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Characterization of the M.S.U.
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CHARACTERIZATION OF THE MSU POWER PLANT FLY ASH FOR CONCRETE AND OTHER APPLICATIONS

By

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ABSTRACT

CHARACTERIZATION OF THE MSU POWER PLANT FLY ASH FOR CONCRETE AND OTHER APPLICATIONS

By

Austin Okwuegbu

Fly ash is a by-product of coal combustion in electrical power plants. It has found growing applications in cement and concrete products, and also in structural fills. Ecological advantages as well as cost savings encourage these applications of fly ash. ASTM C-618 provides the basis for characterization and classification of the fly ashes which are suitable for cement and concrete applications.

The fly ash produced at the MSU power plant was characterized in this investigation, and suitable applications of this fly ash in cement-based materials were distinguished. Sampling and testing of the MSU fly ash were performed using procedures outlined in ASTM C-618. The following tests were conducted on the fly ash: moisture content, loss on ignition, oxide content, density, increase in drying shrinkage of mortar bars, soundness, limit on amount of air-entraining admixture in concrete, air entrainment of mortar, pozzolanic activity index with Portland cement, water requirement, pozzolanic activity

index with lime, and foam index. The uniformity of the MSU fly ash was evaluated by repeating the specific gravity, fineness, and loss on ignition tests on ten fly ash samples. Microstructural studies were also performed on this fly ash.

The MSU fly ash was observed to satisfy most, but not all, the ASTM requirements for Class F fly ash. The soundness and Pozzolanic activity index with lime did not meet the ASTM requirments, and the carbon content of this fly ash, although satisfying the ASTM requirements, was observed to be relatively high.

Microstructural studies indicated that the MSU fly ash, when compared with conventional Class F fly ashes, has a relatively low fraction of spherical particles and its particle size gradation is not smooth. Larger particles of MSU fly ash also seem to become porous and highly irregular in shape when exposed to wetting-drying cycles. All these factors have negative effects on the workability and air-entraining agent requirements of fresh mixtures incorporating the MSU fly ash.

The properties of MSU fly ash seem to suit applications in flowable fill and cement-stabilized fly ash. In spite of its low pozzolanic activity index with lime, the MSU fly ash seems to be capable of satisfying the relatively modest strength requirements in these applications. In the case of cement-stabilized fly ash in particular, noting that strength development partly results from compaction, the low pozzolanic activity index seems to be a cause of even less concern. The high carbon content of the MSU fly ash, which interferes with air entrainment process for increasing the frost resistance of concrete, is also no cause for objecting applications in flowable fill and cement-stabilized fly ash where air entrainment is not practiced. Finally, noting that the MSU fly ash has properties which are not significantly different from those of class F fly ash, its conventional concrete applications should not be completely ruled out, although realization of such applications requires changes in specifications commonly followed in selecting fly ash for concrete applications.

DEDICATION

TO ALL MINORITIES

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CHAPTER I

INTRODUCTION

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INTRODUCTION

1.1 GENERAL

About 600 million tons of coal is combusted annually in U.S. electrical power plants, resulting in the precipitation of about 60 million tons of fly ash.[1] This by-product of coal combustion has found increasing utilization in a variety of areas including cement and concrete products, structural fills, highway road base courses, and grouting. In 1986, about 20% of the fly ash produced in the U.S. was consumed in different utilization categories such as these.[2]

Incentives for the use of fly ash in concrete, structural fills and highway base course are provided by the improvements in some critical aspects of the material performance in the presence of fly ash, and also by the cost savings for utilities and the users of fly ash.

In cement and concrete applications, fly ash provides enhanced fresh mix workability, higher ultimate or long-term strength, chemical resistance, impermeability, reduced heat of hydration and lower alkali-aggregate reactions.[3]

The users of fly ash in cement and concrete, however, should properly proportion the mixtures in order to account for the potential of fly ash to reduce entrained air content and delay the development of strength.[3] Appendix I provides a general background on fly ash production and utilization in concrete. Appendix II provides a more comprehensive review of the effects of fly ash on fresh concrete mix workability, air content and hydration processes.[2] The durability of fly ash concrete is discussed in Appendix III.

ASTM C-618 provides the basis for characterization and classification of fly ash for concrete applications. The ASTM C-618 test results can be used to identify or determine best the utilization categories (i.e., concrete, structural fill, road base, etc.) for a specific fly ash.

1.2 FLY ASH CLASSIFICATION

ASTM C-618 categorizes the fly ashes suitable for concrete applications into two groups: Class F and Class C. Class F fly ash is normally produced by burning anthracite or bituminous coal. It has pozzolanic properties reflecting its reactivity with lime at room temperature. Class C fly ash is normally produced from lignite or sub-bituminous coal, and it has pozzolanic as well as cementitious properties, with the cementitious properties resulting from the inherent high lime content which is sufficient for reaction of fly ash with water. The loss on ignition (LOI), which relates to carbon content, of Class C fly ash is generally lower than that of Class F fly ash. Lower loss on ignition is an advantage as far as air entrainment and stability of the entrained air system in concrete are concerned. Some important chemical and physical requirements for Class F and Class C fly ashes, as suggested by ASTM C-618, are compared in Table 1.1. In addition to these requirements, ASTM C-618 also specifies limits on the soundness, pozzolanic activity with portland cement and lime, and some aspects of fly ash effects in mortar and concrete.

Table 1.1 Some Important Chemical and Physical Requirements of ASTM C-618 for Class F and Class C Fly Ash

Property	Fly Ash			
	F		C	
	Max (%)	Min (%)	Max (%)	Min (%)
$SiO_2 + Al_2O + Fe_2O_3$	--	70	--	50
Loss on Ignition (LOI)	12	--	6	-
SO_3	5	--	5	-
Fineness (Weight fraction greater than 45 microns)	34	--	34	-
Soundness (Auto-clave Expansion or Contraction)	0.80	--	0.80	-

It has been suggested that more reasonable classifications of fly ash for concrete applications may be based on characteristics known to significantly influence significantly their behavior in concrete, as described below:[4]

1. Distinctions should be made between well-burned ashes and badly burned ones that have enough carbon residues to interfere with admixture action in concrete. Well-burned fly ashes are typically characterized as having 0-3% carbon content, while poorly-burned fly ashes have from 3-6%, and very poorly burned ones more than 6% carbon content.

2. Analytical CaO content is also an important basis for classification. For example, ASTM C-618 uses silica plus alumina plus iron oxide content to distinguish between Class F and Class C fly ashes. Low-calcium fly ashes could be designated as having less than 5% CaO content, while moderate calcium groups from 5-15%, and high calcium groups have more than 15% CaO content. The CaO content considered here is the analytical one; the free (crystalline) value is always much smaller.

3. The alkali sulfate content of fly ash can be another factor in classification. The alkali ions contributed by alkali sulfate to the mix water strongly influence the early hydration of Portland cement and can

increase the tendency toward alkali-aggregate attack and steel passivation. An alkali sulfate content of less than 0.5% may be categorized as low, one between 0.5 and 1% can be comsidered intermediate, and alkali sulfate contents greater than 1.0% may be classified as high.

4. The total sulfate content of fly ash may influence the long-term durability and some other properties of concrete. Total sulfate contents of 1% and 3% can tentatively be used to distinguish between low, intermediate, and high sulfate fly ashes.

5. Particle size distribution and the content of hollow particles are also among the factors that could also be considered in fly ash classification for concrete applications.

1.3 OBJECTIVES

The objectives of this research effort have been to: (1) characterize and classify the MSU power plant fly ash; and (2) identify application fields for the MSU fly ash which best suit its particular characteristics.

These objectives were accomplished through classification of the MSU fly ash following the ASTM C-618 guidelines which helped establish the advantages of the MSU fly ash for a variety of applications. The ASTM C-618 guidelines were developed specifically for fly ash applications in Portland Cement Concrete. They do, however, provide valuable information regarding the use of fly ash in other applications; such as flowable fill and cement-stabilzed fly ash. In these specific applications, the requirements for strength development are less restrictive than in conventional concrete, and fly ashes with high carbon contents may be acceptable because they do not adversely influence the mechanisms responsible for the development of frost resistance in flowable fill and cement-stabilized fly ash.

CHAPTER II

EXPERIMENTAL PROGRAM

CHAPTER II

EXPERIMENTAL PROGRAM

2.1 GENERAL

The process of sampling the MSU fly ash is described in this chapter. The experimental procedures followed for characterization and classification of the fly ash are also discussed. The approach to the assessment of the MSU fly ash uniformity is described.

2.2 SAMPLING OF FLY ASH

The MSU power plant generates energy by the combustion of ground coal. The annual combustion of coal in the MSU power plant is about 150,000 tons, resulting in the precipitation of about 15,000 tons of fly ash each year. Different physical and chemical properties of the MSU fly ash were assessed experimentally in this investigation. The action of this fly ash in concrete was also studied and variations in the properties of MSU fly ash were investigated.

The investigation of fly ash characteristics and assessment of its action in concrete were conducted on three 200-16 samples, each representing more than 400 tons of fly ash generated at the MSU power plant in the winter of 1988. These samples satisfy ASTM requirements in the sense that each of them represents more than 400 tons of fly ash. These samples were collected directly from the power plant at the end of the system through which the trucks are loaded with fly ash at time intervals within which at least 400 tons of fly ash were produced at the MSU Power Plant.

Studies on the variations in fly ash properties were conducted on ten samples, each representing at least 400 tons of fly ash.

2.3. PHYSICAL AND CHEMICAL CHARACTERIZATION OF THE FLY ASH

In this experimental study, the physical and chemical properties of the MSU fly ash were assessed, and some key aspects of the action of this fly ash in concrete were investigated. Microstructural studies were also conducted on the MSU fly ash using a scanning electron microscope. All physical and chemical tests on the MSU fly ash were repeated (as required by ASTM C-311) on three different samples of the fly ash (each representing more than 400 tons of fly ash). The following tests were conducted at this stage:

- Moisture Content (ASTM C-311)
- Loss on Ignition (ASTM C-114)

- Oxide Content (ASTM C-114)
- Density (ASTM C-188)
- Increase of Drying Shrinkage of Mortar Bars (ASTM C-157)
- Soundness (ASTM C-150)
- Limits on Amount of Air-Entraining Admixture in Concrete (ASTM C-233)
- Air-Entrainment of Mortar (ASTM C-150)
- Pozzolanic Activity Index with Portland Cement (ASTM C-109)
- Water Requirement (ASTM C-311)
- Pozzolanic Activity Index with Lime (ASTM C-109)
- Foam Index (ref. 18)

A brief discussion of the test procedures and the significance of tests results is presented below.

Moisture Content: The moisture content of fly ash is needed during mixing for determining the exact fly ash and water contents of the mix. In this test, the fly ash is dried in an oven at 105°C (221°F) to constant weight.

