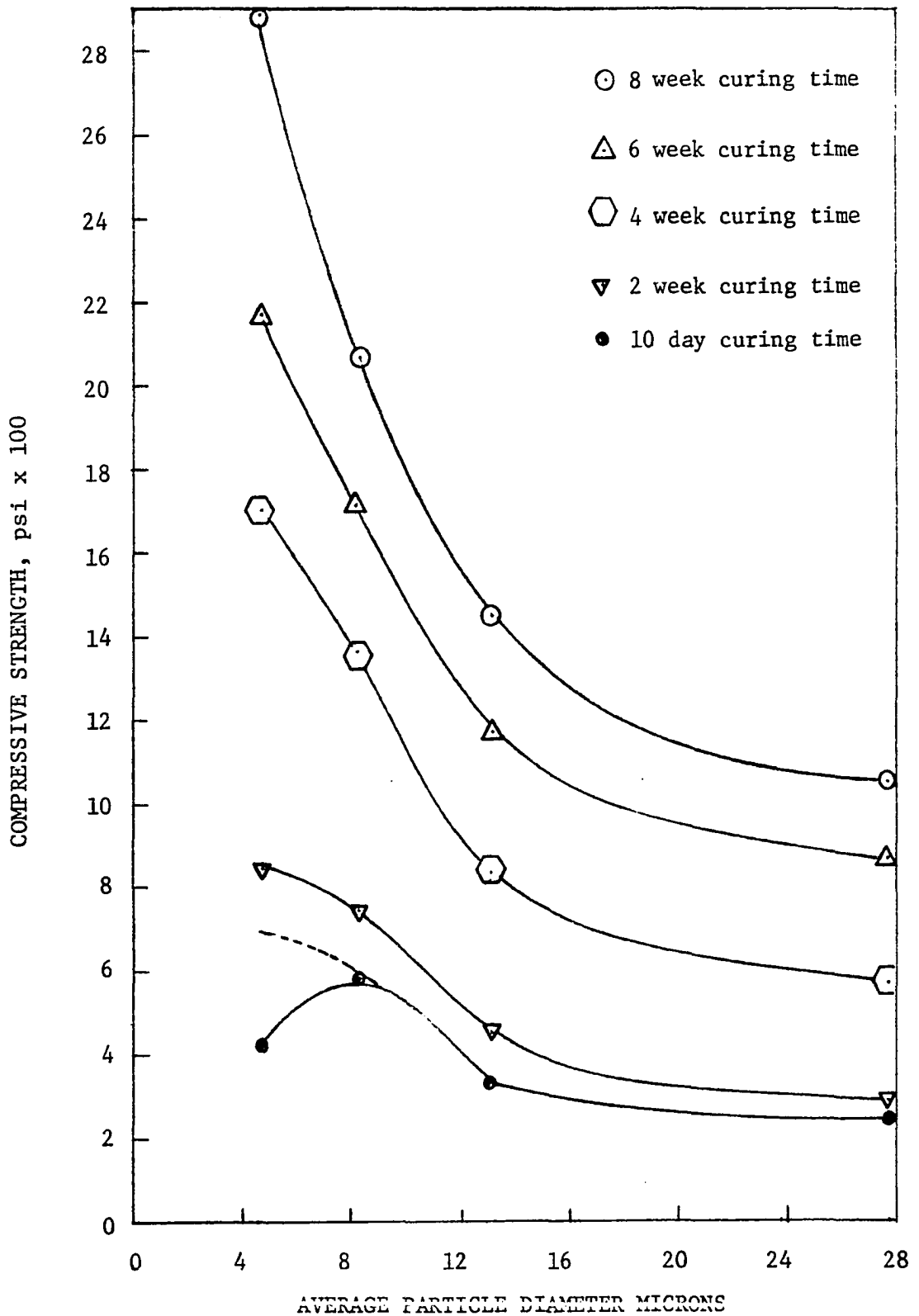The relationship of strength to specific surface area is shown in

Figure 17. Relationship between compressive strength of mortars and average particle diameter of synthetic fly ashes
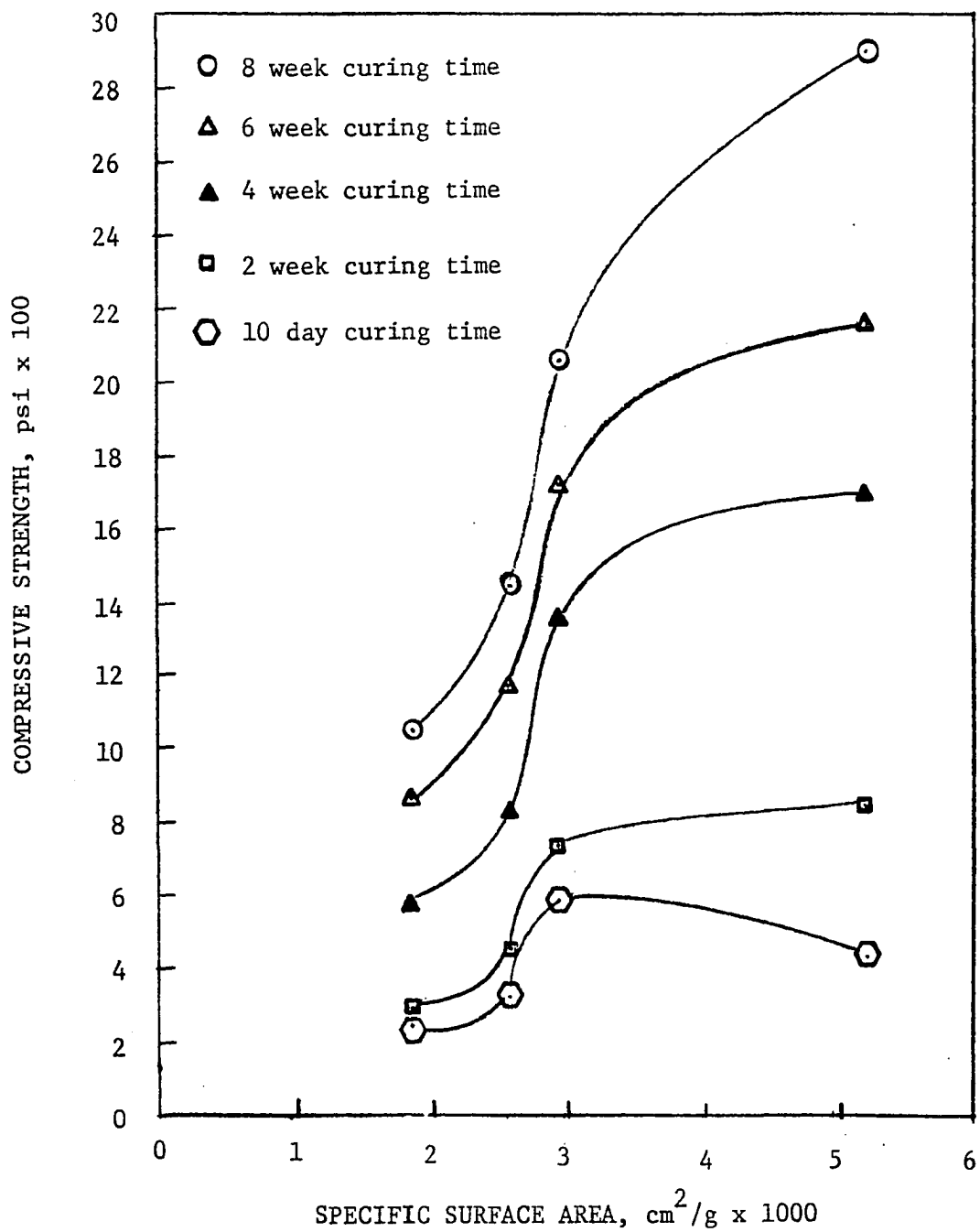
Figure 18. Compressive strength of mortars vs specific surface area (calculated from size distribution) of synthetic fly ashes
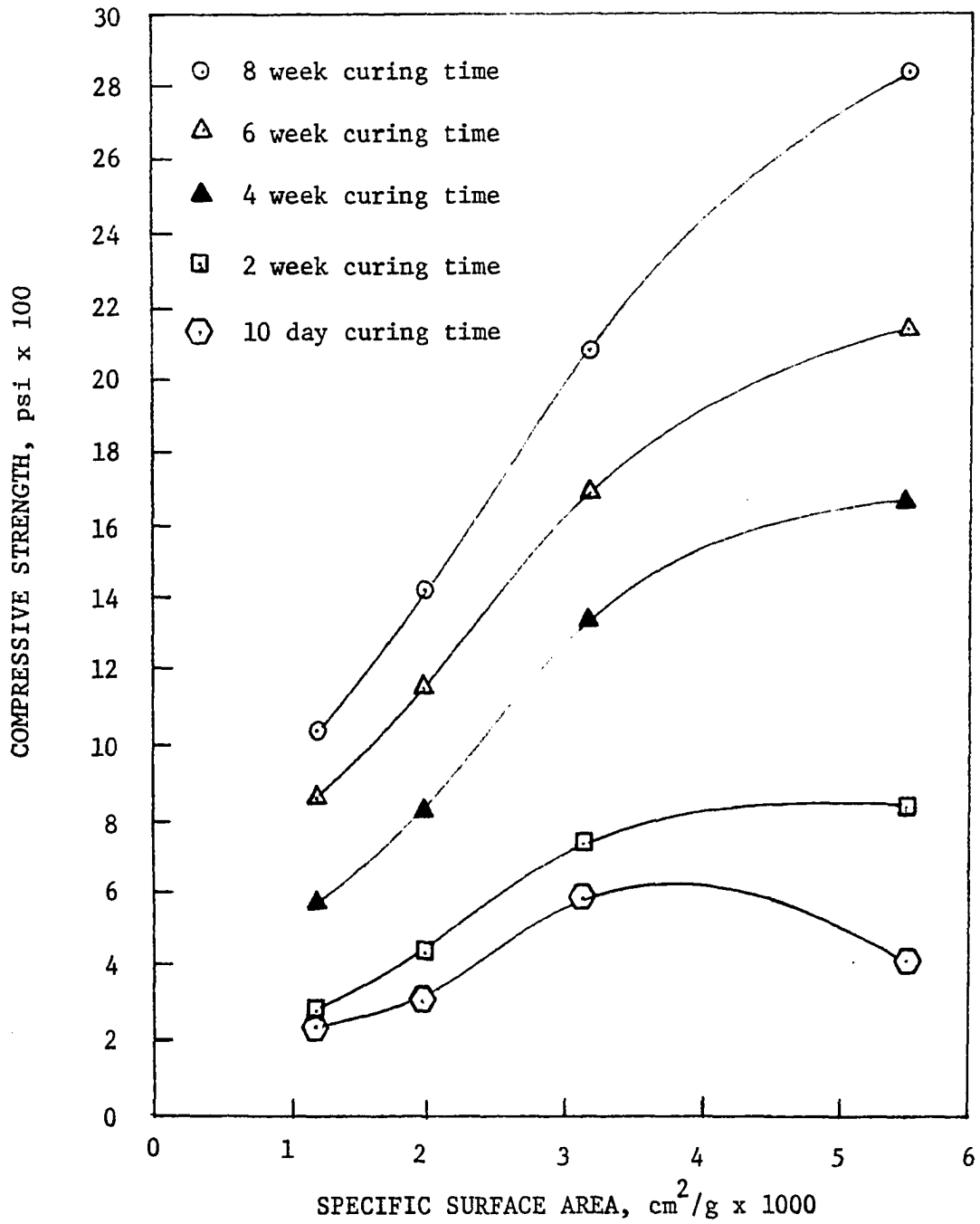
Figure 19. Compressive strength of mortars vs specific surface area
(determined by air permeability method) of synthetic fly ashes

Figures 18 and 19. The shape of curves in these two figures is similar

in that the compressive strength of the fly ash mortars is more sensitive

to specific surface area in the range 1000 to 3000 cm^2/g and reach a

maximum strength at about 5000 cm^2/g as is evidenced by the asymptotic

part of the curves for increased surface area values. This trend is

relatively more conspicuous from Figure 19 in which specific surface area

values obtained by air permeability method are plotted against strength.

It is observed from Figure 20 that strength is directly proportional

to the time of curing, but the rate of strength development is a function

of fineness of the fly ash; the finer the fly ash the higher the rate of

strength development as shown by the increasing slopes in Figure 20.

Figure 21 shows these slopes plotted against average particle size, and

reaffirms the influence of fractions below ≃13 microns. The shape of curve

in Figure 21 is similar to the curves in Figure 17, implying that within

the particle size range of ≃4 to ≃13 microns, the rate of strength develop-

ment of a fly ash, like ultimate strength, is an inverse function of the

average particle size, and any variations in the average particle size

of coarser fly ashes (with average particle size >≃13 microns or fineness

less than 2000 cm^2/g) have relatively little influence on the rate of

strength gain of the fly ashes. The reduction in ultimate strength as

well as rate of strength gain with increase in particle size can be

attributed to their surface characteristics.

Various investigators have pointed out that the pozzolanic reactions

are surface reactions and the surface characteristics of the fly ash

particles control the amount of reaction and thereby the pozzolanic

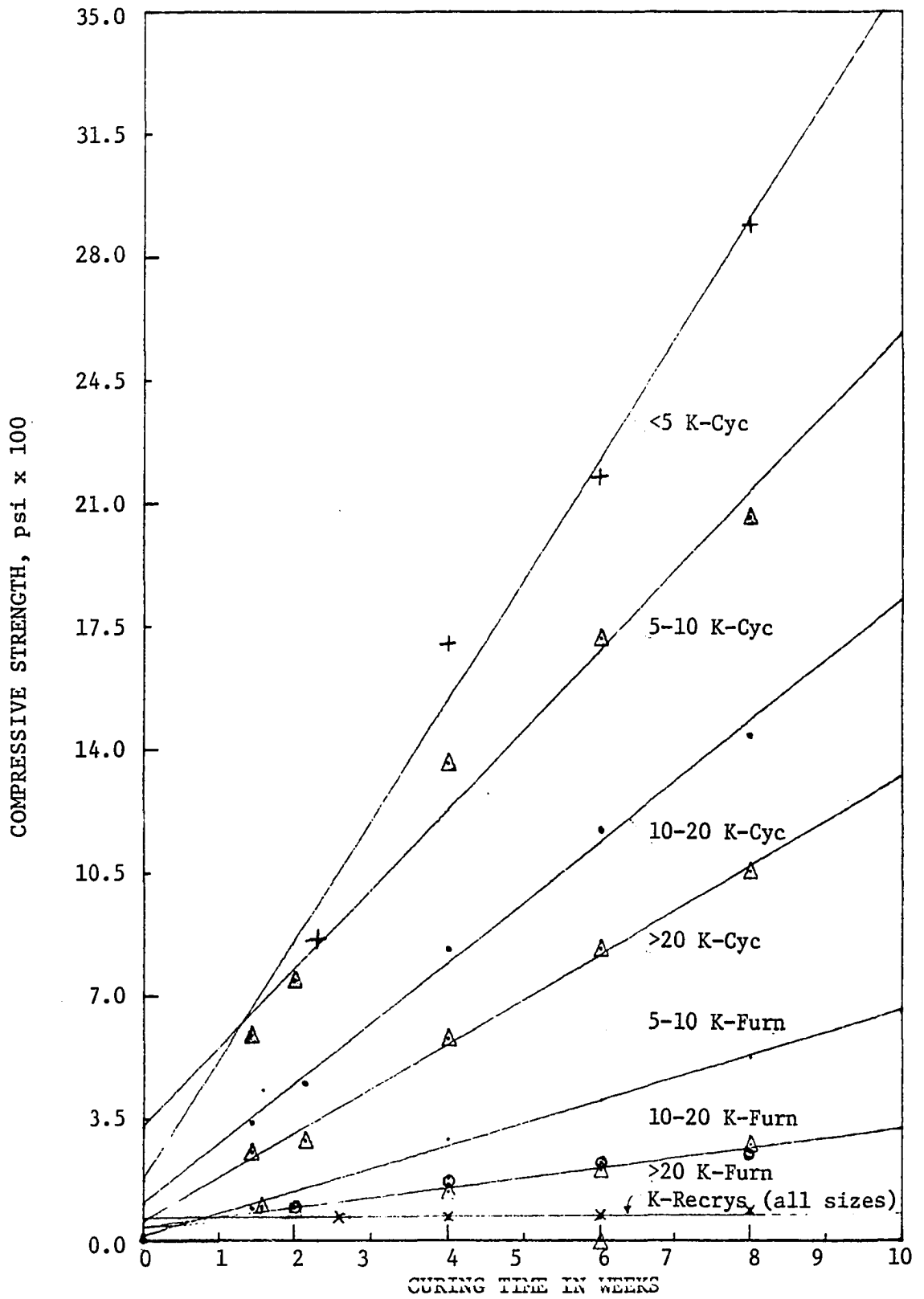strength (137). Snyder et al. (118) report that all other things (physical

