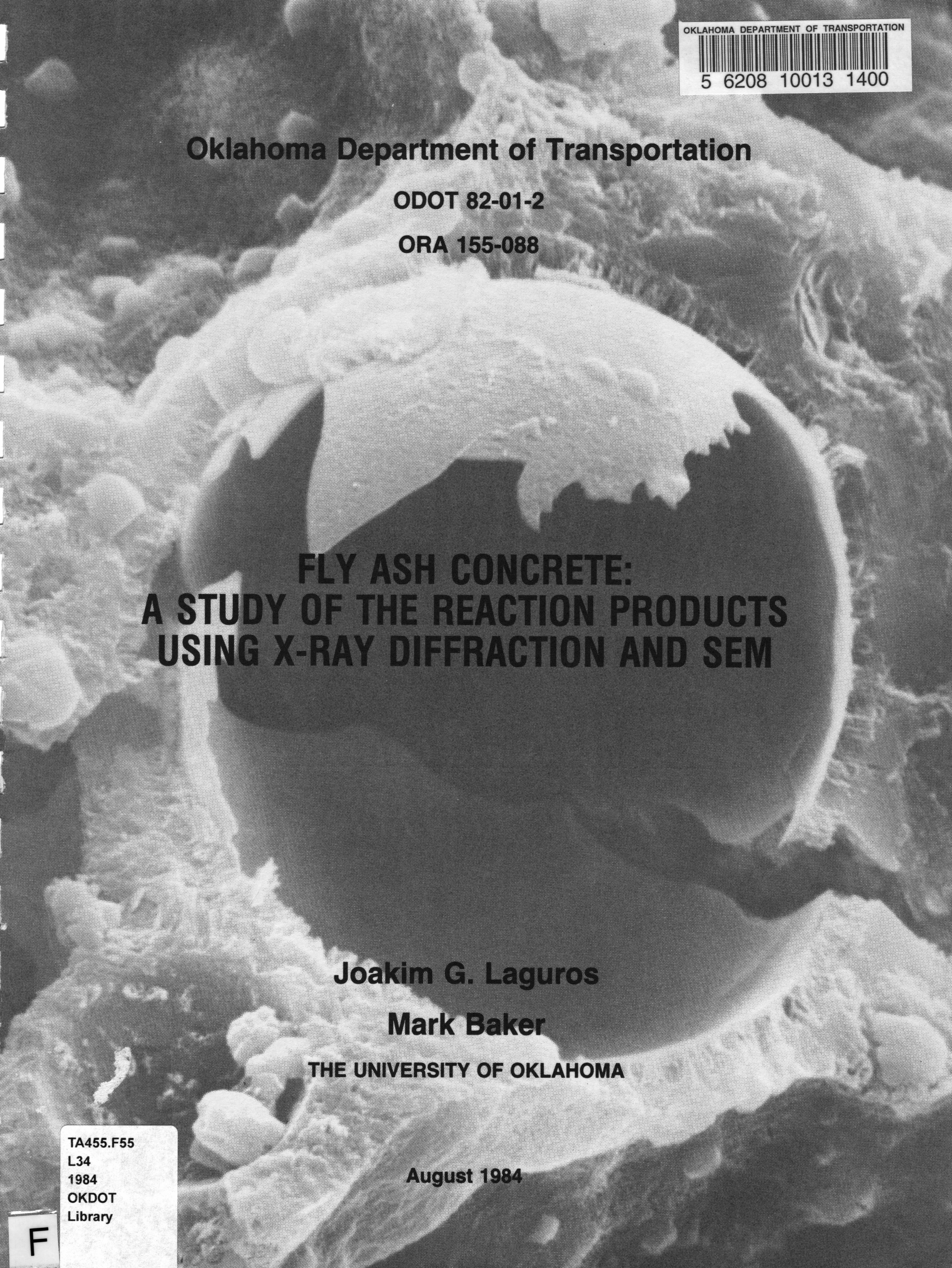

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FLY ASH CONCRETE:
A STUDY OF THE REACTION PRODUCTS USING X-RAY DIFFRACTION AND SEM

Joakim G. Laguros

Mark Baker

THE UNIVERSITY OF OKLAHOMA

August 1984

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FLY ASH CONCRETE: A STUDY OF THE REACTION PRODUCTS USING X-RAY DIFFRACTION AND SEM

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16. ABSTRACT

The setting and strength gaining process of P.C. concrete containing Class C high calcium fly ash were related to the reaction products which were identified using X-ray diffraction and scanning electron microscopy (SEM).

Four fly ash concrete mixes (20, 30, 40 and 50 per cent replacement of cement by fly ash) and similar paste mixes were compared to control mixes for cure periods up to one year. Setting time and early compressive strength were adversely affected by the addition of fly ash. Beyond one week all of the fly ash concrete mixes gained strength at a faster rate than the corresponding control mixes. X-ray diffraction studies suggest that the retardation mechanism may be associated with the high levels of ettringite formed early in the hydration process and its conversion to monosulfoaluminate. A decrease in the level of calcium hydroxide, typical of pozzolanic activity, was not in evidence. SEM micrographs of fly ash spheres in concrete in various stages of hydration reveal an intricate crystal framework and a simple heat of hydration test is presented which helps explain strength gains observed.

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PREFACE

In cooperation with the Oklahoma Department of Transportation a research project was undertaken in 1981 by the University of Oklahoma Office of Research Administration to study the use of fly ash in concrete and specifically the reaction products of fly ash concrete mixes using X-ray diffraction and scanning electron microscopy (SEM).

During the course of this effort, which was conducted by the School of Civil Engineering and Environmental Science, reports were submitted quarterly, and the present constitutes the final report.

The opinions, findings and conclusions expressed in this publication are those of the authors and not necessarily those of the Oklahoma Department of Transportation.

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SUMMARY

In evaluating the differences between plain P.C. concrete and fly ash concrete a series of tests were performed on mix designs of 0, 20, 30, 40 and 50 percent replacement of Portland cement by class C high calcium fly ash. The tests employed both qualitative and quantitative means covering a curing period of up to one year. The X-ray diffraction and scanning electron microscopy (SEM) tests were selected to monitor the chemical composition and crystalline structure of the cementitious minerals participating in the hydration process. These observations combined with the compressive strength data as well as time of set and heat of hydration provide insight especially into the early stages of the hydration process.

The replacement of Portland cement by the type of fly ash used in this study lowers the short term (up to seven days) compressive strength of concrete but increases its long term strength. Furthermore, the strength decrease and retardation of set are directly proportional to the amount of fly ash replacing Portland cement. It appears, however, that certain boundary

conditions are in force such that at high replacement percentages flash setting occurs while for low percentages fly ash causes a retardation of time of setting.

The source of strength is attributed to the early formation of ettringite ($C_3A\bar{S}_3H_{32}$) whose eventual conversion of monosulfoaluminate ($C_3A\bar{S}H_{13}$) causes an increase in the late compressive strength in a way that the higher the amount of fly ash the more rapid the conversion. Too, the size and spherical shape of fly ash contribute to strength gain because they provide a more compact gel and lower the water-solids ratio.

SEM pictures show gel formation about the individual fly ash particles and also a range of reactivity among the various particles.

In general, the addition of fly ash decreases the peak heat of hydration and delays the time in reaching the peak heat. This behavior is believed to be caused by the physical dilution of the Portland cement and by the chemical retardation introduced by fly ash.

It is recommended that better understanding of fly ash concrete will be gained by extending this investigation to cover durability studies, X-ray fluorescence and energy dispersive techniques associated with SEM.

CHAPTER 1

INTRODUCTION

For many years fly ash has been used as an ingredient in Portland cement (P.C.) concrete. Through most of this period, specification writers have considered fly ash as a pozzolanic material, that is, a material which by itself has no cementitious value but in the presence of moisture and calcium hydroxide forms compounds possessing cementitious properties. These pozzolanic fly ashes have been classified under ASTM C618 as Class F fly ashes.

Over the past decade, however, another type of fly ash has gained prominence which contains less pozzolanic material but it possesses cementitious properties of its own. The 1977 version of the ASTM C618 specification recognized this type of fly ash and by adding a new classification, Class C, it differentiated between the two types.

Presently, the state of Oklahoma has an abundant supply of high quality Class C fly ash. As a result of rising costs of cement and energy and the need to find an environmentally acceptable market for this fly ash, greater interest is being shown in its use as an ingredient in ready mixed P.C. concrete. While much research has been conducted with the Class F fly ashes, which are common in the eastern regions of the United States, relatively little is known about the fly ashes produced in Oklahoma or any other Class C fly ash. Consequently, local ready mixed P.C. concrete producers as well as state agencies have been reluctant to widely accept fly ash as an additive in concrete.

Confidence in fly ash concrete will come only through experience and research. Of greatest concern is the lack of knowledge of the chemical processes which occur in fly ash concrete. Understanding such processes would provide insight into problems such as the limits of fly ash concrete strength and durability as well as the time of set. Thus, the present study was undertaken to evaluate the differences in the reaction products of plain P.C. concrete and fly ash concrete in which fly ash is used as a partial replacement ingredient for Portland cement. Specifically, the emphasis of the study is upon the chemical composition and crystalline structure of the reaction products and their role in the compressive strength of concrete.

A number of standard concrete tests were conducted to determine the compressive strength, setting time, slump, air content, and unit weight. Additionally, a crude test for measuring the heat of hydration of the pastes was also devised and utilized. To help interpret the results of these tests, X-ray diffraction testing and Scanning Electron Microscopic (SEM) observations were employed to determine the chemical composition and reaction products of the concrete.

CHAPTER 2

REVIEW OF LITERATURE

2.1. General

The engineering properties of concrete are greatly influenced by the physical and chemical characteristics of its constituents and primarily those of the cementitious materials. Since fly ash used in concrete is typically classified as a cementitious material, variations in either its physical and/or chemical characteristics have a very pronounced effect upon its role in concrete. The first section of this chapter reviews the production, classification and properties of fly ash while the second section addresses the effects of fly ash on the engineering properties of concrete. These effects are more closely examined in the final section of this chapter in which a review of the literature concerning the hydration process is presented.

2.2 Production, Classification and Properties of Fly Ash

Simply defined, the term "fly ash" refers to the by-product produced from the combustion of coal. More specifically, it is a very fine, light weight dust of inorganic residues produced from the combustion of ground coal in electrical generating plants, the fly ash being that portion of the residue which is carried in the air stream to a collector (17). The mineral composition of fly ash originates from the rock detritus which collects in the fissures of coal seams and constitutes 8 to 14 percent of the weight of coal (43,29,31). Other residues, such as slags and bottom ashes, are also produced during the combustion of coal but their characteristics are somewhat different from those of fly ash and will not be discussed in detail in this review.

Physically, one of the most prominent features of fly ash is the spherical shape of its particles. These spheres range in diameter from 1 to 100 microns with the average particle size being about 7 microns (43,31). While most fly ash spheres are solid, especially those of Class C fly ash (21), some fly ashes contain a substantial portion of thin walled hollow spheres. Two types of hollow spheres have been identified: cenospheres, which are completely hollow thin walled particles, and plerospheres which are hollow spheres filled with smaller spheres (17). Some fly ash particles, however, are not spherical. Their irregular shapes are thought to be caused by a variety of reasons ranging from insufficient burning of the coal to the chemical composition of the original coal particle (17). These particles range in size from 10 to 300 microns (43,31).

The chemical composition of fly ash may vary considerably. Most fly ashes contain compounds of silica, alumina, lime, iron, manganese and trace elements. Table 2.1 shows the chemical range in which most coal ashes fall (17). To account for the variation in chemical composition and thus facilitate the use of fly ash in concrete, ASTM C618 specification categorizes fly ash by class: Class F and Class C. Class F fly ash is required to have greater amounts of silica, alumina, and iron oxide (pozzolanic matter) than Class C fly ash and is allowed a higher loss on ignition value than Class C fly ash.

"The chemical composition and physical properties of fly ash are a function of an assortment of factors, including the origin and rank of the coal, the degree of pulverization, the design of the boiler unit, the charging and firing techniques, and finally the processes of collection, handling, and storage" (51).

The type of coal burned, for example, plays a most influential role in the chemistry of fly ash. Generally, bituminous and anthracitic coals yield low calcium, Class F fly ash, whereas subbituminous and lignitic coals yield high calcium, Class C fly ashes. As fly ash represents the inorganic, nonburnable portion of coal, it is useful

Table 2.1 Coal Ash Chemical Composition Ranges

Oxide	Weight Range, Percent
SiO_2	10 - 70
Al_2O_3	8 - 38
Fe_2O_3	2 - 50
CaO	0.5-30
MgO	0.3-8
Na_2O	0.1-8
K_2O	0.1-3
TiO_2	0.4-3.5
SO_3	0.1-30

to consider the mineral components present in various kinds of coals to understand the chemical differences between Class F and Class C fly ashes. In a discussion of the differences in mineral composition of coals Diamond et al. (17) provided a list of mineral components frequently found in coal, as shown in Table 2.2, and offered the following explanation as to the reason that some of these minerals are present in coals while others are not. The minerals at the top of the list in Table 2.2, such as clays, micas, feldspars, quartz, and iron oxides are commonly found in soils. The minerals on the lower portion of the list are also found in soils but as they tend to be more soluble, they are generally found in soils from areas that receive less rainfall and thus are not leached from the soil. Soil scientists classify well leached soils as "pedalfers" ("al" for aluminum, "fer" for iron) and soils from arid regions as "pedocals" ("cal" for calcium). Diamond speculates that "much the same distinction could be made for inorganic components of coals deposited in the 'coal measures' geologically, with the equivalent of pedalfer soils giving rise to low calcium or Class F fly ashes, and pedocals soils to high calcium or Class C fly ashes." Diamond mentions, however, that "the classification of coal by rank is made on the basis of fixed carbon content, the amount of volatile matter, and parameters relating to calorific value, and does not

Table 2.2 Common Mineral Constituents of Coal Ashes

Mineral	Type	Composition
Kaolinite	clay	$Al_2O_3.2SiO_2.H_2O$
Illite	clay	$K_2O.3Al_2O_3.6SiO_2.3H_2O$
Muscovite	mica	$K_2O.3Al_2O_3.6SiO_2.3H_2O$
Biotite	mica	$K_2O.MgO.Al_2O_3.3SiO_2.H_2O$
Orthoclase	feldspar	$K_2O.Al_2O_3.6SiO_2$
Albite	feldspar	$Na_2O.Al_2O_3.6SiO_2$
Quartz	silica	SiO_2
Hematite	iron oxide	Fe_2O_3
Magnetite	iron oxide	Fe_3O_4
Calcite	carbonate	$CaCO_3$
Dolomite	carbonate	$CaCO_3.MgCO_3$
Siderite	carbonate	$FeCO_3$
Gypsum	sulfate	$CaSO_4.2H_2O$
Halite	chloride	NaCl
Sylvite	chloride	KCl
Pyrites	sulfide	FeS_2
Rutile	oxide	TiO_2

intrinsically have anything to do with the chemistry or mineral composition of the inorganic fraction of coal."

The degree of pulverization of the coal and the design of the boiler unit also play an important role in the production of fly ash. "There are three main categories of boiler units in which fly ash is produced: stroker-fired units, cyclone furnace units, and pulverized coal-fired units" (43,31). Typically, stroker-fired units produce coarse fly ashes and cyclone furnace units produce low volumes of fly ash. "In pulverized coal-fired units, finely pulverized coal is burned in suspension, and most of the fly ash produced enters the stream of flue gases and is removed by mechanical collectors or electrostatic precipitators. Pulverized coal-fired units are widely used in the utility industry" (43,31).

Typically, coal for a pulverized coal-fired unit is ground to a fineness such that 80 percent will pass U.S. Standard No. 200 Sieve (74μm) with almost no particles larger than the U.S. Standard No. 50 Sieve size (300μm). Ravina (51) states that "Proper grinding is essential for maximum efficiency" of the coal burning process. "Less than perfect performance and/or insufficient capacity of the pulverizer would not necessarily require a shutdown in the power station but the amount of unburnt carbon in the fly ash may increase under adverse conditions and reach a level that would disqualify it for use in concrete."

The burning process has been described by Diamond (17). When the pulverized coal dust is injected into the furnace, the organic (carbon) component quickly burns. The particles then quickly cool producing nearly amorphous spheres. Some of the particles, particularly the larger ones, cool more slowly so that they tend to have some degree of crystallinity.

Interestingly, Diamond (17) has suggested that the chemical composition of fly ash may vary from particle to particle. "What happens to the inorganic component varies from particle to particle, depending on its size and composition. Each particle constitutes a separate and isolated system and has no appreciable interaction with its neighbors." This fact is significant when attempting to explain differences in the hydration process of individual fly ash particles.

The collection, handling and storage techniques of fly ash also play an important role in the physical and chemical character of the ash. For example the Blaine fineness may range from 1700 cm^2/gm in fly ashes from mechanical collectors to 6400 cm^2/gm in fly ashes from electrostatic precipitators (43,31). This is true in spite of the fact that fineness is primarily influenced by the degree of pulverization (51). In studying variations in fly ash collected in four different storage hoppers of the same plant, Ravina (51) found that while the chemical composition was reasonably constant, the fineness and gradation of the fly ash varied widely. These differences, Ravina further states, may have been responsible for variations in the cementitious properties of the fly ash.

Despite the large variations in the chemical and physical characteristics of fly ash, ASTM C618 specification categorizes all fly ash used in concrete into one of two groups, Class F and Class C. Whether variations within either class of fly ash are significant enough to invalidate the general applicability of research performed on a specific fly ash can not presently be predicted. Scheetz et al. (52) discussed the problem as follows:

> "Currently there is considerable debate about the specifications (ASTM C618-77) in these ASTM Standards. Watt and Thorne (72,73,74) did a careful study of the effect of fly ash on the crushing strength of mortar cubes. These authors found almost no correlation between the crushing strength and the particle size or chemical composition for short curing times (up to 91 days), but for long curing times (365 to 730 days) the crushing strength correlated well with SiO_2 or SiO_2 + Al_2O_3

concentrations in the fly ash. Thus the ASTM specifications may not really help determine if the fly ash will perform well in its intended application."

Improvements in the specification have been suggested by Diamond (17) who argues that CaO content should be included as a basis for differentiating between Class F and Class C fly ash. Diamond states:

> "The present version of ASTM C618 continues the practice of not differentiating Class C from Class F on the basis of CaO content directly, but rather in terms of the combined contents of the other major components, namely, SiO_2, Al_2O_3, and Fe_2O_3. A Class C fly ash is one that may have no less than 50% of this combination of oxides; a Class F fly ash no less than 70% of the combination. The logic is dubious."

Difficulties in improving the specification are made evident by the research of Crow and Dunstan (13) and Abdul-Maula et al. (7) who found that there is no well defined relationship between the strength characteristics of fly ash concrete and the primary oxides of the fly ash.

2.3 Effect of Fly Ash on Properties of Concrete

2.3.1 <u>Fresh Concrete</u>. The work of several researchers (14,44,48) indicates that the addition of fly ash to concrete usually yields improved results in terms of workability, water requirement, and bleeding. The improved workability and lower water requirement are generally attributed to the small size and essentially spherical form of the fly ash particles. In this respect, as noted by Davis et al. (14), fly ash differs from other pozzolans which usually increase the water requirement of concrete mixes for a given degree of workability. The few exceptions from this pattern of behavior generally involve fly ashes of high carbon content (7).

2.3.2 Hardened Concrete. In general, the addition of fly ash to Portland cement concrete is considered to be beneficial to the long term strength and durability of concrete. Most researchers have in some way linked the improved performance of fly ash concrete to the pozzolanic properties of fly ash although there are a few exceptions. For example, the freeze-thaw durability of concrete has been long associated with air entrainment (4). The work of several investigators, including those by Larson (37) and Gaynor (26), has shown that the primary effect of fly ash was upon air entraining agent demand, rather than upon the air entrainment per se. The demand for air entraining agent has, in turn, been associated with the carbon content or loss on ignition of fly ash. These investigators have found that in general the higher the carbon content of a given fly ash, the more air entraining agent is required. Aside from the demand for air entraining agent, the freeze-thaw durability of fly ash concrete and plain P.C. concrete is comparable (37).

The sulfate resistance and alkali aggregate reaction durability of fly ash concrete, however, have been closely linked with the pozzolanic properties of fly ash, Berry and Malhotra (6) state that the main causes of concrete deterioration are the leaching of calcium hydroxide, acidic dissolution of cementitious hydrates, the action of atmospheric and dissolved carbon dioxide, and the reactivity of cement components to ions in solution. As fly ash aids in the removal of calcium hydroxide and helps create more stable C-S-H gel, which improves watertightness, it is generally favorably viewed in applications where concrete is exposed to chemical attack. Recently, however, both the sulfate resistance and alkali aggregate reaction durability of concrete made with some Class C fly ashes have been questioned as these fly ashes may increase rather than reduce the amount of alkali present in these concretes (9,20). In areas which have reactive aggregates, such as California, the amount of Class C fly ash used in concrete has been drastically reduced in response to durability concerns (9).

The strength of various fly ash concretes, mortars, and pastes has been related to several factors including chemical composition of both the fly ash and cement, and various physical attributes such as particle size and shape, and mix proportioning. The chemical composition of the fly ash, which can vary greatly, can affect the rate and extent of the pozzolanic reaction and in some cases even contribute to the amount of basic cement constituents present (17). Physical attributes, such as particle fineness and shape, also effect the development of strength. Like the chemical composition of the fly ash, the fineness of the fly ash also can effect the rate and extent of the pozzolanic reaction, whereas the spherical shape of fly ash particles tends to reduce the water requirement of a given mix thereby improving the long term strength.

Mix proportioning is important to the performance of any type of concrete, including fly ash concrete. The addition of an extra material, in this case fly ash, merely complicates the proportioning process. In reviewing fly ash concrete, Berry and Malhotra (6) state that "apart from the quality of the fly ash and the cement, the method of mix proportioning is the most important single factor influencing the properties of fly ash concrete". They have found that three basic approaches have been developed to either obtain reduced heat of hydration or, more recently, improve strength levels attained in concrete at early ages. The three mix proportioning techniques are:

(1) partial replacement of cement,

(2) addition of fly ash as fine aggregate, and

(3) partial replacement of cement and fine aggregate.

The first approach requires the replacement of a portion of Portland cement with an equal volume or weight of fly ash. "Much research has shown that any percentage replacement of Portland cement in concrete by fly ash on a one-for-one basis (either by volume or weight) results in lower compressive strength up to about 3 months of curing, with the development of greater strengths at and beyond 6 months." These fly ash concretes, which normally exhibit lower heats of hydration, are frequently used in mass concrete applications.

However, more recent research indicates that some fly ash concretes exhibit strengths at early ages equal to or greater than plain Portland cement concretes. These faster strength gaining fly ash concretes are typically made with high lime Class C fly ashes whereas the slower strength gaining fly ash concretes are usually made with low lime Class F fly ashes. Examples of such fly ash concretes may be found in several reports, such as those by Cain (9), Cook (11), Crow (13) and Diamond (20).

The addition of fly ash as aggregate to concrete increases the cementitious content of the mix and it alters the aggregate content. Also, it generally results in increased compressive strength at all ages particularly at three months and beyond (6).

The third method developed for proportioning fly ash concrete involves the partial replacement of cement with an excess of fly ash, by weight, with adjustments made in the fine aggregate content. The purpose of this method is to create fly ash concrete mixes which have comparable early age strengths to control mixes. Lovewell and Washa (40), generally credited with originating the method in 1958, concluded that "in order to obtain approximately equal compressive strengths at early ages, between 3 and 28 days, mixes made with fly ash must have a total weight of Portland cement and fly ash greater than the weight of the cement used in the comparable strength Portland cement mixes."

Cannon (10) further elaborated on Lovewell and Washa's method in 1968 when he reported research conducted by the Tennessee Valley Authority on methods of proportioning fly ash concrete mixes to obtain 28 and 90 days strengths equal to those of conventional control mixes. Cannon's research involved the use of Abrams' (2) relationship between water-cement ratio and strength and resulted in the development of a factor to account for the relative costs of cement and fly ash as well tables and graphs to facilitate the proportioning procedure.

The work of Cannon, and Lovewell and Washa formed the basis for the proportioning procedure recommended by ACI entitled "A Method of Proportioning Structural Concrete Mixtures with Fly ash and Other Pozzolans" by Lovewell and Hyland (39).

The method was further extended in 1975 by Ghosh who, using Abrams' relationship that strength is inversely proportion to the water-cement ratio, or in this case the water (cement + fly ash) ratio, equated the strengths of fly ash concretes to control concretes. This relationship is expressed in the following manner:

$$R1 = M + NR$$

where R1 is the water (fly ash + cement) ratio of the fly ash concrete,

R is the water-cement ratio for the control concrete and,

M and N are empirical constants calculated for different ages and fly ash to cement ratios.

The cases studied included concretes at 3, 7, 28, and 90 days with fly ash to cement ratios ranging from 0 to 1.

Smith (53), using an approach similar to Cannon's but based on the British mix proportioning method of "Road Note No. 4" (16) instead of the ACI 211 proportioning procedure, has modified the conventional mix proportioning procedure so that the cement content and water-cement ratio are found through the use of a "Fly Ash Efficiency Factor." This factor, which is unique for each fly ash, can be determined through testing of various fly ash concrete mixes.

Barker (5) in 1981 extended Smith's work by incorporating a "Water Reduction Factor" with Smith's "Fly Ash Efficiency Factor". Barker argued that the basic problem in using the "Fly Ash Efficiency Factor" as a measure of fly ash quality is that of the variability inherent in concrete. His research showed that differences in performances among fly ashes are much more attributable to water demand than to the cementing efficiency of fly ash.

In a related study, Dodson (23) has attempted to determine the amount of strength contributed by a given fly ash through the use of an "Omega Index Factor" or O.I.F. Dodson defines the factor as the cement factor divided by the water-cement ratio. For a given cement and set of aggregates, Dodson developed graphs which showed a linear relationship between strength and the O.I.F. However the strength of fly ash concretes consistently gave values above this plain Portland cement concrete line. This difference was reasoned to be attributable to the amount of strength contributed by the fly ash.

In similar research, Raba et al. (49) found that fly ashes contributed more strength to leaner concretes as compared to richer concretes. This finding is in agreement with the relationships outlined by Lovewell and Hyland (39).

2.4. The Hydration Process

While mix proportioning procedures are useful in developing fly ash concrete mixes, alone they are insufficient to explain the influence that fly ash has on concrete. In fact, a good mix proportioning technique can mask the effect of fly ash. "Often the influence of the aggregate and mix design features combined with the lesser concentration of cementitious material tend to suppress individual effects of mineral admixtures" (20). Consequently, it is necessary to look beyond mix proportioning techniques to explain the role of fly ash in concrete and it is essential to consider the hydration process of the cementitious materials.

2.4.1 Cement Hydration. Before considering the hydration of fly ash cement mixtures, a brief overview of the hydration of Portland cement alone is imperative, while the hydration process of Portland cement is not completely understood, the basic features and resulting final reactions have long been established. Table 2.3 shows the basic chemical reactions involved in the hydration of Portland cement (12).

Ordinary Portland cement is composed of our princi-

Table 2.3 Chemical Reactions in the Hydration of Portland Cement

$2(3CaO.SiO_2)$ (Tricalcium silicate)	+	$6H_2O$ (Water)	=	$3CaO.2SiO_2.3H_2O$ (Tobermorite gel)	+	$3Ca(OH)_2$ (Calcium hydroxide)
$2(2CaO.SiO_2)$ (Dicalcium silicate)	+	$4H_2O$ (Water)	=	$3CaO.2SiO_2.3H_2O$ (Tobermorite gel)	+	$Ca(OH)_2$ (Calcium hydroxide)
$4CaO.Al_2O_3.Fe_2O_3$ (Tetracalcium aluminoferrite)	+	$10H_2O$ (Water)	+	$2Ca(OH)_2$ (Calcium hydroxide)	=	$6CaO.Al_2O_3Fe_2O_3.12H_2O$ (Calcium aluminoferrite hydrate)
$3CaO.Al_2O_3$ (Tricalcium aluminate)	+	$12H_2O$ (Water)	+	$Ca(OH)_2$ (Calcium hydroxide)	=	$3CaO.Al_2O_3.CaSO_4.12H_2O$ (Tetracalcium aluminate hydrate)
$3CaO.Al_2O_3$ (Tricalcium aluminate)	+	$10H_2O$ (Water)	+	$CaSO_4.2H_2O$ (Gypsum)	=	$3CaO.Al_2O_3.CaSO_4.12H_2O$ (Calcium monosulfoaluminate)

2.4.2 Fly Ash Hydration. Unlike Portland cement, fly ash is typically considered not to have any cementitious properties of its own. Recently, however, this view has been changing due to the upsurge in the production of Class C fly ash. Several studies (15,17,13) have shown that while most Class F fly ashes exhibit virtually no cementitious behavior of their own, many Class C fly ashes possess considerable cementitious potential.

Demirel et al. (15) in a study of six different fly ashes belonging to both classes, F and C, found that the fly ashes which did possess considerable cementitious properties were those which contained significant amounts of tricalcium aluminate and calcium aluminum sulfate cements as well as anhydrite. All of these cementitious fly ashes belonged to Class C. When molded into 2 inch cubes or pastes, these fly ashes exhibited an average compressive strength of 1325 psi after 30 minutes of curing and 2493 psi after three days. The other fly ashes in this study which possessed minimal amounts of these cement minerals appeared to be relatively inert as would be expected of pozzolanic materials.

The primary reaction mechanism of these cementitious fly ashes was explained by Demirel in the following way:

> "Aluminate hydrates appear to be the key reaction products in the case of this fly ash (a cementitious Class C fly ash from a power plant near

Lansing, Iowa). Oscillation diffraction analysis showed formation of ettringite in a period of 4 to 22 minutes, monosulfoaluminate formation in the period of 12 to 58 minutes, and anhydrite removal in the period of 10 to 61 minutes. This seems to represent a good example of Portland cement chemistry and can be rationalized that tricalcium aluminate is present in the fly ash (5.2 percent by weight) and is very reactive with water. Also present is an internal source of calcium sulfate in the form of anhydrite. When hydration begins, the free calcium sulfate content of the paste is high and ettringite begins to form. As the sulfate content decrease, due to consumption by ettringite formation, monosulfoaluminate begins to form and continues to form, at the expense of ettringite formation, until the anhydrite is nearly exhausted. The precise reaction mechanism might be complicated due to the fact that the fly ash contained 2.3 percent calcium aluminum sulfate which might hydrate directly to ettringite."

Diamond (17) reports findings similar to those of Demirel stating "Tricalcium aluminate (in high calcium fly ashes) is quite common, sometimes in appreciable quantities. Where C_3A is present along with anhydrite, the fly ash alone may generate significant amount of ettringite, irrespective of the contribution from the pal cement compounds: tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite. Table 2.4 depicts the chemical formulae and the widely accepted cement industry notation of the principal compounds (12). Tricalcium silicate (C_3S) is principally responsible for the development of early strength and the heat of hydration in Portland cement mixes. Dicalcium silicate (C_2S), on the other hand, hydrates much more slowly than C_3S and is responsible for strength increases at later ages.

"Although about 75 percent of Portland cement is composed of calcium silicates, the remaining compounds are important in determining the type and properties of the cement (12)". Tricalcium aluminate hydrates rapidly, liberating a large amount of heat. This reaction, which must be controlled by the addition of gypsum to prevent flash setting, is responsible for relatively minor strength gains at early ages and virtually for no strength gains at later ages. In sulfate resisting cements the C_3A content is restricted to prevent deterioration of concrete.