Loss on Ignition: The weight loss of dry fly ash is measured after ignition in a Muffle Furnace at 750C (1282F). The loss represents mainly the carbon content which is driven off. The remaining unburned carbon of fly ash will absorb the air-entraining agent and increase the water requirements. Also, some of the carbon in fly ash may be encapsulated in glass or otherwise be less active; therefore, it cannot affect the air content of concrete mixtures. High carbon contents in fly ash lead to an increase in the dosage of air entraining agent required for frost resistance. Variations in carbon content, which contribute to fluctuations in air content, necessitate careful monitoring of the entrained air in fly ash concrete.

Oxide Content: The percentages of silicon dioxide, aluminum oxide, iron oxide, sulfur trioxide and magnesium oxide in fly ash were determined following ASTM C-114. The active compounds in fly ash used for concrete applications are mainly silicon oxide, aluminum oxide, and iron oxide. These compounds react with calcium oxide in solution to produce cementitious materials. Fly ash tends to contribute to concrete strength at a faster rate when these components are mostly present in the finer fraction of the ash. Magnesium oxide, however, can react to produce magnesium hydroxide, which is known to cause deleterious expansions. AASHTO limits the weight fraction of magnesium oxide in fly ash to a maximum of 5%.[3] Sulfur trioxide may also cause expansion and its weight fraction is limited to 5%. Within the specification limits, higher sulfur trioxide weight fractions may, in some cases, result in higher early concrete strengths.

Density: Density, itself, has no major direct effect on concrete quality. It is of definite value, however, in identifying changes in other fly ash characteristics.

Density should be checked regularly as a quality control measure, and should be related to other characteristics of fly ash that may be fluctuating.

Fineness: The percentage of fly ash retained on a No. 325 (45 microns, 0.0017 in.) sieve gives a measure of the amount of very coarse particles which are probably too large to react chemically to any great degree. Fly ash consists largely of solid and hollow spherical particles with some irregularly shaped carbon and other particles. ASTM C-618 suggests a maximum fineness of 34% retained for Class C and Class F fly ashes used in concrete, and ASTM C-595 recommends a maximum fineness of 20% retained for fly ashes used in blended cement (type IP).

Increase of Drying Shrinkage in Mortar Bars: This test compares the drying shrinkage of mortars made using Portland cement and those fabricated using a fraction of cement substituted with fly ash. The purpose of the test is to determine the effects of fly ash on the dimensional stability of concrete.

Soundness: This test determines the soundness (autoclave expansion or contraction) of specimens molded from a paste composed of 25 parts (by weight) of fly ash and 100 parts of Portland cement. ASTM C-618 suggests a maximum autoclave expansion or contraction of 0.80% for Class C and Class F fly ash. Excessive expansions or contractions values are indicative of chemical reactions capable of damaging cement by producing major volume changes.

Limits on Amount of Air-Entraining Admixture in Concrete: This assesses the effects of substituting a fraction of cement with fly ash in concrete mix (with water content adjusted to keep consistency constant, as specified in ASTM C-618) on the increase in dosage of air-entraining agent required to induce a satisfactory level of entrained air content. This test directly studies an important cause of concern for the users of fly ash in concrete; the possible increase in air entraining agent requirements. It also provides practical information for the proportioning of fly ash concrete mixtures. Fly ashes with unburned carbon content may not perform well under this test.

Air-Entrainment of Mortar: This test determines the dosage of air-entraining agent required for achieving a satisfactory level of air content in a fly ash mortar incorporating graded Ottawa sand. The purpose of this test is similar to the previous one (Limits on Amount of Air-Entraining Admixtures in Concrete), but it is performed with a mortar mix incorporating only fine aggregates because it is concerned specifically with mortar applications of fly ash.

Pozzolanic Activity Index with Portland Cement:

Find the pozzolanic activity index is defined as the ratio of 28-day compressive strength of a fly ash cement mortar with graded Ottawa sand to that of a comparable mortar (having similar flow) without fly ashes used in Portland Cement Concrete applications. ASTM C-618 suggests a minimum pozzolanic activity index of 75% for Class C and Class F fly ash, and ASTM C-595 suggests a similar index for fly ashes used in blended cement.

Water Requirement: This test determines the ratio of the water required in fly ash mortars to that required in pure cement mortars (both made using graded Ottawa sand) for achieving a certain level of flow. The maximum water requirement for Class C and Class F fly ash according to ASTM C-618 is 105%. While fly ash, with its round particles, generally improves the workability of fresh concrete mixtures and thus reduces water requirements for workability, some fly ashes (e.g., those with relatively high contents of large carbon particles) adversely influence fresh mix workability and thus increase the water requirements. These test results can be used to identify fly ashes which damage the fresh mix workability and thus change the hardened material properties of the concrete.

Pozzolanic Activity Index with Lime: Considering that the reaction of fly ash with lime produced during cement hydration is a major cause of strength development in fly ash concrete, the pozzolanic activity index with lime provides additional information on the strength development of fly ash concrete. This index is defined as the 28-day compressive strength of mortar incorporating graded Ottawa sand and using a combination of lime and fly ash as binder (with sufficient water added to produce a certain level of flow). The maximum pozzolanic index with lime suggested by ASTM C-618 for Class C and Class F fly ash, and by ASTM C-595 for fly ash in blended cement, is 800 psi (5.5 MPa).

Foam Index: The amount of air entraining admixture needed to initiate a stable foam in a cement paste incorporating fly ash is the foam index amount. Higher foam indices are indicative of fly ashes which result in higher air entraining agent dosage requirements for the production of concrete with sufficient air content.

2.4 ASSESSMENT OF FLY ASH UNIFORMITY

ASTM C-618 has some requirements for insuring the uniformity of the fly ashes used in Portland cement concrete. According to this specification, the specific gravity of each sample of Class C or Class F fly ash shall not vary by more than 5% from the average value established using ten test results. In addition, ASTM C-618 recommends that the maximum percent retained on No. 325 sieve shall not vary by more than 5 percentage points from the average established.[30]

These requirements on fly ash uniformity were checked in this study through specific gravity and fineness tests on ten samples of fly ash. Considering the significance of loss on ignition (LOI) in deciding the performance of fly ash in concrete, it was decided to conduct the LOI tests on all the ten samples of MSU fly ash in order to assess the variations in this important property of fly ash.

2.5 MICROSTRUCTURAL INVESTIGATIONS

In order to develop a more comprehensive understanding of factors influencing the properties of the MSU fly ash, scanning electron micrographs (typically at 1000x magnifications) were produced for: (1) the MSU fly ash as received; (2) a commercially available class F fly ash; (3) residuals of the MSU fly ash on No. 325 sieve after sieving the material in dry condition (by shaking the sieve); and (4) residual of the MSU fly ash on No. 325 after sieving the material in wet condition (by spraying).

Comparisons were made between different micrographs in order to establish differences between MSU fly ash and a typical class F fly ash, and to study the effects of wetting on the larger particles of the MSU fly ash.

CHAPTER III

EXPERIMENTAL RESULTS

CHAPTER III

EXPERIMENTAL RESULTS

3.1 GENERAL

This chapter presents the results of the experimental study conducted to evaluate the MSU physical plant fly ash for concrete and other applications. The results are presented in four parts. First, the major characteristics of the fly ash are given and are compared with the ASTM requirements. In the second part, the results of tests on uniformity of the MSU fly ash are presented. A general analysis of the test results is presented in the third part. The final part of this is the presentation of the microstructural test study (SEM) results.

3.2 MSU FLY ASH PROPERTIES VS. ASTM REQUIREMENTS

Table 3.1 presents the results of tests on the MSU fly ash, and makes comparisons with ASTM C-618 Class F and C fly ash requirements. The MSU fly ash was observed to satisfy most, but not all, of the ASTM requirements for Class F fly ash. Its pozzolanic activity index with lime and soundness, fail to meet ASTM requirements.

Replicated tests were conducted to confirm the pozzolanic activity index with lime and soundness of the MSU fly ash. Figure 3.1 (a) and (b) present frequency distribution curves with corresponding normal distributions for all the test data (a total of twenty measures were made for each property, of the three fly ash samples). Relatively small variations in test results are observed, (5% and 2.5% coefficients of variation for pozzolanic activity index with lime and soundness, respectively). For the pozzolanic activity index with lime and soundness of the MSU fly ash, the twenty replicated tests indicate that the corresponding mean values (638 psi and 0.946%, respectively) are smaller than the 800 psi limit and greater than the 0.8% limit, respectively, specified by ASTM for Class F fly ash.

The loss on ignition of the MSU fly ash, although within acceptable limits for class F fly ash (i.e., below 12%), is relatively high, which is indicative of a poorly burned fly ash. Replicated test data (a total of twenty tests) on the loss on ignition of the three samples of MSU fly ash (see Figure 3.1 (c) for the frequency distribution curve and the corresponding normal distribution) confirmed that the MSU fly ash has a relatively high loss on ignition (mean value 10.08%, with a coefficient of variation of

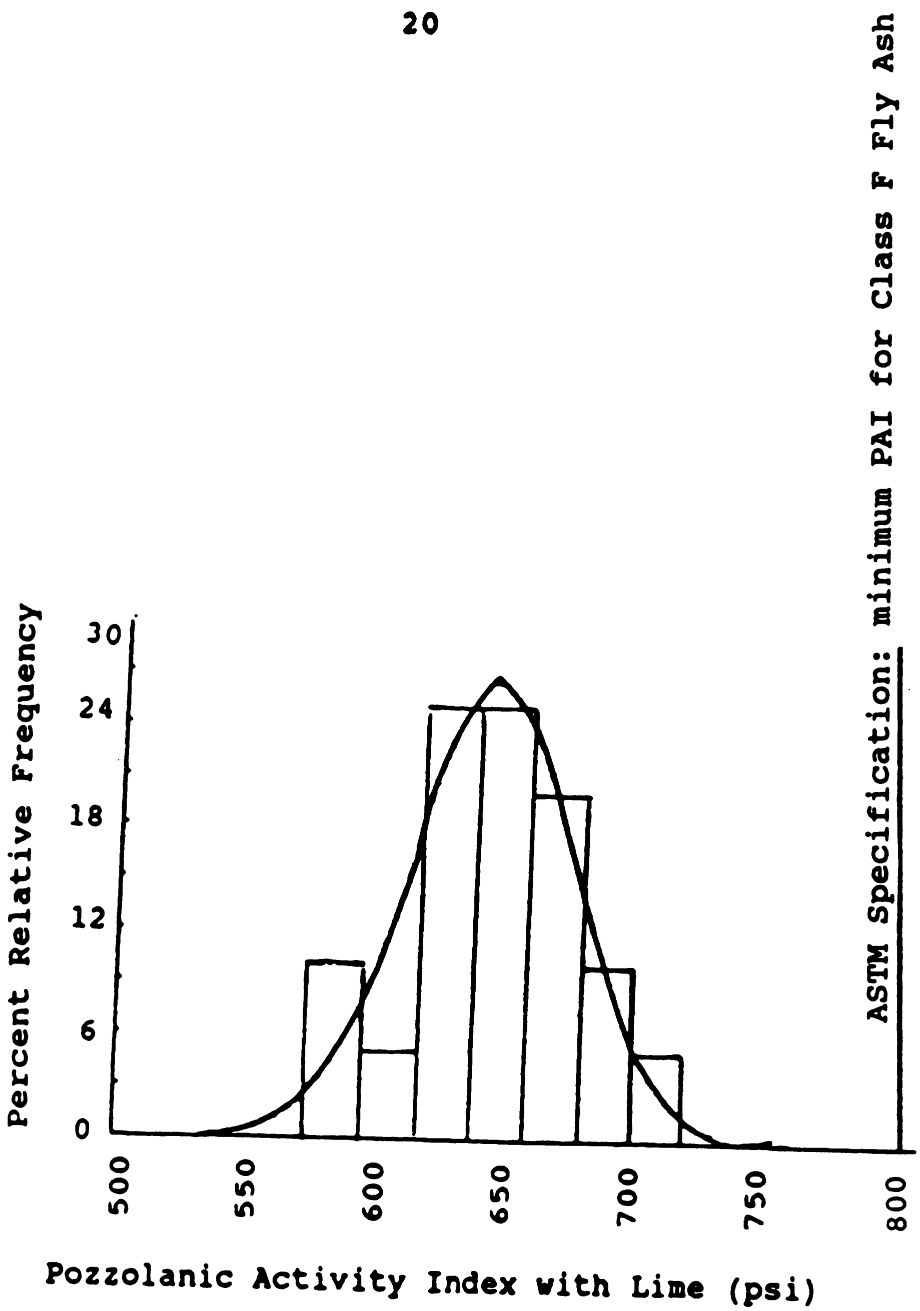
Table 3.1 Properties of MSU Fly Ash vs. ASTM Requirements