Figure 20. Compressive strength of mortars from monomineralic ashes as related to time, fly ash fineness and crystallinity
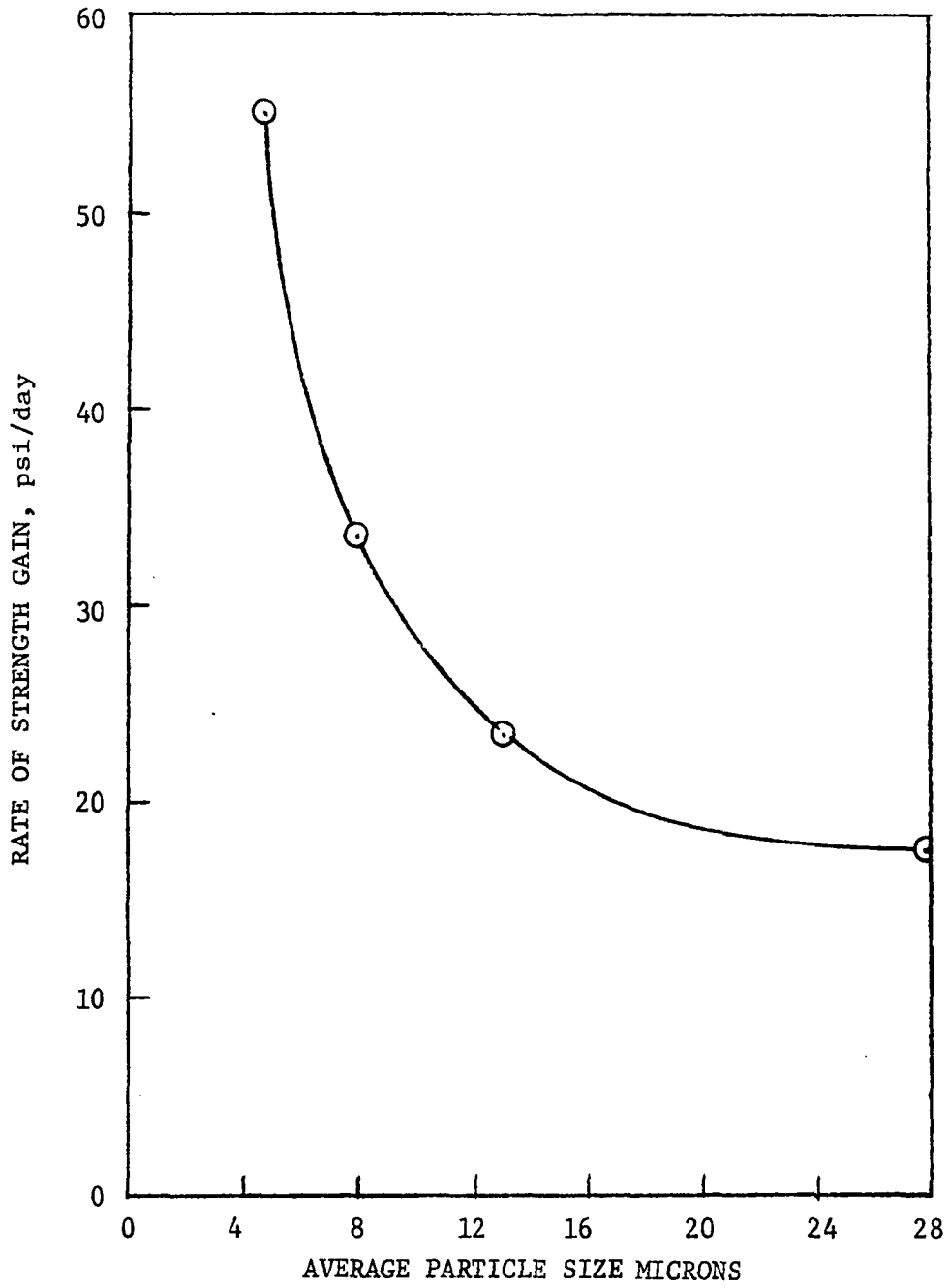
Figure 21. Rate of strength gain up to 8 weeks as related to average
particle size of the fly ash

and chemical properties) being equal, the greater the intrinsic (or inherent) strength of an ash, the higher the strength of mortar or concrete containing it.

The light microscopic examinations of various size fraction of K-Cyc FA showed that the majority of particles in the <5, 5-10, and 10-20 micron size fractions were solid, smooth, glassy and spherical of Type 1 (Table 5, page 59), whereas the >20 micron size fraction contained speckled, grainy, curved and cylindrical and sausage-shaped particles of Type 3 and 5, and the latter had comparatively more inclusions of crystalline substance and air or gas bubbles. This suggests that particles $>\simeq 13$ microns (corresponding to the >20 K-Cyc FA fraction) differed from the finer particles in shape as well as surface characteristics. Although the inherent or intrinsic crushing strength of the particles in the >20 K-Cyc FA was not measured, there is every reason to believe that because of their morphology and structure they would have reduced inherent strength. It appears very likely that the reduced surface area and the changed surface characteristics of the particles larger than $\simeq 13$ microns permit relatively smaller amounts of pozzolanic reaction products to be formed, and the pozzolanic strength is controlled by the inherent compressive strength of particles as suggested by Snyder et al. (118, 119). Furthermore, the crushing strength of particles larger than $\simeq 13$ microns probably does not differ very significantly. As a result, the ultimate strength and the rate of strength gain in the fly ashes containing particles larger than $\simeq 13$ microns does not differ appreciably. This will be further elaborated while discussing the influence of crystallinity on the pozzolanic strength of the fly ashes.

The conclusions drawn regarding the influence of fineness on the

strength development from the strength development from the strength

studies of four synthetic kaolinite fly ashes should also be applicable

to the industrial fly ashes since a large fraction (75-95 wt %) of the

mineral matter in coal is also composed of kaolinite and is believed to

be the source of pozzolanic particles in them (98, 137, 139). Although

these conclusions are in agreement with those of Watt and Thorn (137),

these are very much different from those of Snyder et al. (118) who reports

that as the particle size decreases the pozzolanic strength goes through a

maximum at about 10 micron average particle size attributed to a possible

decrease in the compactibility of the finer particles. They further

report that similar to strength vs. particle size, the pozzolanic activity

also passes through a maximum at about 35 microns and they suggest that

the differences in chemical composition of particles finer and coarser

than 35 microns are responsible for this. The present study shows us

such change in compactability of finer particles. Watt and Thorn (125),

from a comprehensive study of industrial fly ashes, found that there was

hardly any difference in composition of various size fractions of industrial

fly ashes and that the pozzolanic strength as well as reactivity increases

with decrease in the average particle size (or increase in specific surface

area). It does not seem reasonable that particles of a certain size will

attain a particular chemical composition favorable to pozzolanic activity.

As pointed out earlier, the heterogeneous nature of the industrial

fly ashes does not permit separation of particles of similar physical and

chemical properties. It is, therefore, highly probable that the three

fly ashes investigated by Snyder et al. (118) also differed in other ways

such as structure and composition of the glassy substance of the fly
ash particles.

Influence of Crystallinity on Compressive Strength

The three monomineralic fly ashes, i.e. K-Cyc, K-Furn and K-Recrys,
were available to study the parameter of crystallinity. However, their
average particle size was too different to allow comparison of strength
development and hence they were also fractionated with the help of a water
elutriation into four different size fractions similar to those from
K-Cyc FA. The K-Furn and K-Recrys fly ashes had very insignificant
fractions of particles smaller than 5 microns; therefore, only three size
fractions of these fly ashes could be utilized for comparative studies.
The results of chemical analyses revealed that the chemical composition of
the whole samples of the fly ashes and each of the size fractions thereof
is similar. As previously shown, the amount of glass in these fly ashes
as determined by HF-solubility test varied systematically, being highest
in K-Cyc and the lowest in K-Recrys FA with the K-Furn FA intermediate.
The glass content in the various size fractions was found to be no
different from the corresponding whole samples of the fly ashes.

The results given in Table 20 show the strengths of the mortars of
three size fractions of different monomineralic fly ashes for periods up
to 8 weeks. At all periods of curing, even the coarsest K-Cyc FA size
fraction (>20 micron size) gives substantially higher strength than any of
the size fractions (5-10 micron size) of K-Furn and K-Recrys fly ashes.
Figure 20 also indicates that the K-Cyc and K-Furn fly ashes of different
fineness (different size fractions) have constant rates of strength

Table 20. Compressive strengths and rate of strength development of monomineralic fly ashes of different fineness and crystallinity

	Compressive strength psi of mortars of				
Size fraction microns	<5	5-10			10-20
Curing time	K-Cyc FA	K-Cyc FA	K-Furn FA	K-Recyrs FA	K-Cyc FA
10 days	—	588	95.8	86.2	337
11 "	428	—	—	—	—
14 "	—	745	—	—	—
15 "	—	—	—	—	449
16 "	858	—	—	—	—
4 weeks	1700	1362	291.0	68.0[a]	834
6 "	2175	1715	403.0	—	1176
8 "	2890	2060	525.0	86.2	1440
Rate of strength gain[b] psi/day	48.83	32.25	9.25	0.00	24.55

[a]The low value because of zero error in the dial gauge of the proving ring.

[b]Computed from linear regression of data in this table and Figure 20.

| | Compressive strength psi of mortars of | | | |
| 10-20 | | >20 | | |
K-Furn FA	K-Recrys FA	K-Cyc FA	K-Furn FA	K-Recrys FA
—	92.7	254	—	95.0
100.2	—	—	94.2	—
92.5[a]	71.8[a]	—	100.7	68.7[a]
—	—	289	—	—
—	—	—	—	—
143.5	62.3[a]	580	187.5	73.2[a]
205.0	68.2[a]	834	226.0	74.8[a]
278.0	94.0	1055	254.0	92.7
4.06	0.00	18.13	3.55	0.00

development up to a period of 8 weeks but the former have significantly higher rates (3 to 6 times) than the latter. Furthermore, finer K-Furn FA show higher rate of strength development than the coarser, but even the finest K-Furn FA (5-10 micron size) exhibits minimal or rather insignificant rate of strength gain. On the other hand, the K-Recrys FA size fractions, irrespective of their size, do not show any gain in strength with time up to a period of 8 weeks. It is, therefore, evident without any reasonable doubt that crystallinity has much greater influence than the fineness on the compressive strength of lime fly ash mortars or on pozzolanic activity of the ashes.

The relationship between compressive strength of the lime fly ash mortars and the crystallinity of the 5-10 micron ash fractions as determined by HF-solubility test is shown in Figure 22. The asymptotic nature of the curves suggests that irrespective of particle size, there is a sharp decrease in strength with slight increase in crystallinity or decrease in glass content of the fly ash. Figures 23 and 25 further indicate that particle size or fineness of an ash gains significance if the glass content of the ash, as determined by HF test is above 85%. Therefore, the crystallinity of the fly ash particles is the basic parameter which controls the pozzolanic activity and hence its compressive strength.

The question remains as to why even fine fractions of K-Furn and K-Recrys fly ashes develop such low strength in spite of a large amount of glass still present in them. For example, the strength of 5-10 K-Furn FA are about one-fourth of the 5-10 K-Cyc FA, whereas the glass contents are 77% and 87% respectively (Table 19). It is hard to see how a 9% reduction in glass content can impart 75% reduction in strength. Chemical
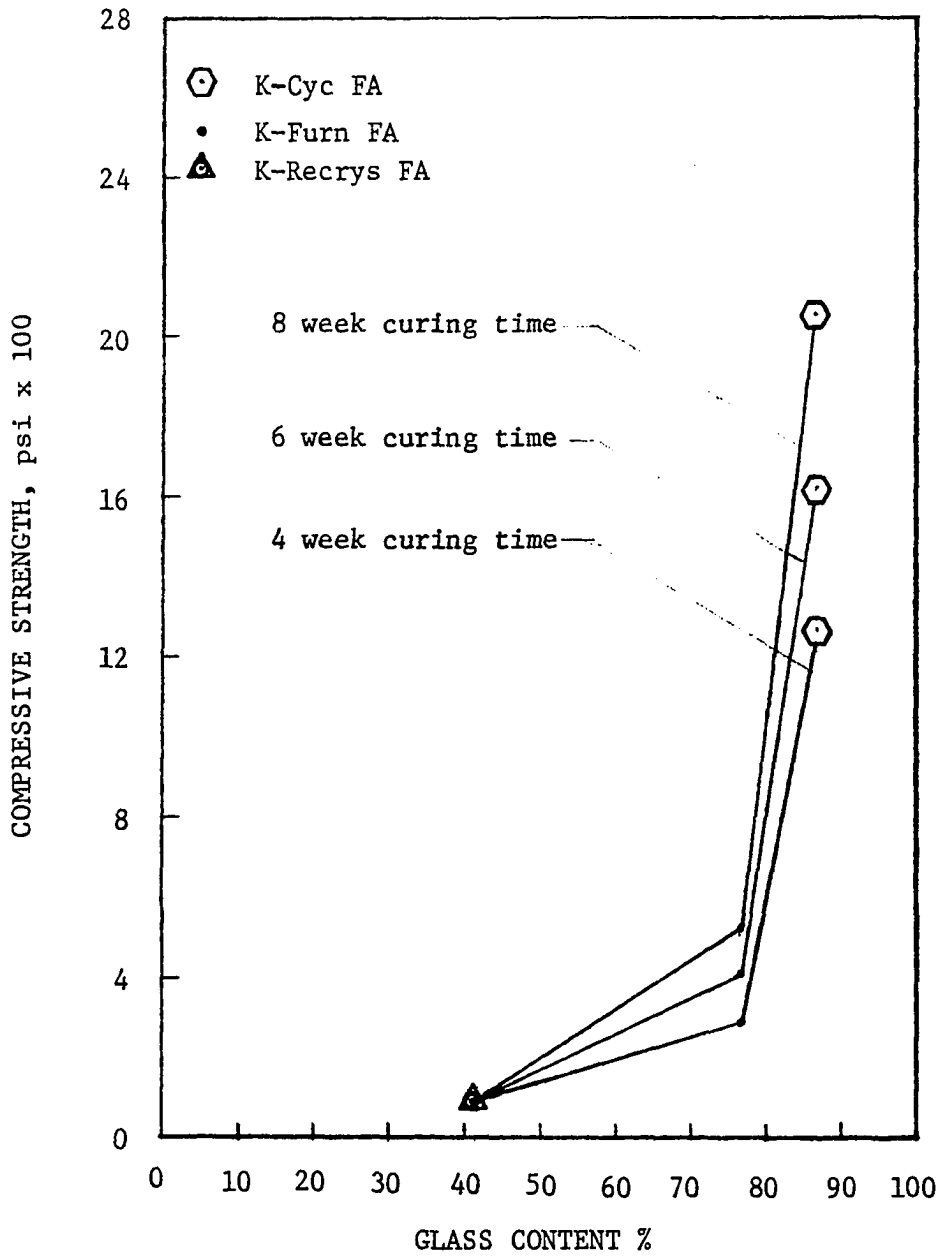
Figure 22. Compressive strength of mortars as a function of glass content of monomineralic fly ashes (5-10 micron fractions)

and particle size differences have been minimized, the main difference

being thermal history. One possibility is residual strains which may be

removed by annealing and/or the observed partial devitrification. The

temperature history of K-Furn and K-Recrys fly ashes is completely different

from that of K-Cyc FA inasmuch as the former two ashes were formed by

cooling the heated powder mass at a slow rate while the latter was formed

by rapid quenching of small particles in molten state. It appears probable

that in the latter the glass exists in a highly strained condition, since

the faster the cooling rate the higher the strains induced in the glass

(113). The glass in the devitrified K-Recrys FA particles, on the other

hand, should be almost in completely relaxed state (unstrained or annealed)

whereas the glass in K-Furn FA particles would be strained but only slightly

because of their temperature history. The HF-solubility test is not

amenable to distinguish strained vs. unstrained conditions since all

aluminosiliceous glasses are soluble in HF.

It can only be concluded from these observations that the structure of

the glass in the fly ash particles influences the pozzolanic activity more

than does size. Turriziani (127) also suggests that structure of glass in

pozzolans plays an important role in their pozzolanic activity. Singer

and Singer (113) state

> Corrosion of glass under strain is higher than that of
> well annealed strain-free glass.

The ceramic literature (63, 89, 113) also suggests that solubility of

various types of glasses is reduced by annealing. It would not be out of

place to mention that in the manufacture of "slag cements" the blast

furnace slag has to be quenched efficiently to a glass, as the slags cooled

at a slower rate are in general crystalline and are of no value as cements

(72, 124). The process and rate of cooling control the amount and degree

of crystallization and thence the structure and composition of the

resultant glass. Nurse (99) suggests that heat-treatment of slag glasses

for removing water possibly anneals them and affects their hydraulic

behavior. The three monomineralic fly ashes are analogues of glassy and

crystalline slags, K-Cyc FA being analogous to the former and K-Furn and

K-Recrys fly ashes to the latter. Therefore, it is reasonable to speculate

that the higher the amount of strain or vitrification in the glass of fly

ash particles the greater the reactivity of the ash.

Another reason for the reduced reactivity of the K-Furn and K-Recrys

fly ashes may be the surficial concentration of crystals in their particles,

which forms an armor coat against pozzolanic reaction. The light

microscopic observations showed that the surfaces of particles in these fly

ashes have higher density of crystals as compared to the interior (Figures

8 and 9). Therefore, such particles have reduced glassy area exposed for

pozzolanic reaction. The K-Cyc FA particles, on the other hand, have almost

all their exposed surfaces frozen in the liquid state due to thermal shock.