Tetracalcium aluminoferrite contributes little to the properties of Portland cement except it is useful in lowering both the C_3A content and the energy required in cement manufacture (12).

Table 2.4 Principal Compounds of Portland Cement

Industry Code	Compound	Chemical Formula
C_3S	Tricalcium silicate	$3CaO.SiO_2$
C_2S	Dicalcium silicate	$2CaO.SiO_2$
C_3A	Tricalcium aluminate	$3CaO.Al_2O_3$
C_4AF	Tetracalcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$

Portland cement. Calcium aluminum sulfate is also occasionally found in high calcium fly ash, but in smaller portions."

Both Demirel (15) and Diamond (20) reported temperature increases for fly ash pastes ranging from 10 to 20 degrees Celcius as well as rapid setting times.

2.4.3 Cement and Fly Ash Hydration.

2.4.3.1 Long term effects - While the hydration process of cement and fly ash mixtures has many similarities to the hydration processes of each material individually, there are additionally unique processes that occur when the two materials are used in combination. Of these processes the best known and documented is the pozzolanic reaction.

Typically, pozzolans are considered to be inert at the early stages of hydration, later forming cementitious materials by reacting with free calcium hydroxide. In plain cement mixtures the level of free calcium hydroxide increases rapidly during the early stages of hydration before leveling off. In pozzolanic cement mixtures, however the amount of calcium hydroxide increases at a less rapid pace and, after peaking, gradually declines. Figure 2.1 illustrates the removal of free calcium hydroxide through reaction with pozzolans as shown by Lea (38).

The addition of pozzolans to Portland cement con-

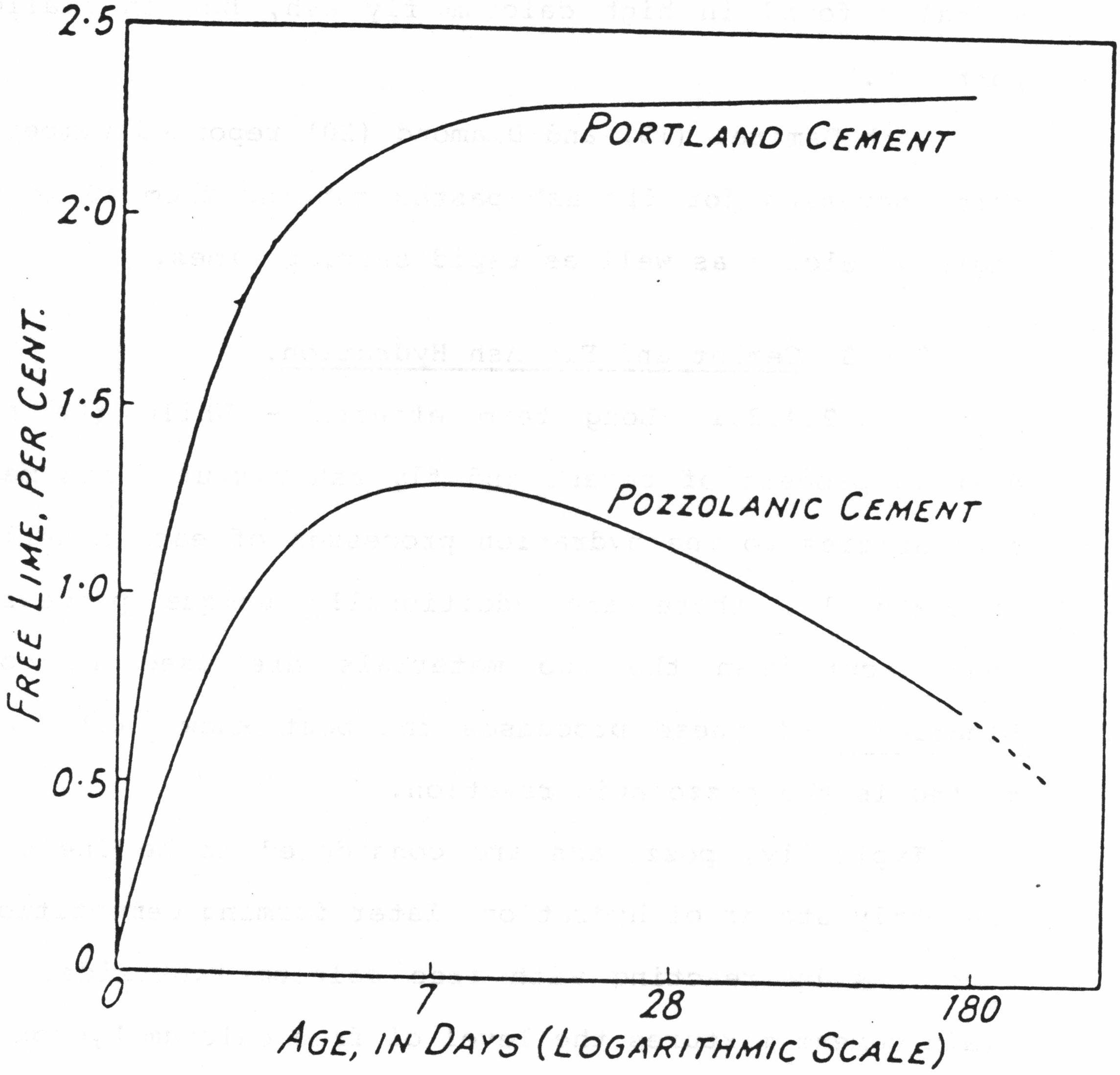

Figure 2.1 Free Lime (Calcium Hydroxide) Content of Cement-Sand Mortars (38)

crete is generally viewed as beneficial to long term concrete properties, such as, watertightness, strength, and resistance to aggressive environments (6). Watertightness and strength are improved since the pozzolanic reaction produces more C-S-H gel and reduces the amount of calcium hydroxide which is of little value to strength (38). Furthermore, the reduced levels of calcium hydroxide improve sulfate resistance since calcium hydroxide is most susceptible to sulfate attack (15).

While the long term strength of fly ash concrete is normally improved, the early strength of fly ash concrete is generally lower than that of plain Portland cement concrete despite the lowered water/cement ratio of the fly ash concrete. Buttler (8) explained this process in the following manner:

> "Although the use of fly ash causes the water/cement ratio to be lowered (where cement is Portland cement + fly ash), the water/cement ratio (where cement = Portland cement) is normally increased. The rates of hydration of both C_3S and C_2S are faster than the fly ash pozzolanic reaction. It follows then that, for short term considerations, the weight of C-S-H gel produced per kg of water used in the mix is less than what would have been obtained with no fly ash substitution. As pozzolanic reaction proceeds, the quantity of gel becomes greater than can form by

hydration of Portland cement alone, and especially if less water has been used, the weight of C-S-H gel per kg of water used becomes much greater."

The pozzolanic properties of fly ash have been studied by several researchers; Kovacs (36), Abdul-Maula (1), Buttler (8), and Takemoto and Uckihawa (20) among others. The following conclusions can be drawn from these studies:

1. The addition of fly ash will reduce over time the amount of free calcium hydroxide present in fly ash cement mixtures,
2. more C-S-H gel is produced in fly ash cement mixtures than in plain cement mixtures, and
3. the extent and rate of the C_3S hydration of cement in fly ash cement mixtures is increased.

Kovacs' (36) observations are presented as typical: "X-ray patterns of plain cement reveal, proportionally to the age of hardening, a reduction of the peak heights of clinker minerals (C_3S, C_2S., etc.) as well as Portlandite [$Ca(OH)_2$] peaks of increased heights. In the patterns of fly ash cements this reduction is even greater than that exhibited by plain cements, which means that the Clinker in fly ash cements will hydrate to higher extent. At the same time the amount of Portlandite, as evidenced by its peak height, is lower; this strongly suggests that it has reacted with the fly ash. These reaction products just like the calcium silicate and calcium aluminate hydrates formed during the hydration of plain cement, are amorphorus character, i.e., undetectable by X-ray diffraction."

The rate of fly ash pozzolanic reaction process has also been studied. Mehta et al. (42) state that the rate of pozzolanic reaction is dependent upon the surface area of fly ash and its degree of amorphousness. Graham (28) suggests that carbon may act as a dilutent of the active pozzolanic materials in fly ash thus affecting the rate of pozzolanic reaction and the rate of early strength development.

While the hydration process of most class F fly ashes may be considered strictly pozzolanic, the hydration process of many Class C fly ashes may be considered a combination of pozzolanic and self-cementitious processes. The effects of Class C fly ash cementitious properties on the hydration process are not as clearly understood as the pozzolanic role of the Class F fly ashes. In general, however, it may be stated that Class C fly ashes tend to become involved in the hydration process much earlier than Class F fly ashes thus typically exhibiting higher strengths than Class F fly ashes (17). Diamond (17) states that this early activity is due to the presence of soluble components such as alkali salts, anhydrite, and CaO, all of which become involved in the hydration reactions from the very beginning. He further adds that the glass in Class C fly ashes might be more "rapidly reactive" than that of Class F fly ashes, with the result of further enhancing the speed of the hydration process.

2.4.3.2 Particle hydration - In order to better understand these and other problems concerning fly ash hydration, many researchers have studied the effects of hydration on an individual particle to particle basis. Idorn (33) lists three mechanisms of particle hydration. The first represents the "classical" pozzolanic effects of fly ash where the particle reacting with calcium hydroxide is surrounded by an integrated layer of C-S-H Gel. The origin of this mechanism is credited to Kobubu (35) in 1968. The second mechanism of particle hydration is credited to Diamond (19) in 1980. It depicts fly ash particles as being completely inert fillers within the surrounding cement paste. The third mechanism of hydration, suggested by Takemoto and Uchikawa (70) in 1980, involves the dissolution of the fly ash particle with the resulting precipitates (C-S-H and calcium aluminate hydrates) located among the ambient C-S-H phases thus leaving a space between the remaining portion of the fly ash particle and cement paste. They claimed that this mechanism was characteristic for alkali-rich environments. Since the chemical composition of fly ash particles varies from particle to particle (17), it is likely that a combination of these or other mechanisms could in effect be in a fly ash cement mixture.

Other studies of particle hydration conducted by Grutzeck, Roy, and Scheetz (30) using a high lime fly ash led to the formulation of a model which assumes that the hydrating particle is a hollow cenosphere and depicts the morphology at various stages of hydration. At early ages little or no particle hydration has occurred and "pull out features" are in evidence. (Pull out features are those in which the fly ash sphere has been cleanly removed or "pulled out" when the sample was broken for observation.) An equal number of smooth surfaced voids and spheres are visible at this stage. At later ages fewer and fewer pull out features are seen as a crust of radiating C-S-H fibers surround the dissolving fly ash sphere. The few pull out features that remain are rough looking. Once a sphere is completely consumed, the mottled interior surface remains as a remnant feature of the original sphere.

Diamond (17) has observed that during the early stages of hydration a "duplex film" of calcium hydroxide and C-S-H Gel are deposited on the surface of the fly ash sphere. "The film is probably not really a result of fly ash reaction per se, but represents precipitation from the supersaturated pore solution onto the fly ash surface." He further states that the film apparently will not protect the underlying fly ash particle from reacting if the particle is capable of reacting, thus erosion of areas under the film may take place. Eventually the film itself may be subsumed into a denser deposit of hydration product surrounding the fly ash sphere.

Observations similar to Diamond's have been made by Ghose et al. (27) who also reported the presence of "duplex film" covering the fly ash spheres. Long term observations revealed that some of the fly ash spheres had not reacted at all while others were very reacted. Generally, the reacted fly ash particle contained more alumina and less silica.

Diamond (17) has also stated that depending upon the chemical composition, many spheres may not react. Despite the absence of reactivity, inert fly ash spheres may not be detrimental to strength. In the study of plain Portland cements, Vivian (71) found that cement "pastes containing as much as one third of their weight of inert quartz particles develop approximately the same compressive strengths as those consisting of cement particles". Thus, it is reasonable to assume that a limited number of inert fly ash spheres would not be detrimental to compressive strength.

2.4.3.3 Short term effects - While the long term effects of fly ash in concrete are generally regarded as beneficial, their short term effects may be regarded as either beneficial or detrimental depending upon the application. In general, fly ash concrete exhibits longer setting times and diminished heats of hydration in comparison to Portland cement concretes (22). Except for mass concrete and hot weather applications these effects are generally regarded as undesirable.

While this behavior has been linked to both physical and chemical factors, the physical dilution of the cement by the fly ash is the most prominent cause. Normally, the amount of cement used in fly ash concrete is reduced or diluted from the amount of cement used in a plain Portland cement concrete, this causes a corresponding reduction in the speed of setting and the heat of hydration given the fact that fly ash is generally not as reactive as Portland cement. In a study utilizing Class F fly ash Ghose et al. (27) noted that the rate of heat evolution of fly ash cement pastes is diminished on addition of fly ash. "However, taking into account the actual amount of cement present in these cement-fly ash pastes, the rate of heat evolution per gram of cement is not materially altered by fly ash addition (27)".

Treating the fly ash as an inert additive, Dodson (22) studied the setting times of several plain Portland cement concrete and fly ash concretes. His work revealed that some ashes, usually Class F fly ash, behaved in an inert fashion while others did not. Some of the fly ashes "accelerated" the set while others "retarded" it. Dodson observed that the fly ashes which accelerated the set hardened quickly when mixed with water alone, forming large amounts of ettringite whereas the fly ashes that retarded the set typically contained large amounts of sulfate, alkali, and occasionally carbonate ions. (It should be reiterated that the terms "accelerated" or "retarded" are expressed relative to fly ash as an inert filler and thus the actual times of set for these fly ash concretes were normally longer than for comparable Portland cement concretes.) From Dodson's research it is clear that while the effect of fly ash on setting times is largely due to the physical dilution of the cement, the chemical characteristics of the fly ash also play an important role.

To understand the chemical effect fly ash has on the setting process and the heat of hydration, it is necessary to understand these processes in plain Portland cement concrete wherein setting is largely dominated by hydration of C_3A. When mixed with water the C_3A hydrates and combines with the gypsum in cement to form ettringite. Vivian (71) states that the product of the reaction (ettringite) between hydrated tricalcium aluminate and calcium sulfate (gypsum) tends to cause the paste to stiffen rapidly. However, the ettringite also tends to coat the cement grains, thus inhibiting hydration, as well as slowing setting and reducing the heat of hydration (46). Once coated, Lea states, "There follows a period of slow reaction, termed the induction period, during which the amount of hydration products gradually builds up with time and slowly increases the plastic viscosity of the paste." This process leads to the eventual setting and hardening of the concrete.

In studies by Cabrera and Plowman (46) fly ash was found to be a more effective retarder of C_3A hydration than gypsum by readily supplying soluble lime and sulfates in the very early stages of hydration (1 to 2 minutes). Their study suggests that rather than ettringite causing retardation, the hydration process is slowed by a retarding layer of lamellar C_4AH_X.

As noted earlier, however, many Class C fly ashes also contain considerable amounts of both C_3A as well as gypsum. The mechanism of how additional amounts of these chemicals affect the early hydration process of cement is still not known. Thus, research done with Class F fly ash is the primary source of information.

In one of the few studies of Class C ash and cement mixes Grutzeck et al. (30) noted the early formation of ettringite and C_2AH_8, later developing into monosulfoaluminate and C_4AH_8. However, the early presence of ettringite and its eventual transformation into monosulfoaluminate has been reported in several studies of Class F fly ash as well. The exception to this would be the research of Abdul-Maula (1) who found that in fly ash (Class C or F) and Portland cement mixes, the amount of ettringite present continuously increased.

In a comparison of low lime and high lime fly ash in mixes, Diamond (20) found that there was not any consistent difference in retarding action between the two mixes. However, the heat evolution characteristic of the two types of fly ash mixes were different. The low lime fly ash mixes displayed 50 percent lower peak temperatures than the control, while the high lime fly ash had little effect on the peak temperatures. From these observations, Diamond concluded that heat of hydration and time of set cannot be directly correlated.

In contrast to Diamond's findings, Jawed et al. (34) found that Class F fly ash significantly delayed the heat of hydration peak of C_3S instead of the time of set. Jawed theorized that the delay could be caused by the "chemisorption" (removal from solution) of Ca^{+2} ion on the fly ash particles and by the "poisoning effect" of soluble silicate and aluminate species. "Since C_3S hydration is essentially a dissolution-precipitation process, any change in ionic composition of the liquid phase of the hydrating system is expected to affect this process."

CHAPTER 3

MATERIALS

3.1 General

All materials tested in this study were provided by the Oklahoma Department of Transportation. The coarse aggregate was delivered in a single three ton load and placed in a stockpile outdoors close to the testing laboratory. The two tons of sand and one ton of both fly ash and cement were delivered in barrels or bags, respectively, and stored in a warehouse also adjacent to the laboratory.

3.2 Coarse Aggregate

The coarse aggregate used in the project conformed to ASTM C33, size #57 limestone quarried near Quapaw, Oklahoma. The stone was found to have a specific gravity of 2.64 and an absorption capacity of 1.44 percent. Table 3.1 details the appropriate measurements and calculations of these properties.

The process of preparing the coarse aggregate for use in the laboratory mixes involved four basic steps. First, the aggregate was oven dried at a temperature of 110°C for a period of 24 hours in accordance with ASTM

Table 3.1 Test Measurements for Coarse Aggregate Specific Gravity and Absorption

Weight, gm	Test 1	Test 2
Oven Dry Specimen, A	987.6	992.5
Saturated Surface Dry (SSD) Specimen, B	1001.6	1007.0
Saturated Specimen in Water, C	621.0	626.5

Specific Gravity (SSD Basis) = B/(B-C)
Absorption, % = [(B-A)/A] x 100]

Table 3.2 Gradation of Coarse Aggregate

Sieve Size or No.	Percent Passing	
	ASTM C-33, No.57	Actual
1 1/2-in	100	100
1-in	95-100	98.5
3/4-in	---	80.0
1/2-in	25-60	60.0
3/8-in	---	35.0
No. 4	0-10	5.0
No. 8	0-5	2.5

C566-78. After cooling, fifty pound lots of material were placed in a shaker and sieved for 10 to 12 minutes in accordance with ASTM C136-80. The material retained on the 1", 3/4", 1/2", 3/8", No.4, and No.8 U.S. Standard sieves as well as the fines were stored separately in 55 gallon barrels. Then, appropriate weights of each stone size were recombined into batch size lots to meet the ASTM C33 specification for size No. 57 stone. Table 3.2 lists the coarse aggregate gradation used for all the concretes as well as the ASTM specification limits. Finally, the coarse aggregate was totally immersed in water for a minimum period of 24 hours. Immediately prior to batching the water was decanted, the stone was weighed, and the weight of free water determined.

3.3 Fine Aggregate

The fine aggregate used in the project was a natural Arkansas river sand produced near Sand Springs, Oklahoma. It was found to have a specific gravity of 2.63 and an absorption capacity of 0.64 percent. Details of these test measurements and calculations are presented in Table 3.3.

The preparation of the sand was quite different from that of the stone. As the sand had been stored in 55 gallon barrels to prevent moisture loss, drying and sieving the entire volume of sand was deemed unnecessary.

Table 3.3 Test Measurement for Fine Aggregate Specific Gravity and Absorption

Item	Weight, gm
Saturated Surface Dry Sample	500.0
Oven-Dry Specimen, A	496.8
Pycnometer filled with Water, B	1308.0
Pycnometer with Specimen and Water, C	1617.9

Specific Gravity (SSD Basis) = 500/(B+500-C)
Absorption, % = [(500-A)/A] x 100

Table 3.4 Typical Gradation of Fine Aggregate

Sieve Size or No.	Percent Passing	
	ASTM C-33	Actual
3/8-in	100	100.0
No.4	95-100	96.9
No.8	80-100	87.2
No.16	50-85	72.0
No.30	25-60	53.1
No.50	10-30	20.0
No.100	2-10	3.5

FM = 2.68
Moisture Content = 2.77%

Instead 200 to 300 pound lots were placed into a 3.75 cubic yard concrete mixer and agitated for 15 minutes to assure a uniform moisture distribution. After mixing, a 600 gram representative sample of moist sand was removed from the mixer, weighed, and placed in an oven for drying. The sample data were then used to determine the moisture content and gradation of that lot. All sand used in this project was processed in this manner which is in accordance with ASTM C192-80 specification. Table 3.4 shows the gradation for a typical lot of sand as well as the limits recommended by the ASTM specification.

3.4 Cement

The Portland cement used in this research was produced by the Martin Marietta Company in Tulsa, Oklahoma. It is classified under ASTM C150 as Type I Portland cement and its chemical and physical characteristics, as reported by Martin Marietta, are given in Table 3.5.

3.5 Fly Ash

The fly ash used in this study was classified under ASTM C618 as Class C fly ash. It was collected from the Oklahoma Gas and Electric Company Thermo Power Plant near Red Rock, Oklahoma and was stored in 30 gallon containers lined with air tight plastic bags. The chemical and physical analyses of the fly ash are presented in Table 3.6.

Table 3.5 Chemical and Physical Characteristics of Portland Cement

Chemical	
Oxides	**Percent of Total Weight**
SiO_2	20.6
Al_2O_3	5.1
Fe_2O_3	2.7
CaO	63.9
MgO	2.0
SO_3	2.9
Loss on Ignition	2.0
Na_2O	0.28
K_2O	0.71
Na_2O Equiv.	0.75
Insoluble Residue	0.26
Cement Minerals	**Percent of Total Weight**
C_3S	55.8
C_2S	17.4
C_3A	9.1
C_4AF	8.1

Physical	
Test	**Value**
Blaine Fineness, sq.cm/gm	3673
Autoclave Expansion, %	0.052
Initial Setting Time, hr:min	2:35
Final Setting Time, hr:min	4:43
Entrained Air, %	9.9
Compressive Strength: (psi)	
1 day	2126
3 days	3533
7 days	4247

Source: Martin Marietta

Table 3.6 Chemical and Physical Characteristics of Fly Ash

Chemical

Oxides	Percent of Total Weight
SiO_2	34.00
Al_2O_3	22.56
Fe_2O_3	7.29
$SiO_2+Al_2O_3+Fe_2O_3$	63.85
SO_3	2.75
CaO	26.88
MgO	5.06
Na_2O	1.46
Moisture Content, %	0.07
Loss of Ignition	0.45

Physical

Test	Value
Fineness (+325 Mesh), %	11.74
Fineness Variation, %	0.35
Specific Gravity	2.74
Soundness	0.43
Lime, Pozz, 7 days, psi	900
Cement, Pozz, 28 days, % of Control	118.4
Water requirement, % of Control	98.0

Analysis conducted by The Bruce Williams Laboratories for the Walter N. Handy Company in accordance with ASTM C-311

CHAPTER 4

TESTING METHODOLOGY

4.1 Fresh Concrete

4.1.1 Mix Design. The mix design for the plain P.C. concrete was based on the Oklahoma Department of Transportation specification for Class A concrete. The fly ash concrete mix designs were similar to the plain P.C. concrete mix design except that Portland cement was replaced by fly ash in percentages of 20, 30, 40 and 50% by weight. The paste samples were proportioned in a similar manner to the concrete samples. The compressive strength of the concrete was measured at 1, 3, 7, 14, 28, 90, 180, and 365 days. It was proposed that by testing at a wide range of time periods and with varying replacement percentages an evaluation of the effect of this particular Oklahoma fly ash could be made.

The mix designs of the control concrete as well as all the fly ash concretes were identical to mixes studied at Oklahoma State University, Stillwater, under a project sponsored by the Oklahoma Department of Transportation (59). As ODOT desired the concretes used in both studies be exactly alike, no adjustments were made in any of the material weights including the weight of the fly ash which normally should be adjusted to account for differences in specific gravity between the cement and the fly ash. Thus while Table 5.1 gives the proportions of each mix per cubic yard, the actual yield of the fly ash mixes is slightly greater than a cubic yard.

4.1.2 Batching Procedures. All concretes made for this study were mixed in a 3.75 cubic foot rotary type mixer in accordance with ASTM C192-76. Three 6 in x 12 in cylinders were cast for each mix design (0%, 20%, 30%, 40%, and 50% replacement) and testing period (1, 3, 7, 14, 28, 90, 180, and 365 days). Thus 24 cylinders per mix giving a total of 120 cylinders were cast excluding rejects. As it was not feasible to cast an entire lot of 24 cylinders from the same batch (due to the limited capacity of the laboratory mixer), the concrete was produced in 2.0 cubic foot batches. This provided ample material for the casting of eight cylinders and made possible the testing of the fresh concrete unit weight, slump, air content, and temperature for each batch.

To start the batching process the mixer drum was first "buttered" with a mixture of water, fine aggregate, fly ash, and cement. The plain P.C. mixes were "buttered" with the same mixture less the fly ash. Once the mixture had coated the drum, the excess material was discharged. The coarse aggregate was then placed in the mixer together with air entraining agent and a small amount of the batch water and mixed thoroughly. Then, the fine aggregate, cement, fly ash (if any) and water were added and mixed.

The mixing process involved three steps: an initial three minute mixing followed by a two minute resting period which, in turn, was followed by a final two minute mixing. If during the first few moments of the initial mixing the concrete appeared to be too stiff, more water was added to the mix. All such additions were duly recorded.

Immediately following the mixing process the concrete was discharged from the mixer into a container to facilitate its handling. At this point, the slump, unit weight, air content, and temperature of the fresh concrete were measured in accordance with ASTM standards (C143-78, C231-78, C138-77), respectively, while the remaining concrete was being placed into the 6 in x 12 in cylinder molds.

After properly compacting the samples and "striking off" the excess material with a steel trowel, air tight lids were placed over the samples to prevent moisture loss. The cylinders were left undisturbed in this state for a period of 24 hours at which time they were stripped from their molds and placed in a lime saturated solution at 70°F to cure. The one day samples were not, of course, placed in the vat for curing as they were tested immediately after stripping.

4.1.3 Time of Set. As insufficient concrete was available from a typical 2.0 cubic foot batch to perform all the required tests, separate batches were prepared to determine the time of set (ASTM C403-77) for each mix. The water contents of the mortars used in the test were determined by the average water cement ratio of each batch.

4.1.4 Heat of Hydration. To measure the effect of the fly ash on the temperature rise of freshly mixed concrete, a simple test was devised. The test involved placing a temperature probe into freshly mixed paste and storing the paste in an insulated enclosure. A strip recorder connected to the probe then continuously recorded the temperature of the paste of a period of 48 hours. For consistency, the test was always performed with the same amount of material (2500 grams of cementitious material and 875 milliliters of water) at the same water-cement ratio (0.35) and near the same initial temperature (70° to 72°F).

Pastes were used instead of concretes when it was found that the aggregate in the concrete so diluted the hydrating materials in the mix that little or no temperature rise could be detected. Table 4.1 lists the

Table 4.1 Paste Mix Proportions

Mix (% Fly Ash)	Material		
	Cement, gm	Fly ash, gm	Water, gm
0	2500	0	875
20	2000	500	875
30	1750	750	875
40	1500	1000	875
50	1250	1250	875
75	625	1875	875
100	0	2500	875

mixes tested and the weights of the materials used for each mix.

4.2 Hardened Concrete

4.2.1 Compressive Strength. The compressive strength of three cylinders from each mix were tested at 1, 3, 7, 14, 28, 90, 180, and 365 days in accordance with ASTM C39-72. The testing procedure was typically initiated by removing the cylinders to be tested from the curing vat and allowing the cylinder surface moisture to evaporate. As soon as the cylinders were dry to touch, they were capped with a sulfur mortar in accordance with ASTM C617-76. After measuring the midheight diameter of each cylinder in two directions, one normal to the other, and the cross sectional area was calculated, the compressive strength of each cylinder was determined in a compressive testing machine (Forney Inc.) having a capacity of 400,000 pounds. A Con Comp CT-5000 (Soil Test Inc.) digital readout and printer was used to monitor and record the compressive strength data of each cylinder.

4.2.2 X-ray Diffraction and Scanning Electron Microscope Samples. Immediately following each series of compressive tests, fragments were removed from each broken cylinder for use in the Scanning Electron Microscopy (SEM) and X-ray diffraction studies. From these fragments, quarter inch specimens of concrete matrix were produced for the SEM observations and finely ground concrete powders were produced for the x-ray diffraction analysis.

Processing these samples involved many steps. First, the fragments were placed in a laboratory jaw crusher and reduced to particles of approximately quarter inch or less in diameter. The crushed material was then sieved through a 1/4 in. U.S. Standard sieve and the passing portion was placed in a laboratory pulverizer where it was ground to a powder. It should be noted that the high percentage of fly ash mixes (40 percent and 50 percent replacement) tested at one and three days responsed poorly to this type of treatment. These mixes tended to be too soft to be effectively ground in the laboratory pulverizer which generally stalled with semi-plastic concrete paste sticking to its grinding surfaces. The material adhering to these surfaces was removed and added to the balance of the ground material.

Placing both the plus 1/4 in. material and the powder for each cylinder into separate pans, each type of material was doused with large quantities of acetone. The purpose of the acetone was to halt the hydration process by evaporating the free mix water as suggested by Diamond*.

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* Diamond, S., Purdue University, Lafayette, Ind., private communication.

After the first dose of acetone was evaporated (this required 12 to 24 hours), the samples were again soaked with a second dose of acetone and again allowed to air dry. The powder material was then sieved through a No. 100 sieve. With the portion retained being discarded, the material passing was stored in one ounce air tight specimen jars for later study. The SEM specimens were stored in a similar fashion.

After an adequate number of samples has been collected, the SEM specimens were prepared for viewing. This process involved first selecting an individual 1/4 inch particle, oven drying the particle at 110°C for one hour to remove any excess moisture, and then cementing it to an aluminum slub using a colloidal silver metal paint. A gold coating approximately 100 Angstroms thick was then applied to the particle using a sputter coater.

Once the coating had been applied, the specimen was ready for viewing in the electron microscope. As the process of photographing each specimen was typically spread over a period of days, the specimens were stored under a vacuum in a dessicator to prevent the entrance of moisture into the sample. (Note: If the specimen contained any excess the electron microscope could not function; thus the drying and dessication procedures were used.)

CHAPTER 5

PRESENTATION AND DISCUSSION OF RESULTS

5.1 Concrete Properties

The Class C high lime fly ash under investigation in this study had a very pronounced effect on all the concrete properties tested. In most cases, the fly ash concrete behaved in a predictable manner, following patterns similar to those of other Class C fly ash concretes described in the Review of Literature (Chapter 2). Table 5.1 summarizes most of the concrete data collected from the testing program.