Property	Fly Ash MSU	Class F Min	Class F Max	Class C Min	Class C Max
$S_iO_2 + Al_2O_3 + Fe_2O_3$	80%	70%	--	50%	--
So_3	4.51%	--	5%	--	5%
Loss on Ignition	9.8%	--	12%	--	6%
Fineness	20.7%	--	34%	--	34%
Pozzolanic Activity Index with Portland Cement	90±4%	75%	--	75%	--
Pozzolanic Activity Index with Lime (psi)	640	800	--	--	--
Water Requirement (% of Control)	96±1.5%	--	105%	--	105%
Soundness	0.95%	--	0.80%	--	0.80%
Multiple Factor (Loss on Ignition Fineness)	255	--	--	--	--
Increase in Drying Shrinkage of Mortar	0.017±0.002%	--	0.03%	--	0.03%
Specific Gravity (g/cm^3)	2.124±0.025%	--	--	--	--
Req'd A/E for Mortar (ml/gr. of binder)	0.64	--	--	--	--

Table 3.1. (cont'd.)

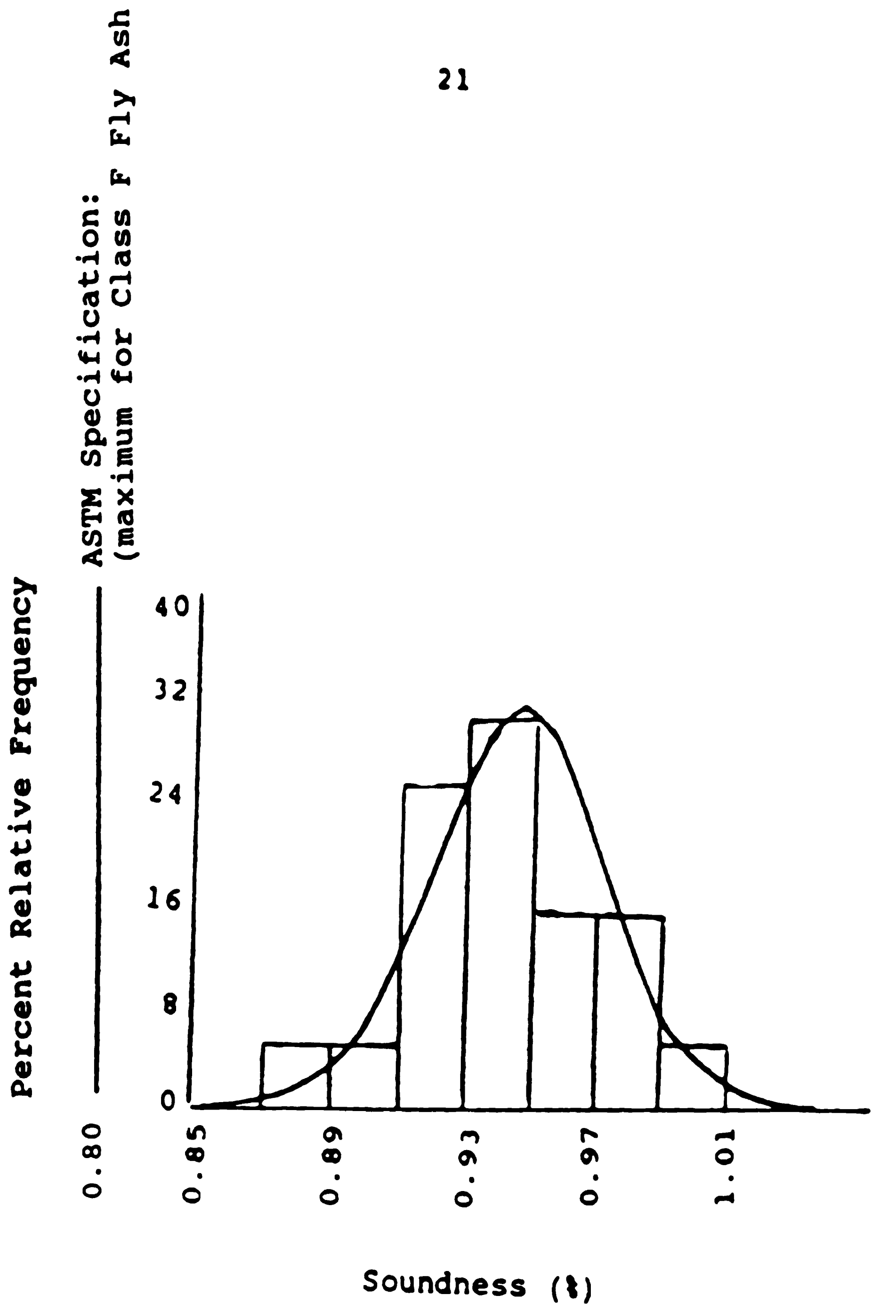
Property	Fly Ash				
	MSU	Class F		Class C	
		Min	Max	Min	Max
Req'd A/E for Concrete (Ratio to Control)	1.91±0.002	--	--	--	--
Foam Index (ml A/E/GR. Binder	0.0046	--	--	--	--

*Max 6% is preferred; for higher LOI acceptable laboratory test results are required.



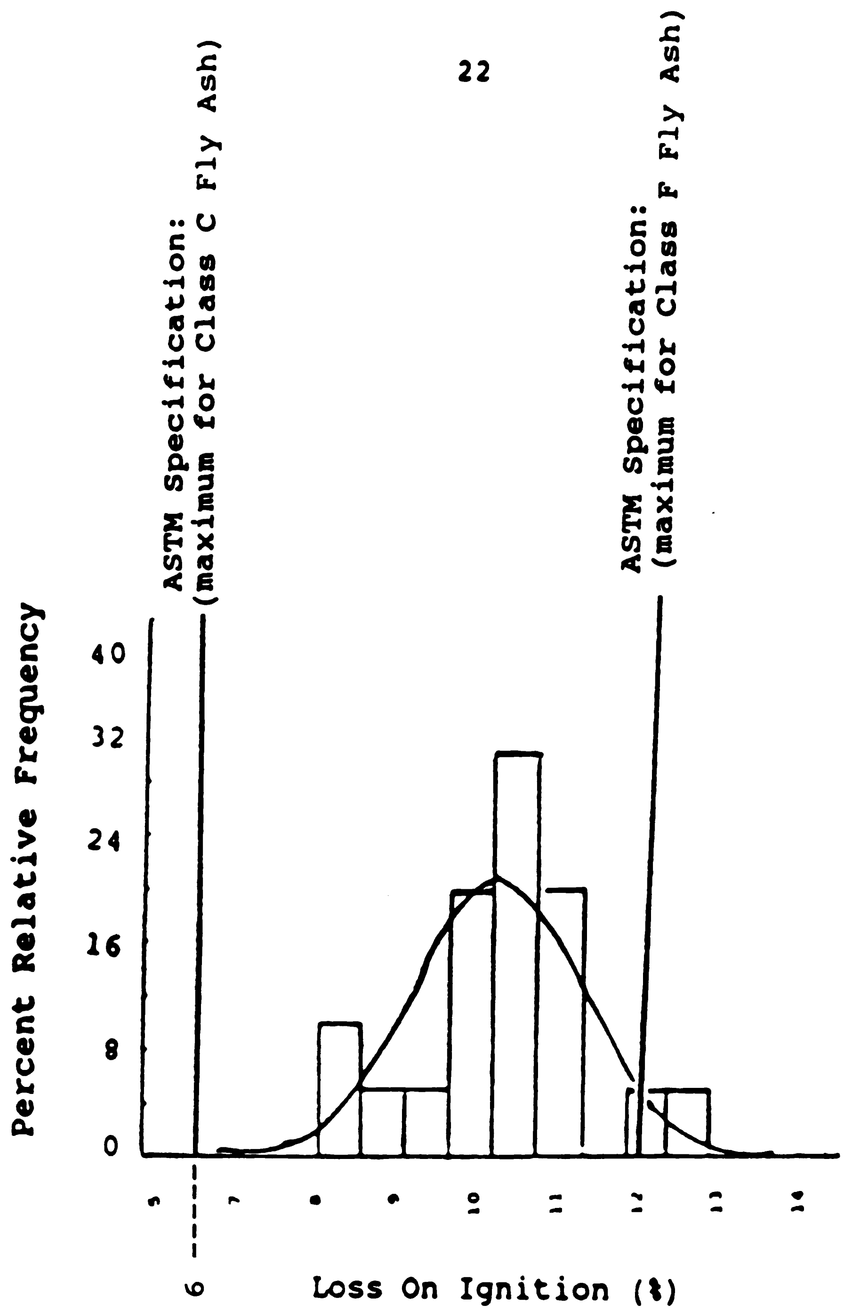
(a) Pozzolanic Activity Index with Lime

Figure 3.1 Frequency Distribution Curves for the Pozzolanic Activity Index with Lime, Soundness and Loss on Ignition of the MSU Fly Ash.



(b) Soundness

Figure 3.1 (continued)



(c) Loss on Ignition

Figure 3.1 (continued)

11.01%). In spite of this, as shown in Table 3.1, the required air-entraining agent dosages for concretes and mortars incorporating this fly ash are not excessively higher than those required in control mixtures without fly ash. The foam index test results are also comparable to those reported for typical class F fly ashes.