If the individual particles in the three monomineralic fly ashes were

essentially similar in shape and size, the reactivity would be the highest

for K-Cyc FA, the lowest for the K-Recrys FA and for the K-Furn FA, it

would be lower than the former but higher than the latter fly ash.

It can therefore be concluded that physical properties (strain and/or

vitrification) of the glass and its relative placement in the particles

rather than the amount of glass are responsible for the reduced pozzolanic

activity of the K-Furn and K-Recrys fly ashes; and the HF-solubility test is not amenable to distinguish the desired glass properties. There is every reason to believe that the industrial fly ashes contain particles similar to the K-Furn FA if not similar to K-Recrys FA in varying proportions. The increased amount of such particles would tend to influence their pozzolanic reactivity to a great extent.

Cockrell et al.(34) has reported that the fly ash emitted by fluid-bed furnaces is less vitrified than fly ash generated by suspension-fired furnaces. Furthermore, results of strength and reactivity tests on some industrial fly ashes presented by Leonards (74) show that the fly ash obtained from a fluid-bed unit showed little or no pozzolanic strength compared to fly ashes from suspension-fired furnaces. It is suggested that of the monomineralic ashes studied, the K-Furn FA most closely resembles the ashes from fluidized-bed units.

Watt and Thorn (125, 136) also report the presence of sintered particles, like K-Furn FA particles, in industrial fly ashes, calling them spongy particles. They found that the fly ash containing sintered and spongy particles was less reactive and developed much less ultimate strength than those fly ashes which contained smooth glassy particles of Type 1, similar to K-Cyc FA.

Although the influence of chemical composition has not yet been presented, it is well known that almost all industrial fly ashes possess some reactivity despite wide variations in their chemical composition. The results presented so far and the published data (72, 74, 99, 125) regarding industrial fly ashes and slag cements lead to the conclusion that the structure (i.e. amount of strain or vitrification, which is controlled by

the temperature history of the particles) of the glass and its relative placement in the particles have an overriding influence on the pozzolanic strength of the fly ash.

This hypothesis can also be applied to explain the minimal differences in the strength development characteristics of the K-Cyc FA particles >≃13 microns as observed from Figure 21. It appears that the surfaces of glassy particles >≃13 microns (corresponding to the >20 K-Cyc FA fraction) are less vitrified than those of particles in smaller fraction. The former particles may have temperature gradient from their surface to the interior during cooling process and, therefore, do not become vitrified as much as the latter. It is also possible that a majority of larger particles are carried away with the flue gases through the furnace by saltation and all the finer particles are carried by flotation. As a result the larger particles are quenched in two or more stages and have a completely different physical and temperature history than the fine particles. The light microscopic observations also indicated that the particles >20 K-Cyc FA fraction were different in shape from those in other three finer size fractions. This may be the reflection of slightly different temperature history of the particles in >20 K-Cyc FA. The similarity of temperature history of larger particles may, therefore, be responsible for minimal differences in ultimate pozzolanic strength and rate of strength gain in >20 K-Cyc FA fraction.

Influence of Chemical Composition on Compressive Strength

The influence of the parameter of chemical composition was investigated by comparing the strength development properties of various mono-, bi-, and

trimineralic fly ashes (Table 21). It was established by physical and chemical tests that, barring their chemical composition, the glassy particles of these fly ashes were similar in fineness, and any differences in their glass content and composition were present as a consequence of their chemical composition and not due to differences in their temperature history.

The results of compressive strength tests of the nine synthetic fly ash mortars cured for 8 to 28 weeks are presented in Figures 23 and 24. The most striking features of Figure 24 is that although the rate of increase of strength is different for different fly ashes, nevertheless all the fly ashes seem to have one fixed rate up to a curing time of 8-10 weeks and another for curing time beyond 10 weeks. The significance of this characteristic common to all the fly ashes will be explained while discussing the mechanism of reaction. Figure 24 further indicates that the difference in the 8 to 10 week strengths of different fly ashes are fairly good measures of the differences in their respective ultimate strengths. It is worth pointing out here that comparison of strength development in industrial fly ashes collected from different sources hardly ever results into such a well defined relationship due to other simultaneously occurring variables.

Influence of iron

The data of Table 21 and Figures 23 and 24 indicate that at all ages of curing up to 28 weeks, the compressive strengths of K+P FA (i.e. iron containing fly ash) mortars are lower than any other fly ash mortars tested in this study. Although strength tests on K+C and K-Cyc FA mortars could
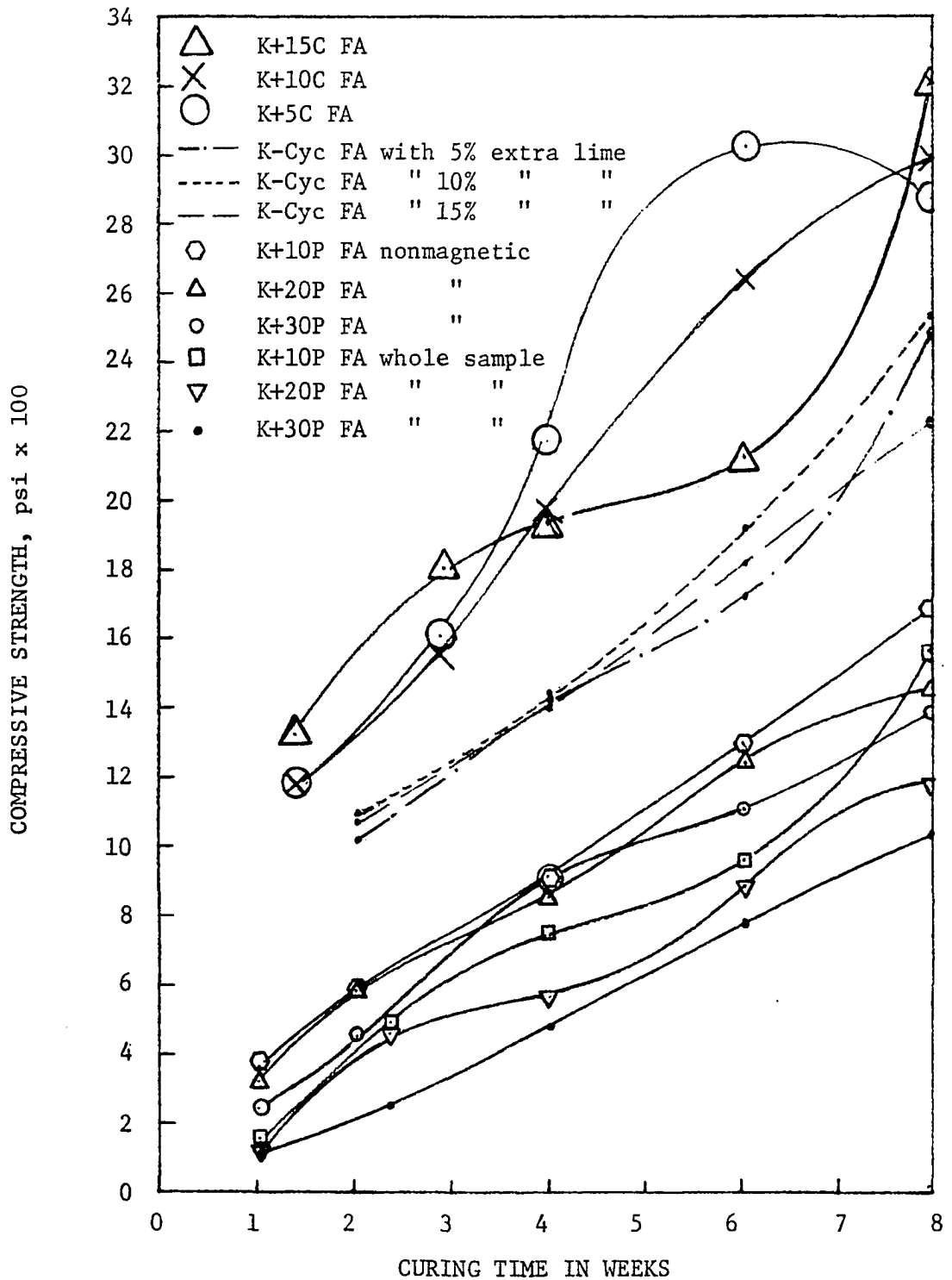
Figure 23. Compressive strength of mortars of bimineralic fly ashes as related to curing time

Table 21. Compressive strengths of mortars of mono-, bi- and trimineralic fly ash

Curing time day/weeks	Compressive strength psi				
	Monomineralic FA Whole sample		Bimineralic fly ashes Whole sample		
	K-Cyc	K-Cyc[a]	K+10P	K+20P	K+30P
1 day	—	79	82	72	73
3 days	—	131	92	94	—
5 "	—	169	—	123	134
7 "	—	207	183	137	137
9 "	—	—	—	—	—
10 "	—	—	—	—	—
11 "	—	—	—	—	—
14 "	1126	448	493	461	261
15 "	—	—	—	—	—
20 "	—	—	—	—	—
3 weeks	—	594	648	550	376
4 "	1550	910	750	563	495
6 "	1915	994	964	890	798
8 "	2445	1425	1575	1180	1035
10 "	2972	1737	1755	1410	1278
12 "	—	1782	1885	1582	1448
14 "	—	—	—	—	—
16 "	—	1710	2210	1840	1755
20 "	—	2035	2740	2350	2230

[a]Only 15 wt % moisture used to make the samples.

| Bimineralic fly ashes | | | | | | Trimineralic fly ashes | |
| Nonmagnetic fraction | | | Whole sample | | | Whole sample | |
K+10P	K+20P	K+30P	K+5C	K+10C	K+15C	K+10P+5C	K+10P+10C
—	—	—	—	—	—	107	106
—	—	—	—	—	—	251	150
—	—	—	—	—	—	294	230
—	—	—	—	—	—	454	324
—	332	228	—	—	—	—	—
374	—	—	—	—	—	—	—
—	—	—	1335	1190	1195	—	—
—	—	431	—	—	—	834	661
—	578	584	—	—	—	—	—
—	—	—	1807	1550	1600	—	—
—	—	—	—	—	—	—	—
912	858	908	1940	1970	2180	1006	932
1295	1240	970	2530	2640	3030	1492	1428
1690	1453	1385	3209	2785	2875	2100	1810
—	—	—	—	—	—	2565	2290
—	—	—	—	—	—	2850	2430
—	—	—	—	—	—	3120	2625
—	—	—	—	—	—	3240	2890
—	—	—	—	—	—	3670	3200
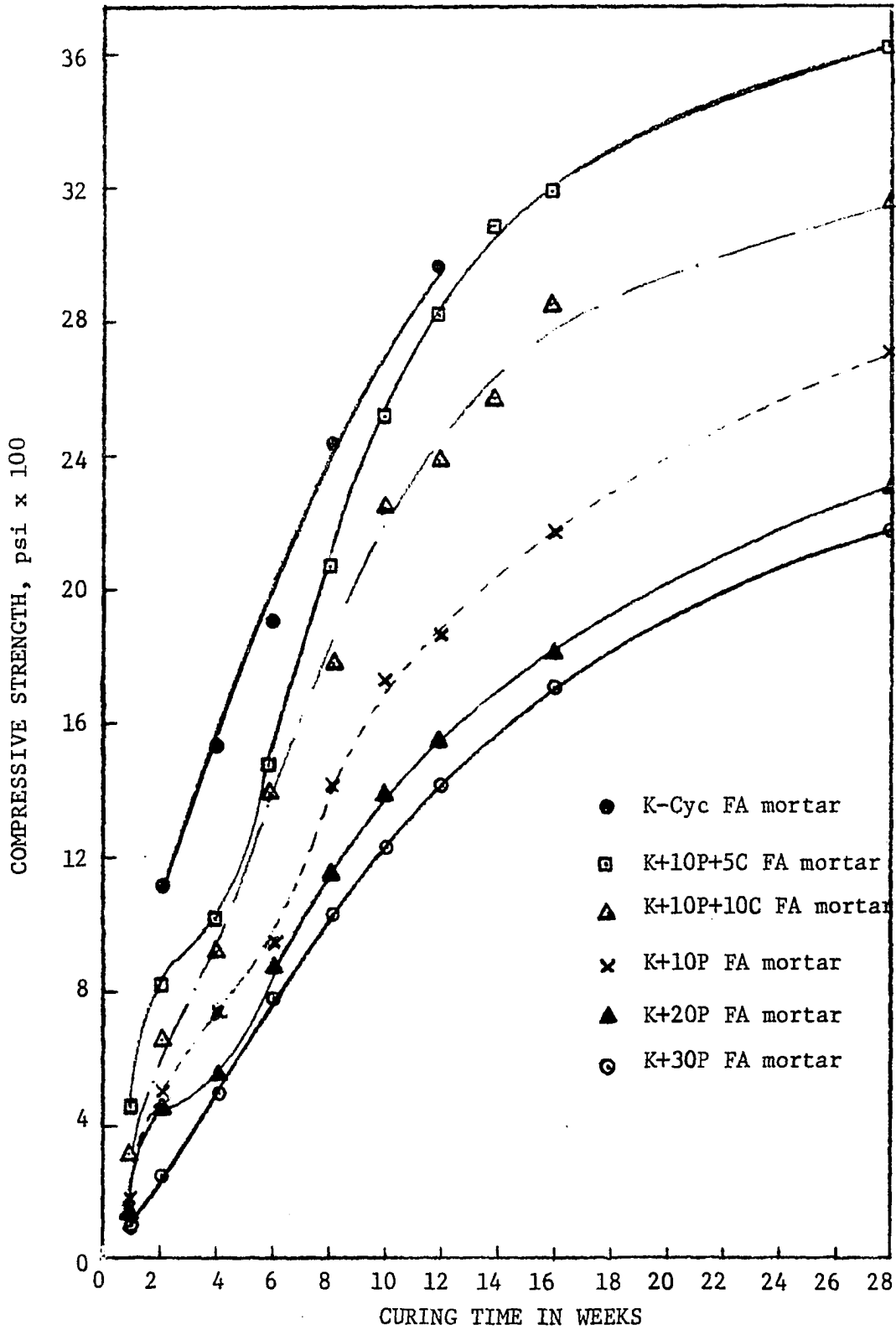
Figure 24. Compressive strength of synthetic fly asn mortars cured up
to 28 weeks

not be run beyond 8 weeks, it is apparent from Figure 23 that ultimate

strengths of these would have been higher than the K+P FA mortars.

Figures 23 and 24 show that the higher the iron content of an ash, the

lower the initial and ultimate strength of that ash. It is reported that

the magnetic separation of iron from the fly ashes significantly bene-

ficiates the fly ashes and improves their pozzolanic strength (90). How-

ever, the data in Table 21 and Figure 23 indicate that benefication by

magnetic separation is not too great since the strengths of mortars of

nonmagnetic fractions of K+P fly ashes, although higher than the mortars

of the corresponding whole samples of the fly ashes, are still much less

than the pure kaolinite fly ash mortar. In addition, the similar trend

of decreasing strength with increasing iron content persists even in the

nonmagnetic fly ash mortars for all ages of curing up to 8 weeks. This

suggests that most of the nonmagnetic iron in the K+P fly ashes is probably

present in the glassy phase and alters their pozzolanic reactivity con-

siderably. The light microscopic examinations also showed evidence of iron

going into solid solution with the alumino-silicious glassy phase. Had

this not been the case, the pozzolanic strength of mortars of nonmagnetic

fractions of all the K+P fly ashes should have been the same and equal to

the strength of pure kaolinite fly ash, i.e. K-Cyc FA.

There is no reason to believe that dilution of glassy phase fly ash

by small quantities of iron not occurring in the glassy phase would tend

to reduce the pozzolanic strength of the ash to such an extent since a

similar dilution by addition of quite a large proportion of aggregates in

sand-lime-fly ash mortars does not reduce the pozzolanic strength of the

mortars appreciably. The magnetic separation simply removes the magnetite

particles (which probably play part of an aggregate) and beneficates in the sense that the glassy phase is enriched. A close examination of published data (90) also indicates that benefication of industrial fly ashes by magnetic separation does not increase their pozzolanic strength significantly. It can, therefore, only be concluded that the iron in fly ashes in nonmagnetic state has the greatest deterious effect on their pozzolanic reactivity probably by forming solid solution in the glass.

The reduced reactivity of the nonmagnetic fractions of K+P fly ashes may be attributed to the reduced strains in the glass by substitution of iron. The size of iron ions varies depending on valence, but is larger than silicon or aluminum ions. Despite this fact, ferric iron substitutes freely for aluminum in octahedral coordination in clay minerals, as in nontronite, and ferrous iron substitutes in limited amounts as in chlorides (43). How such substitutions might structurally affect residual strains in glass is unknown; however iron substitutions will increase the heat capacity of the glass and hence reduce the cooling rate, which should tend to reduce strains. Furthermore iron in slag glasses is also found to reduce their hydraulic activity, and therefore it is reasonable to infer that increasing amounts of iron in fly ashes would also reduce their pozzolanic activity.