The fresh concrete properties, such as water requirement at a given slump, were improved in direct proportion to replacement percentage of fly ash for cement. As shown in Figure 5.1, the water/(cement + fly ash) ratio steadily declined from an average of 0.42 for the plain P.C. mixes to 0.36 for the 50 percent replacement mixes. However, Figure 5.1 also shows that while the water/(cement + fly ash) ratio declined, the water/cement ratio steadily increased from an average 0.42 for the plain P.C. concrete to 0.72 for the 50 percent replacement concrete. To some extent, this may account for

Table 5.1 Summary of Concrete Test Data

Item	Concrete														
	Plain Batch			20% Fly Ash Batch			30% Fly Ash Batch			40% Fly Ash Batch			50% Fly Ash Batch		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Quantities per cu. yd.															
Cement (lb)	564	564	564	452	452	452	395	395	395	338	338	338	282	282	282
Fly Ash (lb)	0	0	0	112	112	112	169	169	169	226	226	226	282	282	282
Water (lb)	233	238	249	237	237	216	219	219	208	200	221	224	184	224	196
Fine Aggregate (lb)	1192	1192	1192	1192	1192	1192	1192	1192	1192	1192	1192	1192	1192	1192	1192
Coarse Aggregate (lb)	1887	1887	1887	1887	1887	1887	1887	1887	1887	1887	1887	1887	1887	1887	1887
Air Ent. Agent (ml)	243	243	243	243	243	243	264	264	264	290	290	290	299	299	299
W/C Ratio	.41	.42	.44	.53	.53	.48	.56	.56	.53	.59	.66	.66	.65	.80	.70
W/(C+F) Ratio	.41	.42	.44	.42	.42	.38	.39	.39	.37	.35	.39	.39	.33	.40	.35
Fresh Properties															
Slump (in)	3	2½	2½	2	2½	2	1¾	2½	2½	2	2	2½	1¾	2½	2
Air (in)	4.9	5.2	6.0	4.8	5.0	5.1	4.6	5.2	6.1	5.4	5.3	5.5	5.0	5.0	5.2
Unit Weight (lb/ft^3)	145	144	143	144	145	146	146	145	145	144	143	145	147	144	144
Temperature (°F)	70	64	65	68	69	66	68	68	65	70	70	70	70	70	64
Strength (psi)															
1 day	1992	2098	2266	2194	2141	2118	1736	1661	1443	1354	1081	1103	575	359	712
3 days	3501	3759	3780	3704	3482	3907	3457	3261	3722	3411	3369	3215	2879	2109	2847
7 days	4241	4385	4116	4322	4462	4448	3160	4374	4716	4871	4840	4161	4702	4035	4466
14 days	4617	4500	4604	4992	5315	5141	4283	4943	5098	4961	5609	5344	5390	4964	4921
28 days	5275	4968	4795	5646	5243	5809	5419	5443	5574	6476	6395	5669	6731	6007	6228
90 days	5492	5362	5439	5887	4610	6229	5774	5553	6744	6767	6469	6591	7627	6564	6333
180 days	5823	5802	5861	6764	6676	6845	6872	6161	6890	7566	5911	6975	8123	7088	6901
365 days	6169	6349	6402	7635	7158	7378	6517	7131	7295	8727	8416	7968	8936	7985	7590

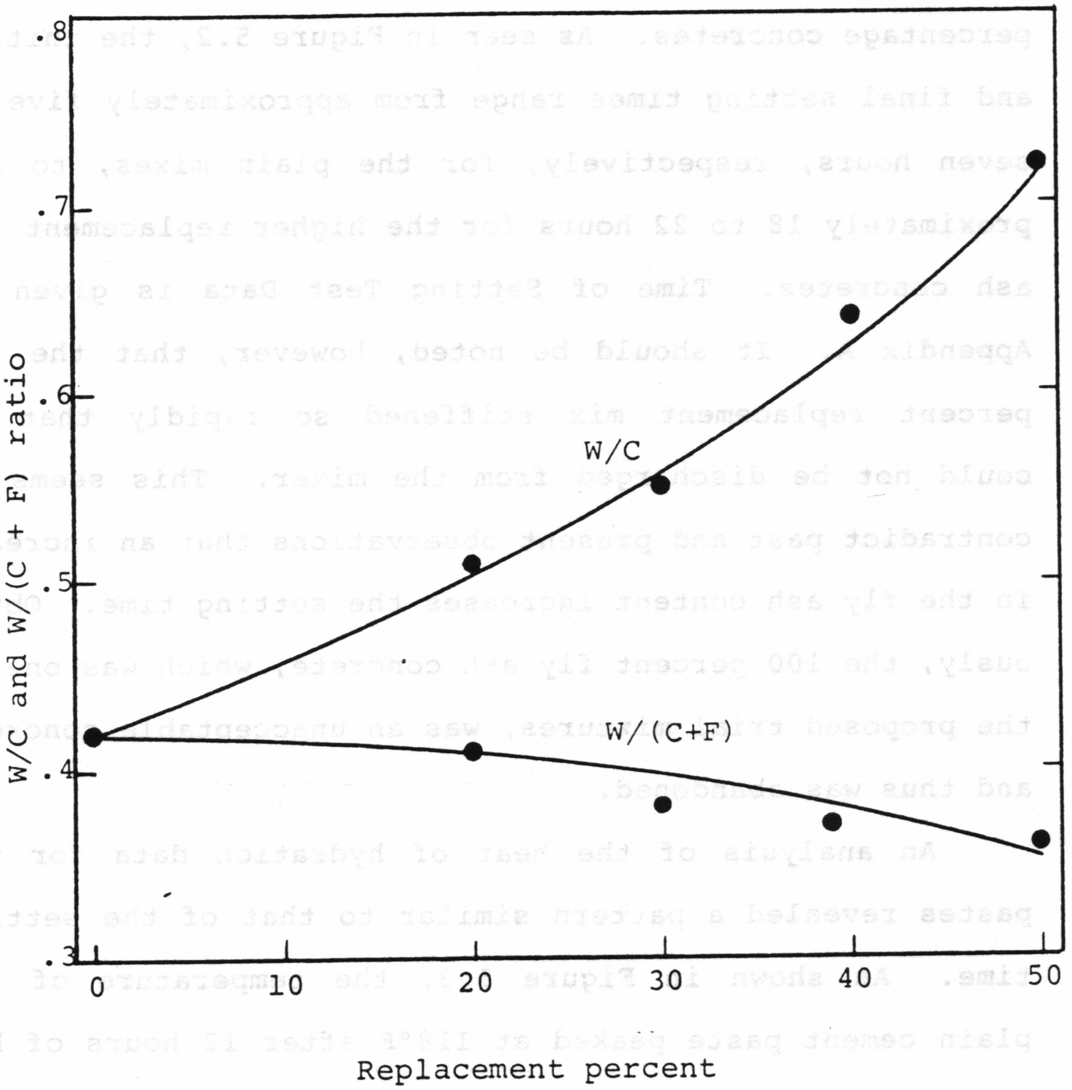

Figure 5.1 Effect of Fly Ash Content on the Water/Cement Ratio and Water/(Cement + Flyash) Ratio

the prolonged setting times for the higher replacement percentage concretes. As seen in Figure 5.2, the initial and final setting times range from approximately five to seven hours, respectively, for the plain mixes, to approximately 18 to 22 hours for the higher replacement fly ash concretes. Time of Setting Test Data is given in Appendix A. It should be noted, however, that the 100 percent replacement mix stiffened so rapidly that it could not be discharged from the mixer. This seems to contradict past and present observations that an increase in the fly ash content increases the setting time. Obviously, the 100 percent fly ash concrete, which was one of the proposed trial mixtures, was an unacceptable concrete and thus was abandoned.

An analysis of the heat of hydration data for the pastes revealed a pattern similar to that of the setting time. As shown in Figure 5.3, the temperature of the plain cement paste peaked at 118°F after 12 hours of hydration while the other mixtures always exhibited lower peak temperatures at different times. In general, the peak temperature was found to be inversely related to the fly ash content, and the time required to reach the peak temperature was found to be directly related to the fly ash content of the paste. However, as in the case of the setting time, the 100 percent fly ash paste did not follow this trend peaking at 106°F in only 30 minutes. A

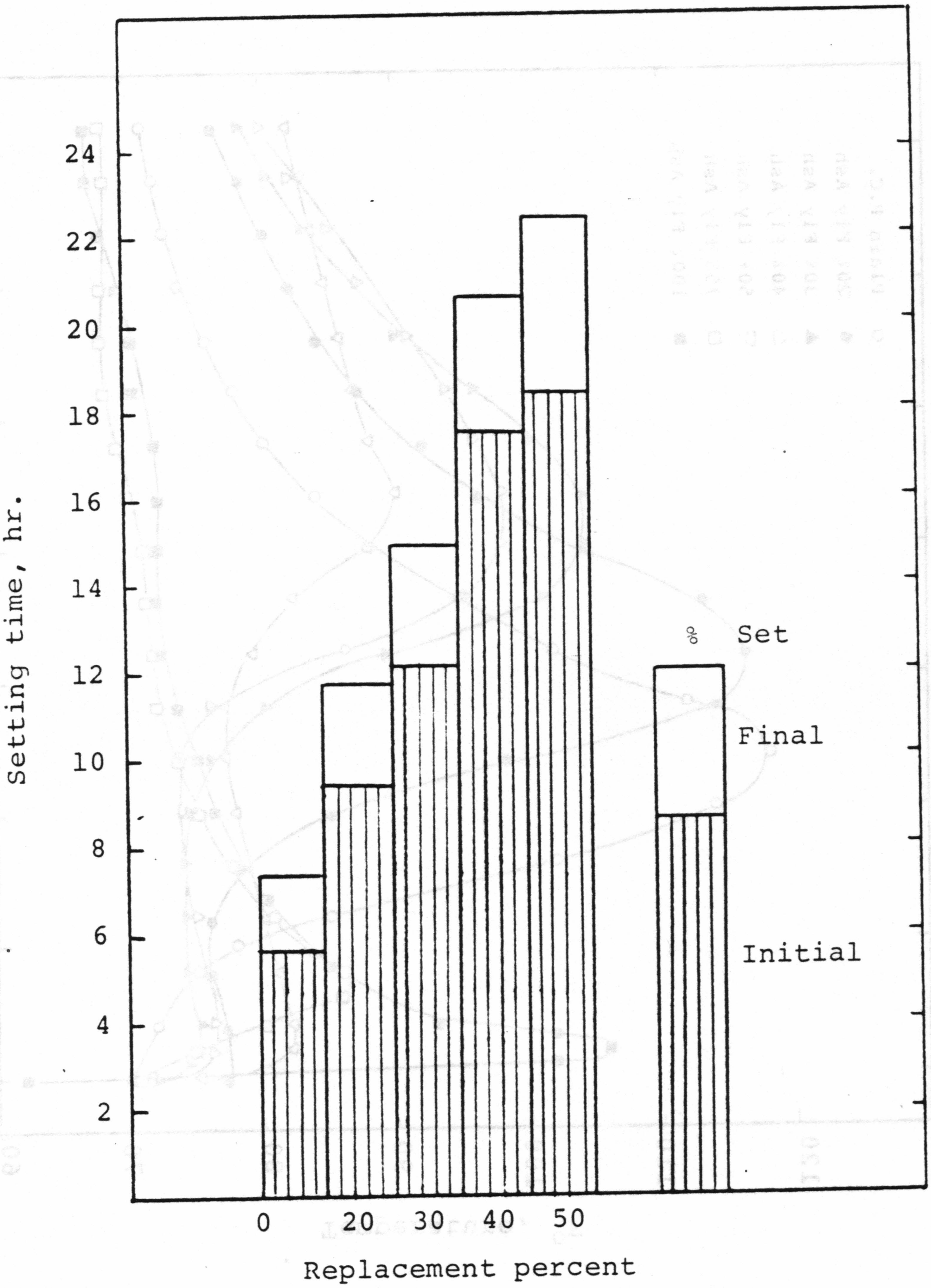

Figure 5.2 Bar Chart of Concrete Setting Time

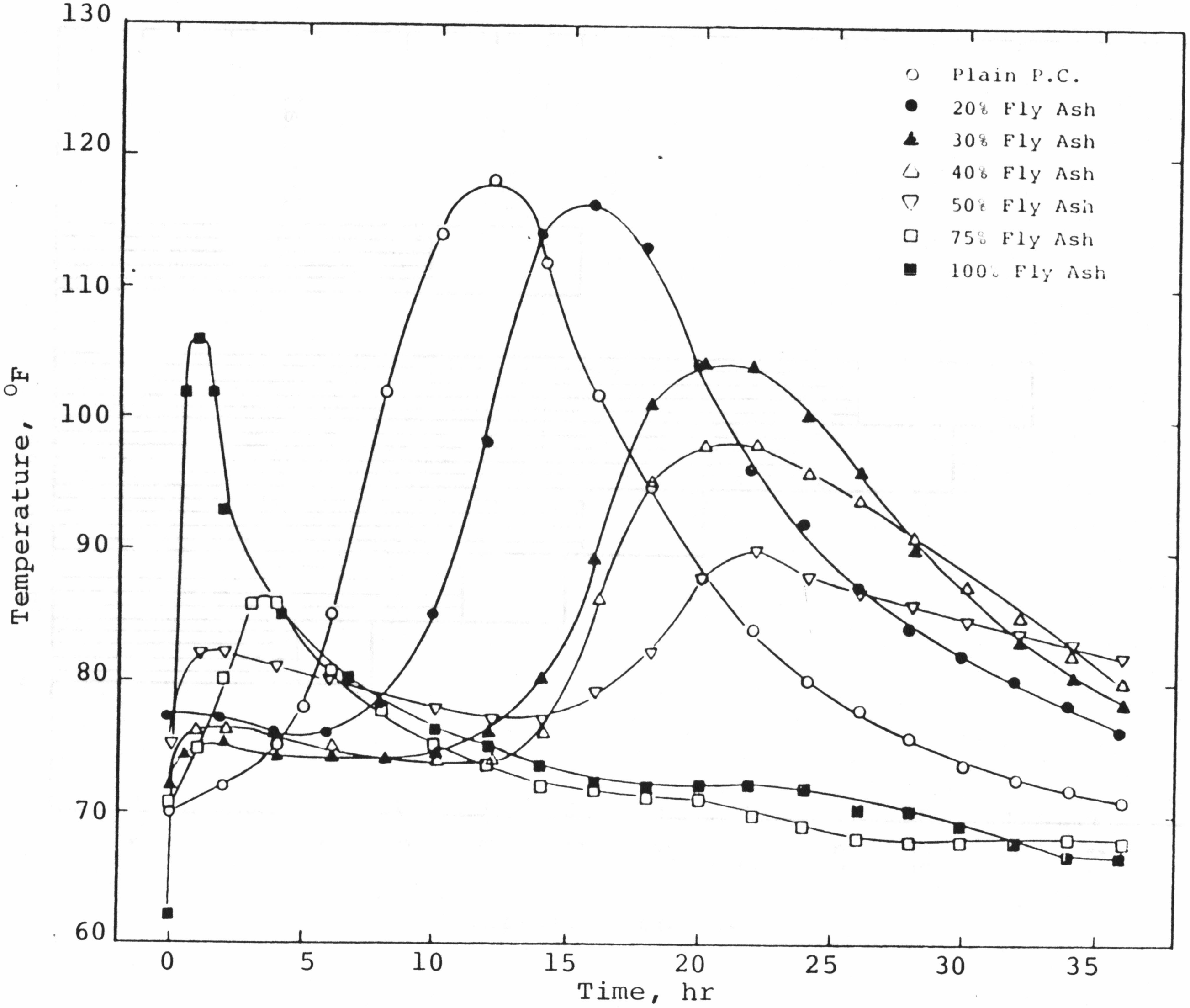

Figure 5.3 Heat of Hydration for Test Pastes

closer inspection of these data reveals that many of the fly ash-cement pastes actually displayed two peaks: The first presumably due to fly ash hydration and the second due to cement hydration. The relative heights of these peaks appear to be roughly correlated with the relative amounts of fly ash and cement present in the paste.

The air content and unit weight of the fly ash concretes appear to be relatively unaffected by changes in the relative amounts of fly ash and cement although the higher replacement concretes required slightly more air entraining agent than the lower replacement concretes. However, this trend is considered to be insignificant since variations in the amount of air entraining agent typically have little effect on the air content of low slump concrete.

Of the properties of hardened concrete, only compressive strength was considered. Generally, in the early stages of hydration the fly ash tended to lower the compressive strength of the concretes in direct proportion to the amount of fly ash present in the concrete. Specifically, concretes with greater than 20 percent replacement exhibited lower strengths at one and three days as shown in Figures 5.4 and 5.5. The 20 percent fly ash concrete at one and three days exhibited strength comparable to the plain P.C. concrete. By seven days, however, the average strength of all the concretes was

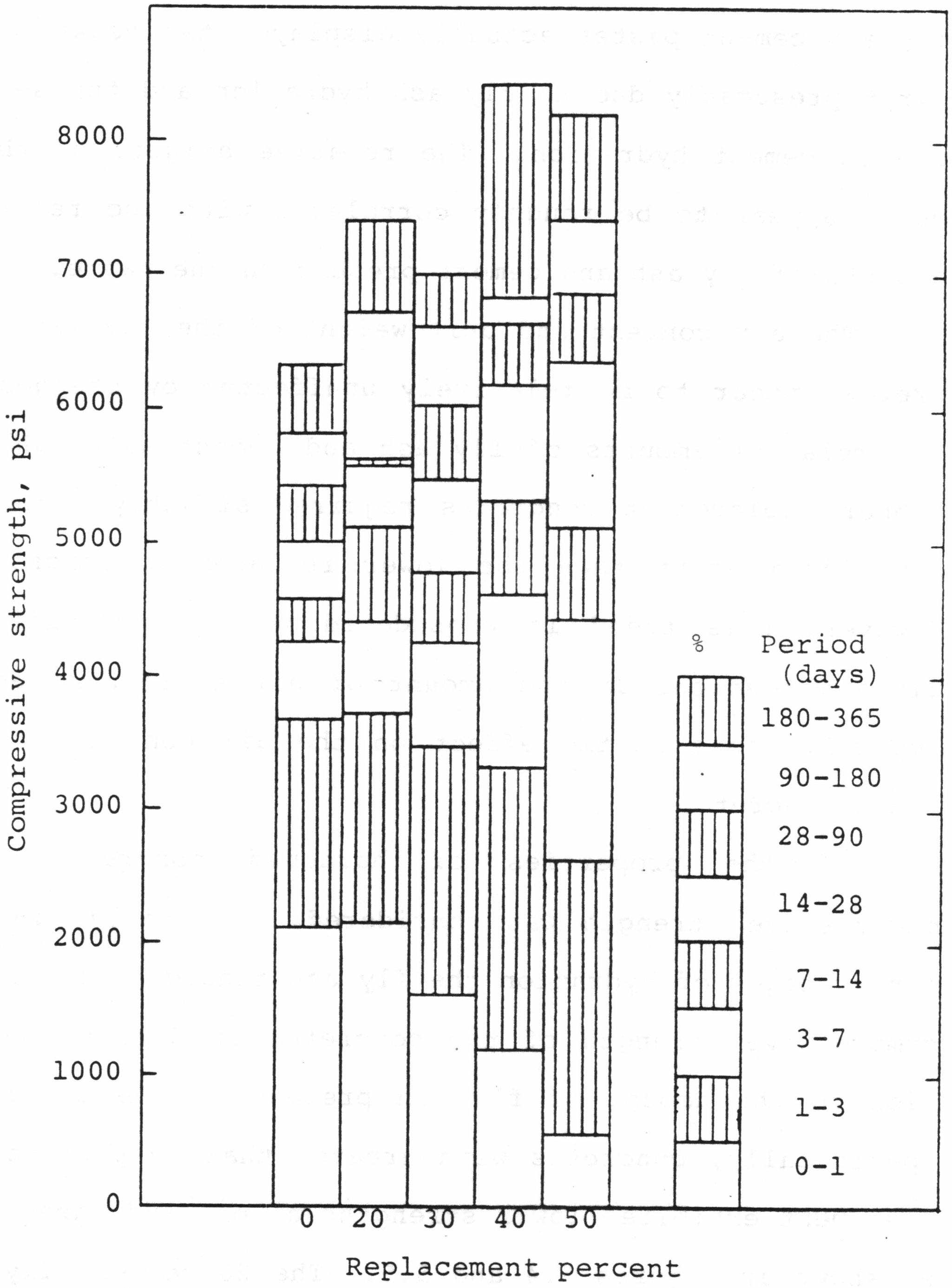

Figure 5.4 Bar Chart of Concrete Compressive Strengths

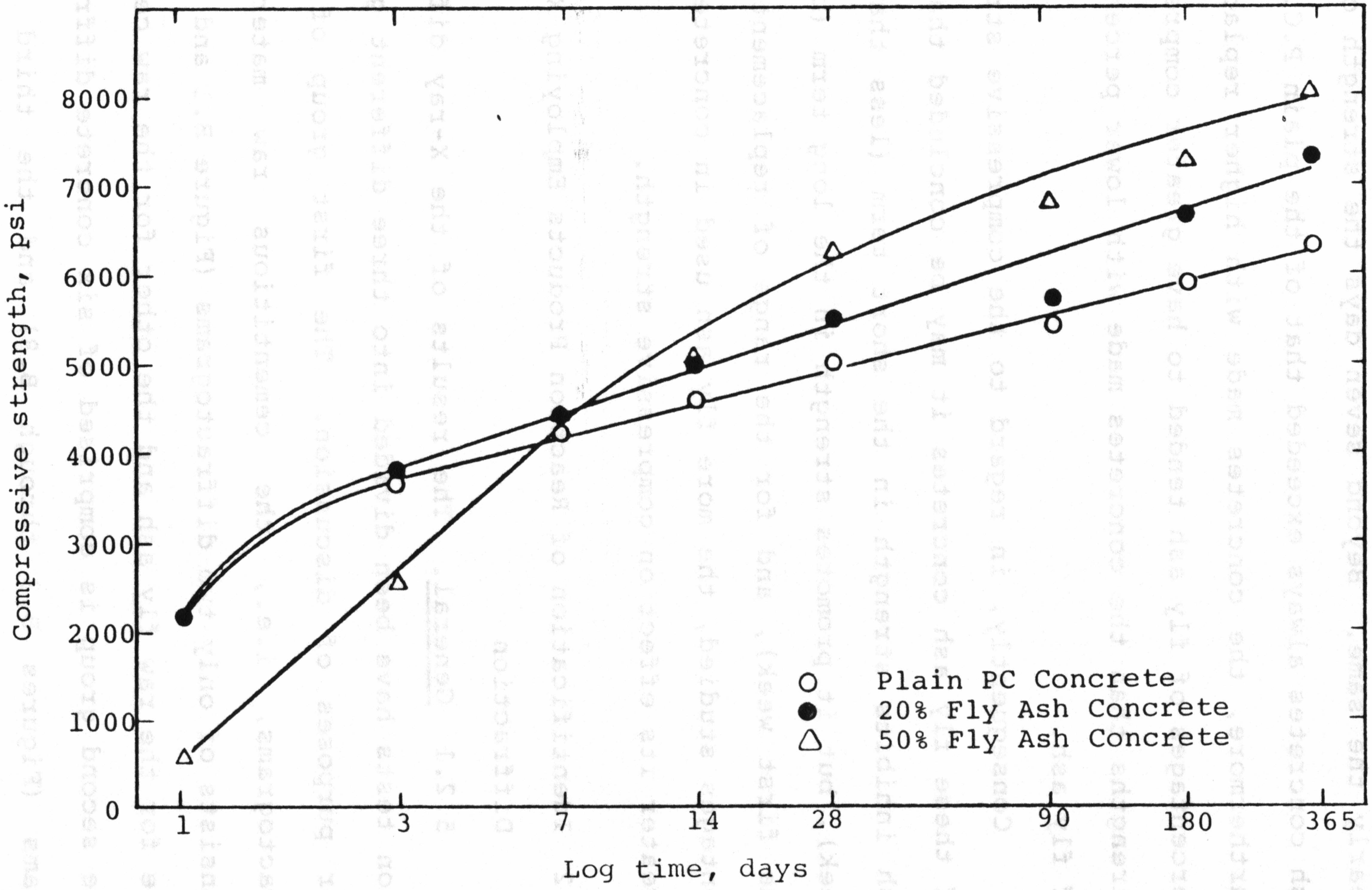

Figure 5.5 Compressive Strengths for 0%, 20%, and 50% Fly Ash Concrete

nearly the same. Beyond seven days the strength of fly ash concretes always exceeded that of the plain P.C. mix. Furthermore, the concretes made with higher replacement percentages of fly ash tended to have greater compressive strengths than the concretes made with lower percentages of fly ash.

Consequently, in regard to the compressive strength of these fly ash concretes it may be concluded that fly ash inhibits strength in the short term (less than one week), but it promotes strength in the long term (beyond the first week), and for the range of replacement percentages studied, the more fly ash used in concrete, the greater its effect on compressive strength.

5.2 Identification of Reaction Products Employing X-ray Diffraction

5.2.1 General. The results of the X-ray diffraction tests have been divided into three different groups for purposes of discussion. The first group of diffractograms, i.e., the cementitious raw materials, consists of only two diffractograms (Figure B.1 and B.2), one for the raw fly ash and the other for the raw cement. The second group is comprised of six concrete diffractograms (Figures B.3 through B.8) and the third group presents twelve paste diffractograms (Figures B.9 through B.20). Also in the third group, Figures 5.6 through 5.9

are presented to allow rapid comparison of variations in peak intensities occurring over time within given replacement percentages. These figures represent a combination of three or four paste or raw material diffractograms in slightly abridged form, whereas Figures B.1 through B.20 in Appendix B represent individual diffractograms in their complete, unabridged form. Table 5.2 summarizes the X-ray diffractograms presented in this study.

The identities of the mineralogical components indicated in each diffractogram were determined using the JCPDS Powder Diffraction File Data (32) and selected X-ray data presented by Lea (38). The probability of a given material being present in a sample was based on a comparison of the peaks found in the diffractogram versus the characteristic peaks of that mineral. Generally, if three or more peaks of proper intensity were found, the mineral was considered to be present. If fewer peaks were found, identification was considered tentative. Obviously, the presence of minerals composed of unlikely elements was rejected. Table 5.3 presents the mineral name, chemical formula, and peak data for all the minerals found in this study.

5.2.2 Raw Materials: Fly Ash and Cement.

The fly ash diffractogram (Figure B.1) indicates the presence of

Table 5.2 List of X-Ray Diffractograms

Group	Figure	Depiction
I	B.1	Raw Fly Ash
The Raw Materials	B.2	Raw Portland Cement
II	B.3	Plain P.C. Concrete @ 7 days
The Concretes	B.4	Plain P.C. Concrete @ 28 days
	B.5	20% Fly Ash Concrete @ 7 days
	B.6	20% Fly Ash Concrete @ 28 days
	B.7	50% Fly Ash Concrete @ 7 days
	B.8	50% Fly Ash Concrete @ 28 days
III	B.9	Plain P.C. Paste @ 7 days
The Pastes	B.10	Plain P.C. Paste @ 28 days
	B.11	20% Fly Ash Paste @ 1 day
	B.12	20% Fly Ash Paste @ 7 days
	B.13	20% Fly Ash Paste @ 28 days
	B.14	20% Fly Ash Paste @ 90 days
	B.15	50% Fly Ash Paste @ 1 day
	B.16	50% Fly Ash Paste @ 7 days
	B.17	50% Fly Ash Paste @ 28 days
	B.18	50% Fly Ash Paste @ 90 days
	B.19	100% Fly Ash Paste @ 7 days
	B.20	100% Fly Ash Paste @ 28 days
	5.6	Plain P.C. Powder & Pastes (ABRIDGED)
	5.7	20% Fly Ash Pastes (ABRIDGED)
	5.8	50% Fly Ash Pastes (ABRIDGED)
	5.9	100% Fly Ash Powder & Pastes (ABRIDGED)

Table 5.3 List of Minerals Identified by X-Ray Diffraction

Mineral Name	Chemical	Diffractogram Symbol	d-spacings (relative intensity) Å			PDF Number[1]
Tricalcium Silicate (C_3S)	$3CaO.SiO_2$	A	2.76 (100)	2.74 (90)	2.59 (90)	11-593
Dicalcium Silicate (C_2S)	$2CaO.SiO_2$	B	2.778 (100)	2.740 (100)	2.607 (100)	*[2]
Tricalcium Aluminate (C_3A)	$3CaO.Al_2O_3$	C	2.70 (100)	1.91 (36)	1.56 (27)	8-5
Tetracalcium Aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	D	2.63 (100)	2.77 (80)	1.92 (80)	*[2]
Calcite (Calcium Carbonate)	$CaCO_3$	Cc	3.04 (100)	2.29 (18)	2.10 (18)	5-0586
Portlandite (Calcium Hydroxide)	$Ca(OH)_2$	P	2.628 (100)	4.90 (100)	1.927 (42)	4-0732
Ettringite ($C_3A\bar{S}_3H_{32}$)	$3CaO.Al_2O_3.3CaSO_4.32H_2O$	E	9.73 (100)	5.61 (80)	3.88 (50)	9-414
Monosulfoaluminate ($C_3A\bar{S}H_{13}$)	$3CaO.Al_2O_3.CaSO_4.13H_2O$	Ms	8.92 (100)	2.87 (70)	4.46 (60)	*[2]
Quartz	SiO_2	Q	3.34 (100)	4.26 (35)	1.82 (17)	5-0490
Periclase	MgO	Mg	2.106 (100)	1.489 (52)	0.942 (17)	4-829
Gypsum	$CaSO_4.2H_2O$	G	7.56 (100)	3.06 (60)	4.27 (50)	6-46
Anhydrite	$CaSO_4$	Ah	3.49 (100)	2.85 (30)	2.33 (20)	6-226
Lime	CaO	L	2.406 (100)	1.701 (45)	2.778 (34)	4-777
Gismondine[3] (CAS_2H_4)	$CaO.2SiO_2.Al_2O_3.4H_2O$	Gs	3.34 (100)	4.27 (35)	3.19 (18)	20-452
Microcline[3]	$KAISi_3O_8$	Mc	3.25 (100)	4.21 (50)	3.29 (50)	22-687

[1] JCPDS powder diffraction file number

[2] From Lea, "Chemistry of Cement and Concrete" ( )

[3] Presence tentative

quartz (SiO_2), lime (CaO), periclase (MgO), anhydrite ($CaSO_4$), and tricalcium aluminate (C_3A). In addition to these minerals, a small amount of dicalcium silicate (C_2S) may also be present.

The cement (Figure B.2) is composed largely of tricalcium silicate (C_3S) and lesser amounts of dicalcium silicate (C_2S), tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF) and gypsum ($CaSO_4.2H_2O$). Table 5.4 lists the minerals found in both the fly ash and cement in descending order of the quantities indicated by X-ray diffraction.

5.2.3 Concretes. Diffractograms of the concrete samples are of limited value in determining mineralogical composition of the paste fraction in the concretes. The limited nature of these diffractograms is the result of the dilution of the paste fraction by the concrete aggregates. Thus, the only identifiable minerals are quartz (SiO_2), calcite ($CaCO_3$), and portlandite or calcium hydroxide ($Ca(OH)_2$). Ettringite ($C_3A\bar{S}_3H_{32}$) may also be present in all of the concretes; however, due to the relative weakness of its peaks, confirmation of its presence cannot be made. Table 5.5 lists the minerals found in the concretes in descending order of the quantities indicated by X-ray diffraction.

With the exception of quartz (SiO_2), all the miner-

Table 5.4 Minerals Identified in Raw Material Samples by X-ray Diffraction

Fly Ash	Cement
Quartz	C_3S
C_3A	C_2S
Periclase	C_3A
Anhydrite	C_4AF
Lime	Gypsum
C_2S (tr)	

(tr) - trace

Table 5.5 Minerals Identified in Concrete Samples by X-ray Diffraction

Curing Time (days)	Concrete		
	Plain	20% Fly Ash	50% Fly Ash
7	Calcite Quartz $Ca(OH)_2$ Ettringite(tr)	Calcite Quartz $Ca(OH)_2$ Ettringite	Calcite Quartz $Ca(OH)_2$ Microcline(t) Gismondine(t) Ettringite
28	Calcite Quartz $Ca(OH)_2$ Microcline(t) Gismandine(t) Ettringite(tr)	Calcite Quartz $Ca(OH)_2$ Microcline(t) Gismondine(t) Ettringite (tr)	Calcite Quartz $Ca(OH)_2$ Microcline(t) Gismondine(t) Ettringite(tr)

tr - trace
t - tentative

als found in these diffractograms are considered to be reaction products of the cement and/or fly ash. It should be noted, however, that the amount of calcite ($CaCO_3$) observed in the diffractograms is probably exaggerated. Normally this reaction product would be present only on the surface of the sample. But since all of the samples, both concretes and pastes, were finely ground, carbonation was permitted to proceed to a greater extent. Thus, all of the diffractograms for both the concretes and the paste are apt to overstate the amount of calcite ($CaCO_3$) actually present in the sample.