3.3 UNIFORMITY OF MSU FLY ASH

The results of measurements made on density, fineness, and loss on ignition of ten different samples of MSU fly ashes are presented in Table 3.2 (noting that each sample is taken from the fly ash storage at sufficiently long intervals to represent at least 400 tons of fly ash and each result presented here is average of three test results). Figure 3.2 presents diagrams which graphically show the observed variations in fly ash properties. Frequency distribution curves (with the corresponding normal distributions) for the thirty test results (three on each sample) on the density, fineness, and loss on ignition of the ten samples of MSU fly ash are presented in Figure 3.3.

Maximum variation from the mean value for density test results of the MSU fly ash is 3%, which is below the maximum value of 5% specified by ASTM C-618. The maximum percentage point difference from mean for the fineness test results is 9.5, but the difference in eight out of ten

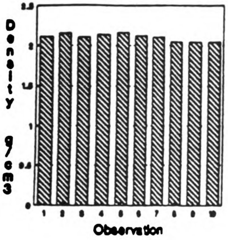
Table 3.2. Uniformity Test Results for MSU Fly Ash

Observation #	Density (g/cm3)	Fineness (%)	LOI (%)
1	2.110	25.1*	10.4
2	2.155	23.3*	10.3
3	2.106	13.6	8.8
4	2.137	15.6	10.1
5	2.165	11.9	10.6
6	2.119	10.6	10.5
7	2.101	13.1	12.0
8	2.041	13.7	10.7
9	2.049	16.4	8.0
10	2.049	13.0	9.4
Mean	2.103	15.6	10.08
Std. Dev.	0.044	4.82	1.11
C.O.V.	2.11%	30.87%	11.01%

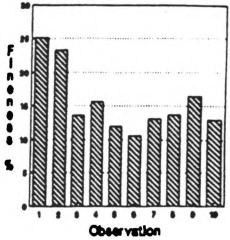
* Does not satisfy the uniformity requirements of ASTM C-618.

Density g/cm3

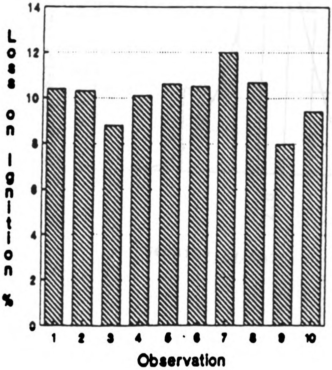
Fi



(a) Density (g/cm3)

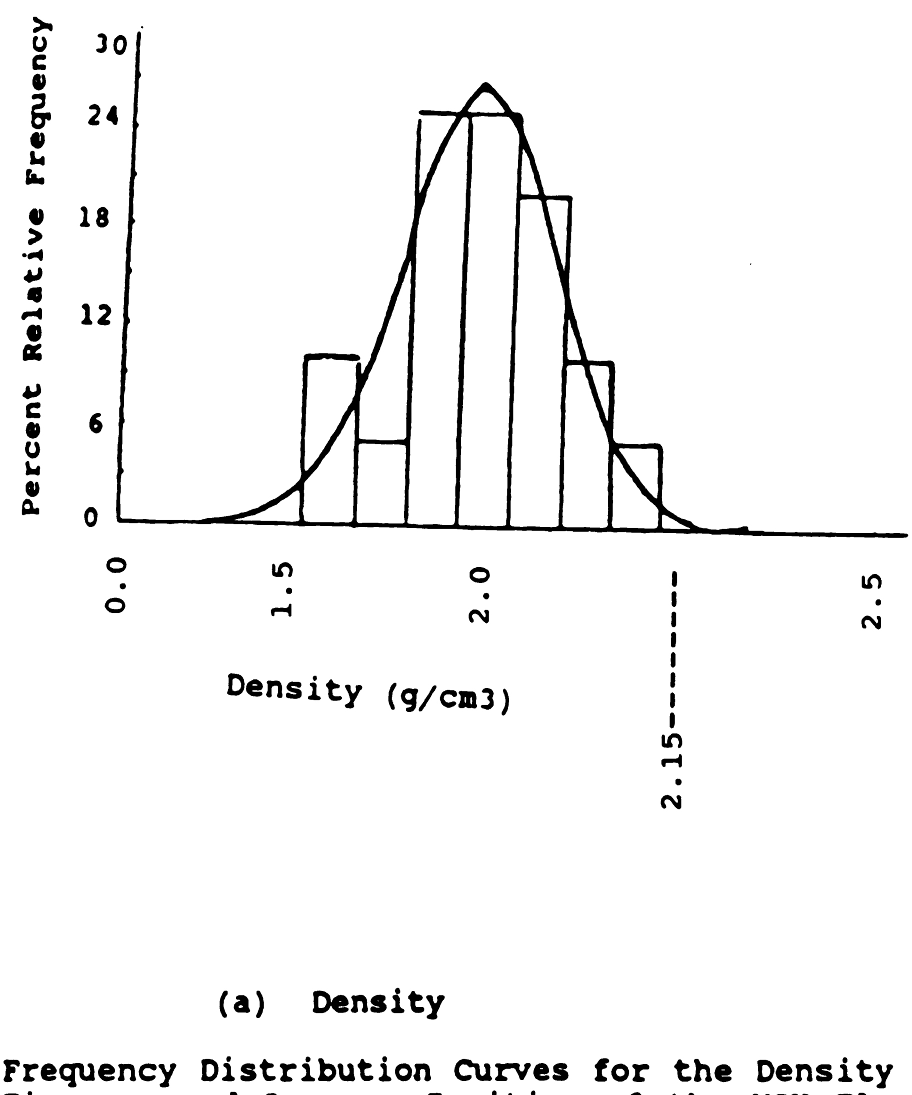


(b) Fineness (%)



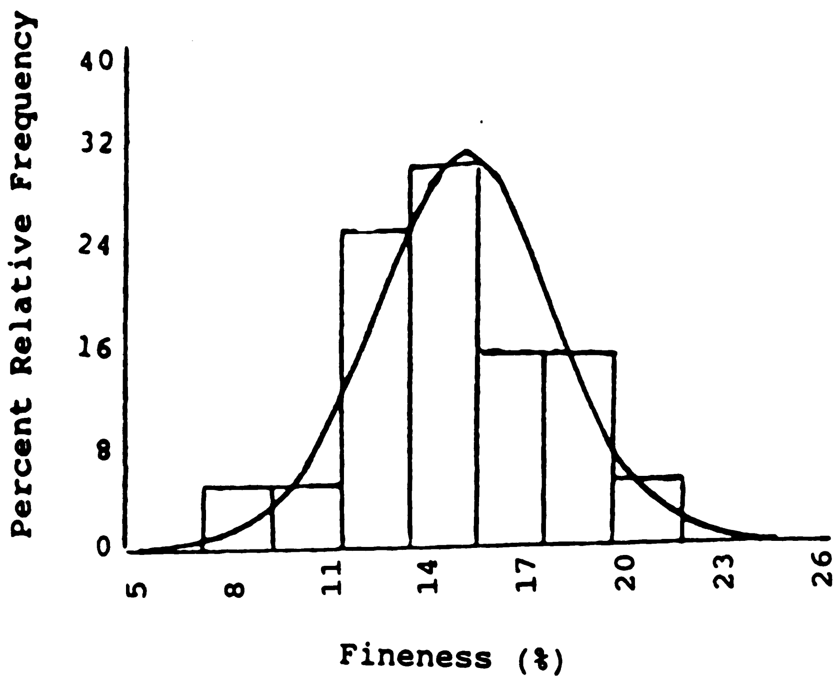
(C) Loss on Ignition (%)

Figure 3.2 Variations in the MSU Fly Ash Properties



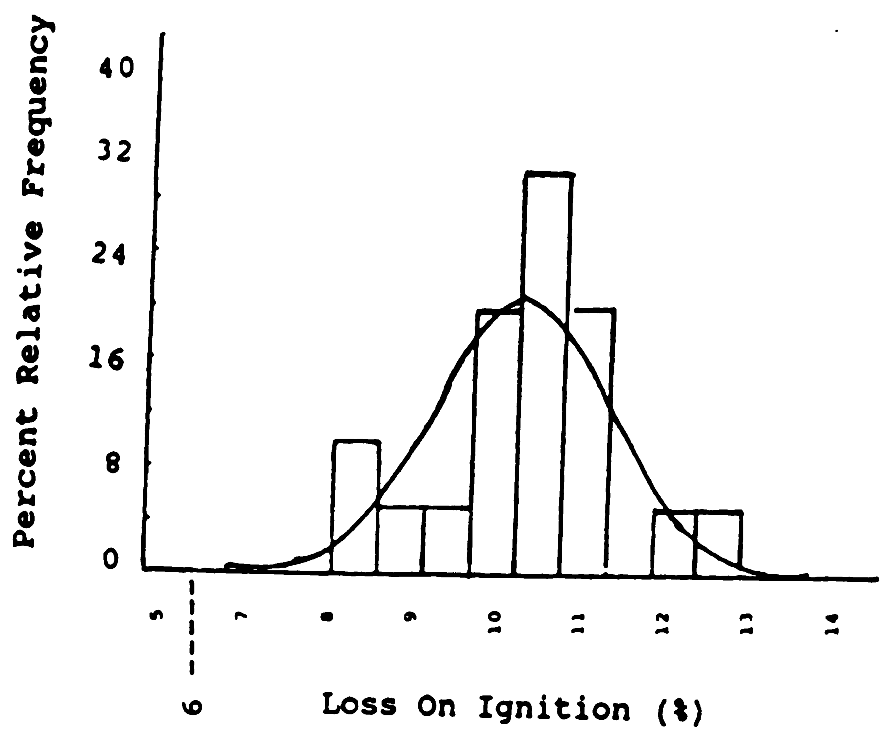
(a) Density

Figure 3.3 Frequency Distribution Curves for the Density Fineness and Loss on Ignition of the MSU Fly Ash



(b) Fineness

Figure 3.3 (continued)



(c) Loss on Ignition

Figure 3.3 (continued)

cases is below the maximum 5 percentage points specified by ASTM C-618. In spite of this, when considering all the samples, the MSU fly ash fails to satisfy the ASTM requirement on the uniformity of fineness. There are no requirements on the variations in loss on ignition (the maximum variation in LOI from average for the MSU fly ash is 21%).

3.4 ANALYSIS OF TEST RESULTS

The MSU fly ash satisfies most, but not all, of the ASTM requirements for class F fly ash. The MSU fly ash, however, fails to satisfy the requirements on soundness, pozzolanic activity index with lime, and uniformity of fineness. It meets the requirements on oxide content, fineness, pozzolanic activity index with Portland cement, water requirement, increase in drying shrinkage, and uniformity of density.