Influence of calcium

Calcium has a beneficial effect on the pozzolanic activity of the fly ash as evidenced by data in Table 21 and Figure 23. At all curing periods up to 8 weeks, the compressive strength of the K+C fly ash mortars are the highest recorded in the entire study. However, there does not seem to be any relation between the pozzolanic strength and the amount of calcium in

the fly ash as evidenced by the erratic trend of rate of strength gain of the three K+C fly ash mortars (Figure 23).

Light microscopy indicated the presence of a few calcite grains, and x-ray analysis showed increasing amounts of $Ca(OH)_2$ with increasing amounts of calcium in the K+C fly ashes. The suspicion immediately arose that, since the ashes themselves contained some $Ca(OH)_2$, this additional lime would lead to higher compressive strengths. Specimens of K-Cyc FA and lime mortars were prepared by mixing additional lime (in addition to the lime required to make 1:2 lime-fly ash mortars) equivalent to the amount of $Ca(OH)_2$ present in K+C fly ashes. The results of compressive strength tests of these specimens along with the corresponding K+C fly ash mortars presented in Figure 23 indicate that adding extra lime to the fly ash mortars does not increase the strength of the resultant mortars. A separate series of tests on lime fly ash mortars of different proportions also indicated that increasing the weight ratio of lime to fly ash above 1:2 decreases the strength (Figure 25). This suggests that all the calcium in the K+C fly ashes is not present as $Ca(OH)_2$ but in some other crystalline or glassy phase which makes these fly ashes more reactive than even the K-Cyc FA. The x-ray analyses of these fly ashes also indicated that there were some additional unidentifiable crystalline phases present in them and there is every likelihood of these being silicate and aluminates of calcium which on hydration produce good cements. Although the refractive index values suggest that both calcium and iron enter into glassy phase, calcium results in increased reactivity whereas incorporation of iron decreases the reactivity. In comparison to the size of iron ion, the calcium ion is much larger than the silicon or aluminum ions and therefore
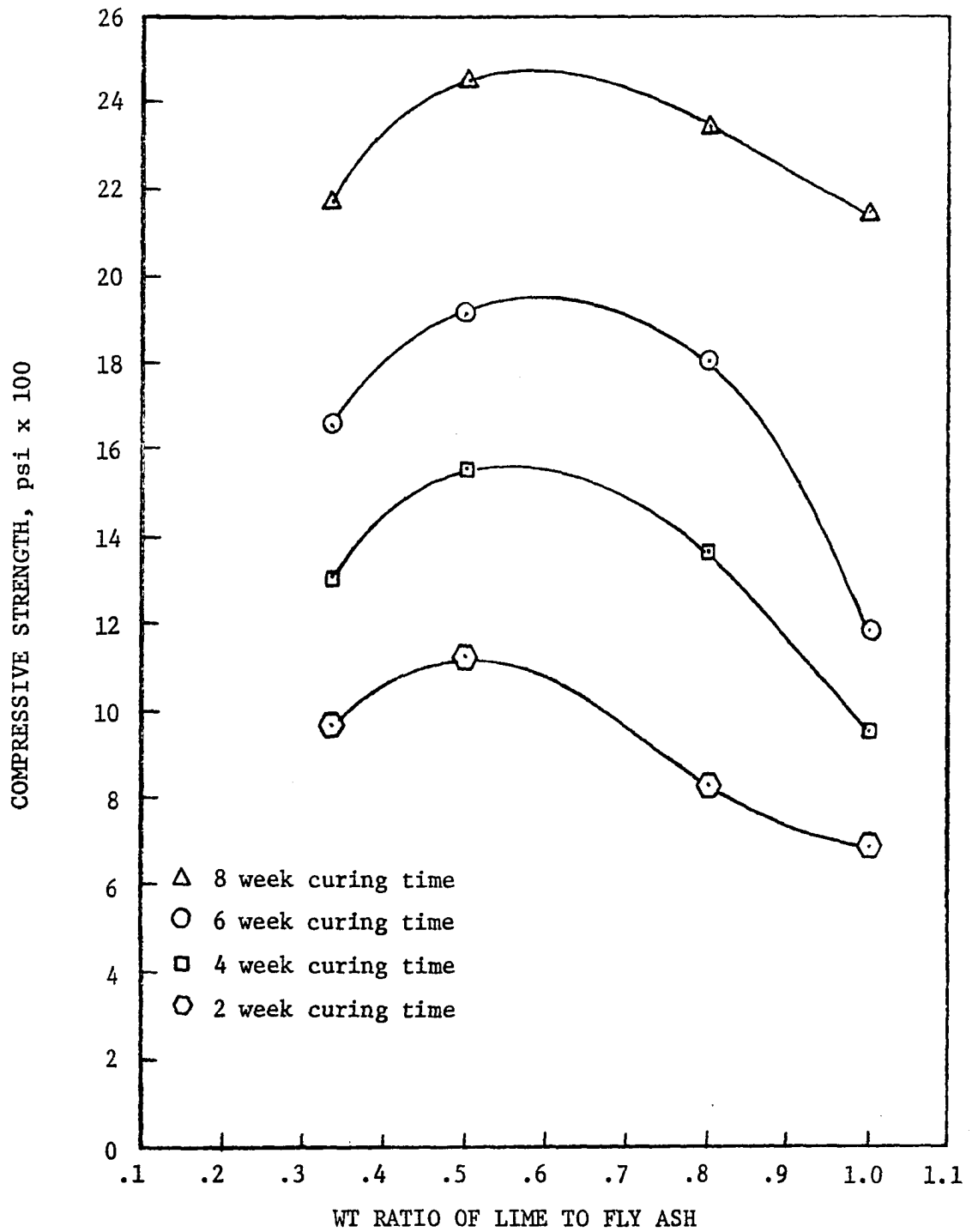
Figure 25. Compressive strength of K-Cyc FA mortars of different lime:fly ash ratio

substitution of calcium in alumino-siliceous glassy particles may induce additional strains which impart increased reactivity to the K+C fly ashes. Lea (72) reports that calcium enters into glassy phase of the slags and to a certain extent increases the vitrification and hydraulic activity of slag cements. Furthermore, unlike glasses of different K+P FA particles, the index of refraction of the glasses of K+C FA particles did not increase with the increasing amounts of calcium, indicating that a maximum amount of calcium may enter into the glassy phase, and larger amounts are excessive. This probably explains the erratic trend of rate of strength development of the mortars of K+C fly ashes. In absence of a direct evidence, it can only be said that the role of calcium in fly ashes is at present not completely resolved.

Influence of calcium and iron together

Figure 24 and data in Table 21 show that the strength of trimineralic fly ashes correlates well with the strength of individual bimineralic fly ashes. The pozzolanic strengths of both the trimineralic fly ashes at all curing periods up to 8 weeks are slightly less than the K-Cyc FA, considerably less than the K+C fly ashes, but higher than the nonmagnetic fractions of the K+P ashes and sufficiently higher than the whole samples of K+P fly ashes. The latter observation suggests that the presence of calcium apparently offsets the expected prominent reduction in the strength due to the presence of iron. It is, however, noticed that K+10P+5C FA has higher early and ultimate strength as compared to K+10P+10C FA. Although some trend was observed even on repeating the compressive strength tests on specimens made to confirm these results, it is difficult to conclude from only two fly ashes that a certain proportion of calcium and iron in a fly ash

(1:2 in the present case) is desirable. The source of increased strength of the mortars of trimineralic fly ashes possibly lies in the particles formed from intermixing of minerals in suspension-fired furnaces. Such particles may have similar composition as that of blast furnace slag cements which are known for their high hydraulic reactivity (45). Although not too many colored particles similar to the ones reported to be abundantly present in some highly pozzolanic fly ashes (137) were observed in the trimineralic fly ashes, it is suspected that even colorless and/or opaque particles may have glass composition favoring high pozzolanic reactivity as was the case in K+C fly ashes.

These observations suggest that calcium tends to nullify the deleterious influence of iron on the pozzolanic strength of the fly ashes.

This observation of significant influence of chemical composition on the pozzolanic strength runs contrary to the observations of Watt and Thorn (125), that the chemical composition has an insignificant effect on the pozzolanic strength of the synthetic fly ashes. However, close examination of the data presented by them and reproduced in Tables 22 and 23 reveals that differences in chemical composition influence the pozzolanic strength almost in a similar way as found in the present study. The data in Tabels 22 and 23 show that the pozzolanic strengths of the fly ashes differ from 6 to 49% as a result of differences in the chemical composition. However, some of the industrial fly ashes in their study with comparable specific surface areas possessed better pozzolanic properties attributed by them to the chemical composition evidenced by an increased number of red colored particles in industrial fly ashes.

Although perhaps coincidental, the study of Watt and Thorn indicated

Table 22. Composition of glasses used in the preparation of fly-ash-like materials (125)

| Glass | Analysis, % | | | | | | | | SiO_2/Al_2O_3 ratio | Refractive index | Density, g/cm^3 |
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Total			
1	55.9	31.9	4.9	3.9	0.0	2.2	1.4	100.2	1.75	1.530	2.55
2	47.9	31.9	7.2	5.3	0.0	5.4	2.2	99.9	1.50	1.545	2.64
3	53.3	29.8	5.7	2.9	1.5	1.9	5.7	100.8	1.79	1.534	2.56
4	55.5	35.8	2.8	1.4	0.9	1.1	3.0	100.5	1.55	1.529	2.51
5	63.8	18.1	7.6	3.9	3.9	1.9	0.8	100.0	3.53	1.530	2.55
6	48.7	36.6	2.9	0.8	1.0	0.5	8.5	99.0	1.33	1.525	2.52

Table 23. Crushing strength of mortars prepared from fly-ash-like products of known compositions and specific surfaces(125)

| Specific surface (size distribution method), cm^2/g | Crushing strength (11-day accelerated cure), p.s.i. | | | | | |
	Glass No. 1	Glass No. 2	Glass No. 3	Glass No. 4	Glass No. 5	Glass No. 6
500	1350	1700[a]	–	–	–	–
1000	4150	4650	–	–	–	–
3200	5800[a]	6800	7350	8300	6300	8200

[a]Values from curves of Figure 7.

that in general higher pozzolanic strength was given by synthetic fly ashes which contained iron and calcium (or calcium plus magnesium) in the ratio of 2:1, and those which contained iron and calcium in almost equal amounts gave lower pozzolanic strength (Tables 22 and 23). This is in agreement with the conclusions drawn from the results of this study.

Various other investigators have also attempted to correlate the pozzolanic strength of the fly ashes with their chemical composition and have suggested limits on different chemical constituents, particularly silica and alumina, to predict the pozzolanic activity of the ash (4, 5, 116). Most organizations also follow this practice because of the general belief that the alumino-siliceous material in the fly ashes is responsible for the pozzolanic reactions in lime fly ash mortars (1, 116). However, it is observed from the data in Tables 20 and 21 that all the bi- and trimineralic fly ashes have considerably higher pozzolanic strength than the K-Furn and K-Recrys fly ashes in spite of the fact that the latter ashes contain almost 100 wt % silica and alumina while some of the former have barely enough silica and alumina (Tables 17 and 18) to meet the required specifications prescribed by certain organizations (116). It is, therefore, apparent that the cement chemical composition specifications are valid indicators of the pozzolanic activity of an ash and the specifications placing limits on chemical composition are superfluous and unnecessarily restrictive. Likewise, various other limits placed on different chemical constituents by various organizations and still others suggested by various other investigators (116), without any consideration to the phase in which these are present, do not seem to be justified.

A close examination of the results of strength tests and glass content

of various mono-, bi-, and trimineralic fly ashes reveals the comparative influence of the three basic parameters on the pozzolanic reactivity of the ash. The results of strength tests on mortars of K-Cyc and non-magnetic K+P fly ashes, which are presumed to be equally strained glass but of different composition, indicate that the glass composition of the fly ash particles has significant influence on their pozzolanic strength. On the other hand, comparison of bi- and trimineralic fly ashes, particularly K+20P, K+30P and K+10P+10C ashes with the K-Furn fly ashes, indicates that the former ashes have several times greater pozzolanic strength than the strength of even the finest of the K-Furn fly ashes. It must, however, be remembered that the substantial amount of iron in bi- and trimineralic fly ashes is present in crystalline form, and the above mentioned three fly ashes have barely as much glass content as the K-Furn fly ashes (Table 19). Nonetheless the glass in the bi- and trimineralic fly ashes is highly strained since they have been prepared in the manner similar to the K-Cyc FA. It is, therefore, once again established that the structure of the glass has overriding influence on the pozzolanic activity in comparison to the fineness of the fly ash.

On the basis of these observations of influence of three basic parameters, it can be concluded that: 1) the amount of strain in the glass has the most significant influence on the pozzolanic activity of the ash; 2) the fineness of the fly ash particles exerts equally important influence provided the glass in them is highly and equally strained; 3) the chemical composition is also of significance but only when the fly ash particles are composed of highly strained glass.

Pozzolanic Reaction Products

The reaction products in different lime fly ash mortars were identified and analyzed with the help of x-ray, chemical and x-ray elemental micro-analytical methods. The diffraction traces indicated that the pozzolanic products in lime fly ash mortars do not differ with the method of curing as adopted in this study and are time dependent, the results of various analyses will therefore be discussed according to curing time. The reaction products in bimineralic fly ash mortars were similar to those from K-Cyc FA mortar; however the reaction products in trimineralic fly ash mortars were different. Therefore the results of x-ray analysis of the K-Cyc and K+P+C ash mortars only will be discussed. The silica and alumina in the acid soluble reaction products are presented in Tables 24 and 25. However, the values for K-Cyc FA mortars are not comparable with others since the specimen were prepared with 15% compaction moisture only and therefore will not be discussed as such.

One day curing

The x-ray diffraction traces for one day curing for all the fly ashes showed that a broad maxima exists in the region corresponding to 8 to 11 $\overset{o}{A}$ d-spacing. No identifiable peaks are seen in any of the diffraction patterns. It suggests that some reaction product(s) has possibly formed but it exists in very poorly crystallized form. There are several hydrates of calcium aluminate and calcium silicate which have their basal spacing between 8-11 $\overset{o}{A}$ and are known to yield poor diffraction patterns (14, 19, 75, 87, 93).

The electron micrograph of one-day-cured mortars of K-Cyc FA

Table 24. Acid-soluble silica in reacted lime fly ash mortars

Curing time	% acid soluble silica in mortars of fly ashes					
	K-Cyc	K+10P	K+20P	K+30P	K+10P+5C	K+10P+10C
1 day	0.600	0.499	0.556	0.512	0.663	0.957
1 week	1.165	1.112	0.886	0.782	2.173	1.827
2 "	1.778	1.835	1.558	1.486	2.791	2.346
4 "	2.450	2.842	2.090	1.579	2.710	2.560
6 "	2.200	2.680	1.960	1.980	3.420	2.680
8 "	2.660	2.800	1.970	2.580	3.780	3.040
10 "	2.900	2.720	2.540	2.400	3.860	3.140
12 "	3.360	3.180	3.400	3.120	4.440	3.660
28 "	3.230		4.410		6.160	5.750

Table 25. Acid-soluble alumina in reacted lime fly ash mortars

Curing time	% acid-soluble alumina in mortars of fly ashes					
	K-Cyc	K+10P	K+20P	K+30P	K+10P+5C	K+10P+10C
1 day	0.11	0.080	0.120	0.110	0.290	0.410
1 week	0.37	0.450	0.300	0.280	0.930	0.710
2 "	0.60	0.690	0.550	0.530	1.180	0.950
4 "	0.94	1.890	0.750	0.690	1.710	1.430
6 "	0.90	1.350	1.050	0.900	1.950	1.660
8 "	1.11	1.120	0.980	1.090	1.610	1.270
10 "	1.23	1.140	1.330	1.200	1.900	1.700
12 "	1.22	1.170	1.470	1.430	2.590	1.830
28 "	2.53		3.040		3.520	3.070

(Figure 26) shows presence of some filmy material in which only calcium was found to be present by x-ray elemental micro-analysis. The particles of filmy morphology failed to give any diffraction patterns on electron microscope. The trimineralic fly ash mortars contained some particles of a different morphology (Figure 27), and they also failed to give any diffraction patterns. The needle-like morphology suggests presence of ettringite.

At one-day-curing the different fly ash mortars contained very little acid-soluble reaction products as determined in terms of alumina and silica (Tables 24 through 26). The trimineralic fly ash mortars had the most acid-soluble silica and alumina whereas the bimineralic K+P fly ash mortars had decreasing acid-soluble products with increasing amounts of iron in the fly ashes.

Three day curing

The diffraction patterns for the three day curing time for various fly ash mortars are essentially the same except that two weak peaks at about 10.8 and 11.8 $^{o}2\theta$ corresponding to 8.18 and 7.49 $\overset{o}{A}$ seem to have started appearing in the mortars of trimineralic fly ashes. The K+P+C FA mortars also showed a feeble peak at about 7.5 $\overset{o}{A}$. No new and identifiable peaks were observed in the diffraction traces of any of the fly ash mortars up to a period of 5 days. However, reduction in the intensity of $Ca(OH)_2$ peaks suggests that lime is being gradually depleted with time.