Variations in peak intensities can been seen in all the concrete diffractograms, depending upon the age of the concrete and its fly ash content. For example, in the plain P.C. concretes (Figures B.3 and B.4) the 2.2 Å peak, representing calcium hydroxide ($Ca(OH)_2$), increases slightly from 7 to 28 days. This same peak in the 20 percent fly ash concrete diffractograms (Figures B.5 and B.6), remains relatively constant over this period, whereas the 50 percent fly ash concrete diffractograms (Figures B.7 and B.8) show a slight decrease in intensity. While this trend of fly ash lowering the long term amount of calcium hydroxide ($Ca(OH)_2$) present in concrete is consistent with the role of fly ash as a pozzolan, it should be noted that a small variation in the intensity of any peak is not necessarily a valid measure of the change in the quantity of a mineral present.

Another example of variations in peak intensities involves the 3.34 Å quartz peak. In all the concretes, a small increase in this peak was noted from 7 to 28 days. The cause of this increase is unknown. However, during this same period more noticeable increases occurred in the 3.24 Å and 3.19 Å peaks. Unfortunately, the minerals associated with these peaks cannot be identified with great certainty due to several overlaps with quartz peaks; possibly they are feldspar (microcline) from the aggregate, and a calcium aluminum silicate hydrate (gismondine), respectively.

5.2.4 Pastes. The diffractograms of the paste samples were more informative than those of concrete since the pastes were not diluted by the concrete aggregates. The minerals found in these pastes are presented in Table 5.6 in descending order of their peak intensities.

5.2.4.1 Plain cement paste - As seen in Table 5.5 the plain cement pastes contain a considerable amount of unhydrated cement minerals (C_3S, C_2S, C_3A, C_4AF) and three primary reaction products: calcium hydroxide [$Ca(OH)_2$], calcium carbonate ($CaCO_3$) and ettringite ($C_3A\bar{S}_3H_{32}$). When the relative intensities of these mineral X-ray peaks in Figure 5.6, are compared at 7 and 28 days, several trends can be noted. One trend, which

Table 5.6 Minerals Identified in Paste Sample by X-ray Diffraction

Curing Time (days)	Paste			
	Plain	20% Fly Ash	50% Fly Ash	100% Fly Ash
1	NA	C_3S C_2S $Ca(OH)_2$ Calcite Ettringite C_3A C_4AF C_4AF Quartz	C_3S C_2S Calcite $Ca(OH)_2$ Ettringite Quartz C_3A, C_4AF Gypsum Anhydrite Periclase	NA
7	$Ca(OH)_2$ C_3S C_2S Calcite Ettringite	$Ca(OH)_2$ Calcite C_3S C_2S Ettringite Monosulfo-aluminate Quartz	$Ca(OH)_2$ Calcite Quartz C_3S, C_2S Ettringite Monosulfo-aluminate Periclase	Quartz Calcite Monosulfo-aluminate C_3A Periclase Ettringite C_2S

continued

Table 5.6 Minerals Identified in Paste Sample by X-ray Diffraction (continued)

Curing Time (days)	Paste			
	Plain	20% Fly Ash	50% Fly Ash	100% Fly Ash
28	$Ca(OH)_2$ Calcite C_3S C_2S Ettringite	$Ca(OH)_2$ Calcite C_3S C_2S Ettringite Monosulfoaluminate Quartz Gypsum(tr)	$Ca(OH)_2$ Calcite Monosulfoaluminate Quartz C_3S, C_2S Ettringite Gypsum Periclase	Quartz Calcite Monosulfoaluminate C_3A Periclase Ettringite C_2S
90	NA	$Ca(OH)_2$ Calcite C_3S C_2S Quartz Ettringite Monosulfoaluminate	$Ca(OH)_2$ Monosulfoaluminate Quartz Calcite C_3S, C_2S Ettringite Gypsum Periclase	NA

NA - not available

tr - trace

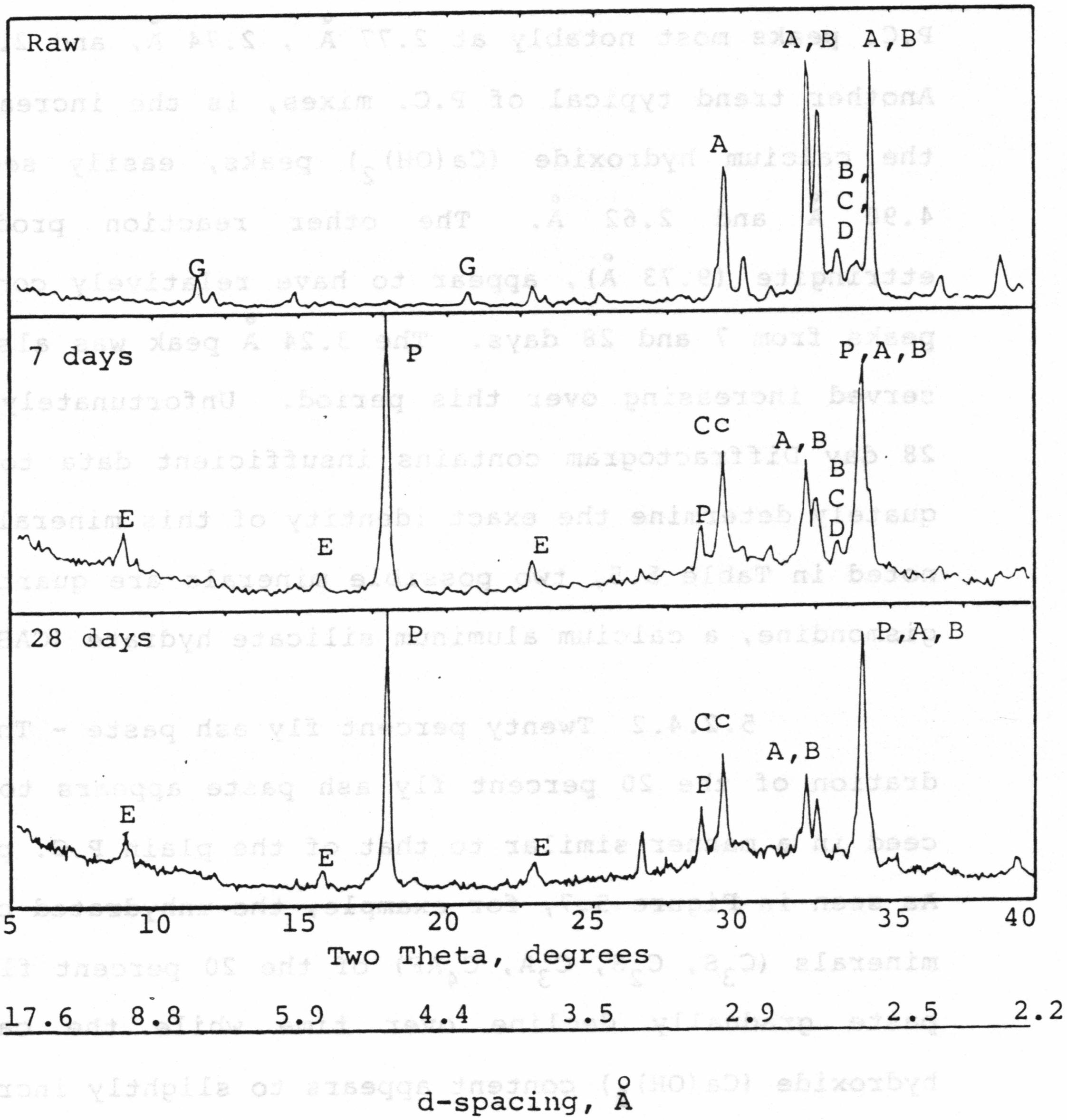

Figure 5.6 X-Ray Diffractograms of Plain Portland Cement Powder and Pastes

is expected to occur, is the decline of the unhydrated P.C. peaks most notably at 2.77 Å , 2.74 Å, and 2.70 Å. Another trend typical of P.C. mixes, is the increase of the calcium hydroxide ($Ca(OH)_2$) peaks, easily seen at 4.90 Å and 2.62 Å. The other reaction products, ettringite (9.73 Å), appear to have relatively constant peaks from 7 and 28 days. The 3.24 Å peak was also observed increasing over this period. Unfortunately, the 28 day Diffractogram contains insufficient data to adequately determine the exact identity of this mineral. As noted in Table 5.5, two possible minerals are quartz and gismondine, a calcium aluminum silicate hydrate (CAS_2H_4).

5.2.4.2 Twenty percent fly ash paste - The hydration of the 20 percent fly ash paste appears to proceed in a manner similar to that of the plain P.C. paste. As seen in Figure 5.7, for example, the unhydrated cement minerals (C_3S, C_2S, C_3A, C_4AF) of the 20 percent fly ash paste gradually decline over time while the calcium hydroxide ($Ca(OH)_2$) content appears to slightly increase. It should be noted that the increase in calcium hydroxide ($Ca(OH)_2$) content appears to contradict the theory that pozzolans remove excess calcium hydroxide ($Ca(OH)_2$).

However, not all of the hydration processes of the 20 percent fly ash pastes are similar to those of the plain P.C. pastes. For example, the amount of ettringite

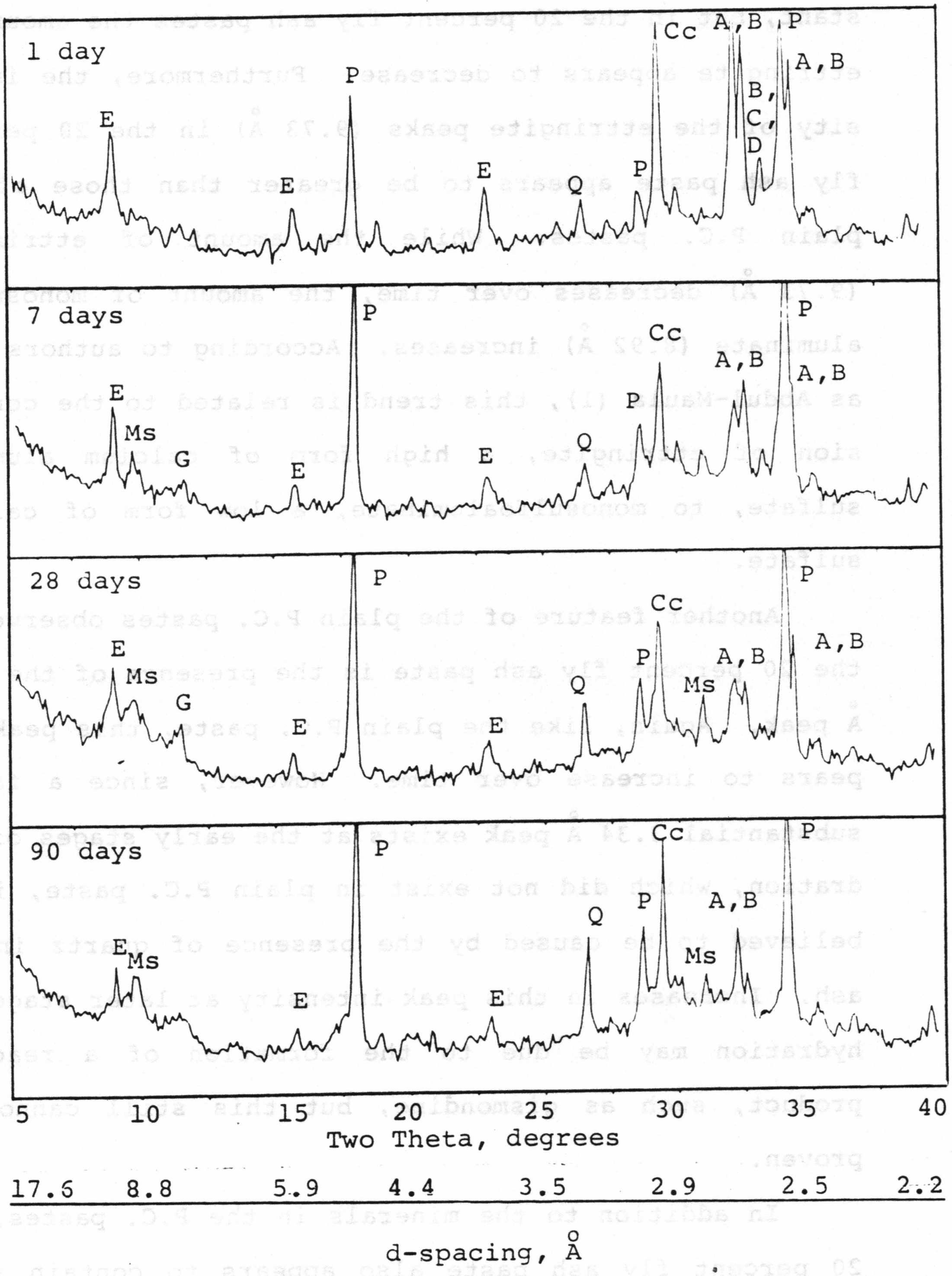

Figure 5.7 X-Ray Diffractograms of 20% Fly Ash Pastes

present in the P.C. pastes appear to be relatively constant, but in the 20 percent fly ash pastes the amount of ettringite appears to decrease. Furthermore, the intensity of the ettringite peaks (9.73 Å) in the 20 percent fly ash paste appears to be greater than those of the plain P.C. pastes. While the amount of ettringite (9.73 Å) decreases over time, the amount of monosulfoaluminate (8.92 Å) increases. According to authors such as Abdul-Maula (1), this trend is related to the conversion of ettringite, a high form of calcium aluminum sulfate, to monosulfoaluminate, a low form of calcium sulfate.

Another feature of the plain P.C. pastes observed in the 20 percent fly ash paste is the presence of the 3.34 Å peak. Again, like the plain P.C. paste, this peak appears to increase over time. However, since a fairly substantial 3.34 Å peak exists at the early stages of hydration, which did not exist in plain P.C. paste, it is believed to be caused by the presence of quartz in fly ash. Increases in this peak intensity at later stages of hydration may be due to the formation of a reaction product, such as gismondine, but this still cannot be proven.

In addition to the minerals in the P.C. pastes, the 20 percent fly ash paste also appears to contain small amounts of periclase (MgO) and gypsum (Figure B.13).

While these minerals cannot be positively identified, their presence is suspected since they are found in some form in the fly ash. Given these conditions, the gypsum peak (7.56 Å) would be a hydrated form of anhydrite ($CaSO_4$).

5.2.4.3 Fifty percent fly ash paste - The hydration processes of the 50 percent fly ash pastes appear to be very similar to those of the 20 percent fly ash pastes. The unhydrated P.C. minerals (C_3S, C_2S, C_3A, C_4AF) slowly decrease over time as they did for the plain P.C. pastes and the 20 percent fly ash pastes. However, the influence of the additional fly ash can be seen in the 50 percent fly ash paste (Figure 5.8) when comparing the relative intensities of C_3S and C_2S peaks at 2.77 Å and 2.74 Å with C_3A peaks at 2.70 Å. The relative amount of C_3A present in the early stages of hydration appears to be much greater in the 50 percent fly ash paste when compared to the plain P.C. pastes and 20 percent fly ash pastes. This increase in the relative C_3A content can be attributed to the fly ash which contains a considerable amount of C_3A. The higher fly ash is also considered responsible for an increase in the intensity of the 3.34 Å peak, which remains relatively constant throughout the hydration process. In the case of the 50 percent fly ash pastes, this peak is probably representative of the

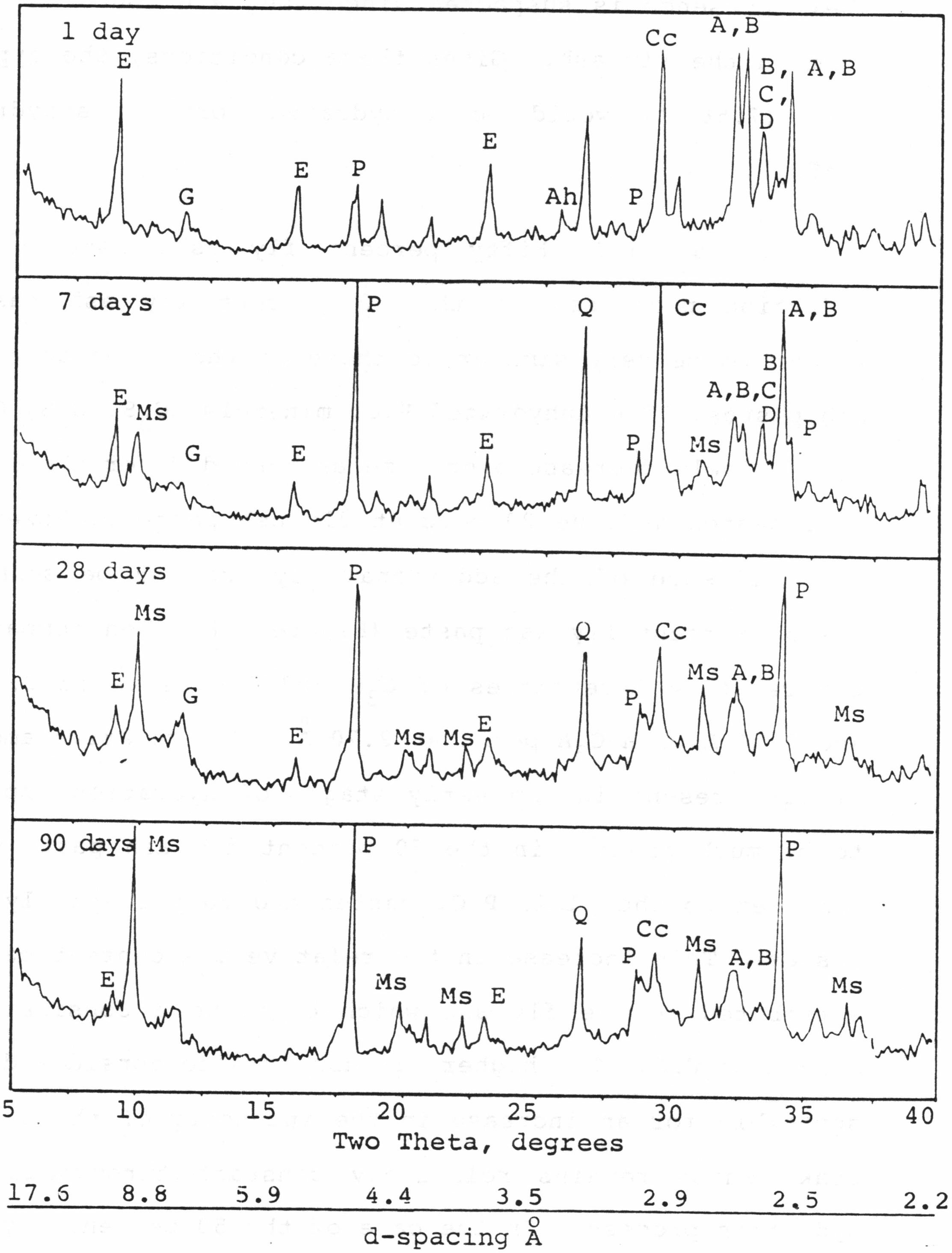

Figure 5.8 X-Ray Diffractograms of 50% Fly Ash Pastes

quartz content of the fly ash.

However, the major constituent of the 50 percent fly ash pastes at seven days and beyond is calcium hydroxide [$Ca(OH)_2$]. The amount of calcium hydroxide [$Ca(OH)_2$] displayed over this period in the diffractograms appears to be relatively constant. Judging by the fly ash paste data, it may be concluded that the fly ash used is not effective in removing the excess calcium hydroxide [$Ca(OH)_2$] from fly ash cement mixes.

Another hydration process similar to that of the 20 percent fly ash pastes is the conversion of ettringite to monosulfoaluminate. In the 50 percent fly ash pastes, however, this process is much more pronounced. At the early stages of hydration (one day) the intensity of the 9.73 Å ettringite peak is much higher for the 50 percent fly ash paste than for the 20 percent fly ash paste. The conversion of the ettringite to monosulfoaluminate beyond this point is greatly accelerated when compared to the 20 percent fly ash paste. In fact, this process is so accelerated that by 90 days the 8.92 Å monosulfoaluminate peak rivals the 4.90 Å calcium hydroxide peak and the 9.73 Å ettringite peak is nearly nonexistent.

Other minerals such as gypsum, periclase (MgO), and possibly anhydrite ($CaSO_4$) are also believed to be present in the 50 percent fly ash paste as a result of the higher fly ash content. The 3.49 Å anhydrite ($CaSO_4$)

peaks which is present in the one day diffractogram only may disappear at later ages because the anhydrite present in the fly ash hydrates and is converted into gypsum or some other hydration product. The 7.56 Å gypsum peak tends to increase over time.

5.2.4.4 One hundredpercent fly ash paste - With the exception of fly ash powder diffractogram, the 100 percent fly ash paste diffractograms bear little resemblance to the other diffractograms in this study. The 100 percent fly ash paste diffractograms appear, instead, to be similar to only the original fly ash powder diffractogram with the peaks of the more soluble or reactive minerals such as C_3A, anhydrite ($CaSO_4$), and CaO weakened by hydration and the new peaks from the reaction products such as ettringite, monosulfoaluminate, and calcite emerging from the background noise.

In all three of the diffractograms, shown in Figure 5.9, the 3.34 Å quartz peak is extremely dominant. The intensity of the quartz peaks, as well as the periclase (MgO) peaks, appear to be relatively constant, indicating that these minerals do not participate in the hydration process. However, the cement mineral, C_3A, does appear to be reactive as its 2.70 Å peak steadily declines over time. Even more reactive, the anhydrite ($CaSO_4$) and CaO peaks are nearly undetectable after seven days of

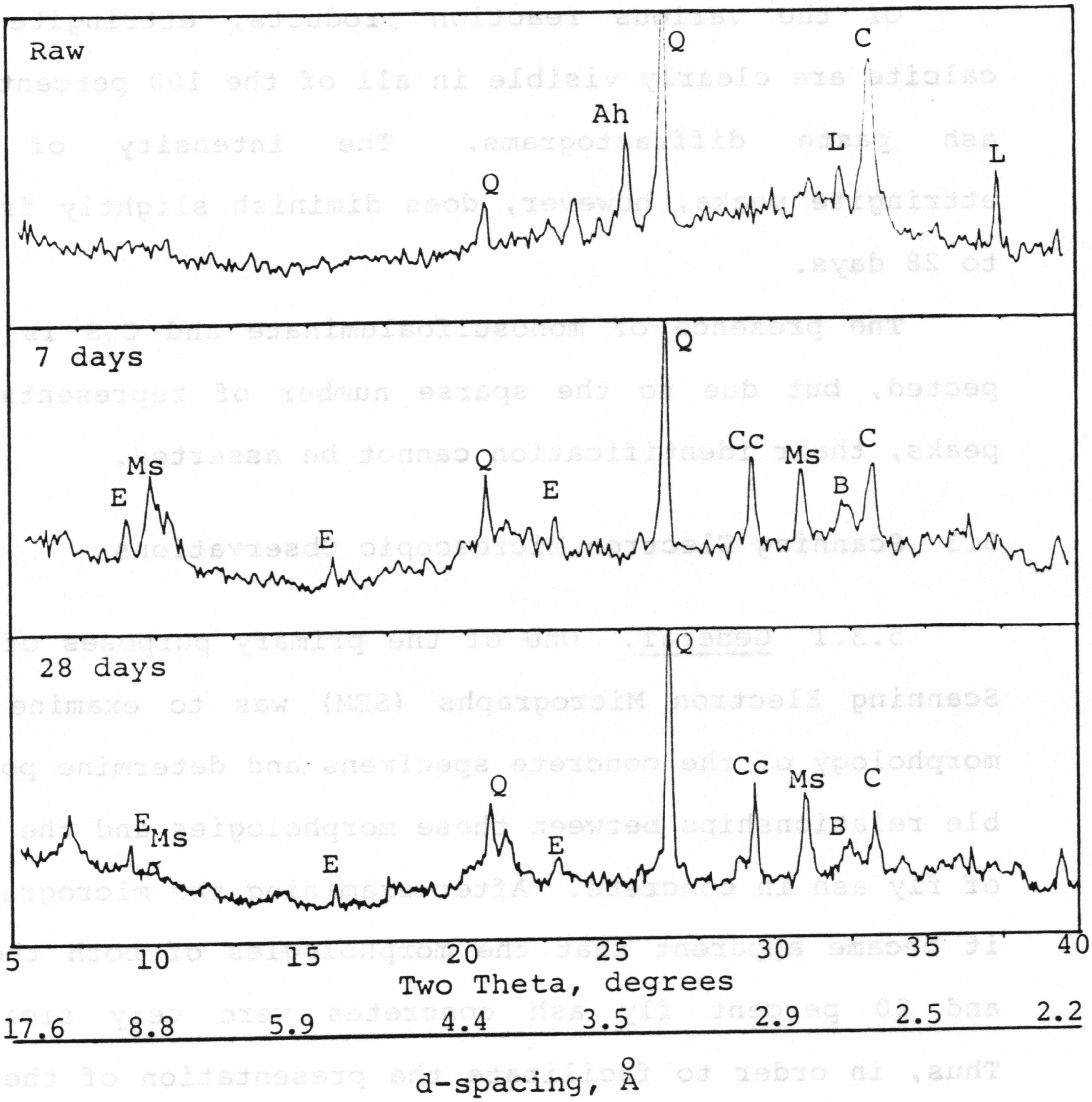

Figure 5.9 X-Ray Diffractograms of 100% Fly Ash Powder and Pastes

hydration.

Of the various reaction products, ettringite and calcite are clearly visible in all of the 100 percent fly ash paste diffractograms. The intensity of the ettringite peaks, however, does diminish slightly from 7 to 28 days.

The presence of monosulfoaluminate and C_2S is suspected, but due to the sparse number of representative peaks, their identification cannot be asserted.

5.3 Scanning Electron Microscopic Observations

5.3.1 General. One of the primary purposes of the Scanning Electron Micrographs (SEM) was to examine the morphology of the concrete specimens and determine possible relationships between these morphologies and the role of fly ash in concrete. After examining the micrographs, it became apparent that the morphologies of both the 30 and 50 percent fly ash concretes were very similar. Thus, in order to facilitate the presentation of the micrographs, fly ash concretes will be discussed as one group. First, however, two other groups of micrographs, the raw materials (fly ash and Portland cement) and the plain P.C. concrete, will be presented.

5.3.2 Raw Materials. Figures 5.10 through 5.13 are micrographs of the raw fly ash and Portland cement. The

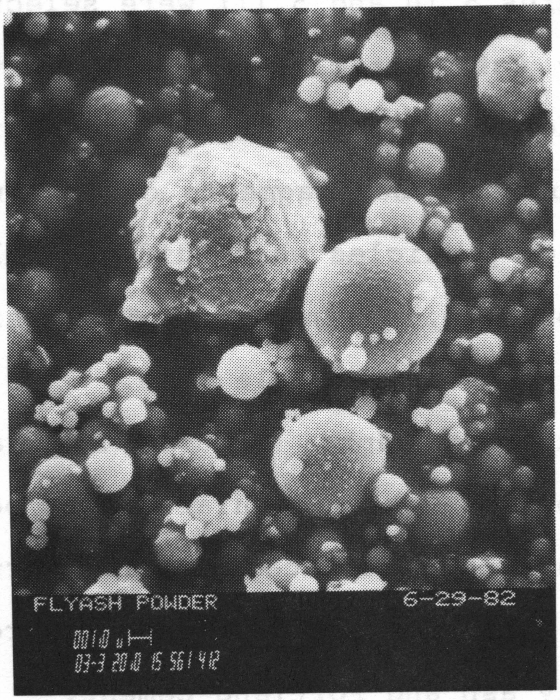

Figure 5.10 Raw Fly Ash (3000X)

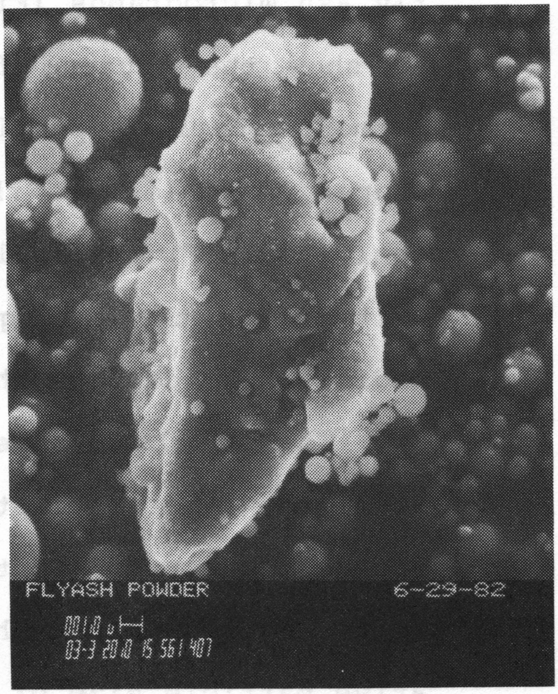

Figure 5.11 Raw Fly Ash (3000X)

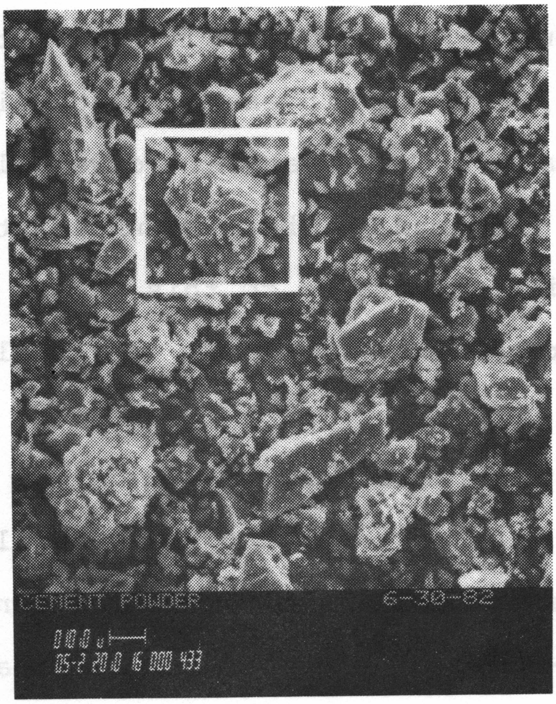

Figure 5.12 Portland Cement (500X)

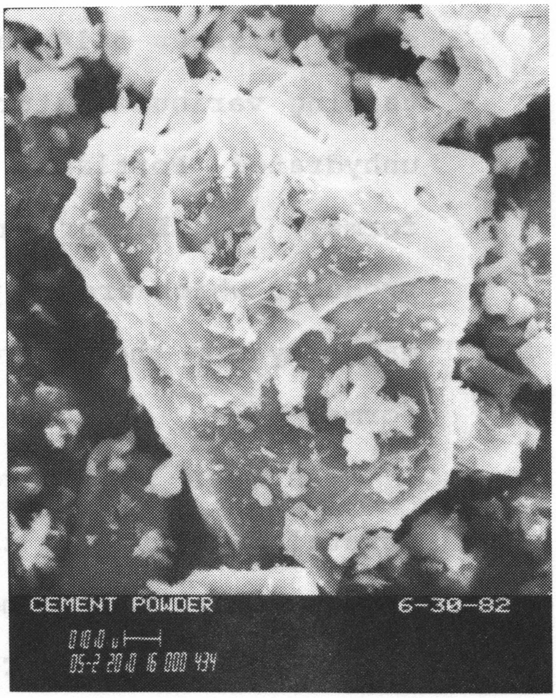

Figure 5.13 Portland Cement (3000X)

fly ash micrographs (Figures 5.10 and 5.11) were selected to show the unusual fly ash particles as well as the common spherical particles. Many of these irregularly shaped particles are thought to be fragments of unburned coal, as in Figure 5.11, or particles which did not fully melt during the firing process, as in Figure 5.10 which additionally depicts the range in particle size.