The average soundness (autoclave expansion) of MSU fly ash is 0.95%, exceeding the maximum 0.8% limit specified by ASTM C-618 for class F fly ash. The minimum limit on pozzolanic activity index with lime (specified by ASTM C-618) is 800 psi, while this index for the MSU fly ash is 640 psi. The maximum percentage difference between the fineness of one fly ash sample and the mean obtained for ten samples is 9.5 for the MSU fly ash which exceeds the maximum limit of 5 specified by ASTM C-618. When compared with class C fly ash, the MSU fly ash also fails to satisfy the requirements on loss on ignition (in addition to the unsatisfied requirements for class F fly ash).

The loss on ignition of the MSU fly ash, although satisfying the ASTM requirements for class F fly ash is relatively high. While a 12% maximum limit is specified for the loss on ignition of class F fly ash by ASTM C-618, many local specifications are more restrictive in this regard and typically require less than 6% loss on ignition for fly ashes used in conventional concrete applications. The MSU fly ash with 9.8% loss on ignition, therefore, does not satisfy typical local specifications for use in concrete.

The MSU fly ash does not satisfy all the ASTM C-618 requirements and it is thus not suitable for regular concrete applications. The fact that it does not satisfy the ASTM soundness requirements implies that, in certain conditions, it might produce deleterious expansion in concrete.

The low pozzolanic activity index of the MSU fly ash with lime is another source of concern. This fly ash, however, showed a relatively high pozzolanic activity index with Portland cement. Noting that reactions of fly ash with lime generated by cement hydration is an important cause of strength development in fly ash cement mixtures, the low pozzolanic activity index may be indicative of problems in strength development of fly ash/cement mixtures incorporating Portland cements with high CaO contents.

Finally, the relatively large variations in fineness may lead to inconsistency in concrete properties. For example, the dosage rate of air-entraining and other admixtures required in concrete is partly dependent on the fineness of fly ash. Hence, concrete produced using the MSU fly ash may have variable air content and, thus, variable freeze-thaw resistance, unless the air content is tested frequently and adjustments are made in the dosage rate of air entraining admixture.

The relatively high loss on ignition (a property related to carbon content) of the MSU fly ash reflects the relatively low efficiency of the coal-burning process of the power plant. Improvements in the efficiency of coal-burning could lower the loss on ignition of the fly ash to more acceptable values. Many local specifications are more restrictive than ASTM C-618 in regard to limits on loss on ignition; typical maximum limits on loss on ignition in Michigan are about 4%. Reduced carbon content of the fly ash may also improve other aspects of its performance. For example, the variations in fineness in the MSU fly ash could possibly result from the variations in the amount of large carbon particles. The pozzolanic activity index with lime of the fly ash could also be improved if the amount of large carbon particles (which increases the water requirements for consistency) is reduced.

It should be emphasized that the ASTM C-618 requirements for Class F fly ash were developed specifically for applications of fly ash in Portland cement concrete. The fact that some of these requirements are not satisfied by this specific fly ash do not necessarily imply problems in other applications. The MSU fly ash, as further discussed in the following chapter may be suitable for applications in areas such as flowable fill and cement-stabilized fly ash foundations. Currently, there are no ASTM requirements for fly ash applications in these fields. Hence, the selection of suitable applications for the MSU fly ash should consider the performance requirements in these fields. For flowable fill, the key performance requirements relate to fresh mix flowability, setting time, dimensional stability, strength development with time, and freeze-thaw durability. The performance requirements in the case of cement-stabilized fly ash relate to compactibility, strength development characteristics, permeability, and durability. These issues are further discussed in the next chapter.

3.5 RESULTS OF MICROSTRUCTURAL STUDIES

In order to develop a better understanding of the MSU fly ash and detect its differences from conventional

classes of fly ash, scanning electron micrographs were produced for the MSU fly ash as well as a commercially available fly ash which satisfies the ASTM requirements for class F fly ash (see Table 3.3 for the physical and chemical characteristics of this fly ash and Table 3.1 for the MSU fly ash properties).

Table 3.3: Physical and chemical characteristics of the class F fly ash considered in microscopic studies.

a. Chemical Composition

Component	Sio2	AL2o3	Fe2o3	Tio2	CaO	MgO	K2O	C
% by Weight	47.0	22.1	23.4	1.1	2.6	0.7	2.0	4.3

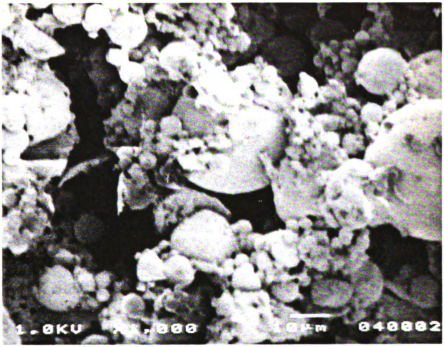
b. Gradation

Sieve or size	0.6mm (600microns)	0.074mm (74microns)	0.045mm (45microns)	0.020mm (20microns)	0.010mm (10microns)	0.005mm (5microns)
% passing	100	92	84	63	36	17

c. Specific Gravity: 2.245

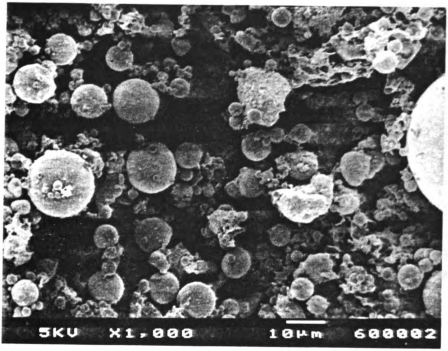
Figures 3.4a and 3.4b present micrographs of the MSU and the Class F fly ash, respectively in as-received conditions. While the class F fly ash consists mainly of round particles with relatively uniform diameters, the MSU fly ash seems to consist of relatively few large spherical particles and a considerable amount of fine particles which are mainly irregular in shape. The irregularity in shape and lack of smoothness in gradation (with many fine and coarse particles, and few particles in between) for the MSU fly ash are expected to negatively influence the workability of fresh concrete mixes incorporating this fly ash. The very coarse particles in MSU fly ash are also expected to be less reactive, a factor which may explain the relatively low pozzolanic activity index with lime of the MSU fly ash.

In order to further study a coarser fraction of the MSU fly ash, this fly ash was sieved (once dry, and once wet) using a #325 sieve. A scanning electrons micrographs were produced for the fraction of the MSU fly ash retained the #325 sieve. Figure 3.5a presents the micrograph with a 1000x magnification for the dry-sieved coarse fraction of MSU fly ash, and Figures 3.5b and 3.5c present micrographs with 200x and 1000x magnifications respectively, of the coarse fraction of wet-sieved MSU fly ash after it has been dried. The washing and drying process seemed to increase



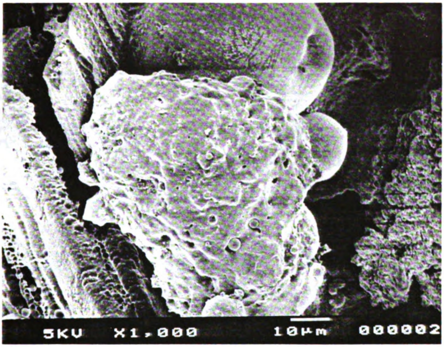
(a) MSU fly ash

Figure 3.4.: Scanning electron micrograph of the MSU and a Class F fly ash (1000x).



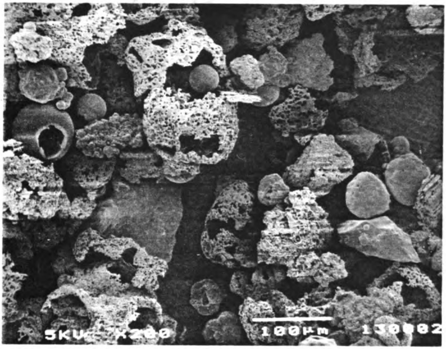
(b) Class F Fly Ash

Figure 3.4 (continued)



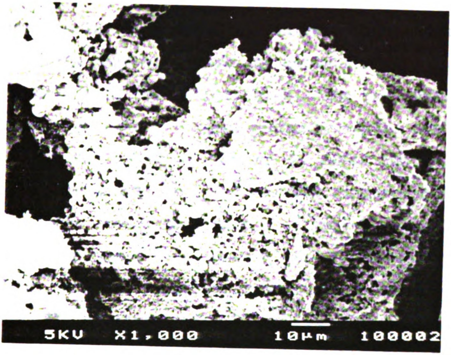
(a) dry sieved (1000x)

Figure 3.5.: Micrographs of the dry-sieved and wet-sieved coarse fraction (particle size greater than 45 microns) of the MSU fly ash.



(b) wet-sieved (200x)

Figure 3.5. (continued)



(c) wet-sieved (1000x)

Figure 3.5. (continued)

the porosity and shape irregularity of the coarse particles of the MSU fly ash as shown in Figure 3.5 b and c. This might be caused by the water solubility of some constituents in coarse particles which could be leached out by water; the drying process may cause further changes in the morphology of coarse particles. The fact that highly porous and irregularly-shaped coarse particles are present in the MSU fly ash when exposed to water can negatively influence the properties of concretes, incorporating this fly ash. The porous particles will tend to absorb water, leaving less water for making the fresh concrete mix workable. Porous particles also tend to consume higher dosages of air-entraining agents, thus reducing the entrained air content and increasing the air-entraining agent requirements.

Finally, the interparticle friction between irregularly-shaped porous particles of fly ash may negatively influence the workability of fresh concrete mixtures.

CHAPTER IV

RECOMMENDED APPLICATIONS OF THE MSU FLY ASH

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RECOMMENDED APPLICATIONS OF THE MSU FLY ASH

4.1 GENERAL

The fly ash produced at MSU satisfies most, but not all, of the ASTM C-618 requirements for Class F and, to some extent Class C, fly ashes used in concrete. This is not a unique situation in Michigan. Utilities operating in Michigan have undergone considerable fuel switching in recent years. One of the consequences of these fuel switching activities has been the production of increased amounts of high carbon fly ash.[6] Michigan utilities have thus devoted major efforts to expand new markets for marginal fly ashes. These efforts have led to development of new application fields for such fly ashes in the recent years.[6]

The growing markets for marginal fly ash can be categorized into three groups:

1. Flowable fill (controlled low strength materials);
2. Cement-stabilized fly ash for highway base courses; and

3. Concrete applications.

Further elaborations on the above application fields as they relate to the MSU fly ash are presented in the following sections.

4.2 FLOWABLE FILL (CONTROLLED LOW STRENGTH MATERIAL)

Flowable fill is an engineered, low-strength material with compressive strength ranging from 50-1500 psi (typically 50-200 psi). The material is generally composed of fly ash, cement and water, or fly ash, cement, fillers, and water which combine to produce a solid mass in a relatively short time. Fillers commonly utilized in flowable fill are sand or some other forms of fine aggregate. A separate mechanical compaction effort is not required to consolidate flowable fill.