The electron microscopic observations and x-ray elemental micro-analysis also did not show any new reaction products since the morphology of the particles was unchanged and no new elements other than calcium could
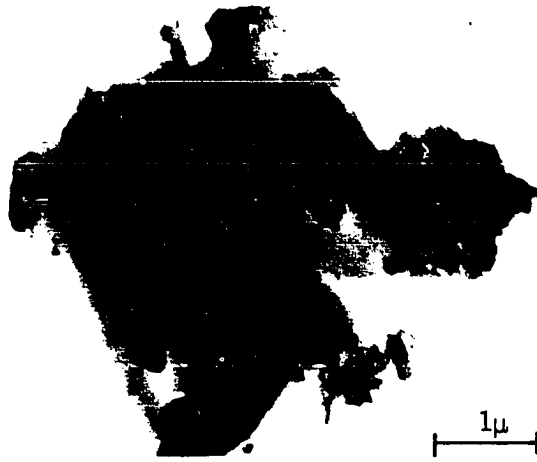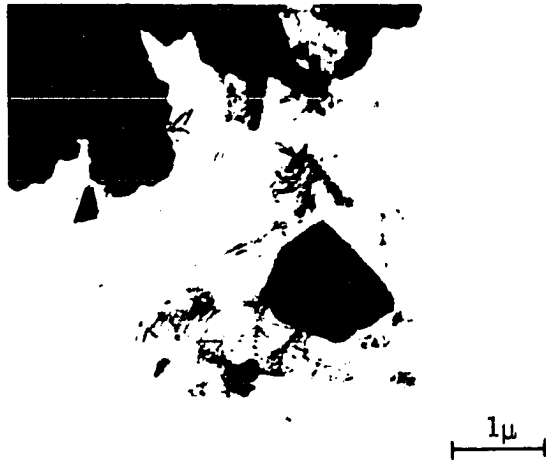
(a)

(b)

Figure 26. Electron micrographs of reaction products common to
all synthetic fly ash mortars: (a) possibly CSH gel,
(b) possibly CSH(I)

(a)

(b)

Figure 27. Electron micrographs of reaction products peculiar to
trimineralic fly ash mortars: (a) possibly ettringite
needles, (b) possibly CO_2 contaminated CSH

Table 26. Total acid-soluble silica and alumina in lime fly ash mortars

Curing time	<5 K-Cyc	>20 K-Cyc	5-10 K-Furn	5-10 K-Recrys	% silica and alumina in mortars of fly ashes					
					K-Cyc	K+10P	K+20P	K+30P	K+10P+5C	K+10P+10C
1 day					0.710	0.579	0.679	0.621	0.956	1.367
1 week					1.535	1.562	1.186	1.062	3.103	2.535
2 "					2.378	2.525	2.108	2.016	3.971	3.296
4 "					3.390	4.732	2.840	2.269	5.420	4.090
6 "					3.100[a]	4.030[a]	3.010[a]	2.880[a]	5.350[a]	4.340[a]
8 "	4.860	2.020	0.970	0.360	3.770	3.920[a]	2.950[a]	3.670[a]	5.390[a]	4.310[a]
10 "					4.130	3.860[a]	3.870	3.600	4.760	4.880
12 "					4.680	5.110	4.590	4.790	7.030	6.590
28 "					5.760		7.450		9.680	8.790

[a]Erratic values possibly due to strength of standard solutions since the values otherwise are in the same order as in other rows.

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Table 27. Silica to alumina ratio in acid-soluble portion of lime fly
ash mortars

Curing time	Silica to alumina ratio in mortars of fly ashes					
	K-Cyc	K+10P	K+20P	K+30P	K+10P+5C	K+10P+10C
1 day	5.460	6.230	4.640	4.650	2.290	2.330
1 week	3.140	2.490	2.950	2.790	2.340	2.640
2 "	2.960	2.650	2.830	2.800	2.360	2.460
4 "	2.610	1.510	2.790	2.290	2.760	1.790
6 "	2.450	1.990	1.870	2.200	1.760	1.620
8 "	2.420	2.500	2.010	2.380	2.340	2.390
10 "	2.360	2.380	1.920	2.000	2.030	1.850
12 "	2.750	1.860	2.210	2.190	1.790	2.080
28 "	1.280		1.450		1.750	1.870

be detected in the filmy material. It was however observed that particles

finer than 2 microns were getting scarce. The acid-soluble silica and

alumina increased in all the mortars in the same general order as for one

day cured samples.

One week curing

A new reaction compound with a peak at 7.6 $\overset{o}{A}$ was found in all the fly

ashes after one week of curing time. The trimineralic fly ash mortars

develop other reaction products in addition to the one formed in mono-

and bimineralic fly ashes as indicated by some of the weak peaks at about

8.5 and 9.2° 2θ corresponding to 10.39 and 9.7 $\overset{o}{A}$. Although presence of

various mullite peaks makes it difficult to detect other peaks of lower

order and thus unambiguously identify these reaction products, the

simultaneous reduction in intensity of $Ca(OH)_2$ peaks suggests the formation

of hydrates of silicates and aluminates of calcium. The 7.6 $\overset{o}{A}$ basal peak

suggests the formation of $C_A AH_X$ in mono- and bimineralic ash mortars while

the 9.7 and 10.39 $\overset{o}{A}$ peaks indicate the presence of some $C_3A_3CaSO_4 32H_2O$

(ettringite) and some other compounds in trimineralic fly ash mortars.

These later convert to other stable compounds since these do not persist

in long-cured samples.

A few particles of somewhat rhombic morphology were observed under

electron microscope in the mortars cured for one week. However, no

elements could be detected in these particles other than calcium possibly

due to low intensity of emission of x-rays. The acid-soluble products

in all these mortars increased almost in the same order as for three day

curing time.

Two week curing

The main distinguishable feature of the diffraction traces for the

two weeks curing time is that the 7.55 $\overset{o}{A}$ peak in mono-, bi- and tri-

mineralic fly ash mortars along with 8.8 $\overset{o}{A}$ peak in the later mortars have

increased in intensity considerably. In addition the broad maxima in the

region of 8-11 $\overset{o}{A}$ seem to be suppressed slightly, and the $Ca(OH)_2$ peaks.

have also reduced in intensity but not too much. This implies that

different varieties of C_4AH_X are probably being formed in mono- and

bimineralic fly ash mortars by crystallization of some poorly crystallized

or gel-like substances. The 8.8 $\overset{o}{A}$ peak suggests the possibility of

formation of monosulphate at the cost of ettringite in trimineralic fly

ash mortars. Although some feeble peaks at about 3.07, 1.97 and 1.82 $\overset{o}{A}$

were seen in the diffraction traces, these and other characteristic peaks

for known crystalline silicate products were not clearly identifiable.

The electron microscopic observations indicate presence of increased

number of particles shown in Figure 27 in the two week cured samples of

trimineralic fly ashes particularly. A few particles of filmy morphology

showed presence of silicon in addition to calcium in x-ray elemental

micro-analyses of different mortars. However, aluminum was not detected

in any of the particles.

The acid-soluble alumina and silica increased further in all the

mortars, and the rate of increase of acid-soluble products seems to be

comparatively more between one to two weeks curing time as compared to

the earlier curing intervals.

Two to eight week curing

There does not seem to be any new reaction products formed between

two to eight weeks of curing period. However, the broad maxima between

8-11 $\overset{o}{A}$ is suppressed, the 7.62 and 8.23 $\overset{o}{A}$ peaks of two varieties of

C_4AH_X in mono- and bimineralic fly ash mortars and 8.92 $\overset{o}{A}$ $C_3ACaSO_4 \cdot 32H_2O$

(monosulphate) have increased and the $Ca(OH)_2$ peaks have simultaneously

reduced in intensity. This suggests that the two varieties of C_4AH_X are

formed, partially at the cost of some transitional reaction product(s)

which are amorphous or very poorly crystallized, and partially from the

hydration reaction between lime and fly ash. At the end of eight weeks a

new reaction product is found to have been formed in all the mortars,

possibly at the cost of other products, as evidenced by the appearance of

12.617 $\overset{o}{A}$ peak and reduction of 7.62 $\overset{o}{A}$ peak of C_4AH_x. The amount or

crystallite size of 8.23 $\overset{o}{A}$ C_4AH_4 also seem to have increased since this

peak has increased in intensity. Although numerous mullite and undepleted

lime peaks make it difficult to identify all the peaks of reaction products,

several clearly identifiable peaks show the presence of calcium silicate

hydrates and calcium aluminate hydrates.

The three peaks of 12.617, 3.07 and 2.80 in the diffraction patterns

of samples cured for 8 weeks and longer are similar to the two major peaks

of calcium silicate hydrate I (19, 124) of tobermorite group. Likewise,

the 8.33 $\overset{o}{A}$ and 7.62 $\overset{o}{A}$ peaks correspond to α-tetracalcium aluminate 13-

hydrate with some essential CO_3 and tetracalcium aluminate carbonate 12-

hydrate (129). It was observed that in spite of all the precautions taken,

carbonation was unavoidable. Other investigators have also reported such

phenomenon of unavoidable carbonation in pozzolanic reactions. These

reaction products have been studied in detail and reported by several

investigators in connection with cement hydration products (19, 62, 124).

The calcium silicate hydrate I is generally formed at temperatures below

$100^{o}C$ with various molar ratios of CaO to SiO_2. The diffuse scattering

of the x-rays by calcium silicate I has been attributed to water of hydra-

tion. The literature indicates that calcium silicate hydrate I is a layer

type mineral similar in structure to swelling clay minerals (14, 26). The

basal reflections are found to be varying with the amount of water between

the layers.

No new compounds are found by x-ray analyses after a curing time of 8

weeks. However, various peaks of the reaction products increased in

intensity, implying either formation of larger quantities of the reaction

products or increase in their crystallite size or crystallinity.

The diffracted x-ray peaks were weak compared to well crystallized silicates and aluminates indicating that the reaction products are present either in very small quantities or have very small crystallite size making them almost x-ray amorphous. Bernal (14) reports that the size of particles that make up some well-known gels are within the range of the calculated dimensions of calcium silicate hydrate I, whereas Watt and Thorn (137) report that in lime fly ash reactions, very small quantities of reaction products are formed.

One more interesting and conspicuous feature of the diffraction traces is that the intensities of the peaks of mullite and other crystalline products in bimineralic fly ashes of K+P series do not change with time. This is in agreement with the observation of Minnick (93) on reacted mortars of industrial fly ashes. In contrast, the $Ca(OH)_2$ of K+C fly ash mortars and calcium compounds of K+P+C fly ash mortars must enter into pozzolanic reactions since they disappear with time.

The electron micrographs of samples of mortars cured for 8 weeks and longer are presented in Figure 28. It is observed that some particles of completely new morphology have formed and the number and size of hexagonal and/or rhomohedral particles has increased in all the mortars. Although no distinct and identifiable diffraction patterns could be obtained from these particles in the electron microscope, the particles of similar morphology are found to be formed in the hydration of cement mortars and have been categorized as calcium silicate hydrate particles (51). The x-ray elemental micro-analysis showed presence of calcium and silicon in increased number of filmy and other particles in mortars cured for more
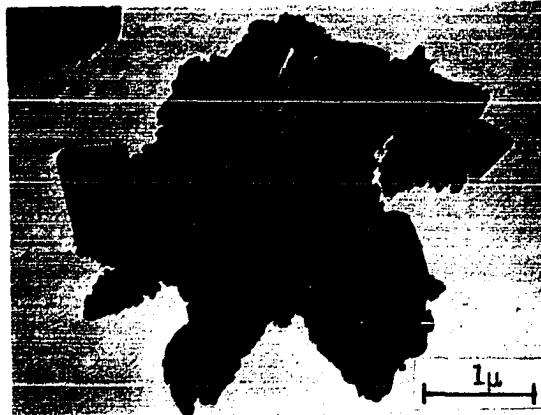
(a)
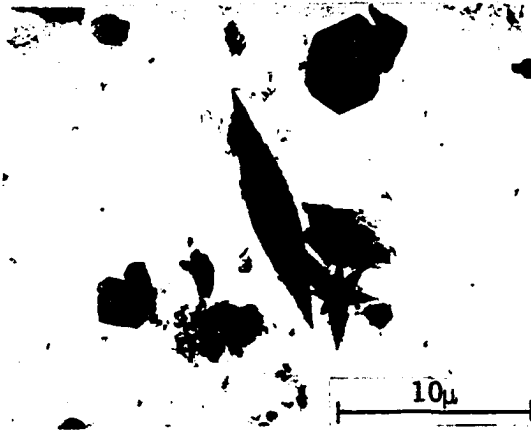
(b)

Figure 28. Electron micrographs of reaction products common to all
synthetic fly ash mortars cured for 28 weeks: (a)
possibly CSH(II), (b) canoe-shaped particles, possibly
CO_2 contaminated CSH(II), hexagonal particles, possibly
C_4AH_x

than 8 weeks. Some of the particles contained calcium and aluminum while a few seemed to contain calcium, silicon and aluminum together. It is possible that aluminum substitution has taken place in some calcium silicate hydrate particles (41, 109). The increased number and size of particles of different morphology and identifiable diffraction from the filmy particles suggests that the pozzolanic products in lime fly ash mortars are probably formed from recrystallization of gel-like substance which is formed immediately in the lime fly ash pastes.

Acid-soluble contents of the reacted mortar samples indicate that the pozzolanic products increase with time; however, the rate of increase of acid-soluble amount tends to decrease especially after a curing time of 12 weeks. The x-ray analysis indicated that although new products are formed in the reacted lime fly ash mortars, immediately, the crystallite size of these increase only after 8 to 10 weeks of curing time, during which formation of new pozzolanic products as determined by the acid-soluble test is considerably reduced. This further suggests that some of the reaction products are formed from recrystallization of the x-ray amorphous material. Therefore, the lime fly ash reaction as studied from cured synthetic fly ash mortars is a consecutive reaction: lime + fly ash → CSH (gel) → CSH (II) + C_4AH_x → CSH (I) + C_4AH_x.

Reaction products by lime depletion method

The results of lime depletion in reacted mortar samples, which indirectly represent the proportion of pozzolanic reaction products, are presented in Table 28 and Figure 29. It should be pointed out that the method as adopted in this study did not yield results within reasonable

tolerance except for the one day cured samples. The results as presented in Figure 43 are averages of three values which were found to lie within $\pm2.0\%$.

Table 28. Lime depletion in fly ash mortars with time

Curing time	wt % of original lime depleted					
	K+10P	K+20P	K+30P	K-Cyc	K+10P+5C	K+10P+10C
1 day	46.3	36.8	41.8	43.6	46.5	59.6
1 week	60.8	52.4	59.8	42.2	49.4	67.3
2 "	72.8	70.2	52.6	55.1	56.5	70.9
4 "	67.8	68.2	75.2	58.7	71.0	65.7
6 "	72.1	-	63.6	80.2	81.8	76.5
8 "	69.4	57.5	67.3	67.6	86.3	74.9
10 "	76.4	81.7	77.6	77.4	84.0	74.6
12 "	71.0	72.6	72.7	72.6	80.5	69.9
28 "	-	65.0	-	65.5	75.8	59.8