The Portland cement micrographs (Figures 5.12 and 5.13) show the contrast between the irregular shaped particles of cement and the smooth surfaced fly ash particles. These micrographs also show the difference in relative particle size of fly ash and Portland cement.

5.3.3 Plain Portland Cement Concrete. The scanning electron micrographs of the plain Portland cement concrete (Figures 5.14 through 5.17) revealed surfaces containing various features, such as air entrainment voids, unhydrated Portland cement, and various crystalline forms. The latter are presumed to be cement reaction products which are of prime importance to this study; the majority of the micrographs present these crystalline forms.

As seen in Figure 5.14, the most prevalent of the crystalline forms in the one and seven day plain Portland cement concrete specimens are foil-like structures tentatively identified as C-S-H gel or a tricalcium aluminate

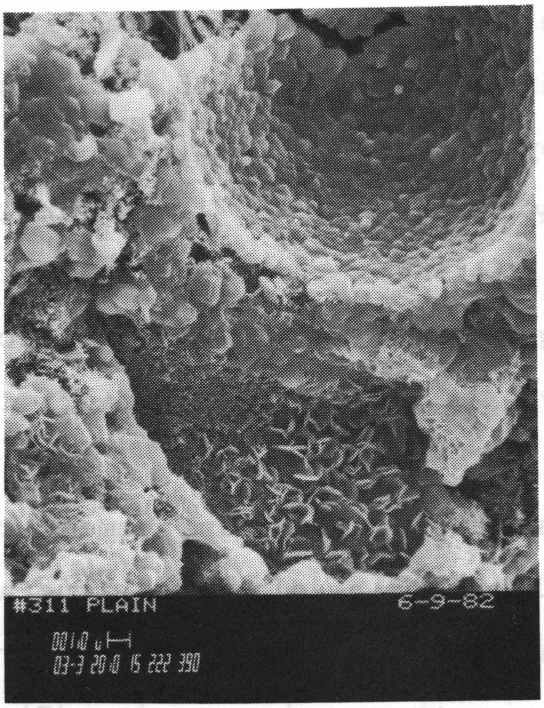

Figure 5.14 Plain P.C. Concrete @ 1 day (3000X)

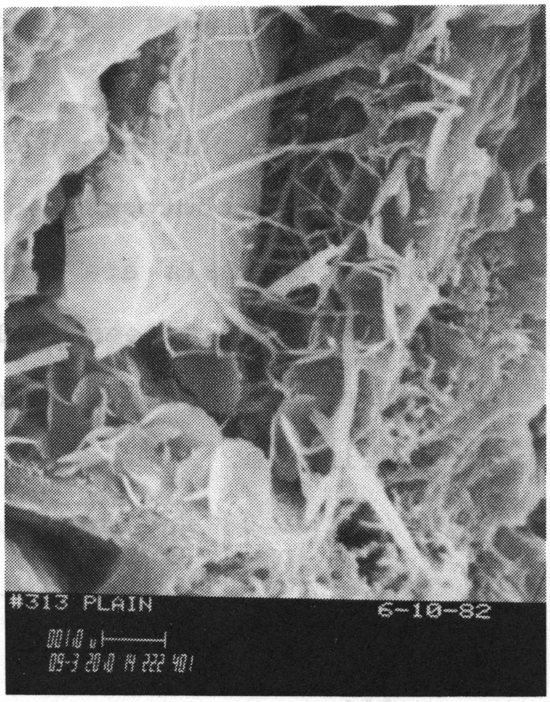

Figure 5.15 Plain P.C. Concrete @ 7 days (9000X)

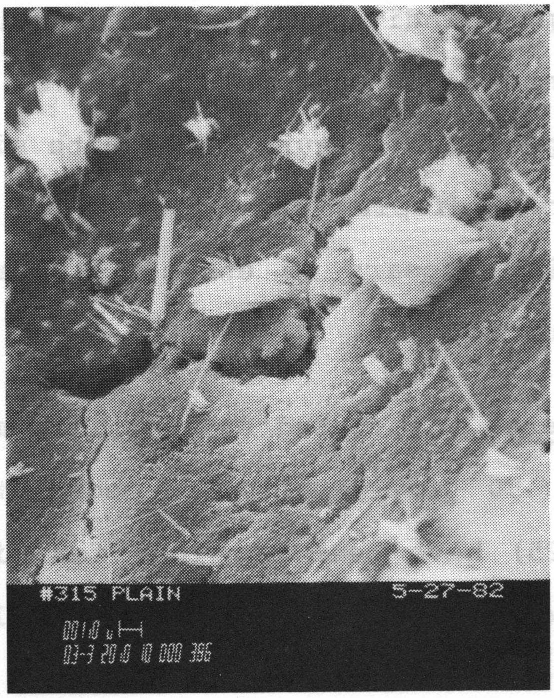

Figure 5.16 Plain P.C. Concrete @ 28 days (3000X)

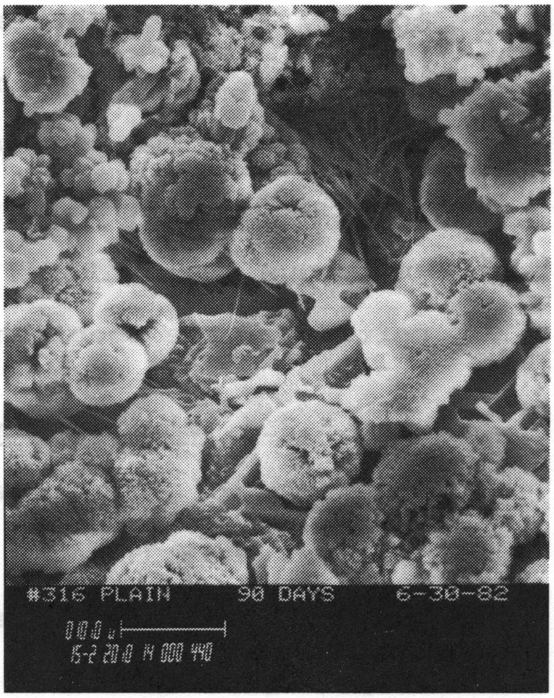

Figure 5.17 Plain P.C. Concrete @ 90 days (1500X)

hydrate. These foil-like structures are similar in appearance to the hydration products of tricalcium aluminate photographed by Plowman et al.(46) and the C-S-H gel photographed by Jawed et al.(34). Typically, these crystals are found filling surface depressions or voids and, as seen in Figure 5.15, are frequently accompanied by needle-like crystals tentatively identified as ettringite.

The 28 day specimens of plain Portland cement concrete reveal fewer foil-like and needle-like structures when compared with the earlier specimens. The few crystalline structures seen in these micrographs (Figure 5.16) are generally needle-like in shape and considerably more slender than the earlier needle-like crystals. Typically, these crystals grow individually or in groups within the air entrainment voids and are thought to be ettringite. The 90 day specimens (Figure 5.17) with similar needle-like structures, display an abundance of an amorphous precipitate which appears to encrust a large portion of the specimen surface.

5.3.4 <u>Fly Ash Concrete</u>. As stated earlier, the micrographs of the 30 and 50 percent fly ash concretes (Figures 5.18 through 5.25) have been combined for discussion since these specimens appear to have similar morphologies.

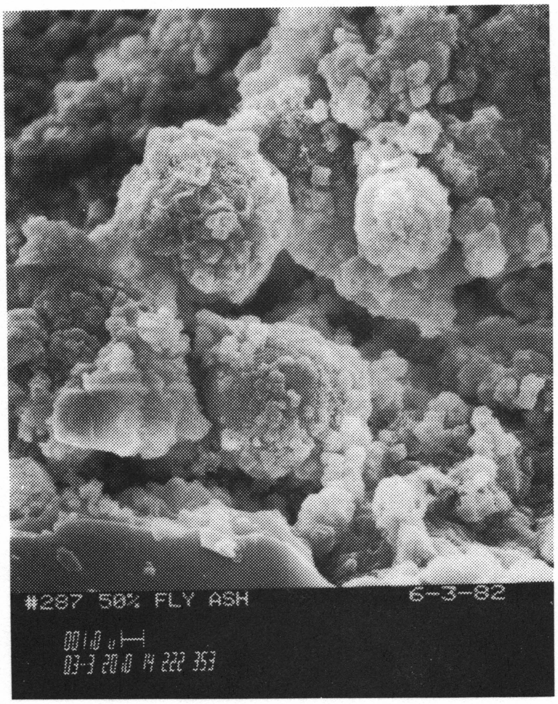

Figure 5.18 50% Fly Ash Concrete @ 1 day (3000X)

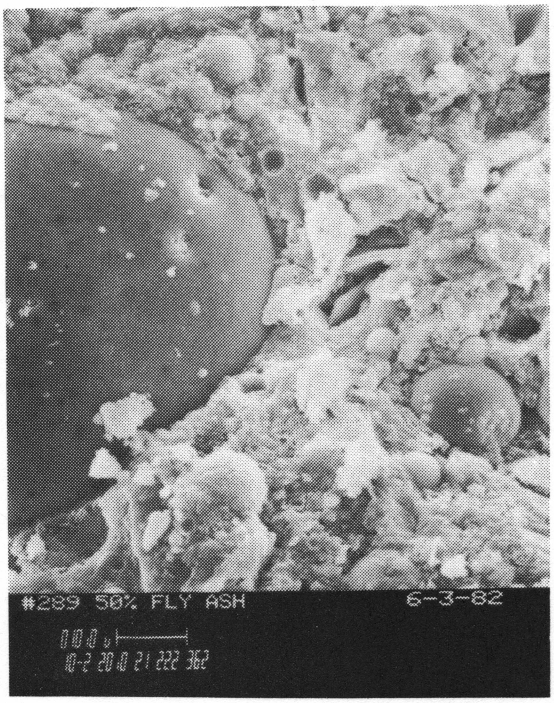

Figure 5.19 50% Fly Ash Concrete @ 7 days (1000X)

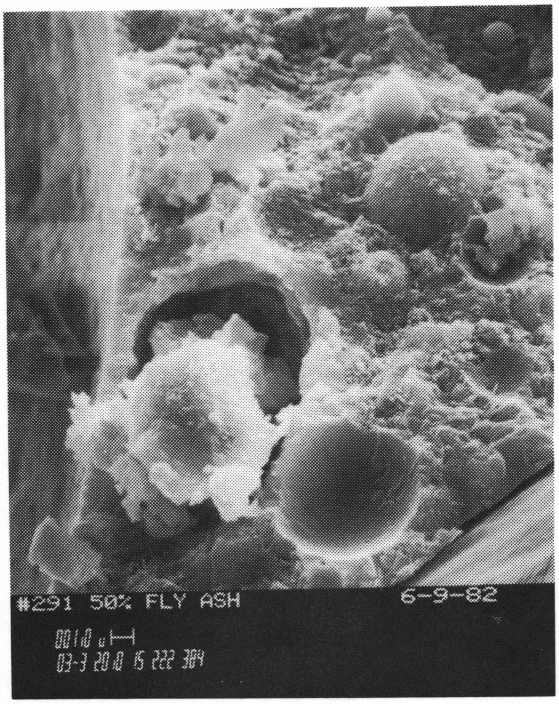

Figure 5.20 50% Fly Ash Concrete @ 28 days (3000X)

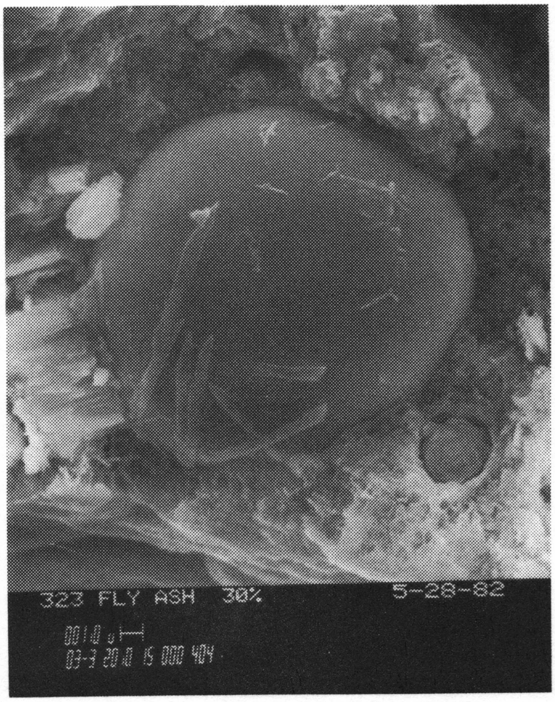

Figure 5.21 30% Fly Ash Concrete @ 28 days (3000X)

Figure 5.22 30% Fly Ash Concrete @28 days (7000X)

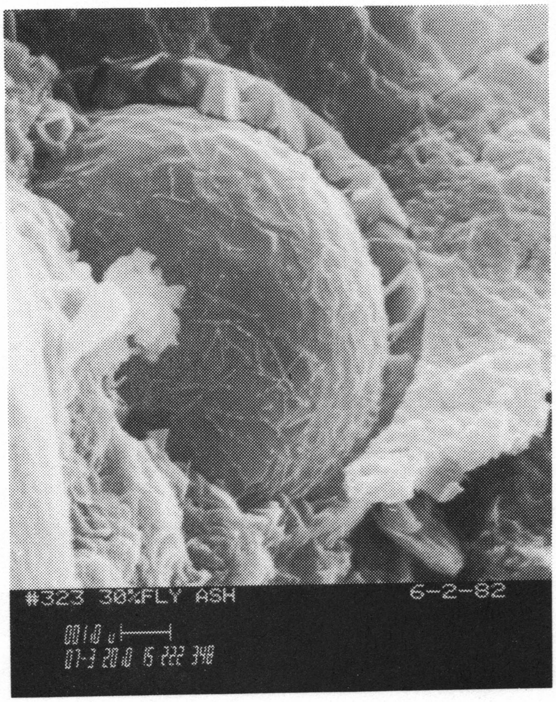

Figure 5.23 30% Fly Ash Concrete @28 days (7000X)

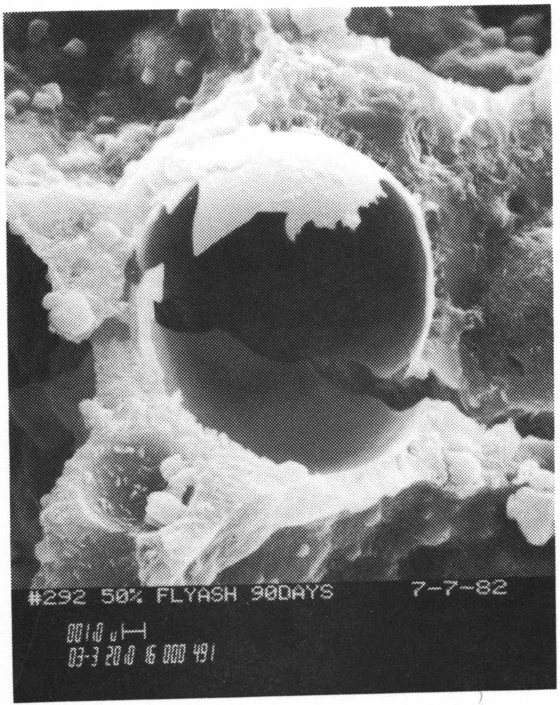

Figure 5.24 50% Fly Ash Concrete @90 days (3000X)

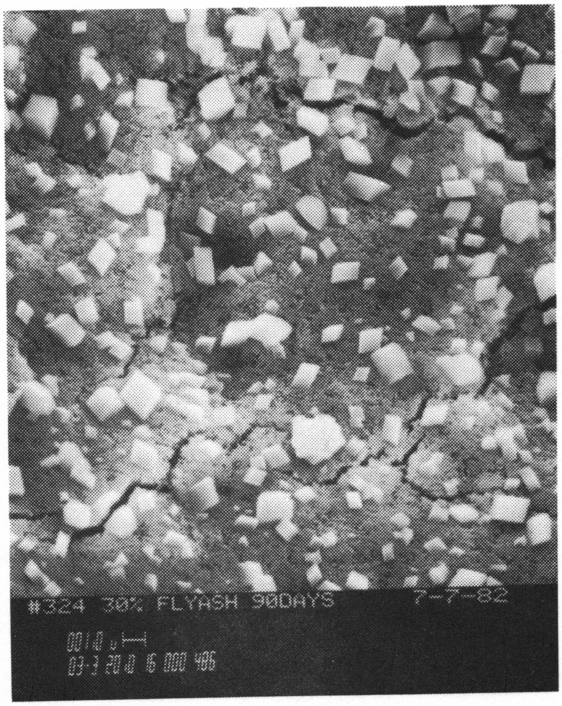

Figure 5.25 30% Fly Ash Concrete @90 days (3000X)

When compared with the one day specimens of plain P.C. concrete, the one day specimens of fly ash concrete (Figure 5.18) display fewer crystalline forms. Among the few crystalline forms observed, are foil-like structures similar to those found in the plain P.C. concretes. However, these structures in the fly ash concretes are much more difficult to detect. Equally difficult to find in the one day specimens, are individual fly ash particles. As seen in Figure 5.18, fly ash particles at this stage of hydration are coated with a "duplex film" similar to that reported by Diamond (17) and Ghose et al. (27). This film camouflages the fly ash sphere, and it is considered to be a precipitated hydration product such as C-S-H gel or calcium hydroxide rather than a reaction product from the fly ash particle itself. Virtually all of the fly ash spheres seen in the one day specimens are coated with this film.

The 7 day specimens of the fly ash concrete (Figure 5.19) reveal a very different situation. Most of the fly ash particles are no longer totally encrusted in duplex film, as they are in one day samples, but are instead fairly smooth with no indication of a coating. These "clean" fly ash particles were apparently detached from the surrounding matrix when the sample was fractured. Several smooth voids can be found where the fly ash had been "pulled out" of the surface. Such "pull out" features, as termed by Grutzeck et al (30), can be observed in several of the micrographs at seven days and beyond (Figure 5.20). The few fly ash particles which are still coated with duplex film are found almost exclusively in air entrainment voids or similar areas where the coating was not attached to the surrounding matrix. At this stage of hydration, none of the fly ash appeared to have reacted.

By 28 days, the morphology of individual fly ash particles has greatly diversified compared with earlier specimens. As in the case of the seven day specimens, several smooth fly ash spheres are present at 28 days. In several instances, crystalline needles are seen growing on the surface of these spheres as in Figure 5.21. Such formations are observed in both 28 day and 90 day fly ash concrete specimens. Heavily coated fly ash particles, like the one in the lower portion of Figure 5.20, are also present, but in greatly reduced numbers when compared with earlier samples. Present for the first time, however, are fly ash particles which appear to have reacted as observed in Figures 5.22 and 5.23. Many of these particles seem to have an etched appearance (Figure 5.22), while other seem to have an encrusted appearance (Figure 5.23).

The particle in Figure 5.22 typifies the etched morphology seen in both the 28 day and 90 day fly ash concrete samples. Although this particle appears to be entwined in a web of interlocking crystalline fibers, it is more likely that this reacted appearance is the result of the etching of the glassy component within the fly ash particle. Based on Diamond's (17) explanation such etching would leave the less reactive crystalline material intact while removing the soluble glassy material.

The encrusted fly ash particle morphology in Figure 5.23, gives some indication of the depth of the hydration surrounding the particle. In this micrograph, a portion of the reacted material of the particle has been broken away revealing a partial cross section of the particle, showing a distinct zone of hydration separating the unreacted portion of the fly ash particle from the surrounding matrix. Similar formations were reported by Grutzeck et al. (30) who observed that:

> "The pattern which evolves is one of in situ hydration of the fly ash sphere, which is gradually consumed in the hydration reaction. The glass sphere is replaced by radiating clusters or bundles of fibrous C-S-H material, which in cross section have a typical honeycomb appearance."

In the 90 day micrograph, Figure 5.24, this same "reacted zone" phenomenon is observed again; however, the fly ash particle is a partially broken cenosphere. The breakage of the particle, which was probably concurrent with the development of an intersecting dessication crack, provided a fortunate opportunity to view the particle cross section. This particular micrograph, which shows a large reacted zone surrounding a very thin shell of unreacted fly ash, conforms perfectly to Grutzeck's model of high lime fly ash hydration.

An additional interesting feature of the 90 day fly ash concrete micrographs is the presence of several cubic and hexagonal shaped crystals. Similar formations are observed through out the 90 day micrographs of both the fly ash and plain P.C. concretes. In the case of the plain P.C. concretes, as described previously, these formations appear to be amorphous (Figure 5.17). However, in the case of fly ash concrete, these formations appear to be more crystalline, as judged by the sharpness of their edges. Figure 5.25 is an example of an area where these formations appear to be very crystalline. While the exact chemical composition of these formations is not known, their shape suggests that they may be composed of calcium hydroxide.

5.4 Correlation of Strength Data with other Tests

One of the primary purposes of this study was to address some of the questions concerning the differences in the hardening or strength-gaining processes between plain P.C. concrete and fly ash concrete. In this section some of these questions are explored by relating the results of the compressive strength tests with the other analyses, such as X-ray diffraction, scanning electron microscopy, etc.

The effects of fly ash on the hardening process are manifested as early as the setting stage, which is the first step in the hardening process. During this period fly ash has a retarding effect upon concrete, the extent of which is in direct proportion to the amount of fly ash used as cement replacement. While the physical dilution of the cement by the less cementitious fly ash is partially responsible for this behavior, it does not completely explain the apparent paradox that 100 percent fly ash concrete will set almost immediately. However, the heat of hydration curves (Figure 5.3) of the fly ash pastes and the X-ray diffractograms of the raw fly ash and the early fly ash pastes (Figures 5.7 through 5.9), are useful in advancing some suggestions. The fly ash paste heat of hydration curves indicate that the fly ash in these pastes hydrates very rapidly with cement hydration being delayed several hours. The X-ray diffractogram of the raw fly ash (Figure 5.9) indicates the presence of gypsum, anhydrite, lime, and C_3A. All of these are very soluble and contribute to the formation of ettringite, which is believed to play a major role in the retardation of Portland cement, either by forming an impervious layer about the cement grains or reducing the amount of water in the vicinity of the hydrating compounds (46). Since fly ash supplies these ettringite-forming minerals in both greater amounts and finer form compared to Portland cement, it seems reasonable to expect that fly ash chemically inhibits the cement hydration in the fly ash cement mixtures. This would help explain why the heat of hydration curves of the fly ash cement pastes display a small early peak (fly ash hydration) followed by a delayed large peak (cement hydration). As the replacement percentage approaches 100 percent, the weak ettringite structure, formed by the hydrating fly ash, apparently is adequate to produce a low level of strength and the hardening process of such high percentage fly ash mixtures is nearly complete at this early time.

As in the case of the heat of hydration tests and the time of setting tests, the one day compressive strength tests reflect the retarding effect of the fly ash on fly ash-cement mixtures. The strength gains beyond one day, however, were significantly greater for the higher percentage replacement concretes. To explain this phenomenon, it is helpful to review the causes that induce compressive strength in plain P.C. concrete.

The compressive strength of concrete, as stated by Philleo (45a), is affected by a number of factors including the gel strength and concentration, the degree of saturation of the concrete, the paste-aggregate bond, and the aggregate strength, size, and gradation. As all of these factors, with exception of the gel strength and concentration were kept constant, it is reasonable to assume that these two factors are responsible for the differences in strengths among the test concretes. It is also reasonable to assume that the gels produced in fly ash concrete possess similar strength properties to those produced in plain P.C. concrete. Thus, the gel concentration would then be the determining factor in the hardening process of fly ash concrete.

The concentration of the gel is affected by many factors, the most important being the water-cement ratio. Plain Portland cement gels typically contain a minimum of 25 percent empty space (using the lowest water-cement ratio possible to permit complete hydration). In fly ash-cement gel, however, the percentage may be lower since fly ash particles are smaller than cement particles thus permitting the gel to be better graded and more compact. Assuming that a large portion of the fly ash particles in the gel are gel-forming like the plain cement gels, it is probable that fly ash-cement gels are more concentrated than plain cement gels and thus stronger. The long term compressive strengths of the test concretes agree with this explanation in that these strengths are higher for the higher replacement, low water-solids ratio concretes.

Additional support and assertion come from the scanning electron micrographs. While no quantitative measurements were made, it is observed that fewer fly ash particles are visible than expected assuming that the fly ash particles acted as inert fillers. Thus it may be concluded that many of the fly ash particles had already hydrated.

The fly ash particle size and shape may also improve strength by reducing the amount of bleeding in fly ash concrete. Bleeding tends to destroy paste-aggregate bonds when bleed water collects on the under side of the coarse aggregate. From subjective observations, bleeding of the fly ash concretes appeared to be less than the plain P.C. concrete.

Another factor affecting the compressive strength of fly ash concrete through gel concentration is again related to the ettringite. The crystalline network formed by ettringite during the setting stage is thought to provide the framework in which the C-S-H gel forms (38). It is possible, then that an early abundance of ettringite may provide more sights for the formation of the gel to commence and thus enhance strength. After the gel formation is well underway, however, the ettringite is considered as a source of weakness and its destruction is considered advantageous (38).

As noted earlier, the X-ray diffractograms of the pastes indicate that an early abundance of ettringite exists in the higher replacement mixes. At later periods, ettringite is converted to monosulfoaluminate and gypsum. These trends tend to be accentuated by higher amounts of fly ash in the mixes, with the plain P.C. paste containing the lowest amount of ettringite at the earlier stages and virtually none of the ettringite being converted to other minerals. Thus, there appears to be a relationship between the level of ettringite and the development of strength in fly ash concrete.

The conversion of ettringite to other minerals may also be helpful in explaining an apparent discrepancy in the levels of calcium hydroxide. Normally the level of calcium hydroxide decreases as it pozzolanically reacts with the silica and alumina in the fly ash. As stated earlier, however, no such decrease occurs in any of the pastes. Assuming that the gel formed in the fly ash-cement pastes is partially pozzolanic in nature, there must be a source of lime available to the silica and alumina other than the crystalline calcium hydroxide detected by X-ray diffraction. The lime in solution from the fly ash would constitute such a source. If the lime in solution is utilized in a pozzolanic reaction, the ettringite may decompose into monosulfoaluminate and gypsum since, according to Lea (38), ettringite requires a saturated solution of lime and calcium sulfate to prevent decomposition. Further supporting evidence comes from the micrographs which suggest that the pozzolanic reaction of some fly ash particles occurs between the fly ash particle and a surrounding lime solution rather than a nearby calcium hydroxide crystal (Figures 5.23 and 5.24).

In conclusion, the effect of fly ash on the compressive strength of concrete, as observed in this study, may primarily be linked with two factors: the physical size and shape of the fly ash particles, and the chemical composition of the fly ash which controls the amount of calcium sulfoaluminates (ettringite and monosulfoaluminate) present in the concrete paste.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 General

The purpose of this study was to evaluate the differences in the hydration processes between plain P.C. concrete and fly ash concrete in which fly ash was used as partial replacement ingredient for Portland cement. To accomplish this task, a series of qualitative and quantitative tests were performed to monitor the hydration process of concretes and pastes with varying fly ash replacement percentages for periods up to one year. Of the possible qualitative tests that could have been used, X-ray diffraction and scanning electron microscopy techniques were selected to monitor the chemical composition and crystalline structure of the cementitious minerals participating in the hydration process. These tests, combined with the use of compressive strength tests as a quantitative measure, provided the primary basis of this study. Additional tests, such as time of set and heat of hydration measurements, were conducted to provide insight into the early stages of the hydration process.

6.2 Conclusions

Based on the data obtained and observations made in this study, the following conclusions have been drawn:

1. For the range of replacement percentages studied, the replacement of Portland cement with fly ash on an equal weight basis in concrete tends to lower the short term compressive strength (before seven days) and increase the long term compressive strength (after seven days).
2. The effect of lowering short term compressive strengths and raising long term compressive strengths appears to be directly proportional to the replacement percentage of the cement.
3. The use of the particular fly ash studied in concrete has a negligible effect on the long term level of calcium hydroxide [$Ca(OH)_2$]. This effect is contrary to the normal view that fly ash, through a pozzolanic reaction lowers the long term level of $Ca(OH)_2$. However, this does not imply that pozzolanic reaction involving fly ash does not occur; rather, it indicates that the pozzolanic reaction probably has a source of lime other than the crystalline calcium hydroxide found in the X-ray diffractograms. The fly ash is possibly a source of

this lime.

4. While the long term calcium hydroxide levels are relatively unaffected by the presence of fly ash, the levels of other minerals such as ettringite $(C_3A\bar{S}_3H_{32})$ and monosulfoaluminate $(C_3A\bar{S}H_{13})$ are significantly affected. The amount of ettringite present at the early stages of hydration and the rapidity of its conversion to monosulfoaluminate, appear to increase with increases in the replacement percentage in the paste. This effect may partially be due to the relative increase in the amount of tricalcium aluminate (C_3A) and anhydrite from the fly ash.

5. The development of compressive strength of fly ash concrete has been associated to two factors, one physical and one chemical. Physically, the fly ash contributes the strength by its size and spherical shape both of which help make the gel more compact and thus lower the water-solids ratio. Chemically, the development of strength appears to be related to the early presence of ettringite and its transformation into monosulfoaluminate as described above.

6. Scanning electron microscopic (SEM) observa-

tions of both unreacted and reacted fly ash particles, at advanced stages of hydration, tend to support Diamond's findings (17) that the chemistry of fly ash varies from particle to particle. Without such variation in chemical composition, it is difficult to explain the differences in the morphologies of unreacted and reacted fly ash particles.

7. Some of the morphological features of the micrographs (SEM) agree closely with Grutzeck's model of high lime fly ash hydration (30). These features include "pull out" features and the presence of reacted zones surrounding the remains of the original fly ash particle. Diamond's "duplex film" of C-S-H gel coating fly ash particle in the early stages of hydration is also observed in this study(17).

8. Within the range tested, the setting time of fly ash concrete is retarded in direct proportion to the fly ash content. However, this does not mean to imply that a 100 percent fly ash concrete will set more slowly than any concrete using both cement and fly ash. On the contrary, attempts to batch 100 percent fly ash concrete were futile because the mixtures undergo flash setting. This behavior has ten-

tatively been associated with the mineral ettringite which is thought to retard the early hydration of cement and the physical dilution of the cement by fly ash.

9. In general, the peak heat of hydration for fly ash/Portland cement pastes is inversely related to the fly ash content of the paste. Furthermore, the time required to reach the peak heat of hydration is directly proportional to the fly ash content of the paste. However, as in the case of the time of set tests, 100 percent fly ash mixtures do not follow these patterns. Instead, they peak very rapidly and at only a slightly lower temperature than plain P.C. mixtures. Again, this behavior is thought to be related to the mineral ettringite and the dilution of the cement.