Flowable fill has been utilized in light weight fills, trench backfills, utility backfills, mud mats, structural fills, sewer abutments, underwater backfill, foundation backfill, bridge abutment, fills, and slope stabilization. Application volumes for flowable fill may vary from 10 cubic yards for filling abandoned underground storage tanks, to one or more orders of magnitude greater for backfill application over buried plains around residential and commercial basement walls and behind bridge abutments fills.

The Michigan Department of Transportation (MDOT) has a specification for flowable fill that presents a range of mixtures that can be delivered from ready mix concrete plant.[36] The materials section requires a fly ash generally meeting the requirements of ASTM C-618, except that there is no limit on LOI (carbon content).[2] This specification recognizes appropriately that fly ash for controlled low-strength materials does not need the restrictions on carbon content that are imposed on fly ashes used in normal concrete.

The following reasons indicate that the MSU fly ash, with properties discussed in the previous chapter, has potentials for successful use in flowable fill:

(1) Flowable fill has a more porous structure than conventional concrete and it is thus highly permeable. The effect of frost action in flowable fill is expected to be different from that in concrete and air-entrainment does not seem to help in increasing the frost resistance of such a porous media. In such conditions, the relatively high carbon content of the MSU fly ash and the consequent problems with air-entrainment are not causes of major concern in flowable fill.

(2) An important aspect of flowable fill properties relates to the workability and flowability of the material. The water requirements of the fly ash

(for achieving reasonable workability) is thus an important property if this fly ash is to be used in flowable fill. The MSU fly ash has desirable water requirement characteristics which satisfy the ASTM C-618 requirements (see Table 3.1). It is thus expected that the flowability requirements for flowable fill can be conveniently satisfied with the MSU fly ash;

(3) The strength requirements of flowable fill are very modest. In spite of having an acceptable pozzolanic activity index with Portland cement, the MSU fly ash does not satisfy the ASTM C-618 requirements on pozzolanic activity index with lime (see Table 3.1). This may not be a major problem when the fly ash is used in flowable fill, (which does not rely heavily on the strength development characteristics of fly ash). Furthermore, any strength deficiencies can be addressed by adjusting the cement content of the flowable fill.

Flowable fill is playing a growing role in efforts aimed at replacing existing worn out roadways, bridges, sewage systems, and water supply facilities. Expenditures of many billions of dollars are expected to be made over the next decade on replacing the aged infrastructure in Michigan. Fly ash in flowable fill applications is a potential resource for cost-effective rebuilding of many infrastructure components.[33, 34, 35]

4.3 CEMENT STABILIZED FLY ASH HIGHWAY BASE COURSE

The pozzolanic properties of fly ash which enable it to react with lime to form cementitious products have made fly ash a high-quality base/sub-base course material when used with cement to stabilize aggregates and soils, or when used only with cement.[7] In such applications, high-carbon fly ash can be substituted for many conventional materials which are dwindling in supply or escalating in cost.[8] Typical construction procedures utilize standard techniques for central or in-place mixing operations.

The ASTM specification C-593 (fly ash and pozzolanic materials for use with lime) establishes minimum confined compressive strength and durability requirements for mixtures using coarse-grained soils. Unconfined compressive strengthes of 400 psi in seven days under accelerated curing conditions have proven to be quite acceptable.[7,8] The durability requirements of ASTM C-593 relate to the performance of the material under repeated cycles of freezing and thawing.

High-carbon fly ash has been used with cement and lime to modify subgrade soils in order to provide additional permanent support or to expedite construction.[8] Fly ash in these applications reduces the plasticity, improves the drainage characteristics, and reduces the shrinkage of many soils. It also produces a cementitious matrix which further increases the strength and durability of the soil. In-place construction procedures are commonly used for stabilizing or modifying soils with fly ash and cement or lime.

In the specific case of the MSU fly ash, applications to cement-stabilized highway base course are encouraged by the following factors:

1) Strength development in cement-stabilized fly ash results from the mechanisms of physical compaction, and also from cement hydration and pozzolanic reaction of fly ash with the lime produced by cement hydration. Strength requirements for a cement stabilized fly ash are also modest (400-450 psi, 2.75 - 3.09 Mpa, compressive strength at 7 days).[32] Hence, the material relies only partly on the pozzolanic reactivity of fly ash to develop relatively low strengths. The relatively low pozzolanic reactivity of the MSU fly ash with lime is thus of less significance in cement- stabilized fly ash than in concrete.

2. Fly ashes with relatively high carbon contents (about 10%) have been successfully used in cement- stabilized fly ash highway base courses.

This is partly due to the fact that air entrainment (which could be disturbed by the presence of high carbon contents in fly ash) is not the mechanism through which cement-stabilized fly ash develops frost resistance. The potential problems with frost heaving in cement-stabilized fly ash are effectively overcome through stabilization with cement,[32] and the cement content (typically ranging from 5% to 15%) can be adjusted for controlling heave. Hence, the relatively high carbon content in the MSU fly ash is not expected to cause freeze-thaw durability problems in cement-stabilized fly ash.

3. The MSU fly ash has a relatively high soundness, indicating expansive tendencies in the presence of cement. Due to the relatively low cement content in cement-stabilized fly ash materials, however, only a minor pozzolanic reaction would be taking place in large volumes of the material. Thus potentially expansive tendencies may not play a significant role in cement stabilized fly ash materials.

4.4 CONCRETE APPLICATIONS

The ASTM C-618 requirements for fly ash types suitable for concrete applications allow the use of fly ashes with carbon contents as high as 12%. For carbon contents exceeding 6% (as in the MSU fly ash), however, ASTM C-618 requires that the decision on the utilization of a fly ash in concrete should be based on evaluating its performance in trial concrete mixtures. Hence, although the fly ashes used in concrete typically have a carbon content below 6%, high-carbon fly ashes satisfying the ASTM C-618 requirements also have potential for concrete applications.

In the evaluation of a high-carbon fly ash for use in concrete mixtures, one should pay attention to the following effects of the fly ash carbon content on the performance of fly ash concrete mixtures:

1. The required dosage rate of air-entraining agent for the production of sufficient air content in fly ash concrete tends to increase with increasing carbon content of fly ash, and the developed air content with high-carbon fly ash also tends to be unstable during transportation of concrete from plant to the job site.

2. The higher carbon content of fly ash, especially when carbon particles are relatively large, tends to damage the workability of fresh fly ash concrete mixtures, thus increasing the water requirements for workability.

3. The increase in carbon content of fly ash reduces the pozzolanic reactivity of fly ash, and thus reduces the effectiveness of fly ash in increasing the strength, sulfate resistance, and impermeability of fly ash concrete.

The rate of hydration heat generation and the alkali-aggregate expansion of fly ash concrete also tend to increase with increasing carbon content of fly ash.

4. Fly ash concretes incorporating high-carbon fly ashes may require longer curing periods in order to develop their full strength.

5. High-carbon fly ashes may influence the color of concrete surfaces.

In order to specify a high-carbon fly ash for specific concrete applications, trial batches must be made and tested, with due consideration given to the above concerns in order to develop proper mix proportions for specific job conditions.

Regular concrete applications have low priority for the MSU power plant fly ash, which fails to satisfy the ASTM C-618 requirements on soundness and pozzolanic activity index with lime. The relatively high variations in the fineness of this fly ash cause further problems in the proportioning of concrete mixes with the MSU fly ash. Flowable fill and cement stabilized fly ash seem to provide more promising areas for the applications of the MSU power plant fly ash.

CHAPTER V

SUMMARY AND CONCLUSION

CHAPTER V

SUMMARY AND CONCLUSION

About 60,000,000 tons of fly ash is produced annually by the combustion of coal in U.S. electric power plants. About 20% of this fly ash is now being consumed in different utilization categories, including cement and concrete products, structural fills and road bases. These applications are encouraged by technical advantages, cost savings and ecological benefits.

In cement and concrete applications, fly ash can be partially substituted for higher-cost cement to provide enhanced fresh mix workability, higher strength, chemical resistance, impermeability, and reduced heat of hydration and alkali-aggregate reactions. The fly ash concrete mixtures should be properly proportioned and cured in order to avoid reducing the air content and delaying the development of strength.

ASTM C-618 provides the basis for characterization and classification of fly ashes which are suitable for concrete applications. Two classes of fly ash are distinguished: Class F and Class C. Class F fly ashes have pozzolanic properties and their loss on ignition (carbon content) can reach as high as 12%. Class C fly ashes have both pozzolanic and cementitious properties and their maximum loss on ignition is 6%. The research reported herein has been concerned with the characterization of the MSU fly ash and identification of application fields which best suit the properties of this specific fly ash.

In order to characterize the MSU fly ash and assess its action in concrete, three samples, each representing 400 tons of fly ash, were taken in the winter of 1989 following the ASTM C-618 guidelines. Studies on fly ash uniformity were conducted on ten samples, each representing 400 tons of the MSU fly ash.

The following tests were conducted for the characterization of the MSU fly ash:

- Moisture content
- Loss on ignition
- Oxide content
- Density
- Increase of drying shrinkage of mortar bars
- Soundness
- Limits on amount of air entraining admixtures in concrete
- Air entrainment of mortar
- Pozzolanic activity index with Portland Cement
- Water requirement
- Pozzolanic activity index with lime

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- **Foam index**

The uniformity of the MSU fly ash was evaluated through conducting the specific gravity and fineness (ASTM C-618) as well as the loss on ignition tests on ten samples of fly ash in order to assess the variations in fly ash quality.

Microstructural studies were also conducted on the MSU fly ash (as received) and the fraction of this fly ash which is greater than 45 microns (after dry and wet sieving of the fly ash). Scanning electron microscopy techniques were used in these microstructural studies.

The MSU fly ash was observed to satisfy most, but not all, of the ASTM requirements for physical and chemical properties as well as fly ash action in concrete. The requirements on the uniformity of the fly ash density was satisfied by the MSU fly ash. The MSU fly ash, however, did not satisfy the requirements on the uniformity of fineness. The carbon content of the MSU fly ash, although satisfying the ASTM C-618 requirements for class F fly ash, is near the upper limits specified by ASTM C-618. This is by no means a unique situation in Michigan, where utilities have been producing increasing amounts of high-carbon fly ash in the recent years (due to some fuel-switching activities). Michigan utilities have successfully expanded new markets for high-carbon fly ash in the following applications:

- Flowable Fill
- Cement stabilized fly ash for highway base course
- Concrete Applications

The MSU fly ash has potentials for use in any of the above applications, although concrete applications can be materialized only if some changes are made in the coal-burning process at the MSU power plant. An efficient burning of coal at the MSU power plant can potentially improve not only the loss on ignition, but also the uniformity of fineness and the pozzolanic activity index with lime as well as many other properties of the MSU fly ash.