In addition to a general trend of increasing lime depletion with time, a very important feature of Figure 29 is that more than 40 wt % lime in all the fly ash mixes is depleted within 24 hours of curing time. This probably explains the broad maxima in x-ray diffraction patterns of one day cured samples and the presence of particles of filmy morphology which showed nothing but calcium by x-ray elemental micro-analysis. It appears lime gets loosely attached to the amorphous silica and alumina in the fly ash and gives rise to a material of filmy morphology which is x-ray amorphous.
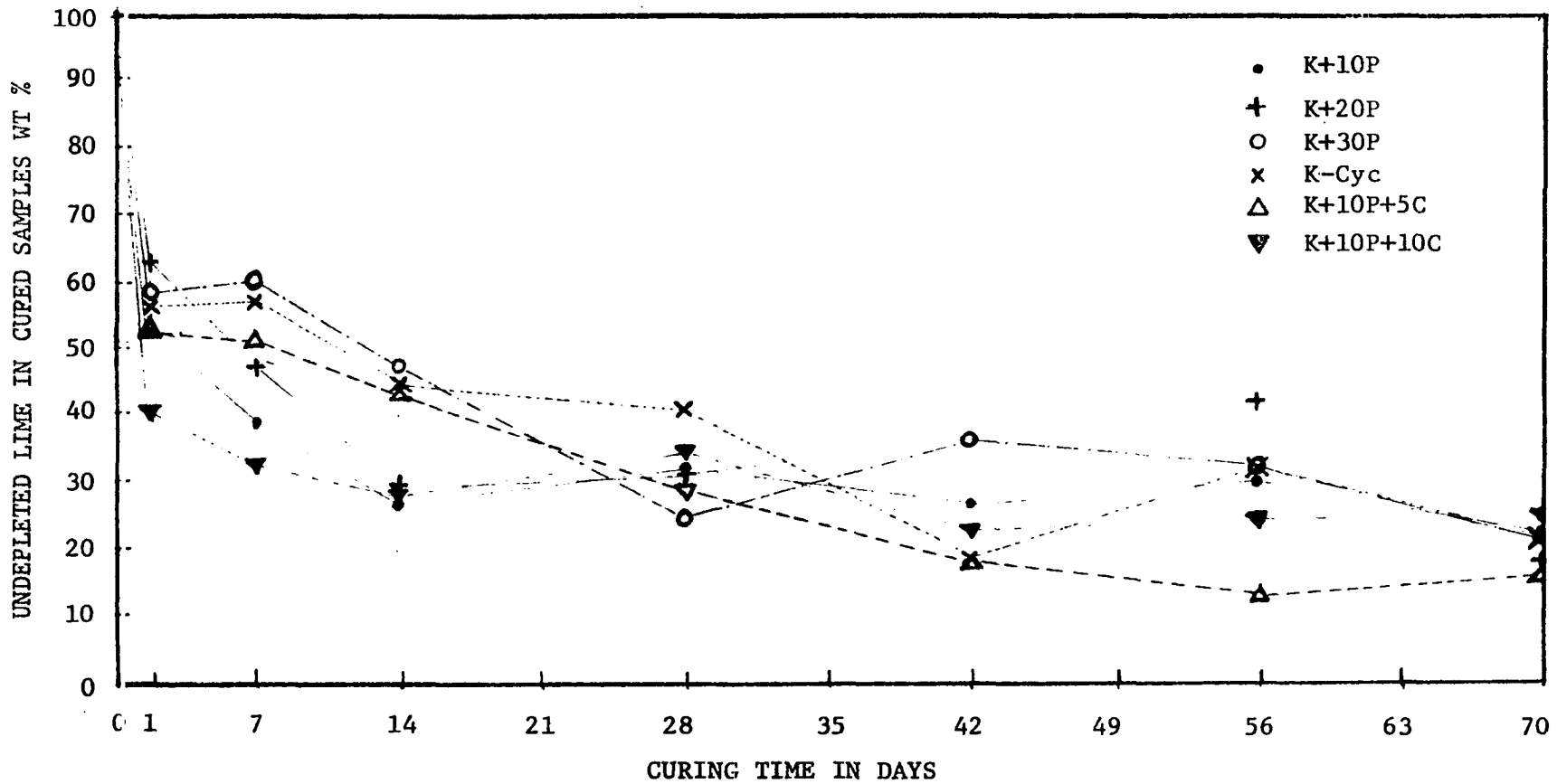
Figure 29. Undepleted lime in cured lime-fly ash mortars in relation to curing time

This filmy material is probably a calcium silicate hydrate gel of high C/S

(calcium/silica) ratio since it contains very small amounts of silica as

determined by chemical tests (Table 24). With time this gel-like substance

becomes enriched in silica by reaction with fly ash particles and also by

removal of calcium to form tetracalcium-aluminate hydrates. It appears

both the reactions proceed simultaneously. The lime for tetracalcium-

aluminate hydrates may be derived either from the gel or from undepleted

lime. In any case, the consumption of alumina from the fly ash particles

will free more silica and thus enrich the gel. When the C/S ratio of the

gel approaches approximately two or less, the calcium silicate hydrates of

tobermorite group crystallize. It is suspected that some of the hydrated

aluminates and silicates of calcium and also the gel of high C/S ratio

decompose in cold water, giving variable values of undepleted lime. This

test method is therefore suspect for determination of lime in samples cured

for a long time.

Minnick (93) determined the comparative amounts of undepleted lime in

fresh and cured lime-fly ash mortars by comparing the x-ray diffraction

intensities of the lime present in the samples. His data (Figure 30)

indicates that 30 to 70% lime is depleted within first 4 weeks of curing

time and beyond that the rate of depletion is very gradual and depends on

the availability of water for hydration. In addition, the fresh lime-fly

ash pastes containing excess water showed about 10% less lime present in

them than the pastes containing a limited amount of water. In absence of

the data for depletion of lime within one day curing time, it is not

possible to positively conclude that most of the lime depletion shown to

have occurred in 4 weeks actually occurred within the first few days.
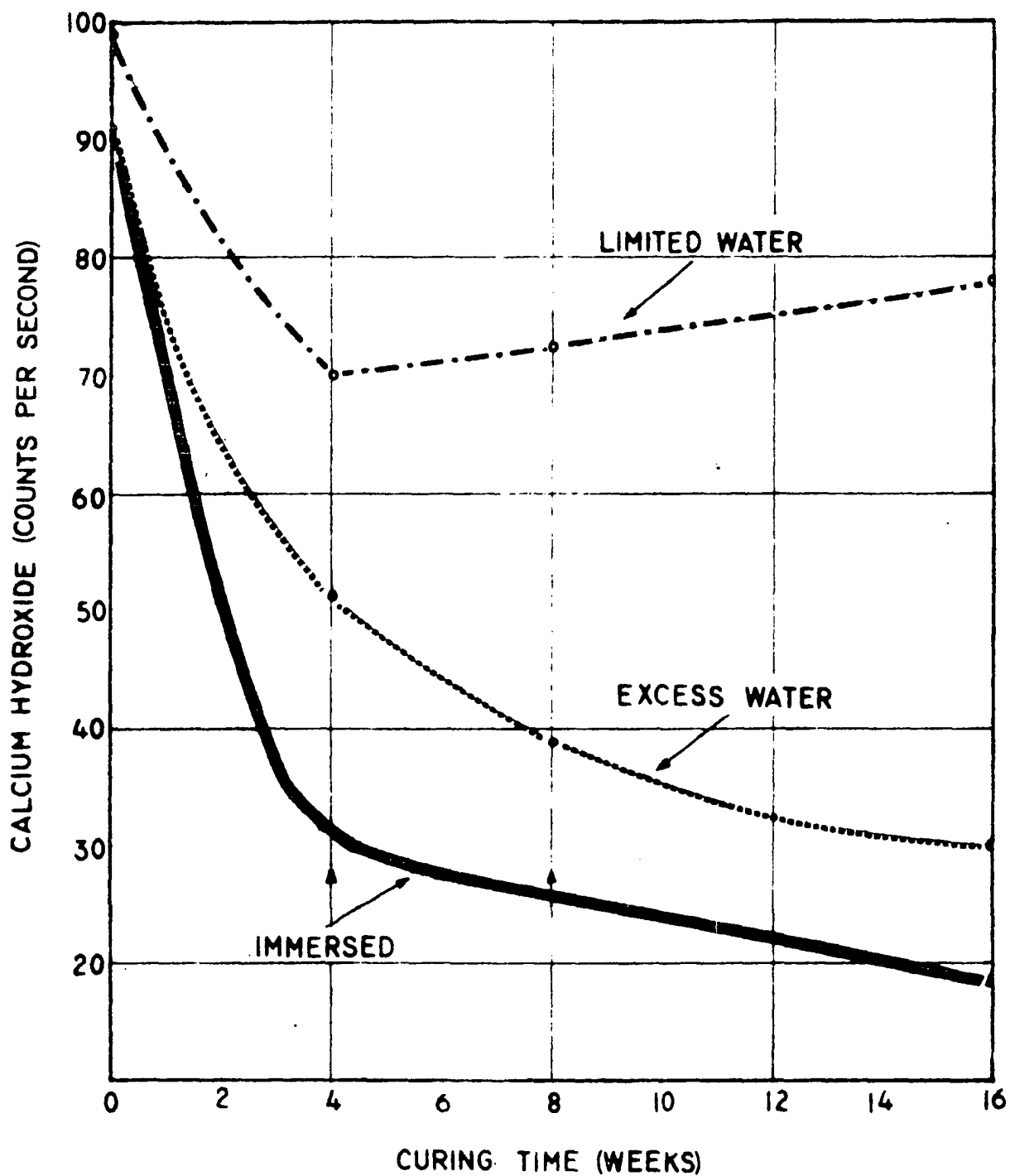
Figure 30. X-ray diffraction data. Effect of curing conditions on rate of calcium hydroxide consumption (dolomitic monohydrated lime C with fly ash C) (93)

Nonetheless, it is fairly evident from his data that the lime depletes at an abnormally fast rate within the first 4 weeks, and beyond 4 weeks curing time, the rate of lime depletion is rather minimal. These observations partially support the present hypothesis.

The data of Snyder et al. (118) reproduced in Figure 31, on the other hand, indicates that no lime is depleted in the lime-fly ash mortars up to 4 weeks curing time. They determined undepleted lime by the Franke method, which is essentially a method used to determine the lime in the portland cement hydration reactions. It is reported that the lime as determined by this method is always more than the lime present in the reacted samples since the lime solvents used decompose the tetracalcium-aluminate hydrates and dissolve the lime from them. Therefore, the lime loosely attached to the fly ash particles in lime-fly ash mortars would certainly be extracted by the solvents used in Franke method and reported as undepleted lime. It is not feasible that the lime-fly ash mortars develop pozzolanic strength without using lime.

S/A ratio of reaction products

Table 27 gives the ratio of acid-soluble silica to alumina at different curing times and mortars. With the exception of one day curing time the S/A ratio of the reaction products for almost all the mortars lies between 1.75 to 2.75. The average S/A ratio of the reaction products is 2.03 whereas that of the synthetic fly ashes is 1.16. It must be pointed out that all the fly ashes contained some mullite which never reacted with lime. The average S/A ratio of the alumino-siliceous glass therefore will be approximately 1.8 or almost similar to the reaction products. This
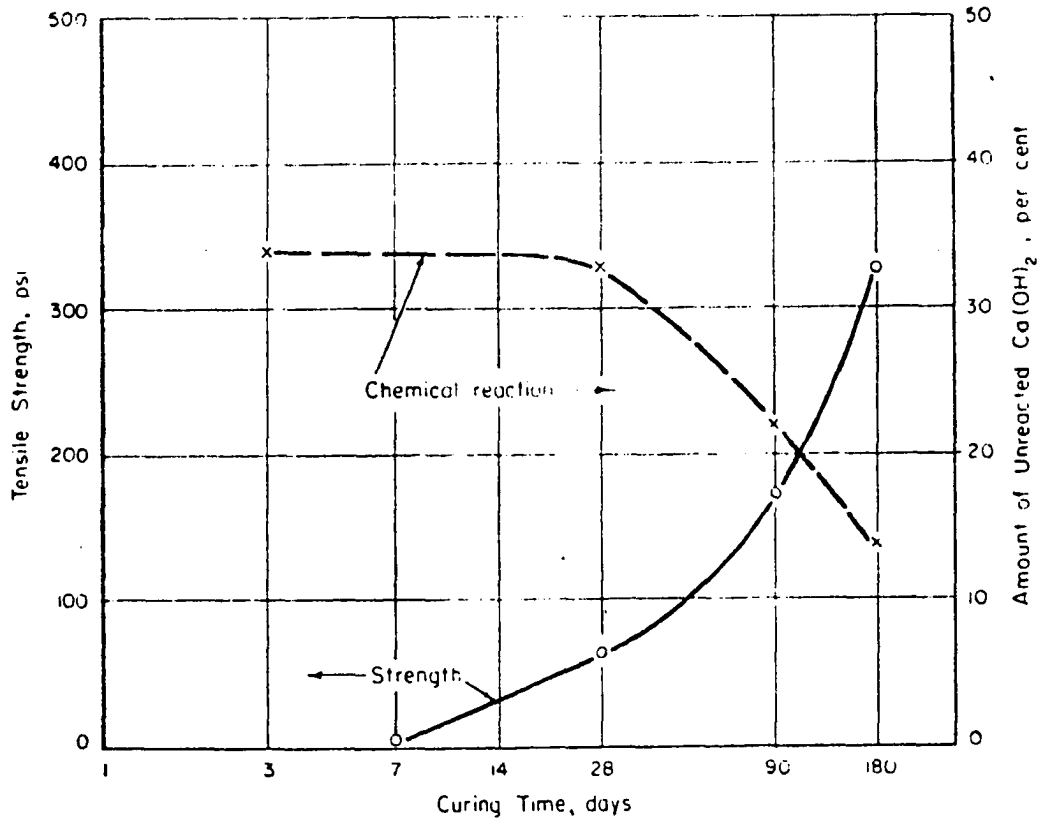
Figure 31. Pozzolanic reaction of fly ash with calcium hydroxide (118)

indicates that the fly ash particles were attacked from all the sides and the glass was equally consumed in the reaction without any preferential reaction between lime and silica in the glass.

Influence of Reaction Products on Pozzolanic Strength

Figures 32 and 33 show the compressive strength of mortars as a function of acid-soluble silica plus alumina in the cured lime-fly ash mortar samples. Although there is a large amount of scatter in the data in both these figures, it is evident that irrespective of the chemical composition of the fly ash, the pozzolanic strength increases with the increase in the amount of reaction products (Figure 32) and the amount of reaction products increases with curing time (Figure 33). The general form of the relationship between crushing strength and the amount of reaction products is approximately linear. This is in agreement with the observations of Watt and Thorn (137) and Ruff (109).

On the basis of Figures 32 and 33, it can only be concluded that the cured samples which have the largest amount of acid-soluble reaction products or the most depleted calcium hydroxide will have the highest pozzolanic strength.

Furthermore, it is observed from Figure 33 and Table 26 that after a curing time of 8 weeks, the <5 K-Cyc FA mortars had a greater amount of reaction products as well as pozzolanic strength than the mortars of whole samples of K-Cyc FA. These observations confirm that strength is a function of cementitious reaction products and that the formation of reaction products is a function of fineness. Obviously, a coarser fly ash would have a smaller number of contacts per unit volume compared to a
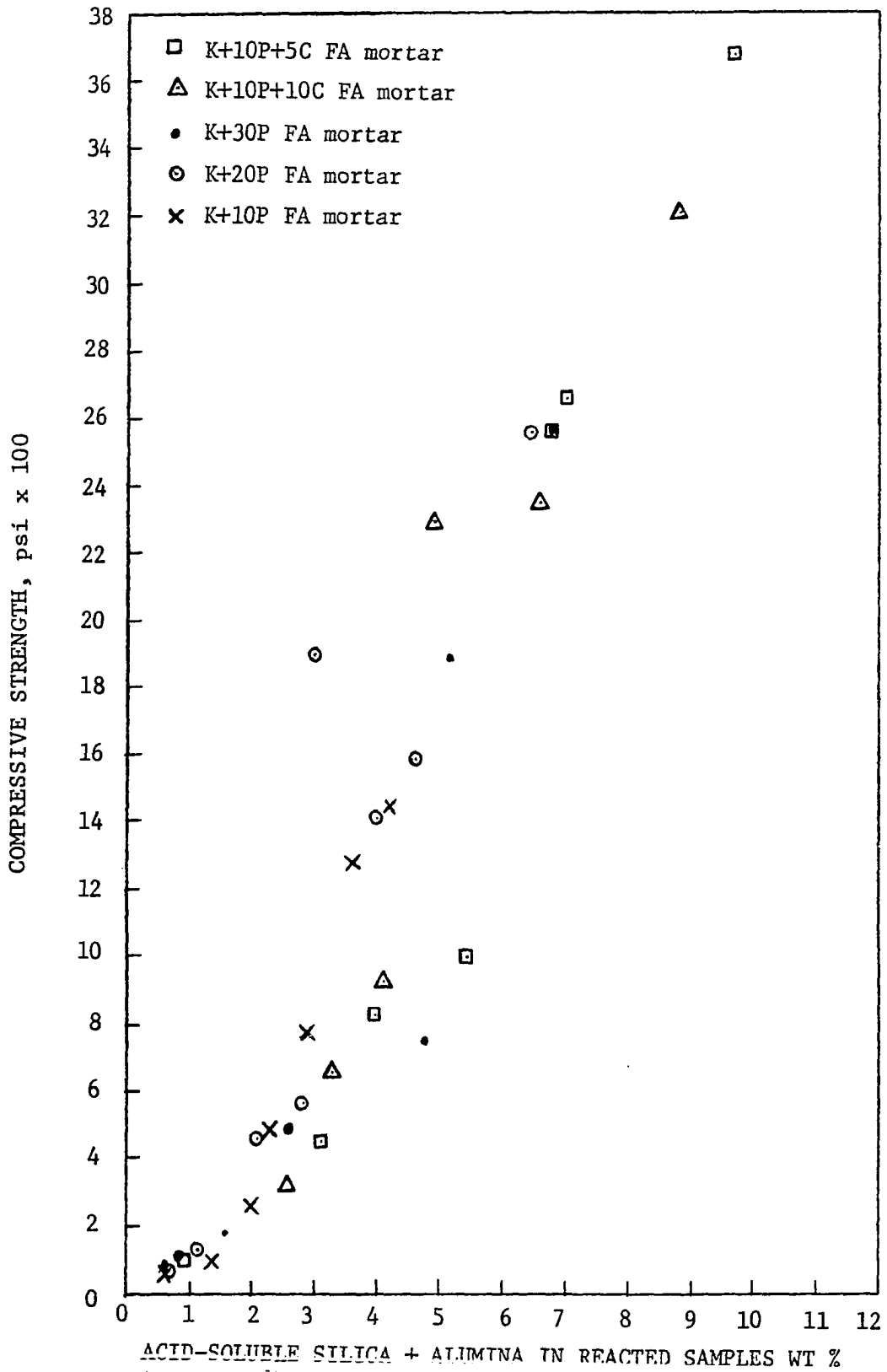
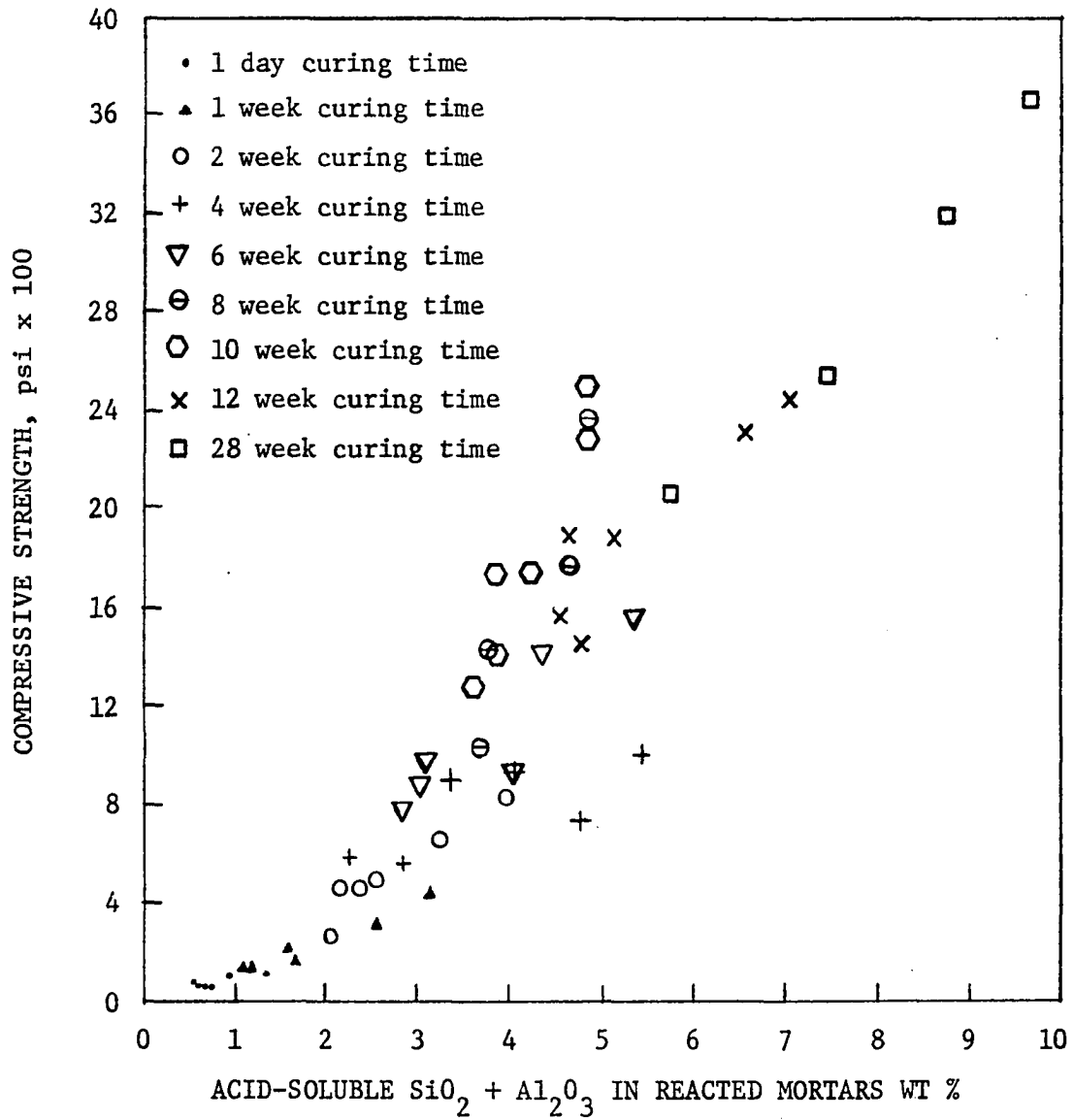Figure 32. Compressive strength vs reaction products as related to fly ash composition