6.3 Recommendations

While most of the test results from this study may be considered as positive arguments for greater fly ash utilization in concrete, there still remain several unanswered questions concerning the use of this locally produced fly ash in concrete. Thus, the following recommendations appear to be in order:

1. Considering the relatively high amount of

tricalcium aluminate (C_3A) and anhydrite present in this fly ash and knowing that these minerals are limited by ASTM in Portland cement to prevent volume stability problems, there is a need to study the durability of fly ash concrete exposed to alternate wetting and drying cycles. Furthermore, the durability of fly ash concrete exposed to chemical attack should be investigated in light of the relatively high levels of calcium hydroxide which exist late in the hydration process.

2. To improve the quantitative measurements of the mineral content of fly ash concrete, it is suggested that X-ray fluorescence be used in combination with X-ray diffraction in future studies. Additionally, the methods of processing the X-ray specimens should also be reevaluated so that carbonation of the specimen be minimized. This may allow some measurements of the various gel products to be made which would be extremely useful in explaining differences in compressive strengths of fly ash concretes.
3. The SEM studies should be extended to include energy dispersive techniques and thus improve the identification process of various mineral formations.

4. The study of setting time should be extended to investigate the physical and chemical differences between fly ash concrete and plain P.C. cement concrete at prior to set. From such an investigation insights may be gained into the problem of retarded set of fly ash concrete.