Factors encouraging applications of the MSU fly ash in flowable fill include: (1) the porous nature and high permeabilty of flowable fill eliminate the need for air entrainment for the development of frost resistance. The relatively high carbon content of the MSU fly ash, which interferes with the air entrainment process, is thus not cause of major concern; (2) the MSU fly ash, in-spite of its low pozzolanic activity index with lime, should still be capable of satisfying the modest strength requirements in flowable fill applications; and (3) the relatively high soundness of the MSU fly ash which is indicative of expansive tendencies in the presence of cement, is a cause for less concern in flowable fill which incorporates minimal cement contents and thus produces minor pozzolanic activity in a relatively large volume of material.

In the case of cement-stabilized fly ash, the following factors encourage this application of the MSU fly ash: (1) cement-stabilized fly ash relies as much on compaction efforts for strength development as on cement hydration and pozzolanic reaction of fly ash. The low pozzolanic activity index of the MSU fly ash with lime is not thus a major problem in this application which has relatively modest strength requirements; (2) air entrainment is not the mechanism through which frost resistance is developed in cement-stabilized fly ash. Hence, the relatively high carbon content of the MSU fly ash is not a major cause for concern in this application; and (3) cement-stabilized fly ash incorporates relatively low cement contents and thus expansive tendencies associated with pozzolanic reactions, which seem to be a problem in concrete applications due to the relatively high soundness of the MSU fly ash, would be a cause for less concern in cement-stabilized fly ash where minor pozzolanic activities take place, noting that relatively low cement contents are placed in this application in a relatively large volume of material.

Microstructural studies on the MSU fly ash indicated that this fly ash, when compared with typical class F fly ashes, has a relatively low fraction of round particles which are typically large in size. The gradation of particle sizes in MSU fly ash is not smooth and a relatively high fraction of fine and irregularly-shaped particles are present in this fly ash. Washing and drying seem to make large particles of the MSU fly ash porous and highly irregular in shape, indicating the presence of soluable compounds in this fly ash.

Shortage of round particles, lack of a smooth gradation, and increase in porosity and irregularity in shape of the MSU fly ash particles all negatively influence the workability of fresh concrete mixtures incorporating this fly ash. The porous particles also tend to consume higher dosages of air entraining agents, further interfering with the process of air entrainment in concretes incorporating the MSU fly ash. Larger fly ash particles, which constitute a relatively high fraction of the MSU fly ash, are also less reactive, a factor which can illustrate the relatively low pozzolanic activity index with lime of the MSU fly ash.

APPENDICES

APPENDIX I

FLY ASH PRODUCTION AND USE IN CONCRETE

APPENDIX I

FLY ASH PRODUCTION AND USE IN CONCRETE

Fly ash is finely divided residue that results from the combustion of ground or powdered coal.

The present annual world combustion of coal in electrical power plants is about 4 billion metric tons, resulting in the precipitation of about 400 million tons of fly ash. Handling and disposing of such large amounts of fly ash as waste is not economically or environmentally sound if viable alternatives exist.[9]

Traditionally, the cement and concrete industries have significant markets for fly ash. Basically, fly ash is being used as a partial replacement of Portland cement in concrete and concrete products, as an ingredient in blended cement (IP cement), and as a raw material for cement production. Fly ash is used in concrete not only for economical and ecological benefits, but also to improve the properties of concrete. The improvements in concrete properties resulting from the use of fly ash (either as a separately batched material or as an ingredient in blended cement) result mainly from the favorable effects of fly ash on fresh mix workability, and also from the pozzolanic properties of fly ash. pozzolanic materials including fly ash possesses little or no cementitious value by themselves but, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.[10] The calcium hydroxide required for the pozzolanic action of fly ash in concrete is generated by the hydration of cement.

Four major incentives can be distinguished for the serious consideration of fly ash applications to concrete, which impact on far more than only the construction material industries:[11]

1. The beneficial use of a material that would otherwise have been wasted, is environmentally acceptable in land filled operations.
2. A reduction in the average amount of energy required for the production of a cubic yard of concrete.
3. The ability to provide an alternative for reducing the demand for portland cement during periods of exceptionally high demand, thus reducing construction delays and the need for cement.
4. The ability to provide concrete with certain improvements in quality which could not be otherwise reached economically.

Concrete is by far the most-used solid commodity in the world and is, literally, the fundamental material for housing and industrial construction. Fly ash has been increasingly used in different countries as a substitute for part of the cement in the production of concrete. Table I.1 gives a few figures to demonstrate the order of magnitude of fly ash utilization in cement as a fraction of total collected quantities. This gives a rough idea of the achievements and opportunities in the field. In a number of countries, including the United States and Canada, there seems to exist major opportunities for increasing the utilization of fly ash in the cement and concrete industries.

Table I.1: Percentage of Collected Fly Ash Used in Cement and Concrete in Eight Countries[12]

Country	%	Year
France	24	1978
UK	19	1978
Poland	14	1975
Denmark	14	1981
W. Germany	8-10	1978
U.S.	6	1978
Canada, Ont.	3	1978
India	1	1978

APPENDIX II

ACTION OF FLY ASH IN CONCRETE

APPENDIX II

ACTION OF FLY ASH IN CONCRETE

This section describes the mechanisms through which fly ash modifies the fresh concrete mix workability and air content, the process of cement hydration, and concrete engineering properties.[13]

II.1. Fresh Mix Workability and Air Content

One of the main advantages of using fly ash in concrete is that many fly ashes improve the workability of concrete, thereby permitting reductions in water content. This water reduction is extremely important, as it affects all concrete properties; therefore, it should be properly understood. The water reduction is commonly attributed to the spherical shape of many of the fly ash particles, by analogy with similar effects of microscopic aggregate particles. It has, however, been suggested that[14] for flocculents such as cement paste, besides the shapes of individual particles, the floc sizes distribution and the strength of the interparticle forces also determine the flow.

The flow and workability of mortar and concrete (incorporating aggregates) depends upon not only paste consistency but also on its volume. The volume of pastes is important in producing adequate separation of aggregate particles. Fly ash can be used to increase the volume without increasing the water or cement content.

The particles of the dispersed aggregates for achieving desirable levels of consistency must be at least equal to the largest particles of cement or fly ash that are present in significant amounts. Hence, the volume of paste required for a given mortar or concrete consistency depends upon the paste volume as well as the maximum size of the particles in the paste. It has been shown that the fineness of fly ash has a strong effect on the workability of the resulting fly ash concrete. The loss on ignition of fly ash also influences fresh mix workability because of absorption of water by porous carbon particles. In general, finer fly ashes which have a higher loss on ignition tend to lead to fly ash concretes with higher water requirements and therefore lower strengths.[14]

Fly ash may also affect the air content in fresh concrete and the stability of entrained air. The form of carbon particles in fly ash may be very similar to porous activated carbon, which is a product manufactured from coal for use in filtration and absorption processes. In concrete, the porous carbon particles can absorb air-entraining admixtures, thus reducing their effectiveness.[15] Adjustments must be made as necessary in the admixture dosage to provide fly ash concrete with desirable air-contents at the point of placement. To maintain a constant air content, admixture dosages must usually be increased depending on not only the carbon content, but also on the fineness and the amount of organic materials in the fly ash.[10] Cement type and alkali content, and water-to-cement ratio are also among the important factors deciding the effectiveness of air-entraining agents in fly ash concrete.

The presence of fly ash in concrete also seems to influence the rate of loss in concrete air content with prolonged mixing or agitation prior to placement. There appears to be a relationship between the required dosage of air-entraining admixture to obtain the specified air-content and the loss of air content in fly ash concrete over time.

II.2. Hydration Process

Fly ash is characterized as an artificial pozzolan. "Pozzolans" are defined as[16] natural artificial solids involving constituents which react with Ca^{2+} or $CaOH_2$ and form new binding compounds in the presence of water. The constituents may be mineral, crystalline, and non-crystalline materials, and glasses. "Pozzolanic reactivity" is defined as an index of the reaction degree at ordinary temperatures between pozzolans and Ca^{2+} or $CaOH_2$ with water, or between pozzolans, water and minerals which produce $CaOH_2$ in the presence of water.

The pozzolanic reaction of fly ash in concrete involves fly ash reaction in hydrating Portland cement with the lime which is liberated by the hydrating C_3S and C_2S (which are some key cement compounds) leading to the formation of additional C-S-H (a key cement hydration product) which precipitates in the pores of cement pastes.

There are three broad areas of interest regarding the reaction chemistry and pozzolanic activity which differ considerably with the composition and reactivity of different fly ashes, the vs forming the basis for classifying fly ashes into "Class F" bituminous coal fly ashes and "Class C" lignite and sub-bituminous coal fly ashes. The three areas are:[17]

1. The effects of fly ash on the early reactions;
2. The long-term reaction and composition of hydration products after sufficient curing; and
3. The way in which the pore spaces are filled with reaction products (which directly affects strength development and durability).

The effects of fly ash on the early hydration chemistry of Portland cement depends mainly on the rate of release of water-soluble phases and also on the amount and kinds of solid surfaces provided for the early formation of the reaction products. Soluble alkalies and sulphates are most important for the control of the reaction of tri-calcium aluminates (C_3S) in Portland cement; they also influence the rate of hydration of calcium silicates (C_2S). The early rate of reaction is accelerated by the presence of fine powders, and also influences the spatial distribution of the hydrates as well as the physical properties.[17]

The heat generated by cement hydration fly ash pozzolanic reactions in Portland Cement is an activator of fly ash, which causes an increase in the density and ultimate strength characteristics of concrete. Hence, heat, in addition to lime, alkalies and sulfates, is also an activator and accelerator of the fly ash reactions in concrete.

The composition of fly ash concrete hydration products after long-term curing depends upon the proportion of reactive materials in fly ash and Portland cement (or lime). The aluminum-silicate glasses in fly ash react with calcium hydroxide to produce low lime content calcium silicate hydrates and gephenite hydrates with lower lime/silicate and lime/alumina ratios than the ordinary hydration products of Portland cement.[17]

Strength development of hydrating Portland cement has been reasonably well understood for many years, but it does not appear that similar descriptions have been adequate for fly ash cement mixes. The process is more complex because of the differences in the rate of reaction, differences in reaction products, and intricate porosity of some of the fly ash particles.

II.3. Engineering Properties

The actions of fly ash in concrete described above lead to the following effects on engineering properties of concrete:[18]

1. The workability of fresh concrete is influenced by the incorporation of fly ash; many but not all fly ashes reduce water demand and the "harshness" of fresh concrete mixtures is usually reduced with fly ash, promoting a creamier texture and body of the material.
2. Most fly ashes increase the dosage rate of air-entraining admixture required for achieving a certain air-content, and also accelerate a loss of air from concrete in prolonged mixing and agitation conditions.
3. Fly ash concrete typically has lower water content than conventional concrete, and thus it has a lesser tendency to bleed.
4. Most fly ashes have some retarding influences on set, especially at low temperatures.
5. Heat evolution at early ages is usually reduced in fly ash concrete as compared to conventional concrete mixes.