Figure 33. Relationship between compressive strength and reaction products (silica + alumina) and curing time

finer fly ash of the same density and less cementing material would be formed in the mortar. Therefore, the resultant strength of such a mortar would also be less than mortar of an equally reactive but finer fly ash.

Data in Table 26 further indicates that the K-Furn and K-Recrys fly ash mortar developed an insignificant amount of reaction products even after a curing time of 8 weeks as compared to any other mortar. It implies that the reactivity of an ash is influenced to a greater extent by the structure of the glass in the fly ash particles. This is in conformity with the results of strength tests in the mortar of K-Furn FA.

Figure 32 also indicates that the reaction products as well as strength of the bimineralic fly ashes is less than that of trimineralic fly ashes. In addition the data in Table 26 shows that the amount of reaction products in reacted mortars of K+P fly ashes generally decreases with increasing amounts of iron in the fly ash. It leads to confirm the earlier observation that the pozzolanic reactivity of an ash is a function of glass composition. Thus, the conclusions drawn about the influence of various fly ash parameters of fly ash on the basis of compressive strength tests are also confirmed by the results of pozzolanic reaction products.

Mechanism of Pozzolanic Reaction

It is observed from Figure 24 that although the rate of strength development for different fly ashes is not the same, the change of rate of strength development with curing time is almost identical for all the ashes. Generally the rate of strength development is slow initially, i.e., up to 5 to 7 days curing period, rapid from 7 to 14 days, and after slowing down between 2 to 4 weeks to almost initial rate, it increases and

remains almost constant from 4 to 10 weeks curing period. Beyond the curing time of 10 weeks the rate of strength gain is very much reduced. Although strength tests could not be performed on samples cured for longer periods of time, it is evident the increase in strength of lime-fly ash mortars beyond 28 week curing period will be minimal or zero (Figure 21). The long term compressive strength studies by Watt and Thorn (136, 137) also indicate that after a curing period of 26 weeks the rate of strength gain is minimal.

The results of compressive strength tests of mortars of various mono- and bimineralic ashes indicated that the pozzolanic strength is directly proportional to the curing time at least up to 8 weeks (Figures 20 and 23). Since the amount of reaction products in various mortars is found to have linear relationship with pozzolanic strength, the relationship between strength and time in Figure 24 can be utilized to study the reaction rates and therefore the type of reaction in the lime-fly ash mortars.

Close examination of Figure 24 confirms that up to a curing time of 8 to 10 weeks the pozzolanic is reaction-controlled as is first-order as evidenced by almost linear relationship between strength and time. From 10 weeks onwards, the shape of the curve changes to an exponential and asymptotic curve suggesting the possibility of a second-order or diffusion controlled reaction. This is further confirmed by plotting strength versus log time on semilogrithmic paper (Figure 34), which shows almost a linear relationship between pozzolanic strength and logrithmic of reaction time. It can therefore be said that the pozzolanic reaction after about 10 weeks of curing time is a diffusion-controlled reaction.

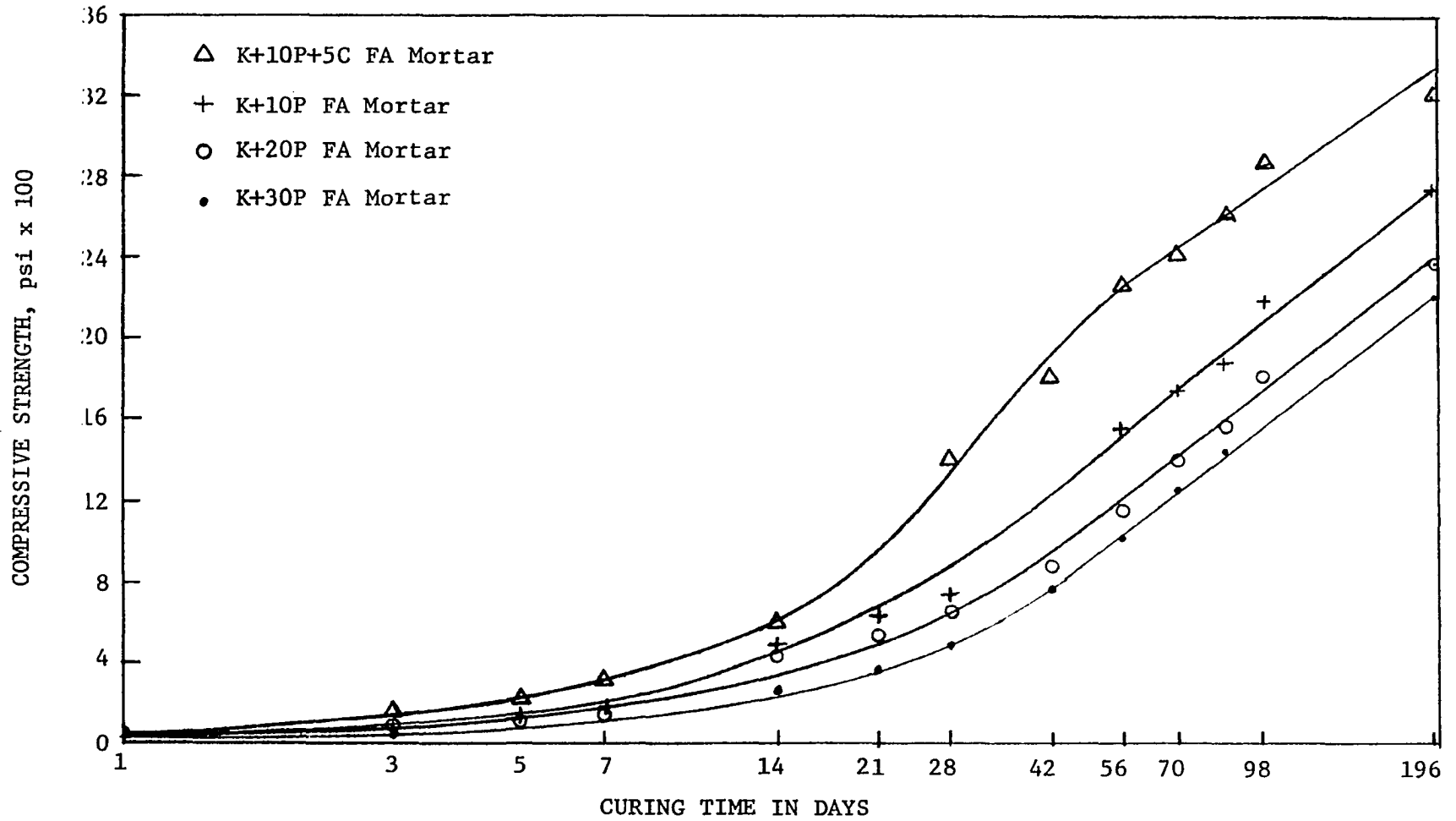Furthermore, the results of x-ray and electron microscopic studies

Figure 34. Relation between compressive strength and logathrim of curing time

lend support to this hypothesis and probably provide an explanation for the change of rate of strength gain for different curing times. Some reaction product forms immediately on the surface of the particles which is a gel-like substance and x-ray amorphous. This gel-like substance in time gives rise to different crystalline products under hydrothermal conditions. The first crystalline product was detected at about the same time when the rate of strength gain increased, i.e., 5 to 7 days curing period. The simultaneous decrease in $Ca(OH)_2$ and crystallization of reaction products from gel probably accounted for the increased rate of strength gain up to 2 weeks. From 2 to 4 weeks curing period there was not any new compound forming. It appears that formation of calcium silicate hydrate I of tobermorite group started forming from the calcium silicate hydrate gel about 4 weeks after reaction was first begun, and by the end of 8 weeks of curing time, it was sufficiently crystallized to be identified by x-ray analysis. About 70% of the $Ca(OH)_2$ had been depleted by this time and had probably gone into further gel formation. The calcium silicate hydrate I is a cementitious compound (19, 25, 124), and the increased strength of lime-fly ash mortars is a reflection of increased amount of this product. However, after a period of 10 weeks, the lime depletion rate is substantially reduced and so is the increase in calcium silicate hydrate I as observed by results of x-ray and chemical analysis. It once again points out that the compressive strength of lime-fly ash mixes is dependent on the amount of the cementitious material.

Once the cementitious reaction product such as calcium silicate hydrate forms on the surface of a particle, it follows that for any more reaction product to be formed, the additional $CA(OH)_2$ must penetrate

through this reacted layer to reach the enclosed particle. The mechanism of the pozzolanic reaction therefore is one of simultaneous diffusion and chemical reaction of the calcium. The formation of reaction product therefore controls further reaction between the reactants. In the present case of lime-fly ash mortars, the rate of reaction is controlled by the rate of diffusion of the reactant ($Ca(OH)_2$ through the reaction products. It is for this reason that in spite of availability of $Ca(OH)_2$ and fly ash particles, the rate of strength gain is reduced or approaches zero since the new cementing material is formed either at a very slow rate or does not form at all. The presence of fly ash particles in the lime-fly ash samples cured for 28 weeks in this study and in the samples several years old reported by Minnick (93) further suggests that the reaction for long term curing beyond 10 weeks is diffusion controlled.

SUMMARY AND CONCLUSIONS

The work presented in this report covers the results of experiments conducted to prepare synthetic fly ashes and to determine the source of pozzolanic activity from the mortars of these ashes. Based on the results of this research, the following conclusions were reached.

(1) It is possible to prepare synthetic fly ashes of known physical and chemical properties similar to the industrial fly ashes from various minerals associated with the coal.

(2) The temperature history of the fly ash particles controls the strain and/or divitrification of the glass in the particles.

(3) The mineral particles intermix in suspension-fired furnaces and therefore the composition of the resultant glass in the fly ash particles is governed by the parent mineral composition.

(4) Various mineral particles not only give rise to smaller particles on dissociation but also to some larger particles due to agglomeration and/or intermixing of two or more mineral particles.

(5) Added pyrite and calcite give rise to different crystalline phases in addition to altering the glass composition of the fly ash particles formed from kaolinite which can be identified by x-ray analysis. The following glassy and crystalline phases result from calcination of different minerals: a) Kaolinite gives rise to mostly alumino-siliceous glassy particles and very few mullite particles due to rapid heating and subsequent quenching. Most mullite particles are of minute size and are frequently associated with glassy particles; b) Added pyrite to kaolinite gives rise to ferrugenous-alumino-siliceous glass, however most of iron

from pyrite produce magnetite and hematite crystalline phases in the fly ash; c) Calcite added to kaolinite produces calcic-alumino-siliceous glassy phase. The main crystalline phase is calcium hydroxide, however, trace calcium silicates and aluminates are also suspected to be formed; d) The calcite added to kaolinite along with pyrite does not produce any calcium hydroxide but calcium sulphate and some other unidentifiable compounds of complex chemical composition. Most of the iron from pyrite is converted to magnetite and hematite. The glassy phase also seem to contain small amounts of calcium and iron.

(6) Although size does not necessarily control the crystalline substance in a fly ash, particles larger than 20 microns seem to contain increased amounts of inclusions of mullite as compared to particles smaller than 20 microns. Those particles which have numerous inclusions of mullite also have a different glass composition, as evidenced by change in refractive index of matrix glass. Likewise, particles having a different temperature history also have different composition and amount of strain in the glass. The magnetic particles exist in all sizes but seem to be more predominant in size fraction larger than 10 microns.

(7) Numerous particles contain bubbles in them; the larger particles seem to contain more than the smaller ones.

(8) The magnetic particles are probably coated with a thin surface layer of ferrugenous glass.

(9) Despite the presence of particles 100 microns or larger in diameter, the average mean diameter of the synthetic fly ashes and very possibly of most industrial fly ashes is less than 20 microns.

(10) The fineness as determined by the wt % passing 44 micron mesh

sieve is no indication of the fineness of the fly ash.

(11) The particle size distribution and average particle size can be determined very accurately by combined data of electron microscope count method and sieve analysis.

(12) Solubility of HCl leached fly ash sample in HF is a good indication of its total glass content, however it does not give any idea about pozzolanic reactivity.

(13) The pozzolanic activity of an ash resides primarily in its glassy particles. However, the amount of strain in the glass produced by rapid quenching of the slagged mineral particles appears to have an overriding influence on the reactivity of the ash as compared to fineness, composition and total amount of the glass.

(14) Therefore, the fly ashes containing increasing number of particles with a temperature history other than rapid quenching would tend to have substantially reduced pozzolanic activity.

(15) The pozzolanic strength of the fly ashes containing equally and highly strained glass is inversely proportional to its average mean weight diameter in the range of 4 to 13 microns; however, coarser fly ashes having average mean weight particle diameter $>\simeq 13$ microns differ only slightly in their pozzolanic strength. In terms of specific surface area per unit weight, the pozzolanic strength of the ashes increases directly with the increase in the specific surface area of the fly ashes from 1000 cm^2/g to 3000 cm^2/g, beyond which the relationship between specific surface area and pozzolanic strength is not linear and appears to taper off.