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APPENDIX A

Time of Setting Test Data

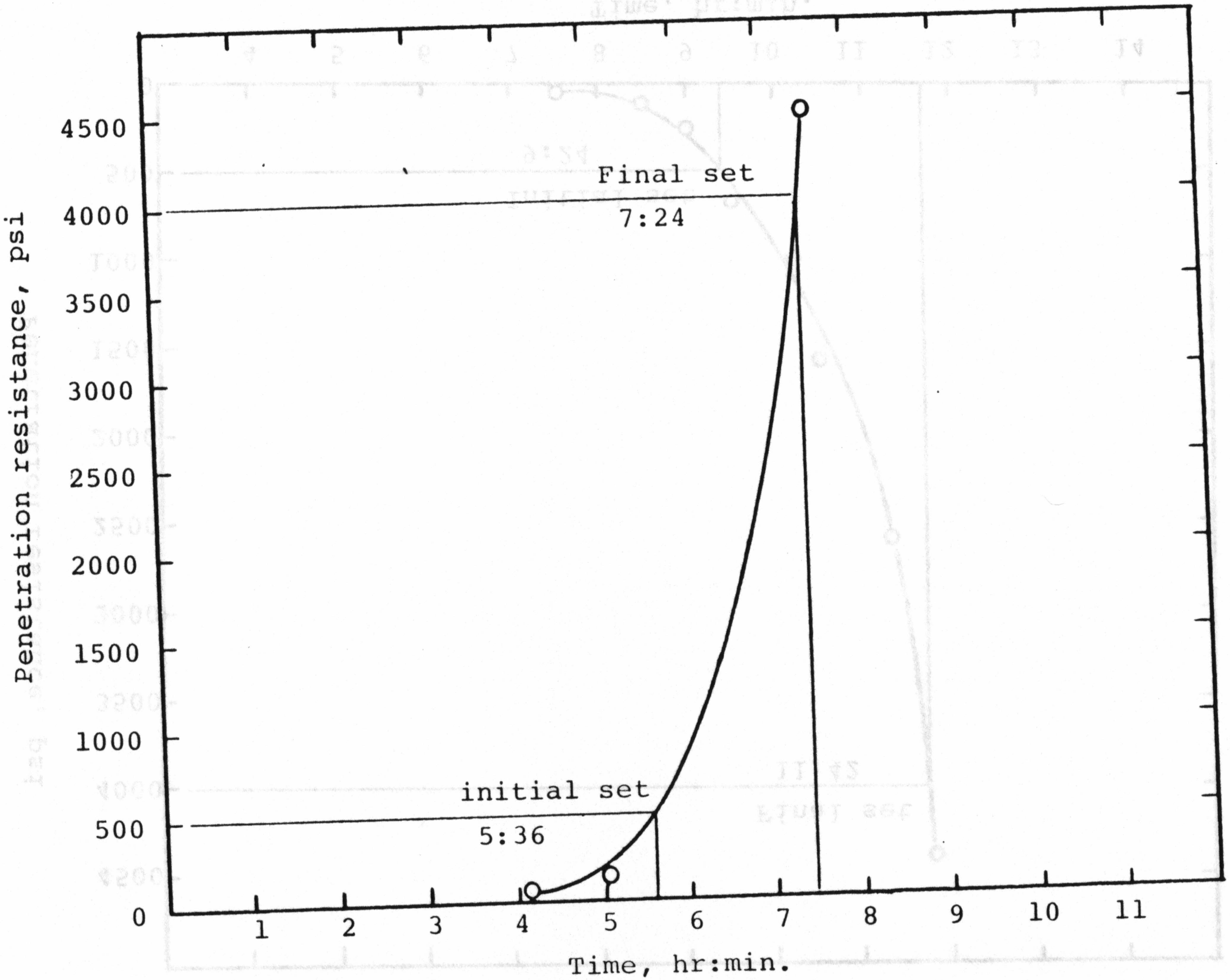

Figure A.1 Time of Setting Test for the Plain P.C. Concrete

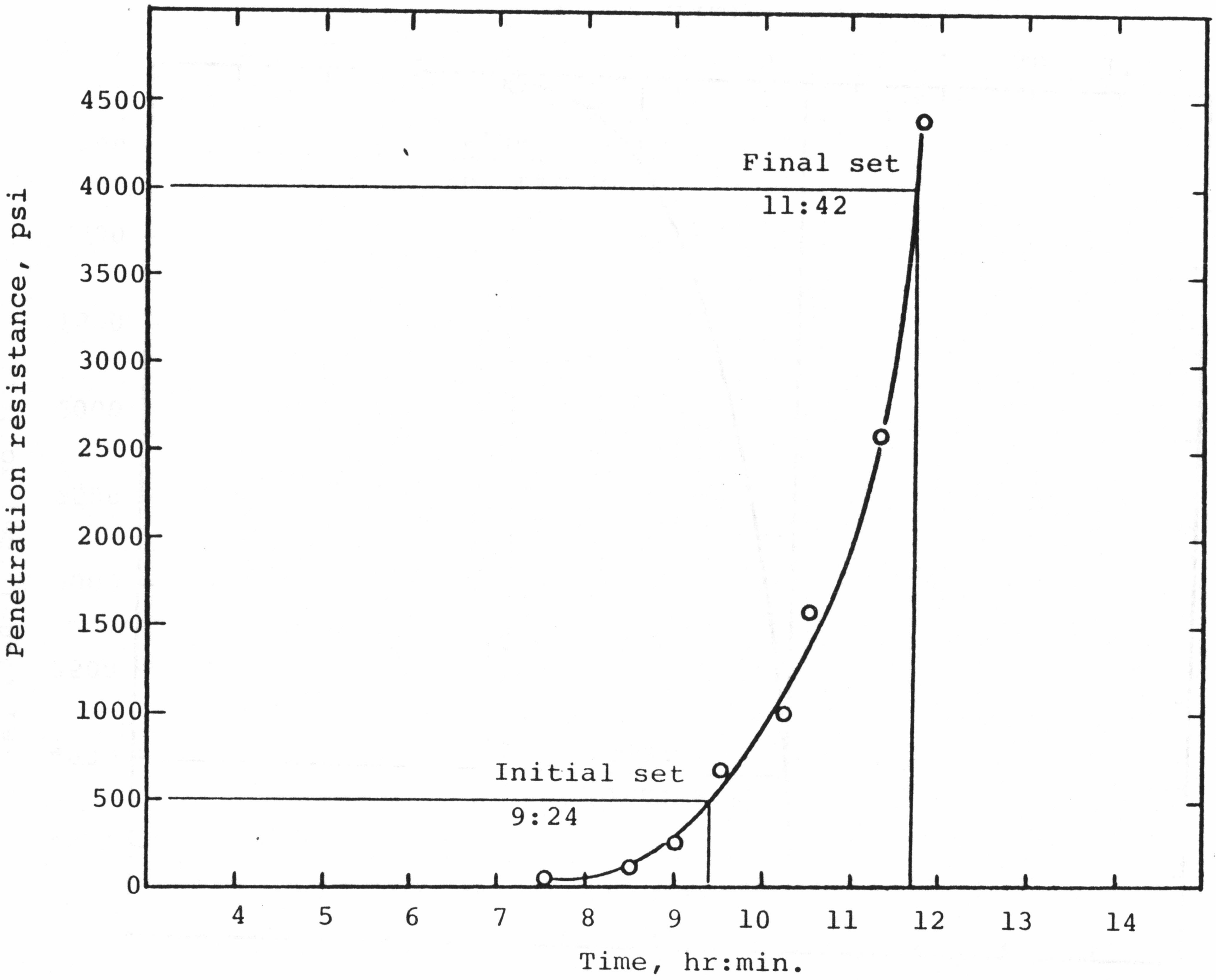

Figure A.2 Time of Setting Test for the 20% F.A. Concrete

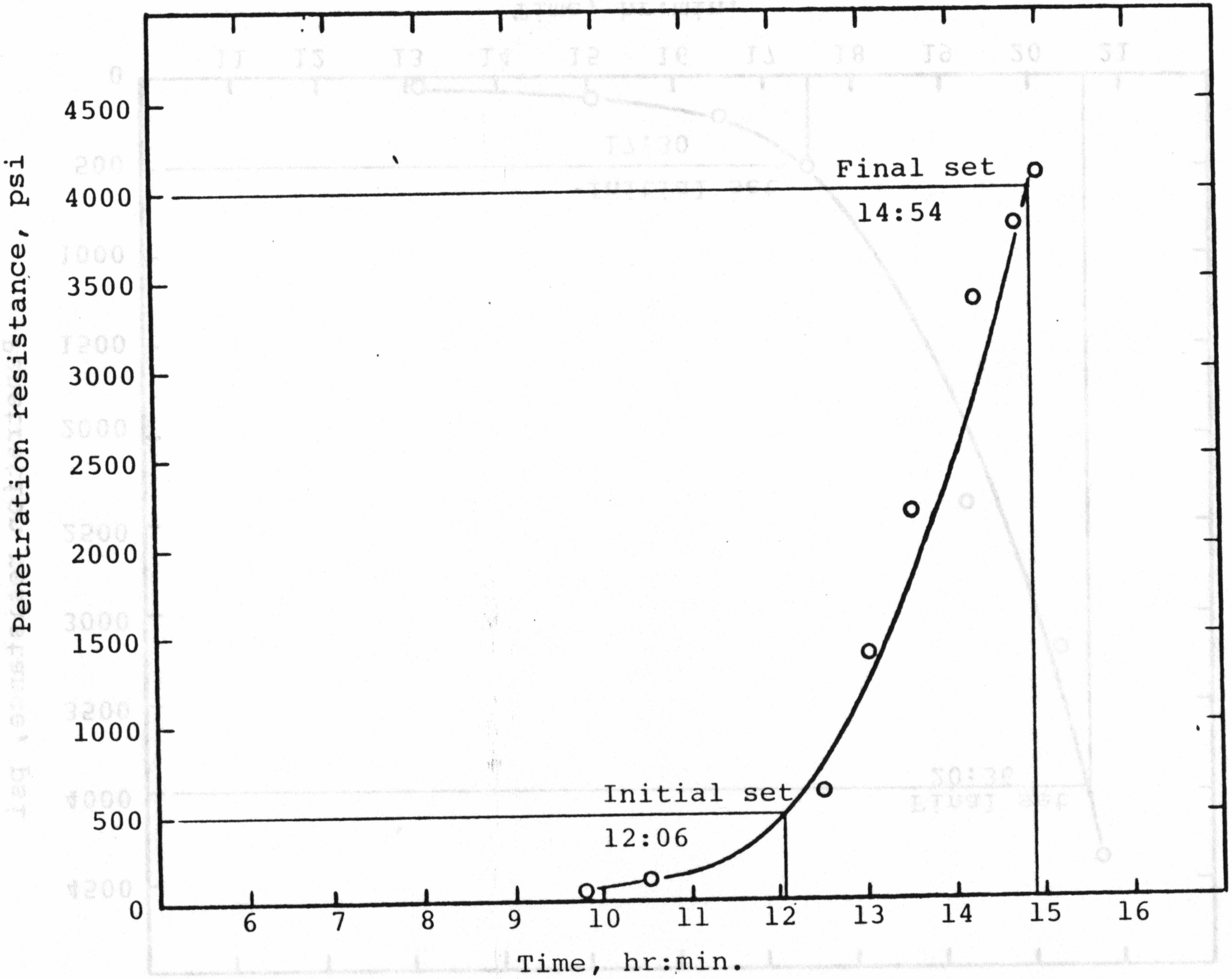

Figure A.3 Time of Setting Test for the 30% F.A. Concrete

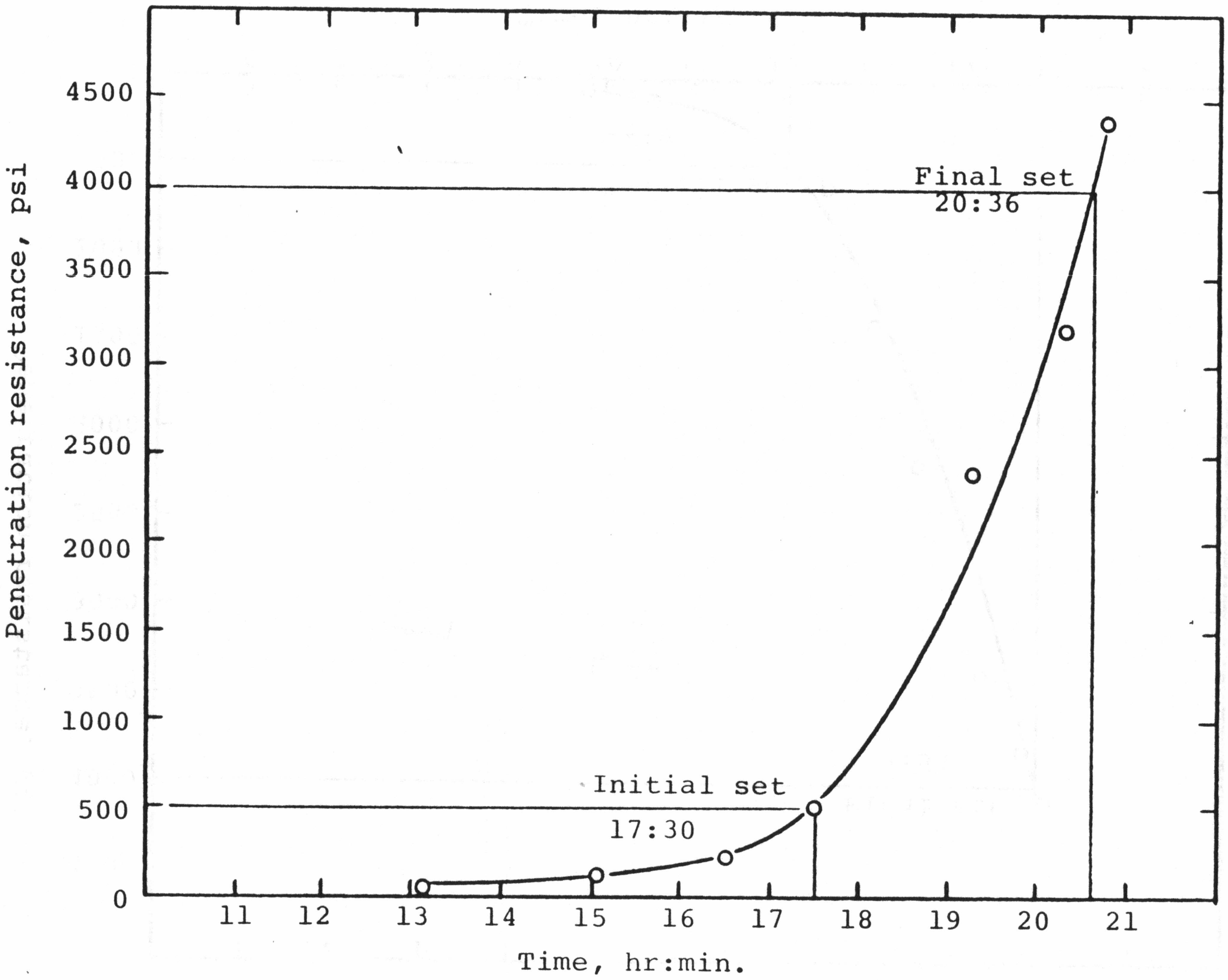

Figure A.4 Time of Setting Test for the 40% F.A. Concrete

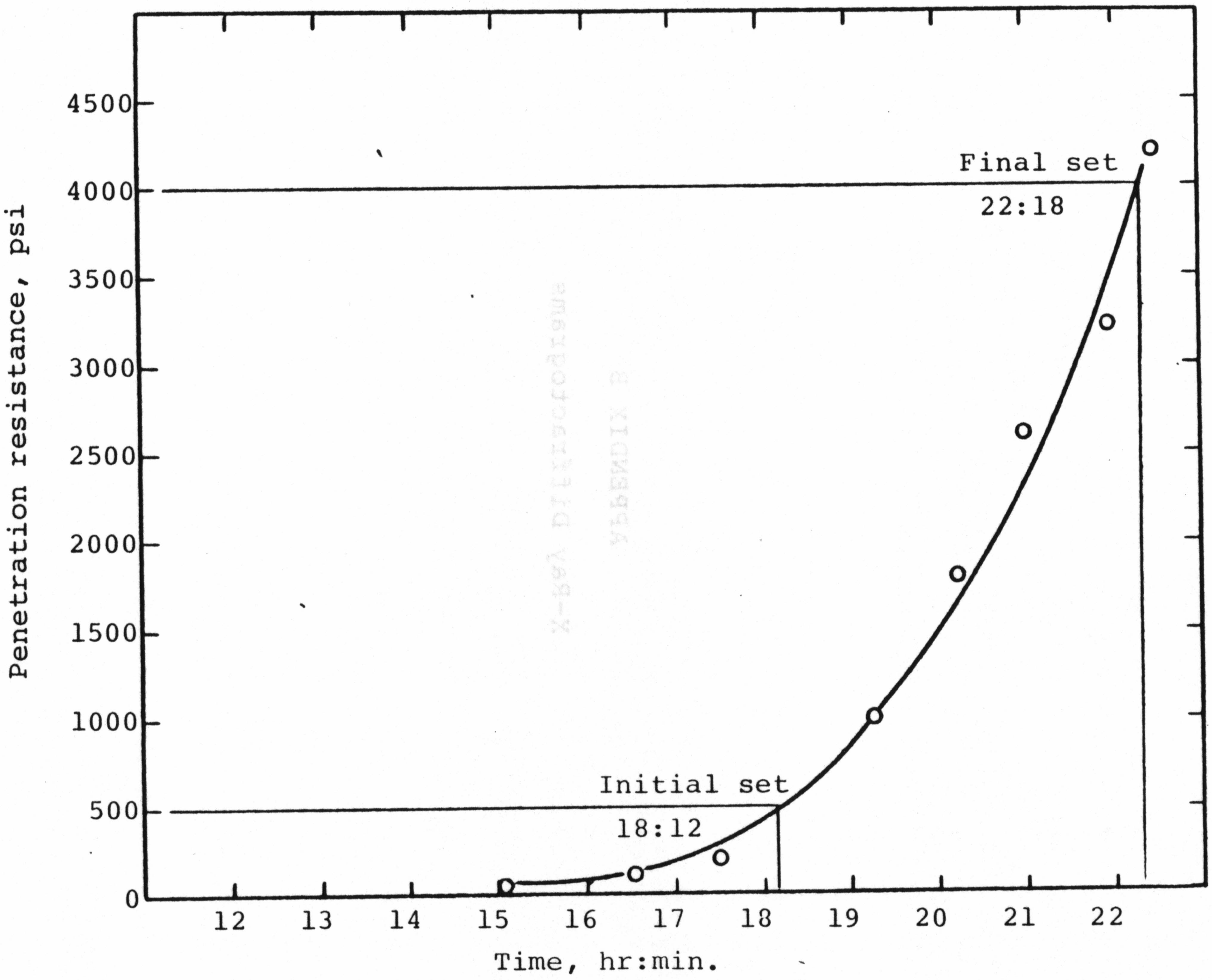

Figure A.5 Time of Setting Test for the 50% F.A. Concrete

APPENDIX B

X-Ray Diffractograms

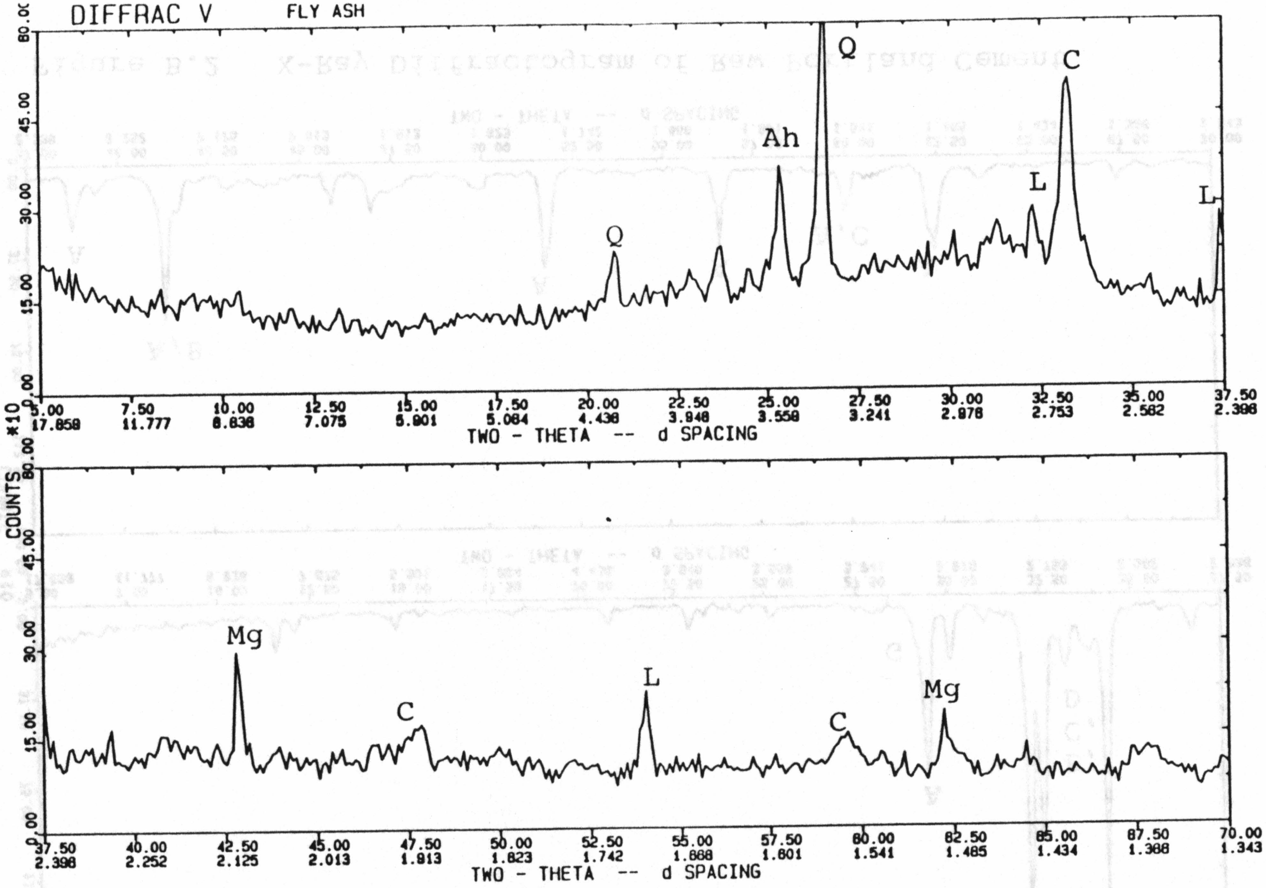

Figure B.1 X-Ray Diffractogram of Raw Fly Ash

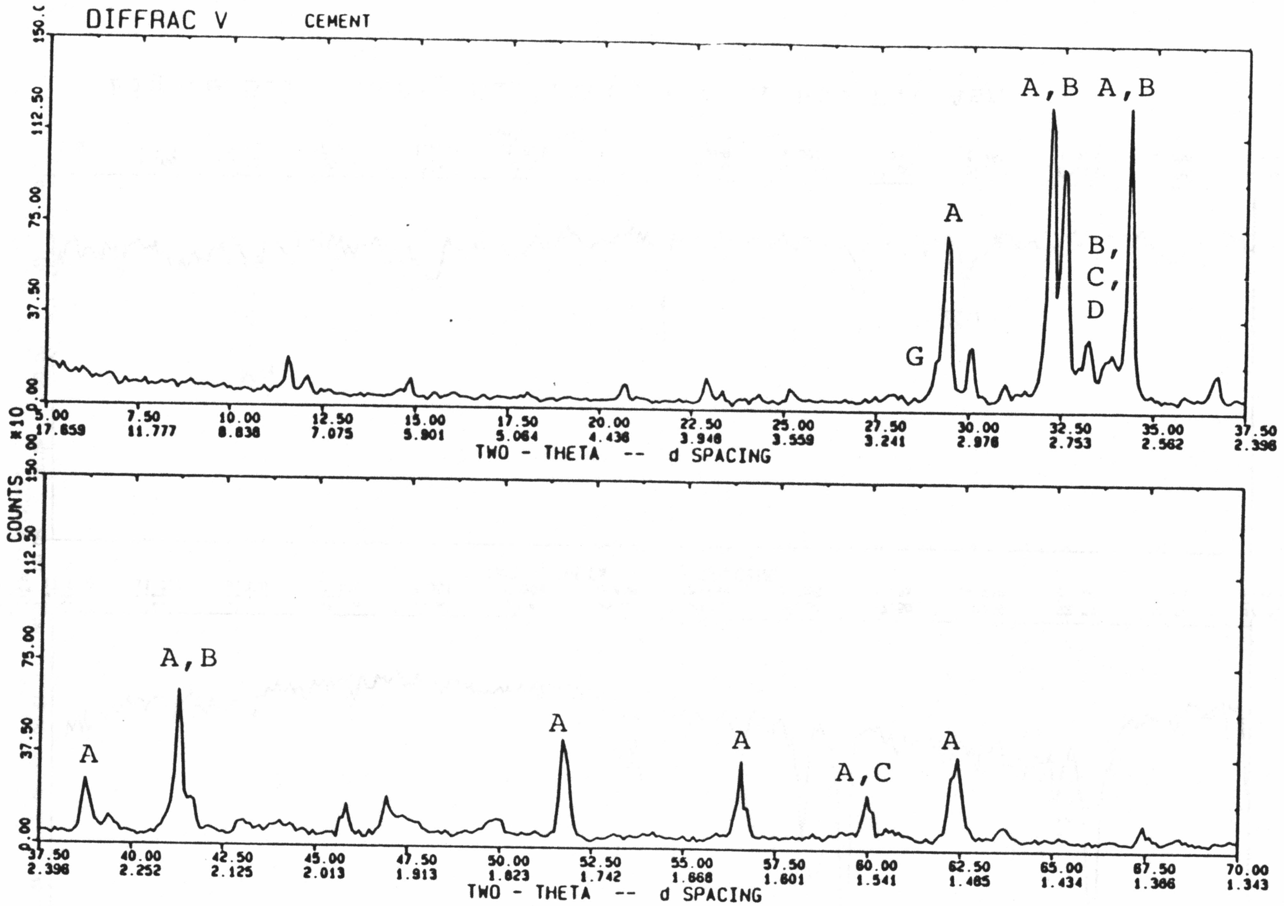

Figure B.2 X-Ray Diffractogram of Raw Portland Cement

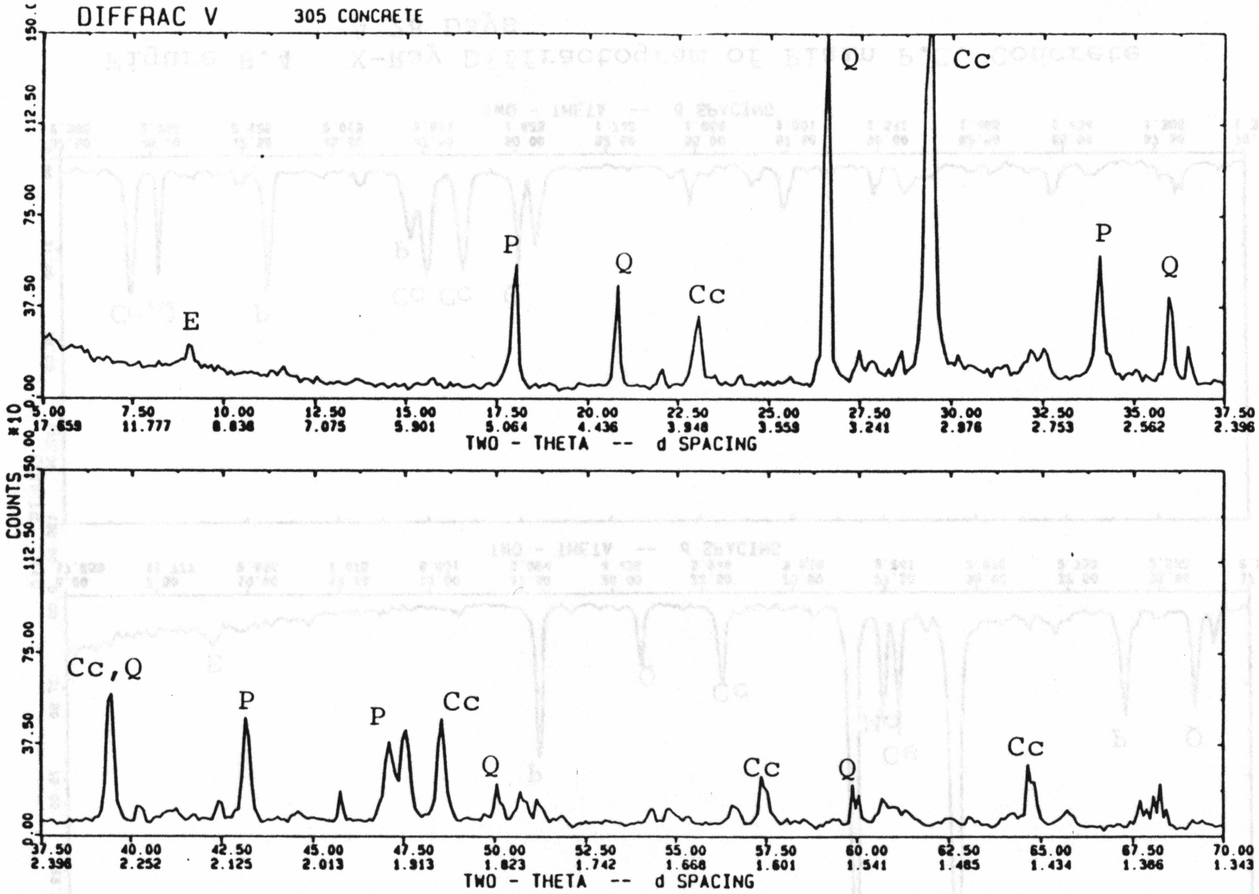

Figure B.3 X-Ray Diffractogram of Plain P.C. Concrete @ 7 Days

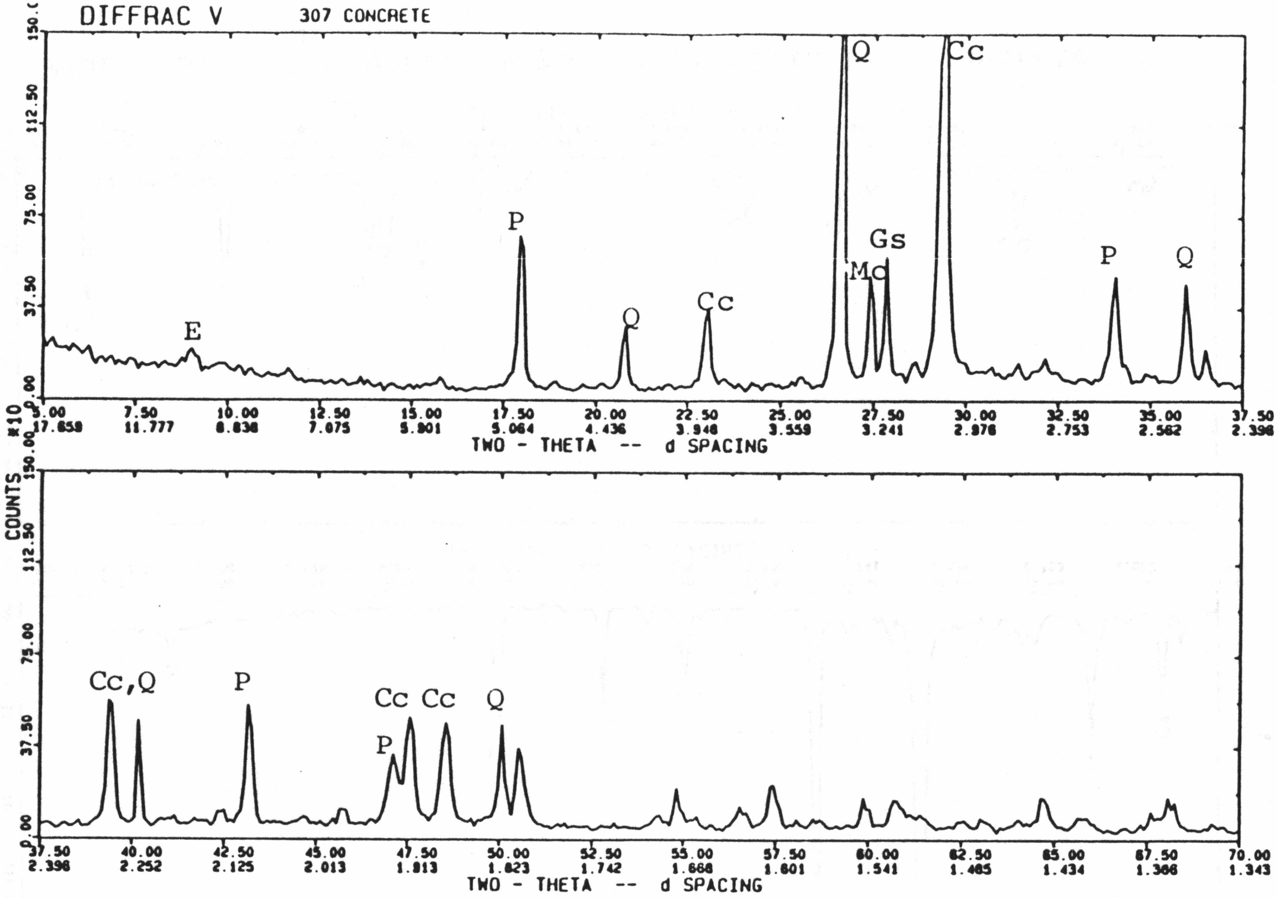

Figure B.4 X-Ray Diffractogram of Plain P.C. Concrete @ 28 Days

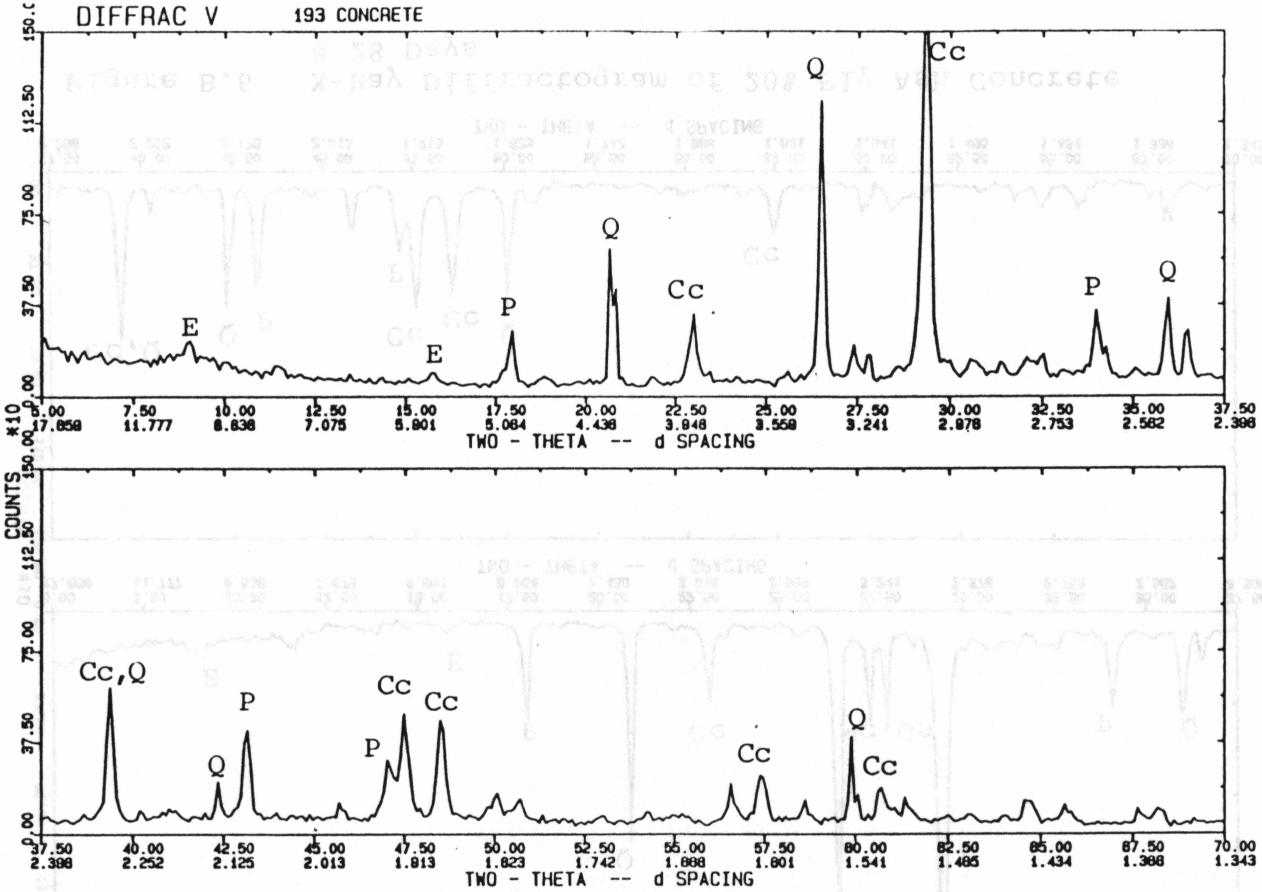

Figure B.5 X-Ray Diffractogram of 20% Fly Ash Concrete
% 7 Days

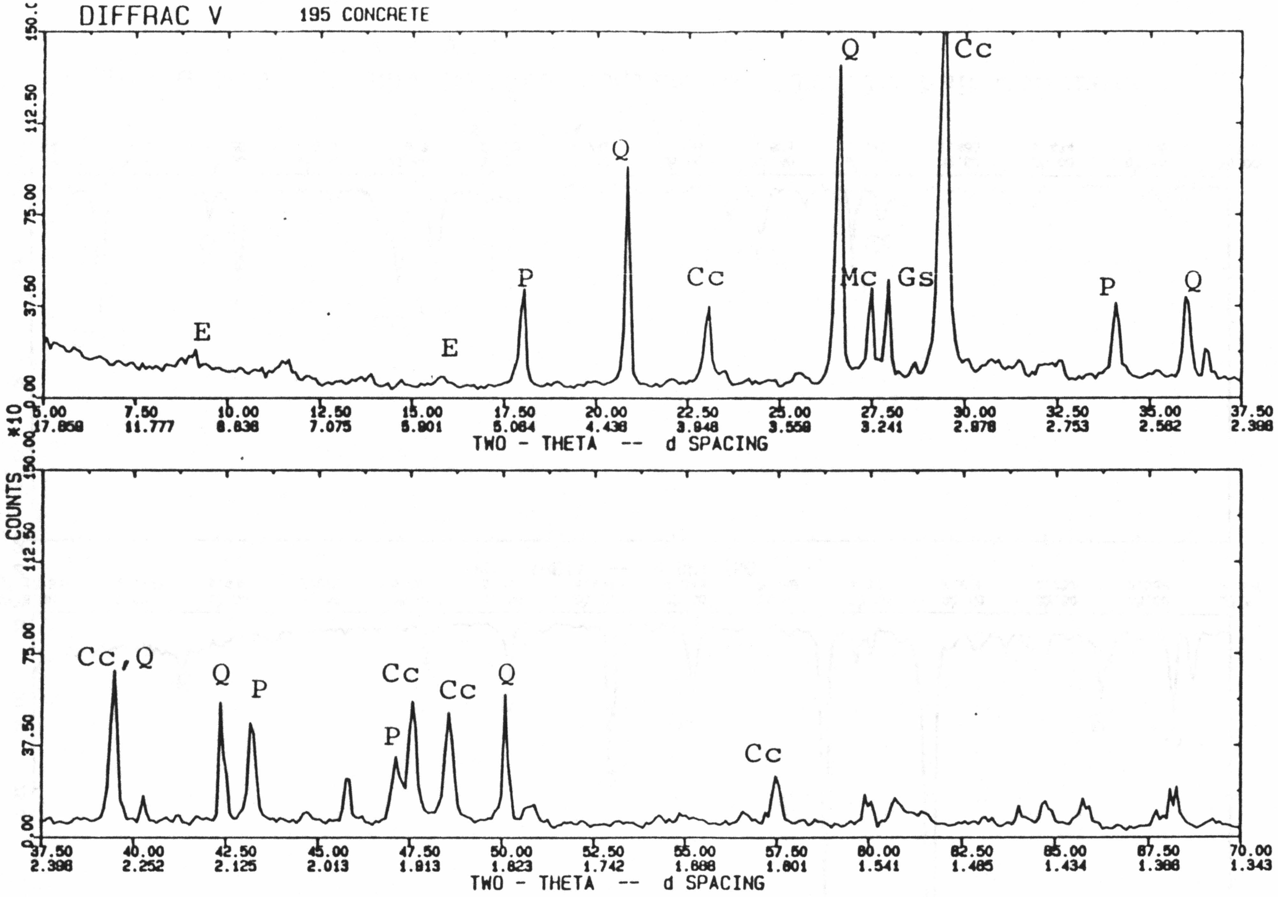

Figure B.6 X-Ray Diffractogram of 20% Fly Ash Concrete @ 28 Days

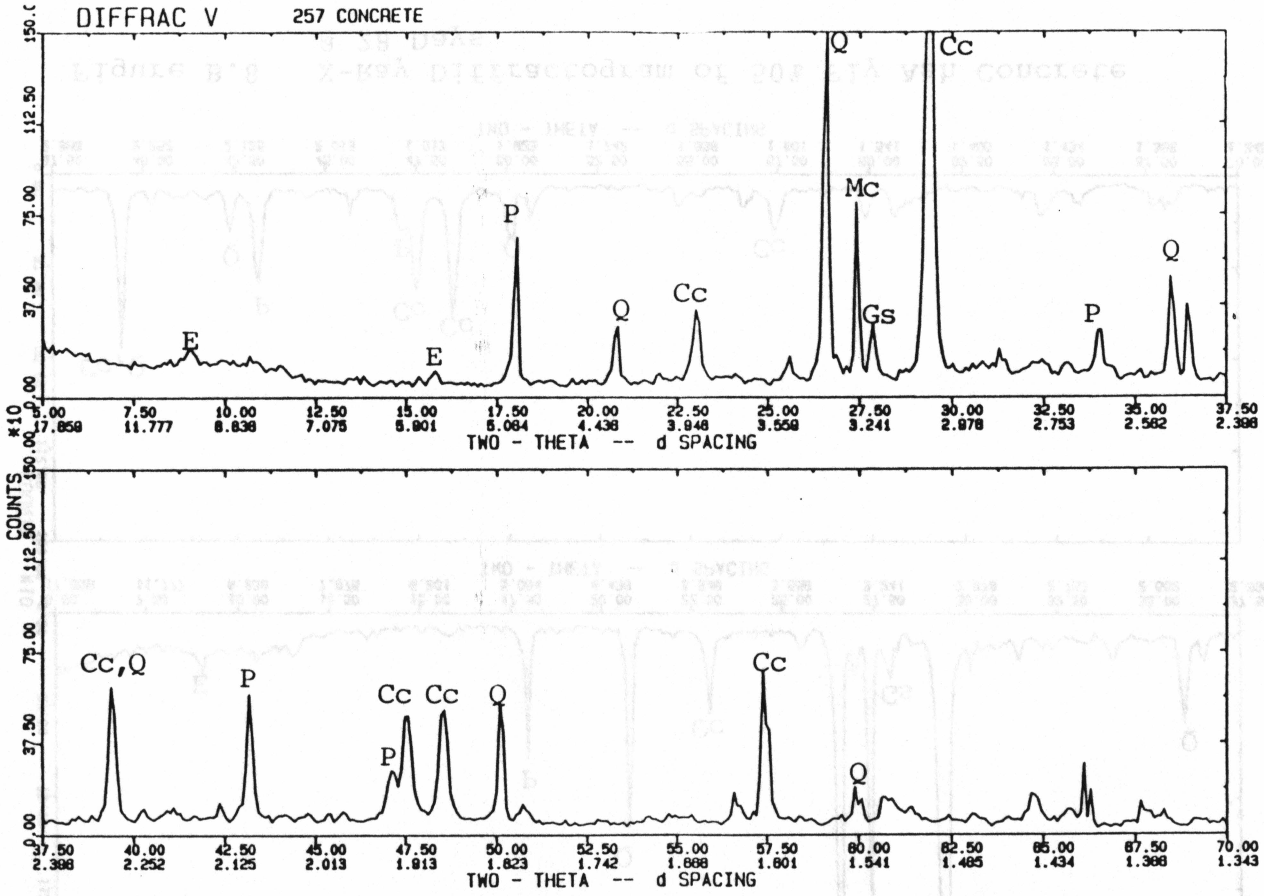

Figure B.7 X-Ray Diffractogram of 50% Fly Ash Concrete