6. Most fly ashes reduce the early rate of strength gain when incorporated in concrete. This is less true for high calcium fly ashes. Often, fly ashes incorporation permits redesign of concrete mixes so as to eliminate early strength differentials.

7. Fly ash usually increases the strength of concrete at later ages, with the "cross-over" being at about a month or so.

8. Fly ash effects in concrete tend to be pronounced through thermal and steam curing.

9. Fly ash incorporation modifies the pore structure and pore system distribution of pastes and presumably of concretes into which it is incorporated. Capillary space may be increased at early ages, but a more compact structure may eventually develop. use of superplastizers seems to accelerate phenomenon.[19]

10. The compact structure of fly ash concrete generally leads to reduced permeability of the material when compared with conventional concrete. Through its pozzolanic properties, fly ash chemically combines with calcium, potassium and sodium hydroxides to produce C-S-H, thus reducing the amount of calcium hydroxide, which is water soluble and thus leads to leaching of concrete. The reaction between siliceous parts in fly ash and the alkali hydroxide in the Portland cement paste consumes alkalies, and reduces

their availability for expansion reaction with reactive silica aggregate. The use of adequate amounts of some fly ashes can reduce the amount of aggregate reaction and reduce or eliminate harmful expansion of concrete.

11. Some fly ashes, however, add some alkali to that already available in the cement, leading to an increase in the alkali-hydroxide concentration in concrete pore water. This may be beneficial to the preservation of embedded steel, but may lead to greater, rather than lessened, likelihood of alkali-aggregate reactions. Other fly ashes may have substantial alkali contents, but do not readily liberate the alkalies; these alkalies are apparently tied up in relatively insoluble glass.19

12. The composition of the glass, especially calcium aluminate glass found in high calcium fly ashes, may influence resistance to sulphate attack of concretes in which fly ashes are incorporated. As a general rule, **Class F fly ash** will be found to improve the sulfate resistance of any mixture in which it is included. Evidence suggests that **Class C fly ashes** may reduce sulfate resistance when used in normal proportions. Others suggest that using **Class C fly ash** at relatively high proportions of the total mix

cementitious materials may yield mixtures with improved sulphate resistance.

APPENDIX III

FLY ASH EFFECTS ON CONCRETE DURABILITY

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Concrete construction must be durable when exposed to natural weathering and aggressive environments. It must also be sound, i.e., it must not undergo internal disruptive reactions that cause deterioration.

This section deals with the fly ash effects on durability characteristics of concrete. In particular, the permeability, carbonation and steel corrosion, sulfate resistance, and alkali-aggregate reaction of fly ash concrete are discussed.[15, 20]

III.1. Fly Ash Effects on Concrete Permeability and Corrosion of Steel

Continued long-term pozzolanic reaction of fly ash in concrete reduces the size of pore spaces in cement paste.[13] Permeability and the rate of diffusion of moisture and aggressive chemicals into concrete is thus reduced. This, in turn, reduces the danger of damage due to steel corrosion.[20]

Some fly ashes add soluble alkali to that already available from cement, leading to an increase in alkali hydroxide concentration in pore solution. This may be beneficial in preserving passivation of embedded steel, thus reducing the possibility of steel corrosion in concrete. Some fly ashes with substantial alkali content do not readily liberate these alkalies (they are apparently tied up in relatively insoluble glass).

Another factor deciding the potential for steel corrosion is the **carbonation** resistance of concrete.[16] Carbonation effects can reduce the passivation of embedded steel, thus encouraging steel corrosion.

The presence of fly ash in concrete is suggested by **Nagatoki, Ohga, and Kim**[16] to reduce the depth of carbonation in concretes with comparable water contents. **Roper, Kirkby and Baweja**[20] on the other hand, suggest that fly ash might increase the carbonation effects on concrete; they, however, concluded that fly ash concrete provides embedded steel with a protection against corrosion which is at least as good as that of Portland cement. In studies of fly ash effects on the carbonation resistance of concrete, one should consider that the key factor deciding carbonation effects is the **water cement ratio** of concrete. Fly ash can increase the carbonation resistance of concrete by reducing the water content, while maintaining the compactibility of concrete at a desirable level.

III.2. Sulfate Resistance

Sulfate attack possibly represents the most wide-spread and common form of chemical attack on concrete. Sulfates are often present in groundwater particularly when high proportions of clay are present on the soil. Sea water also has sulfates as a major constituent. Groundwater may have local concentrations of sulfates in the vicinity of industrial wastes, such as mine tailing, slag and rubble-fills. Sulfates present in laying water from pollution, or produced by biological growths, may cause slow deteriorations even in concrete above ground.[21]

Sulfate attack can be considered as a sequence of three processes, as outlined below:

1. The first process is the diffusion of sulfate ions into the pores of the concrete, which is controlled by the permeability coefficient for sulfate ions.

2. Sulfate attack starts with an initial reaction between sulfate ions and calcium hydroxide resulting in the formation of gypsum.

3. The gypsum reacts with the C_3A of Portland cement to form **ettrigite**, leading to a very large increase in solid volume which causes a volume expansion within the pastes, and which generates internal stresses causing internal cracking. The subsequent increase in

concrete permeability accelerates further sulfate attack.[21]

The water-cement ratio is an important factor in controlling sulfate attack because it determines the permeability of concrete. The use of **Type V cement** (which has relatively low C_3A content) or the use of blended cements (incorporating pozzolans) can also improve sulfate resistance. Curing in high pressure steam at temperatures above 100°C, with the use of **silica additives**, removes calcium hydroxide from the hydrated cement paste and causes formation of alternative cement hydration products, which lead to higher resistance to attack by sulfate ions.

Although calcium hydroxide does play an important role in sulfate attack, the successful ability of a cement to resist sulfate attack depends on how much ettrigite can potentially form. This can usually be related back to the C_3A content of cement. The form of aluminum that occurs in some pozzolans can also react with sulfates to form ettrigites, and this should be kept in mind when using such admixtures.[19, 22]

Fly ash, by its continued long-term reaction with concrete, reduces the size of the pore spaces in the cement paste phase of concrete. Permeability and the rate of diffusion of moisture and aggressive chemicals into concrete is reduced, thereby reducing the danger of damage due to sulfate attack.[22, 23] The continued reaction of fly ash with calcium hydroxide in concrete, which reduces the **calcium hydroxide** content and forms additional **calcium silicates hydrates**, helps in reducing the sulfate attack in concrete.[23] As a general rule, **Class F** fly ash will be found to improve the sulfate resistance of any mixture in which it is included. The situation with **Class C** fly ash is somewhat less clear. Evidence suggests that some **Class C** fly ashes may reduce sulfate resistance when used in normal proportions.

The sulfate resistance of fly ash concrete is influenced by the same factor which affects concrete without fly ash; **water-binder ratio, curing condition, and exposure**. The effects of fly ash on sulfate resistance will be dependent upon the type, amount, and individual chemical and physical characteristics of the fly ash and cement used. Ref. 11 suggests that the composition of glass, especially of calcium alluminate glasses found in high calcium fly ash, may influence resistance to sulfate attack of concretes in which those fly ashes are incorporated. Ref. 25 presents an indicator **(R-value)** of the relative sulfate resistance of a fly ash as the ratio of calcium to alluminum oxide.[24, 25, 26]

$$R = \frac{\text{Percent CaO} - 5}{\text{Percent } Fe_2O_3}$$

The higher the R-value of fly ash, the lower the sulfate resistance of the resulting concrete.

III.3. Alkali-Aggregate Reaction

The reaction caused by a chemical reaction between the alkalies contained in the cement paste and certain reactive forms of silica within the aggregates can lead to extensive map cracking or pattern cracking on the concrete surface, frequently accompanied by gel exgilding from the cracks, or leading to spalling and surface deterioration. **Opal and chit** are common forms of reactive silica, but the list is considerably broader, and naturally occurring volcanic glasses constitute a wide-spread form of reactive silica.[19, 27, 28] The mechanism of alkali-aggregate reaction is suggested to involve four steps:

1. Initial alkali development and dissolution of reactive silica;
2. Formation of hydrous alkali silica gel;
3. Attraction of water by the gel;
4. Formation of fluid sol (a dilate suspension of colloidal particles.

During Steps 1 and 2, the integrity of aggregate particles tends to be destroyed. The attraction of water by the gel in Step 3 is accompanied by a volume expansion, which might crack the weakened aggregate and the surrounding cement pastes. The final step takes place after the critical expansion has occurred, when further injection of water turns the solid gel into a fluid sol which escapes into the surrounding cracks and voids.

Secondary reactions with calcium hydroxide in the cement paste may also take place, forming deposits of a calcium alkali-silica gel at the periphery of distressed aggregates.

Pozzolanic admixtures such as fly ash are commonly stated to control the expansions associated with the alkali-aggregate reaction (see Figure III.1). One reason suggested for the beneficial effects of pozzolans is that they react with the calcium hydroxide in the paste and thus lower the pH of the pore solution.[29] The highly reactive silica in a finely divided pozzolan may consume the alkali in the cement in a rapid but harmless alkali-pozzolan reaction which proceeds rapidly to Step 4 above with damaging reactions of Step 3. Reduced permeability of concrete in the presence of fly ash may also help to limit the supply of water needed to cause the alkali-silica reactions.[19, 30, 31]

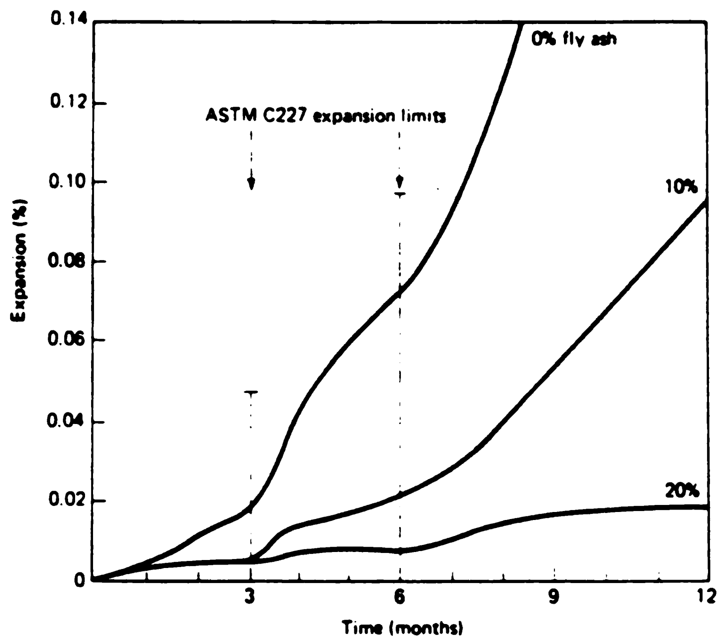

Figure III.1: Effects of Fly Ash Additions on the Process of the Alkali-Aggregate Reactions[19]

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