(16) The composition of glassy fly ash particles as well as the total fly ash composition influence the pozzolanic activity of the ashes as found

from the study of bimineralic fly ashes. Iron in any state, glassy or crystalline, has deleterious effect on the reactivity of the ash; the presence in the former state is more deleterious than in the latter. The iron in glassy phase changes the composition and possibly the strain of the glass and hence reduces its pozzolanic reactivity because of change in chemical properties as well as reactivity of the glass. On the other hand, iron in crystalline phase simply dilutes the proportion of glass content in the fly ash and influences the pozzolanic strength by its physical presence as does increased amount of aggregate in a cement concrete. Therefore, beneficiation by magnetic separation does not increase the pozzolanic activity significantly. Comparison of published data shows that the same is the case with the industrial fly ashes.

(17) Although calcium increases the reactivity of synthetic fly ashes considerably, the role of calcium is not completely understood.

(18) The presence of calcium in trimineralic fly ashes seem to offset the deleterious influence of iron. It is however not clear whether it is because of change of glass composition or formation of crystalline substances of calcium similar to those present in the portland cement that the calcium nullifies the harmful effect of iron. Available data seems to indicate the possibility of former reason being mainly responsible for increase in reactivity of the ash.

(19) A weight ratio of calcium oxide to iron oxide of 1:2 in the fly ash seems to be optimum according to the results of this study and data of Watt and Thorn (136, 137) for high initial and ultimate pozzolanic strengths of the fly ash.

(20) Although reaction products similar to the hydration reactions in

portland cement are formed in the hydration reactions of lime-fly ash mortars also, the rate of formation and amount of products in the latter is much less.

(21) Calcium silicate hydrate of tobermorite group and tetracalcium aluminate hydrates with variable amounts of water of hydration and partially carbonated are the main products formed in the mortars of synthetic fly ashes containing alumino-siliceous and ferrugenous glass, while ettringite and monosulphate are also formed in mortars of fly ashes containing both iron and calcium. The presence of gypsum in the latter is probably responsible for the formation of ettringite.

(22) The tetracalcium aluminate hydrates appear within a week of curing of lime-fly ash mixtures, however, the calcium silicate hydrates take about 8 weeks to be sufficiently crystalline for being detected by x-ray diffraction.

(23) Quantitative chemical analysis can be successfully used to accurately determine the amounts of reaction products in reacted lime-fly ash mortars. However, out of the two methods adopted in this study, the method of determining silica and alumina from the acid-soluble portion of reacted samples proved to be better than the method of determining undepleted lime by extraction in ice cold water to determine the amount of reaction in the lime-fly ash mortars.

(24) It is possible to detect the reaction products by their morphology in electron microscope; however, the light microscope does not seem to be suitable for this purpose.

(25) Irrespective of curing time, the amount of reaction products in the reacted samples of mortars of synthetic fly ashes is directly

proportional to their pozzolanic strength.

(26) The pozzolanic reactions are consecutive first and second order reactions. That is, for a curing time of up to 8 weeks, the reactions are primarily reaction-controlled, whereas beyond this they appear to be second order diffusion controlled reactions.

(27) Most of the conclusions drawn should be true for industrial fly ashes also as observed from the comparison of results in this research and the data in published literature. Consequently, the specifications prescribed by various organizations are faulty and do not take into consideration the basic fly ash parameters, such as nature (strained and/or devitrified) and composition of the glass in fly ash particles. Within ranges of Ca, Fe, Si and Al investigated, the total chemical composition of the mineralic fraction of an ash is in no way related to its pozzolanic strength. The specific surface area of the reactive particles only is of significance and not the whole fly ash.

(28) Last but not the least it is established that technique of preparing synthetic fly ashes from coal minerals has proved to be very successful in revealing some of the fundamental properties which were either obscurely understood or not known at all.

Suggested Research

Obviously more basic research is required in order to obtain complete knowledge of pozzolanic activity of the ashes. The parameters of strain and composition of the glassy material of the fly ashes need to be explored further to predict the activity of an ash. The influence of fineness on fly ashes of different glass composition also needs to be found out. If

quantitative influence of the three basic parameters can be estimated, the prediction of pozzolanic activity of a fly ash would become simple. Further, the knowledge so gained can be utilized to produce industrial fly ashes of desired properties eventually leading to a solution to the problem of enormous wastage of resources on disposal and pollution control of fly ash.

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ACKNOWLEDGEMENTS

APPENDIX A

Pioneer air floated kaolin, which is one of the high purity kaolins, was supplied by Georgia Kaolin Co., Elizabeth, New Jersey. The physical and chemical properties of the kaolin as given in specification sheet of the suppliers are reproduced below in Table 29 and Table 30.

Table 29. Typical particle size analysis of the clay

Equivalent spherical diameter in microns	Percent finer by weight
20	98
10	91
5	76
3	65
2	55
1	40
0.8	35
0.6	28
0.4	22

Table 30. Typical chemical analysis of the clay

Constituents	Percent by weight
Silicon dioxide	45.68
Aluminum dioxide	38.51
Iron oxide	0.44
Titanium dioxide	1.43
Calcium oxide	0.24
Magnesium oxide	0.14
Sodium oxide	0.04
Potassium oxide	0.14
Loss on ignition	13.5

APPENDIX B

Rising Current Elutriator

A rising current elutriator consists of one or more vertical tubes of different internal diameters through which a constant volume of liquid flows from the bottom to the top. Particles suspended in the liquid will rise with or fall through the liquid depending on their size and the velocity of the rising current. Specific gravity of the particles as well as the liquid must be considered.

The elutriator used in this research was constructed of Pyrex glass and modified after the version described by Handy (54) (Figure 35). The vertical tubes were placed one above another; the one with the smallest diameter on the bottom. Thus, although the volume flow through all tubes is constant, the velocity through any given tube is a function of its internal diameter (i.e. faster, through a narrow tube; slower, through a wide tube). Three elutriator tubes having internal diameters of 1.5, 3 and 6 inches were fabricated. The lower end of each tube was tapered for a length twice its diameter to ensure laminar flow and a No. 3 stop-cock was sealed to the bottom of each. Although tube length is unimportant as long as laminar flow is maintained, they should be long enough to allow accumulation of sufficient fractionated material. The tubes were connected to one another by appropriate rubber stoppers; the tubes themselves were clamped to a steel rod for stability. A constant head of distilled water was supplied by a glass container placed above the uppermost tube. A constant flow of distilled water was maintained by use of a floating-ball flow meter in the line immediately ahead of the lowermost tube. Tygon
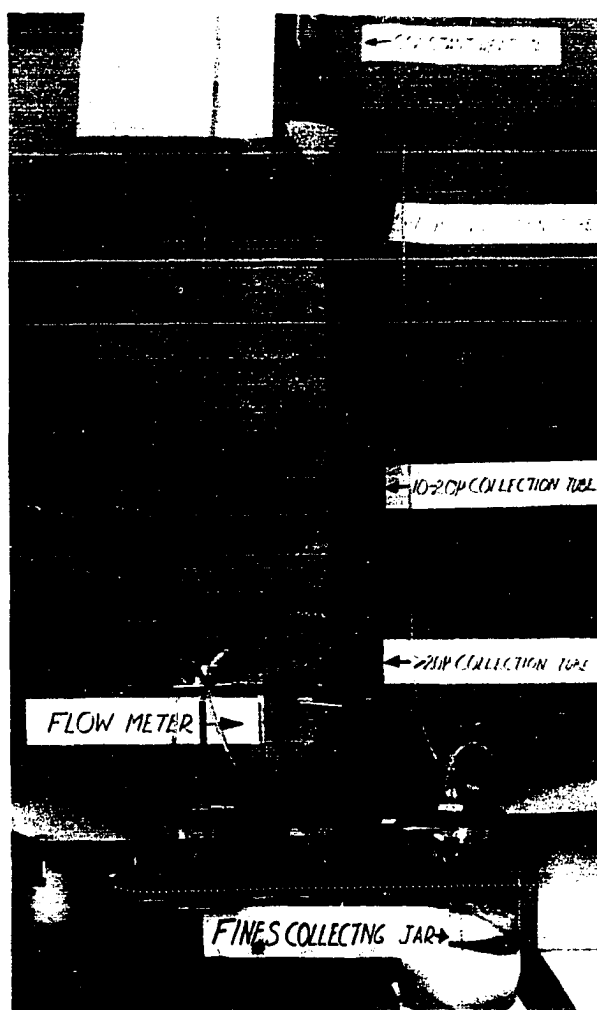
Figure 35. Rising-current ellutriation used for fractionating monomineralic fly ashes

tubing was connected to the top of the uppermost tube and lead into a large settling jar where the effluent water and particles were collected.

The theory of operation of the rising current elutriator is based on Stokes law in which the velocity of a settling spherical particle in the liquid depends on the viscosity of the liquid. This is given by

$$V = \frac{2 (d_1 - d_2) gr^2}{gn} = \frac{Q}{\pi r_t^2 T} \tag{15}$$

where V is the settling velocity of the particle in cm/sec; g, the acceleration due to gravity in cm/sec^2; r, the particle radius in cm; n, the viscosity of the settling liquid; d_1 and d_2, the specific gravity of the particle and the liquid respectively; and Q, the discharge of the liquid in time T through an elutriator tube of radius r_t cm. Since tubes of known diameters are used, it is possible to estimate the quantity of water fed per unit time into the elutriator in order to maintain a certain velocity and thereby retain particles coarser than certain size in a particular tube. For example, to retain particles of 5 microns or larger in diameter having a sp gr of 2.449 g/cm^3 in the top tube of 3 in. radius, at 68°F., and $n = 0.01009$ poise, the discharge which must be maintained can be calculated as follows:

$$\frac{Q}{T} = \frac{2 \pi (2.449 - 1.00) \times 980 \times (.0025)^2 \times (3 \times 2.54)^2}{9 \times 0.01009} \tag{16}$$

$$= .365 \ cm^3/sec \tag{17}$$

$$= 21.9 \ cm^3/min \tag{18}$$

This volume of water through the elutriator automatically allowed particles

10 to 20 microns to be retained in the middle tube and particles coarser

than 20 microns to be retained in the lowermost tube. Since their

diameters were one-half and one-quarter, respectively, that of the top

elutriator tube. The water discharged from the top tube carried away

particles finer than 5 microns in diameter. The desired discharge was

maintained with the help of flow meter and also by counting drops falling

in the bottle. The latter was found to be more accurate. Since the

viscosity of water depends on temperature, the discharge must be adjusted

according to the change in water temperature. However, temperature

measurements indicated variations were too small to require corrections.

The elutriator column is first filled with water and the volume of

water rising through the column and discharging into the collection bottle

is adjusted to about 22 cm^3/min using the flow meter. The supply of water

is then stopped and the three stopcocks in the elutriator tubes are closed.

The lowermost tube is removed, emptied, and refilled with a water suspension

of fly ash containing about 100g solids and a small quantity of sodium

pentaphosphate as a dispersing agent. This tube is then filled brimful

by adding more water before replacement into the column. Complete filling

of the lower tube is necessary to avoid introducing air bubbles into the

column. The stopcock controlling the water supply is opened, and then

the other stopcocks in the elutriator column are reopened in turn. The

flow of water must be readjusted to the predetermined value of 22.1 cm^3/min.

Within 2 hours the suspension of particles is carried upwards into

all the tubes. Since flocculation was observed in the lowermost tube, a

solution of dispersing agent was injected through the Tygon tubing into the

system using a hypodermic needle and syringe. About 8 hours were required to fractionate 100g of fly ash. Complete fractionation of a given fly ash sample is indicated with the upper 3/4 to 7/8 of each of the elutriator tubes is clear, i.e. contains no observable particles. Dispersing agent was once more injected at this stage to see if any flocculated particles have been left in any of the columns. After about an hour and a half, all the stopcocks were closed, and the contents of the elutriator tubes were emptied into individual beakers for drying at $60^{\circ}F$. The fly ash fraction less than 5 microns collected in the large settling jars was salvaged by continuous centrifuging with a Servall Type KSB-3 (4) "Szent-Gyorgyi and Blum" 8-tube continuous flow centrifuge operated at a speed of 12,000 rpm.

The various fractions thus collected from a known weight of fly ash were found to be very comparable with the calculated weights of identical fractions as measured in the electron microscopic count of the whole kaolinite fly ash. All of the monomineralic kaolinite fly ashes were fractionated in this manner.

APPENDIX C

Table 31. Maximum limits of impurities in the reagent grade calcium
hydroxide

| Constituents	wt %
Amonium hydrate Ppt	0.60
Chloride (cl)	0.005
Heavy metals (as Pb)	0.003
Insoluble in HCl	0.05
Iron (Fe)	0.05
Magnesium and alkali salts as sulfates	2.0
Sulphate	0.40

APPENDIX D

Curing Compartment

An ordinary 6 cu ft household refrigerator[1] was used. A stainless

steel air duct of having a rectangular cross-section of 8 x 1 3/4 in. led

from the rear opening of the freezer chamber to the bottom of the refrigera-

tor compartment. The freezer chamber was lined with 3/16 in. Masonite

and the front end was closed with a 3/16 in. thick sheet of Plexiglas

which had an inlet for feeding nitrogen. A small 1/32 H.P. fan with a

2 1/2 in. blade diameter was placed in the freezer chamber to aid in

circulation throughout the refrigerator compartment. A drip pan fabricated

from 1/4 in. sheet asbestos was mounted below the freezer chamber, and

water collected here was drained into a stainless steel water try at the

bottom of the refrigerator compartment. The freezer chamber was insulated

from the main refrigerator compartment with a 1/4 in. Masonite sheet.

A small heater, consisting of chromel-A wire (#34) wound around a

1/2 in. porcelain tube, was placed across the opening of the duct work

coming from the freezer chamber. The heater was controlled externally.

A one-and-a-half-gallon capacity room humidifier[2] was installed in the

lower right-hand corner of the refrigerator compartment. With the help of

a small motor and gear system, placed outside of the cabinet, the

humidifier could be operated for desired length of time at suitable

intervals. The top of the humidifier was covered with a sheet of Corform

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[1]Kelvinator, Model CS-7-R.

[2]De Vilbiss Model 238.
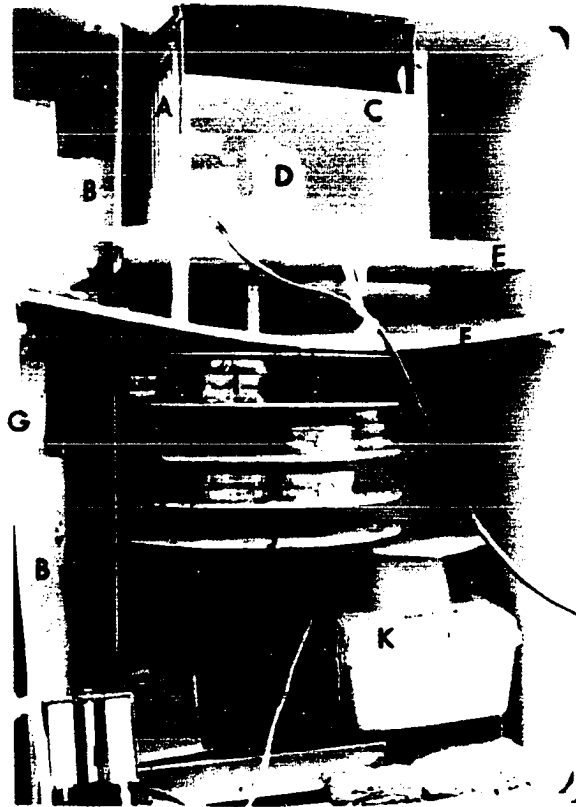
A. Freezing compartment
B. Stainless steel duct
C. Fixed Plexiglas shutter
D. Fan inside the enclosed compartment
E. Tray of asbestos sheet
F. Masonite board partition
G. Nitrogen feed line
H. Thermometer
I. Perforated plastic containers
J. Perforated steel shelf
K. Humidifier
L. Dry and wet bulb hygrometer

Figure 36. Interior of the curing compartment (front doors swung aside)

which allowed air to enter the motor space but eliminated water droplets and thus avoided damage to the motor. A Mason hygrometer (wet-bulb, dry-bulb thermometer) was used for humidity measurements and placed in the lower left-hand corner of the curing chamber opposite the humidifier. Two thermometers, readable to within $0.1^\circ F$ and $1^\circ C$ respectively, were installed in the curing chamber so they could be read externally.

Five perforated circular steel shelves, 14 in. in diameter and 1/8 in. thick, were installed on a vertical steel shaft in the center of curing compartment. These shelves could be rotated externally.

The original door of the refrigerator was replaced by two large hollow Plexiglas doors hinged at the outside. Foam rubber strips and rubber gaskets were used to seal the doors against the surface of the refrigerator. Electrical and gas lines were led into the cabinet through the Plexiglas refrigerator and freezer chamber doors.

The refrigerator, fan, heater and humidifier were operated on 110V and appropriate Variac controls. Nitrogen was continuously fed into the freezer chamber at a pressure of 15 psi. The nitrogen was bubbled through a flask filled with water. The fan in the freezer compartment forced the cooled and moist nitrogen down into the duct where it passed over the heater. The voltage to the heater was adjusted with a Variac to maintain a temperature of $73 \pm 2^\circ F$ in the curing compartment. The nitrogen was allowed to seep through holes provided for this purpose near the top of the curing compartment. Trial runs indicated that operation of the humidifier for 50 seconds every 15 minutes provided the desired relative humidity of $98 \pm 2\%$.