@ 7 Days

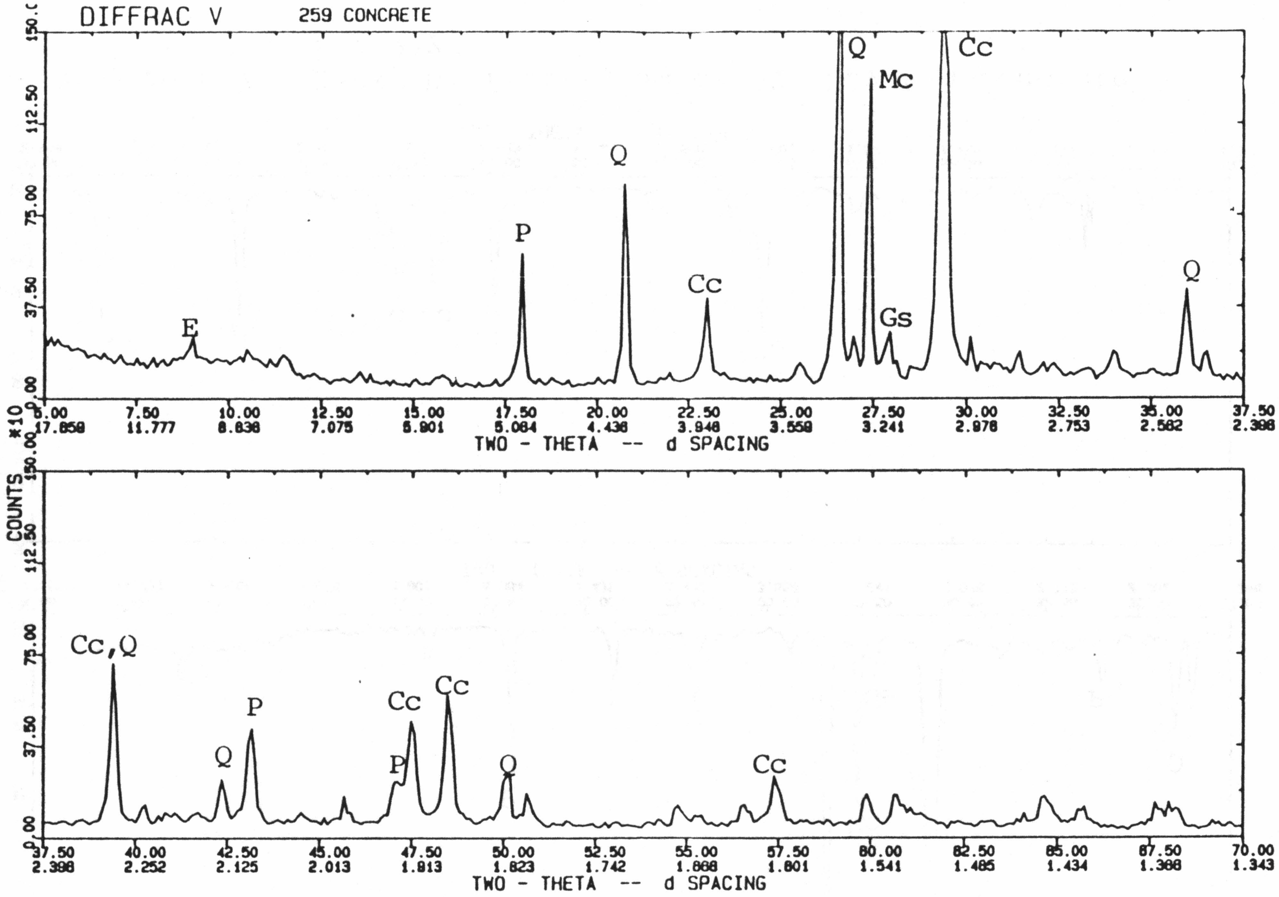

Figure B.8 X-Ray Diffractogram of 50% Fly Ash Concrete @ 28 Days

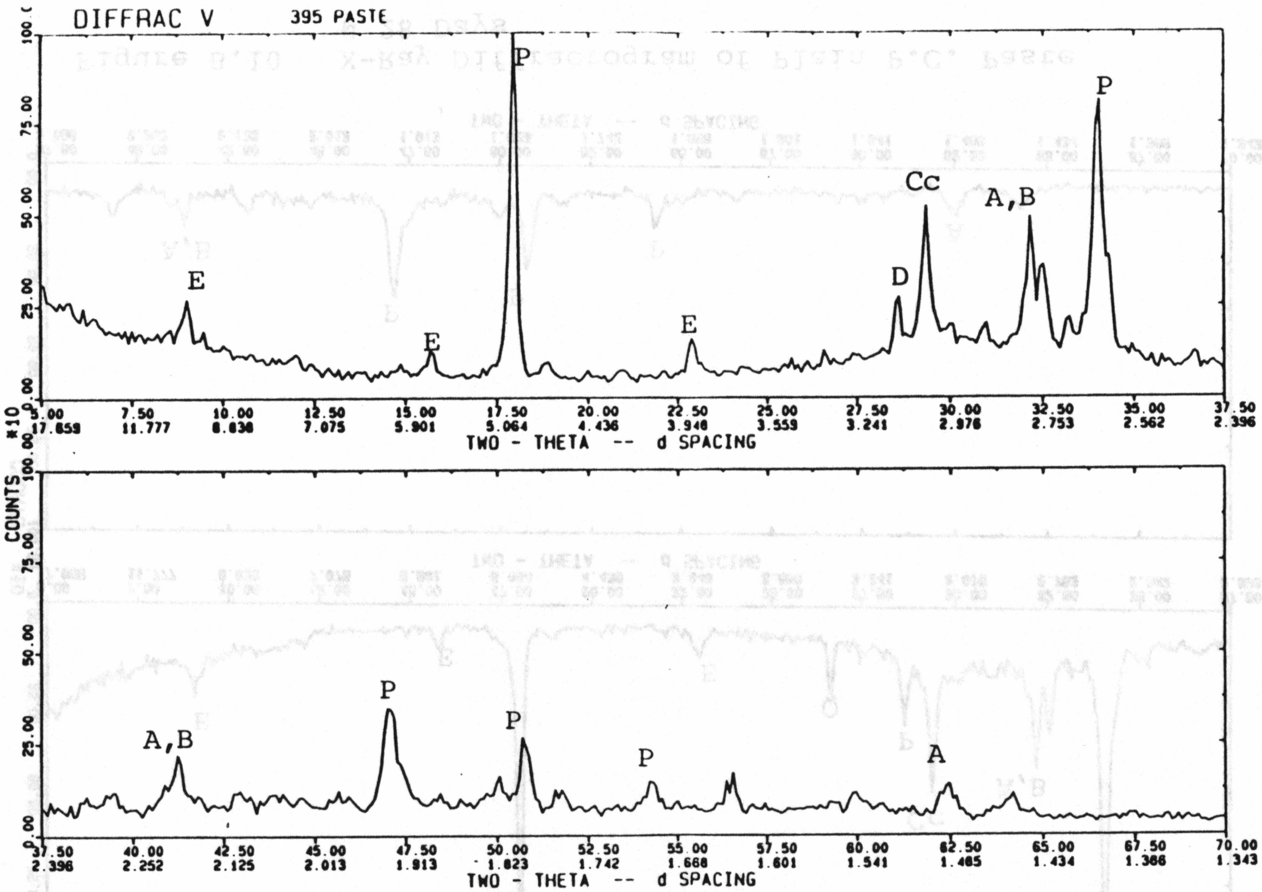

Figure B.9 X-Ray Diffractogram of Plain P.C. Paste @ 7 Days

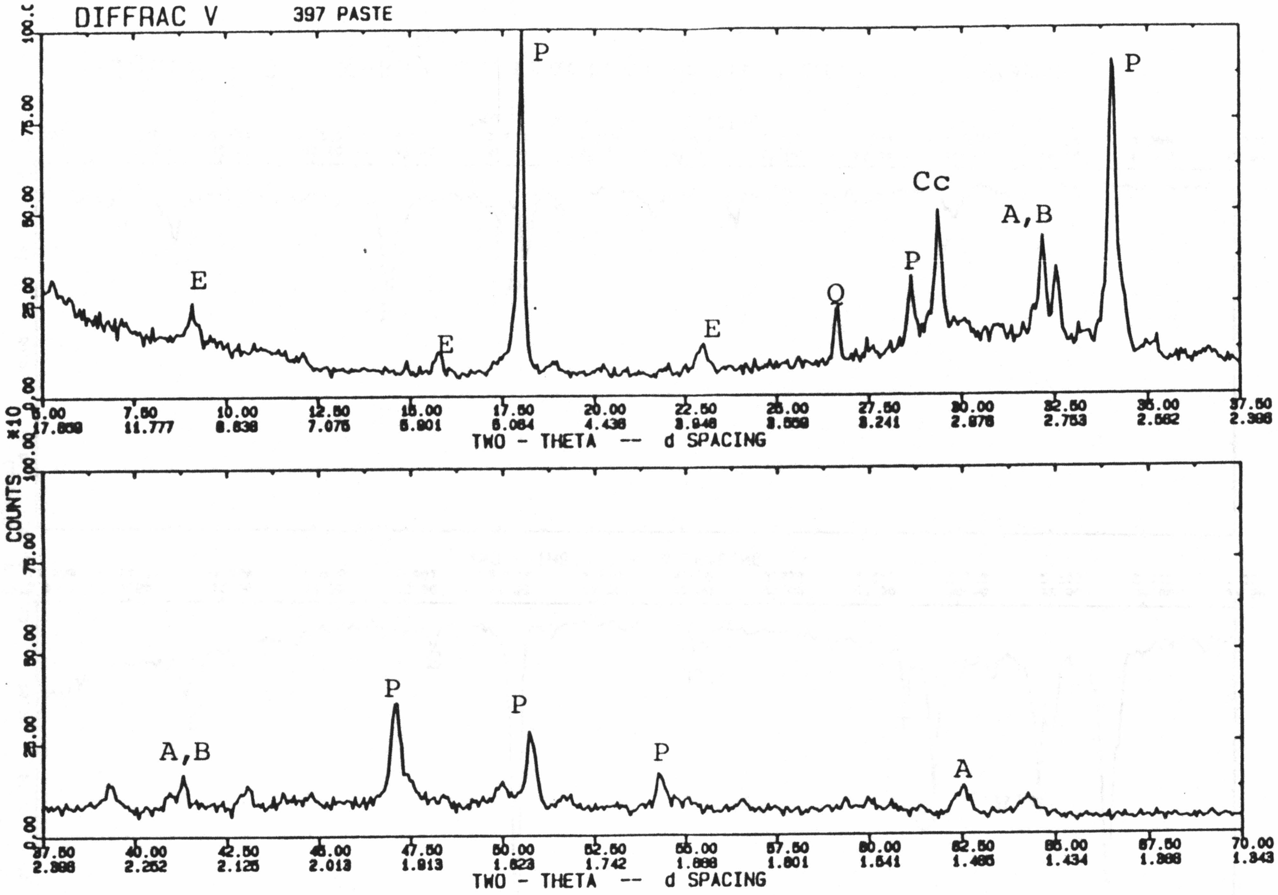

Figure B.10 X-Ray Diffractogram of Plain P.C. Paste @ 28 Days

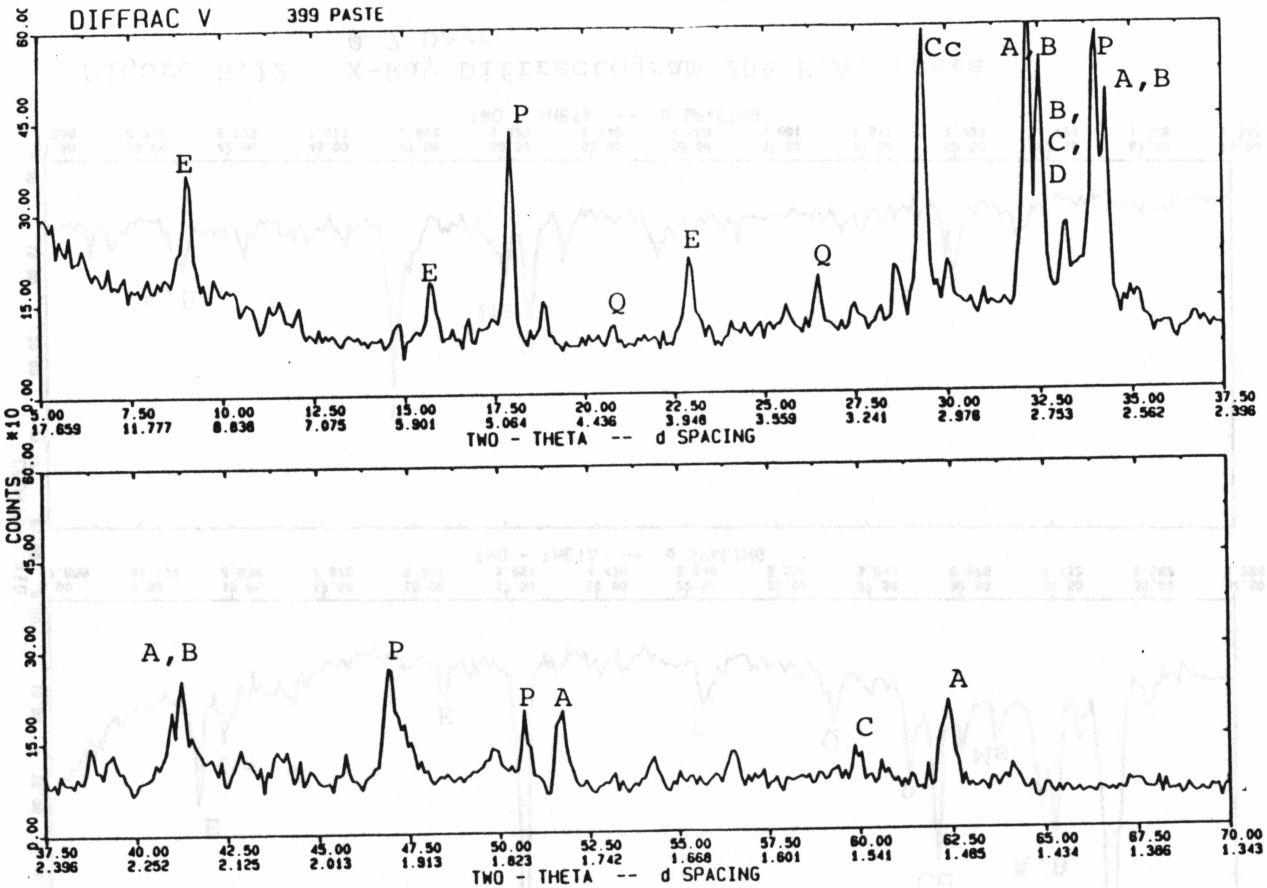

Figure B.11 X-Ray Diffractogram 20% Fly Ash Paste @ 1 Day

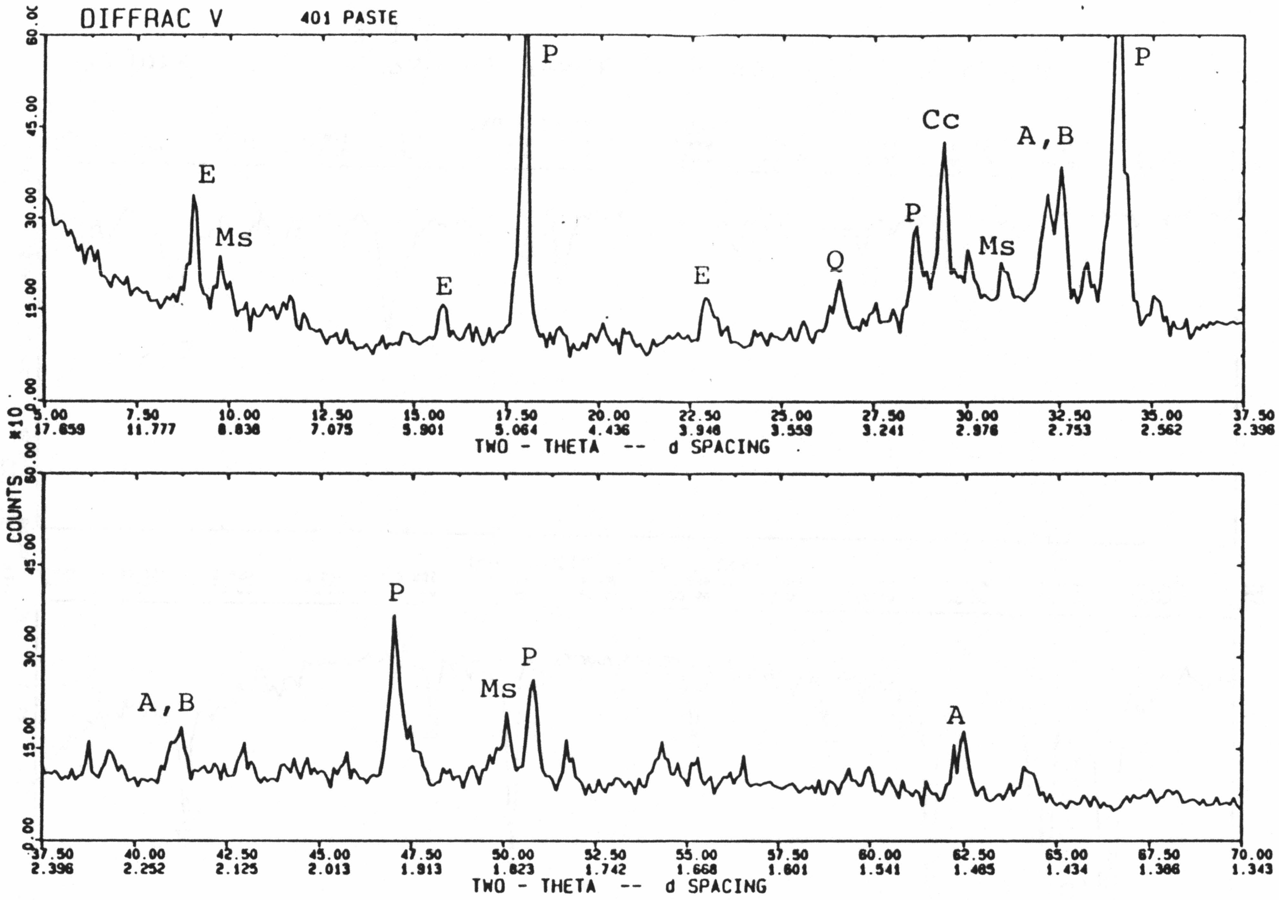

Figure B.12 X-Ray Diffractogram 20% F.A. Paste @ 7 Days

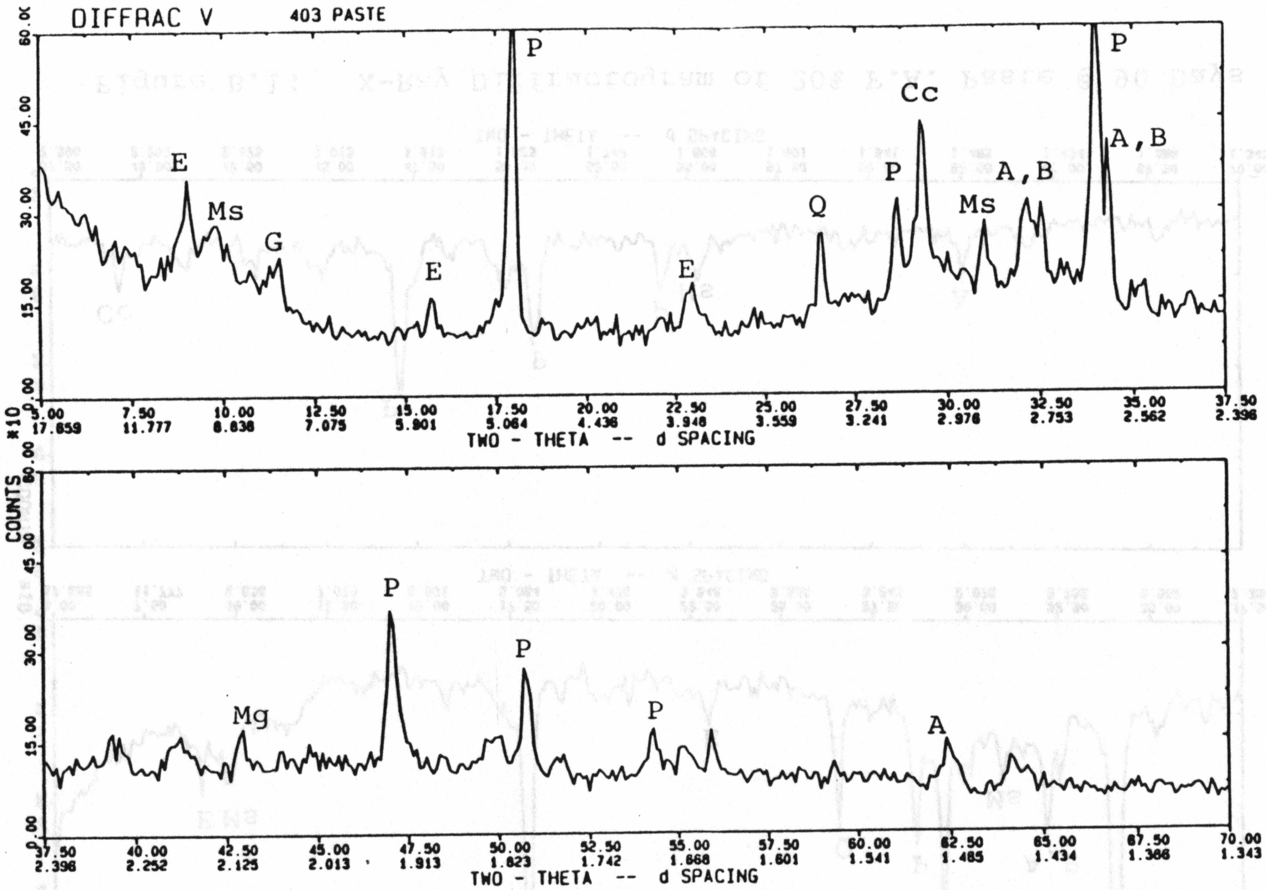

Figure B.13 X-Ray Diffractogram 20% F.A. Paste @ 28 Days

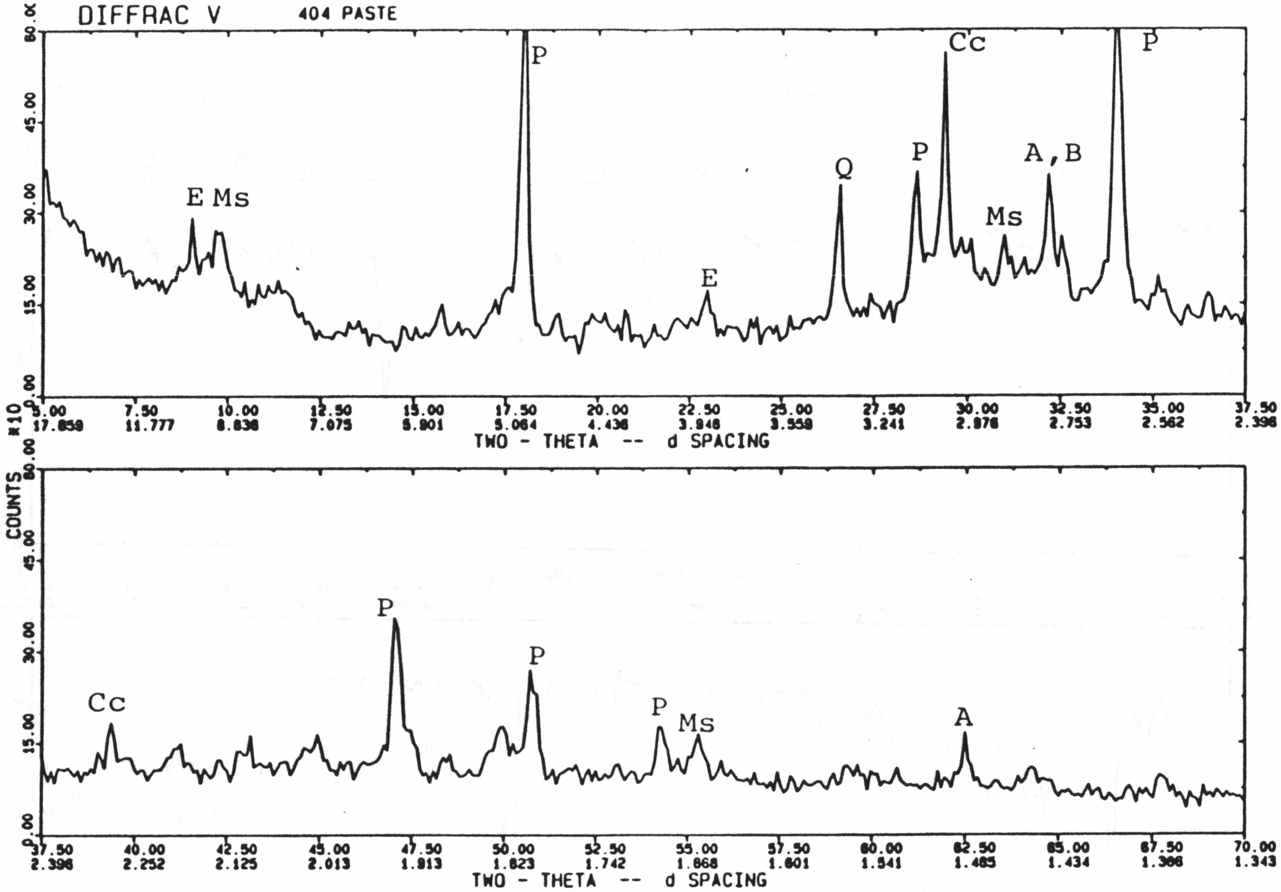

Figure B.14 X-Ray Diffractogram of 20% F.A. Paste @ 90 Days

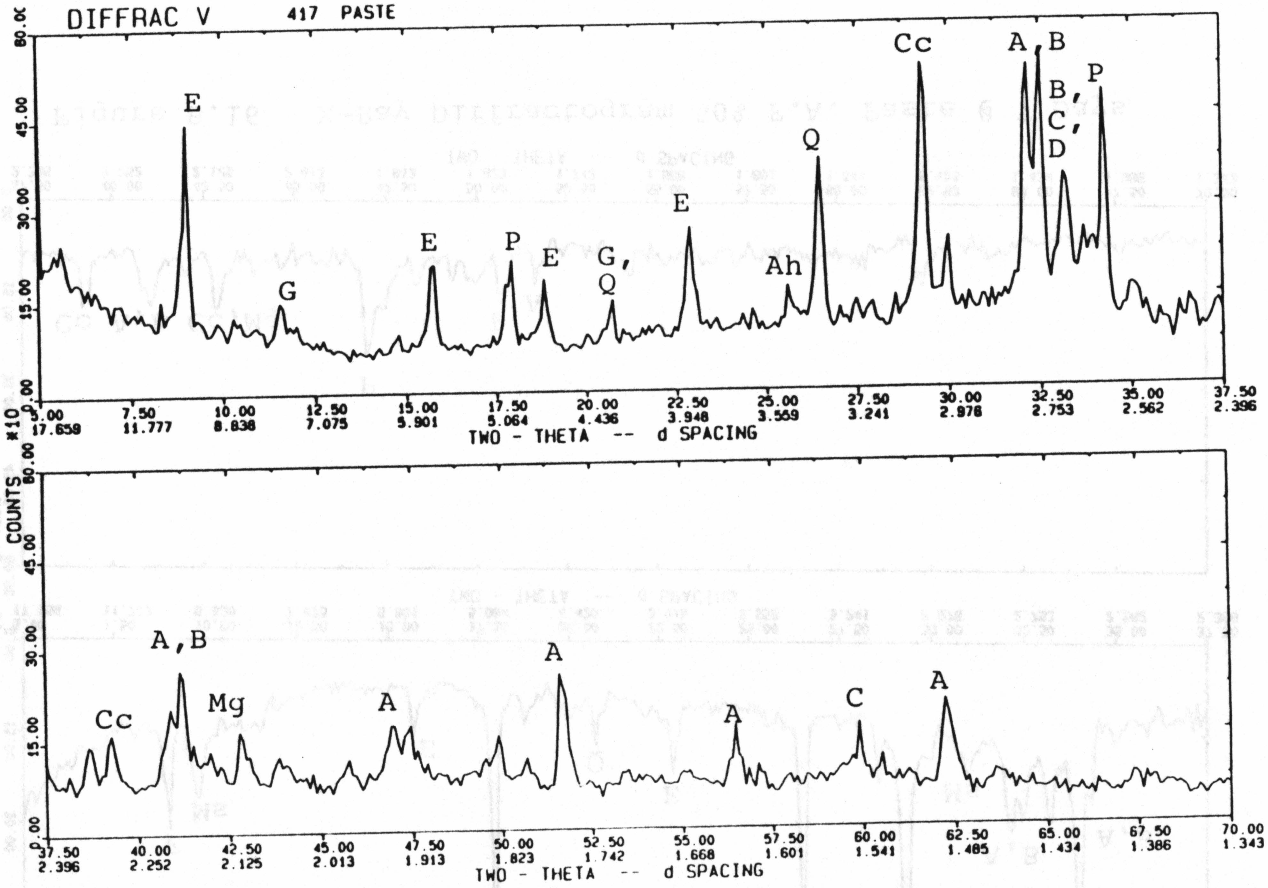

Figure B.15 X-Ray Diffractogram 50% F.A. Paste @ 1 Day

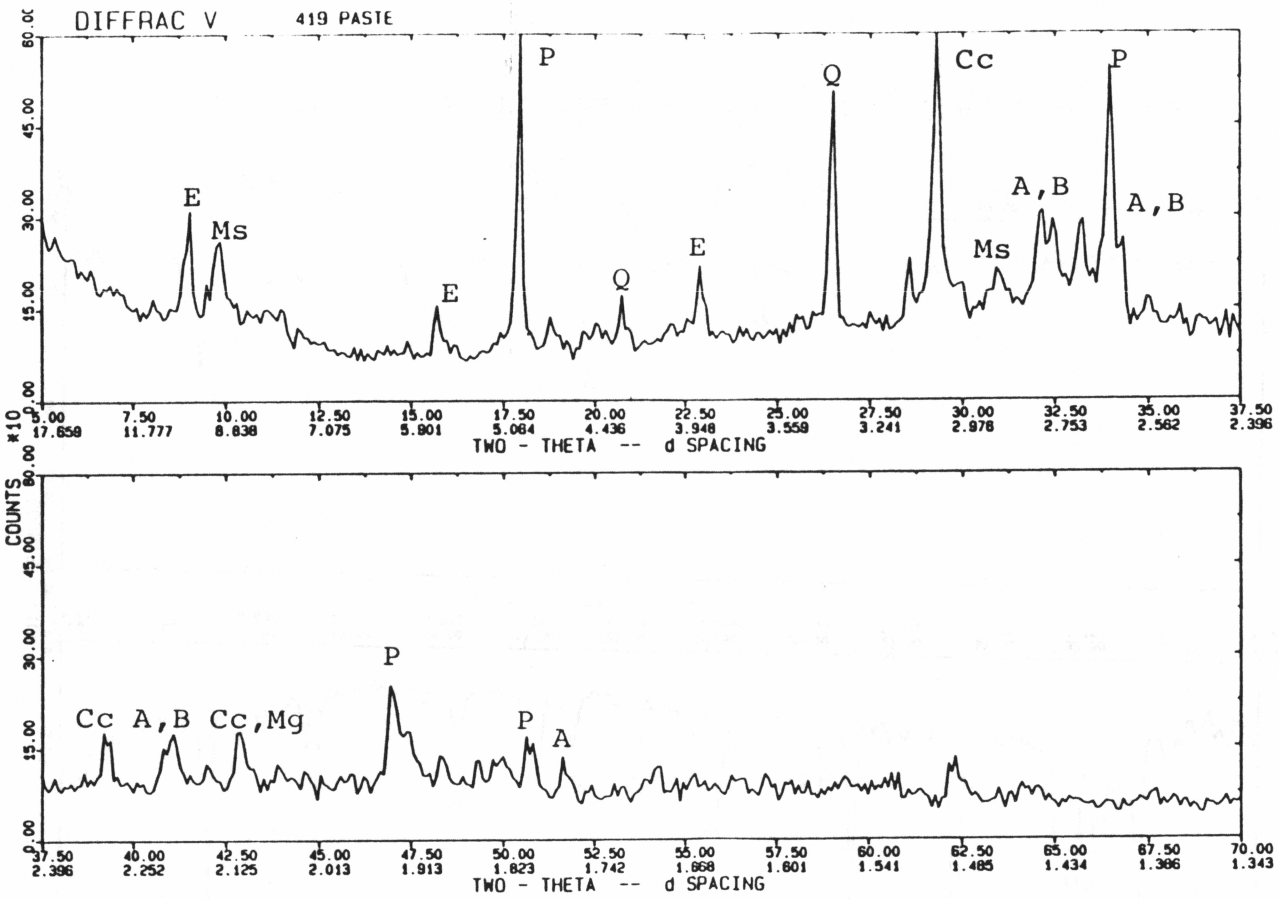

Figure B.16 X-Ray Diffractogram 50% F.A. Paste @ 7 Days

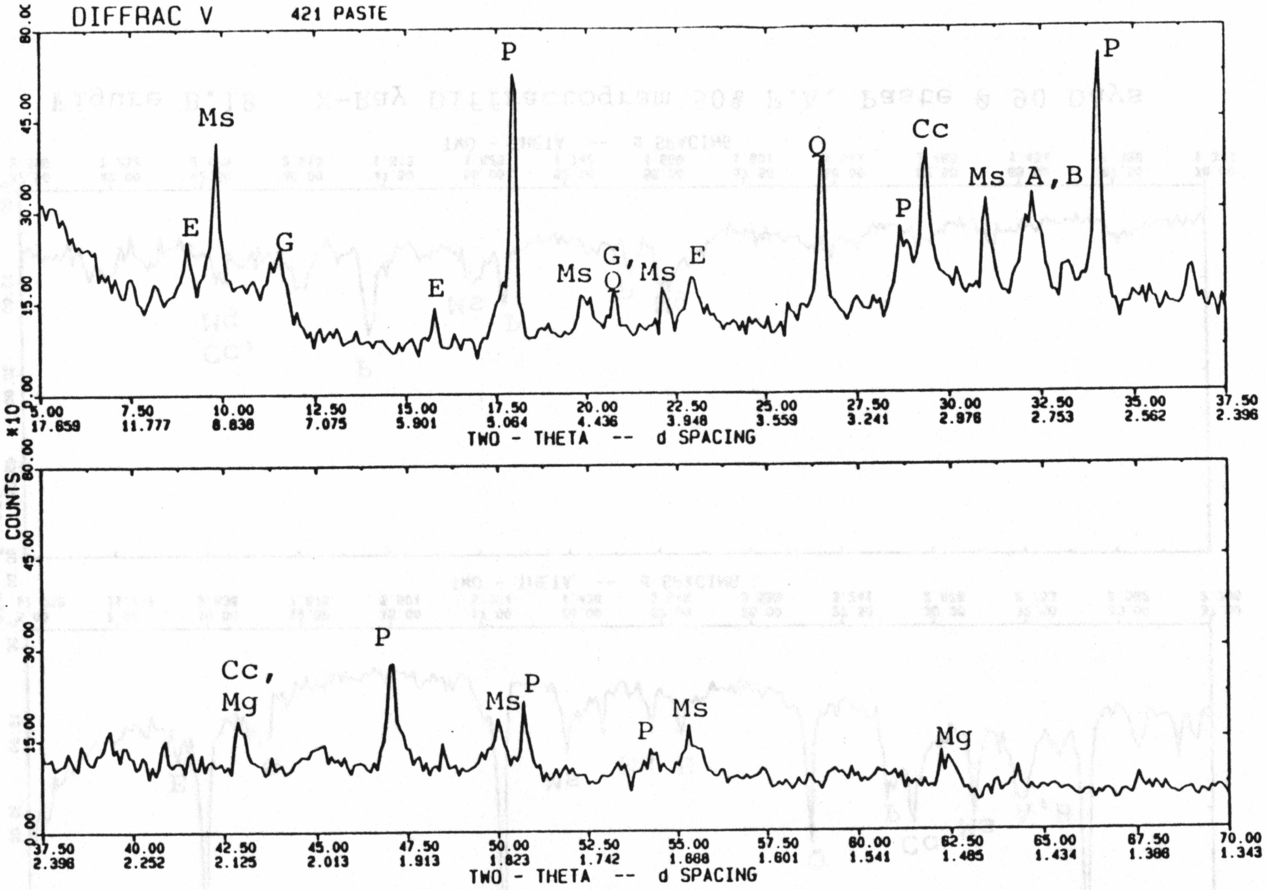

Figure B.17 X-Ray Diffractogram 50% F.A. Paste @ 28 Days

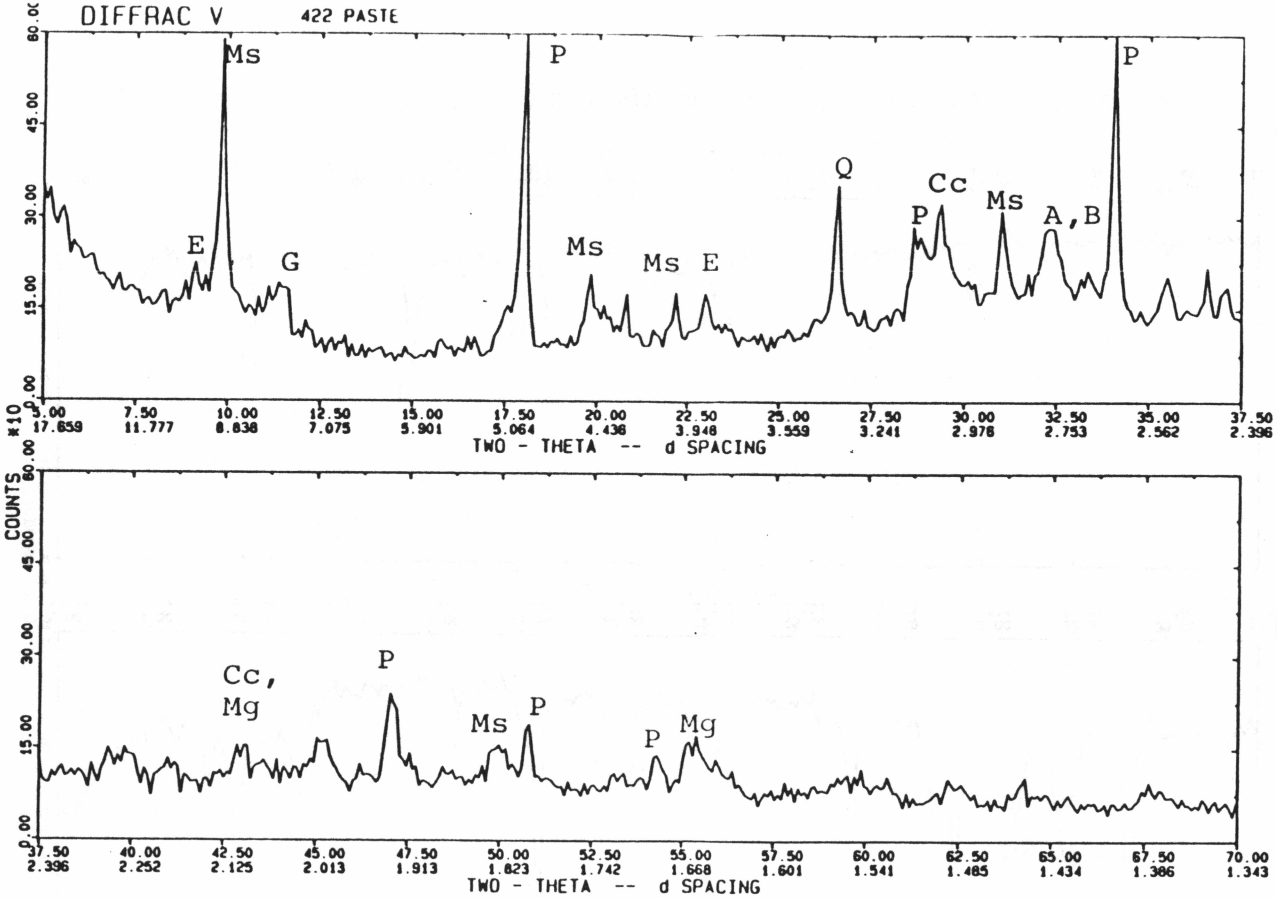

Figure B.18 X-Ray Diffractogram 50% F.A. Paste @ 90 Days

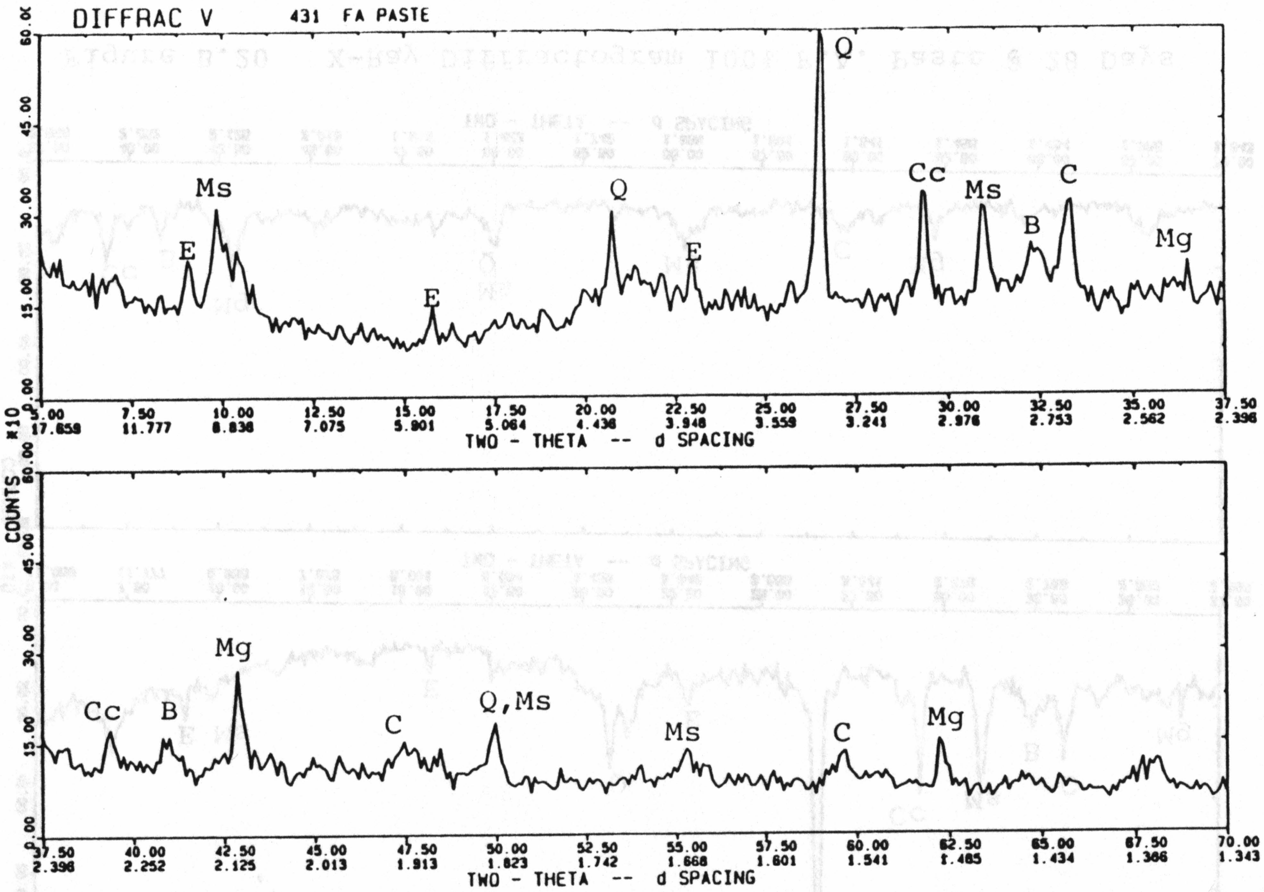

Figure B.19   X-Ray Diffractogram 100% F.A. Paste @ 7 Days

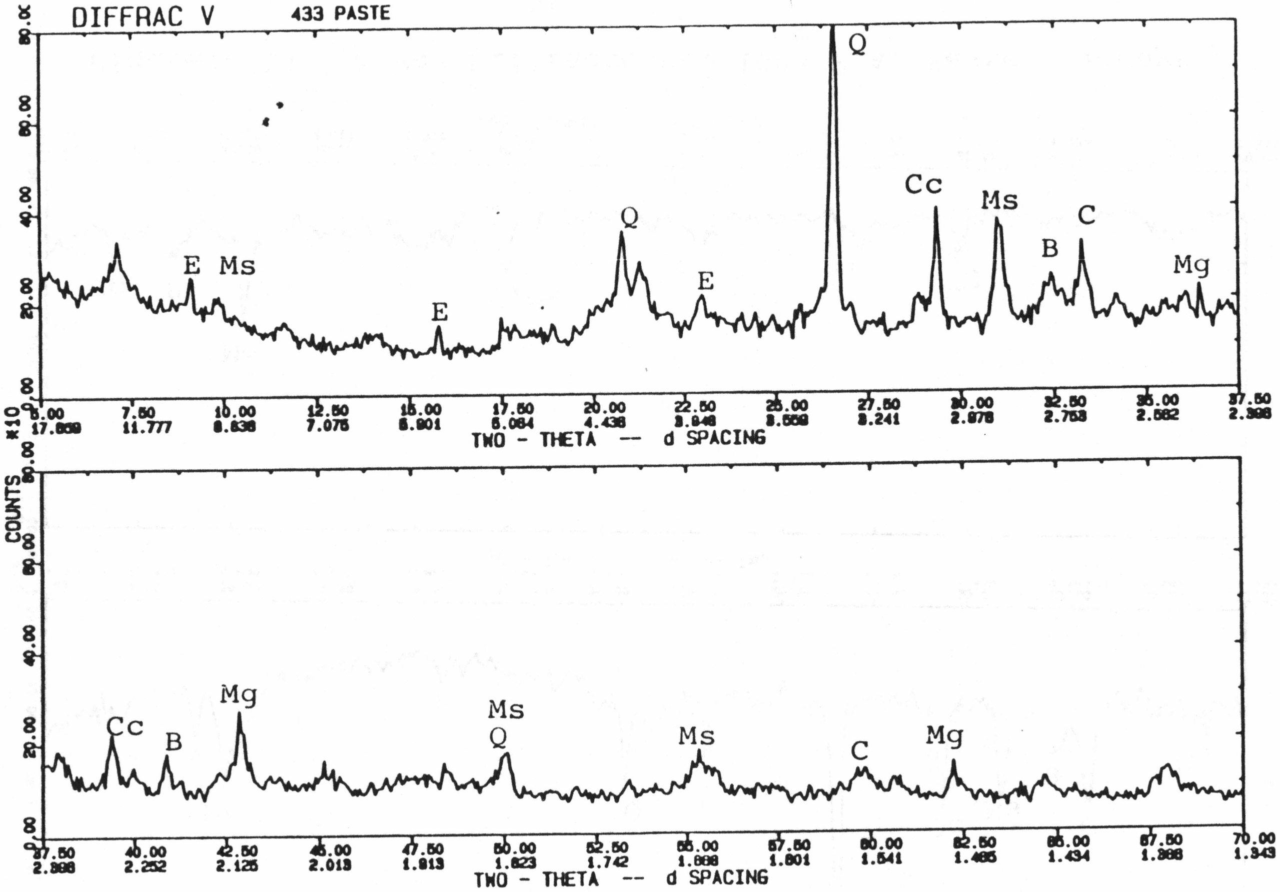

Figure B.20 X-Ray Diffractogram 100% F.A. Paste @ 28 Days