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16. Abstract

The durability of concrete is determined by its ability to endure the physical and environmental surroundings without losing the functional properties and structural integrity of the original design. Concrete containing fly ash can be proportioned to meet the durability requirements of a wide range of applications, such as concrete for mass structures, pavements, structural members, and high strength applications. One area where the long term performance of concrete containing fly ash is not clearly understood is in sulfate environments. The sulfate attack mechanism in concrete containing fly ash has been related in recent years to the mineralogical and chemical composition of the cementitious and pozzolanic material. This study investigated the interrelationship between the physical, mineralogical and chemical characteristics of portland cement, fly ash, and their proportions, and the sulfate resistance of concrete containing fly ash. Eighteen fly ashes and five portland cements have been studied at four levels of volumetric replacement of fly ash for portland cement. Other variables studied were workability, air content, curing conditions, and permeability. The fly ashes were characterized by performing chemical, physical and mineralogical analyses. Over 700 specimens were submerged in a 10 percent sodium sulfate solution. The specimens were measured for expansion, mass change, and cracking. The study has revealed a strong correlation between the glassy composition of fly ash and the sulfate resistance of concrete.

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THE EFFECT OF FLY ASH ON THE SULFATE RESISTANCE OF CONCRETE

by

P.J. Tikalsky and R.L. Carrasquillo

Research Report Number 481-5
Durability and Performance of Concrete Containing Fly Ash
Research Project 3-5/9-481

Conducted for

Texas
State Department of Highways and Public Transportation
in cooperation with the
U.S. Department of Transportation
Federal Highway Administration

by

The Center for Transportation Research
Bureau of Engineering Research
The University of Texas at Austin

August, 1989

PREFACE

This is the fifth in a series of reports summarizing the durability and performance of concrete containing fly ash. This report summarizes the results of a three-year study of the effect of fly ash on the sulfate resistance of concrete. Other reports address the topics of scaling resistance, abrasion resistance, freeze-thaw durability, and creep and shrinkage at early ages.

This work is part of Research Project 3-5/9-87-481, entitled "Durability and Performance of Concrete Containing Fly Ash." The study described in this report was jointly conducted by the Center for Transportation Research, Bureau of Engineering Research, The Ferguson Structural Engineering Laboratory at the University of Texas at Austin and private industry. The work was co-sponsored by the Texas State Department of Highways and Public Transportation and The Federal Highway Administration.

The overall study was directed and supervised by Dr. Ramon L. Carrasquillo.

SUMMARY

The use of fly ash in concrete is becoming the standard rather than the exception throughout Texas in highway and structural applications. The economic and technical advantages of using concrete containing fly ash have been well documented, but there remain material considerations which limit specific applications of concrete containing fly ash. One of these applications is in concrete exposed to sulfate environments.

This report addresses the effect of fly ash on the sulfate resistance of concrete, the material characterization of fly ash, and the permeability of concrete containing fly ash. The results of the study presented herein establish interim guidelines for the selection of fly ash for use in concrete exposed to sulfates. A specific class of fly ash can be used to improve the sulfate resistance of concrete, while a separate class of fly ash will decrease the sulfate resistance of concrete. In addition, this study shows that concrete containing fly ash is less permeable to chloride ion intrusion than concrete without fly ash.

This study investigated eighteen fly ashes and five different portland cements. The fly ash was used as a volumetric replacement for portland cement in the quantities of 25, 35 and 45 percent. Curing time, air content, and slump were also varied to investigate their effect on the sulfate resistance of concrete containing fly ash. Each of the fly ashes differed in chemical and mineralogical composition. A material phase analysis was performed on the fly ashes to determine the crystalline and noncrystalline phases present. The sulfate resistance of concrete containing fly ash was found to be related to the composition of the noncrystalline glassy phases of the fly ash. Concrete containing low calcium fly ash was found to have a sulfate resistance greater than that of concrete containing only portland cement. Concrete containing high calcium fly ash was found to have a lower sulfate resistance than similar concrete containing no fly ash.

Although a reduction in the water content, the addition of entrained air, and extended moist curing of concrete are known to improve the overall durability of concrete, test results from this study showed the chemical and mineralogical composition of fly ash to be the most relevant factor governing the effect of fly ash on the sulfate resistance of concrete. Extended moist curing, the addition of entrained air or a reduction in the water content did not improve the sulfate resistance of concrete containing high calcium fly ash to the level of sulfate resistance of similar concrete without fly ash.

IMPLEMENTATION

This report summarizes the findings of a three-year study on the sulfate resistance of concrete containing fly ash. The results show a relationship between fly ash composition and the sulfate resistance of concrete containing that fly ash.

Several recommendations are made to improve the quality of concrete exposed to sulfate environments. These recommendations are as follows: wherever a specific type portland cement is specified for the express purpose of providing sulfate resistant concrete, fly ashes conforming to the Texas SDHPT D-9-8900 Type A standard with a total calcium oxide content less than 10 percent can be used as a partial portland cement replacement to increase the sulfate resistance of the concrete. Fly ashes containing greater than 10 percent calcium oxide and conforming to the Texas SDHPT D-9-8900 standard specification for either Type A or B should not be used in concrete exposed to sulfate environments unless sulfate exposure testing has verified the performance of the concrete using the proposed materials for the particular job. Pozzolans should be specified in concrete where low permeability is required.

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CHAPTER I
INTRODUCTION

1.1 General

The disposal of by-products from spent natural resources is, in itself, a monumental task. In an effort to legislate a solution to the problem of diminishing natural resources and increasing environmental pollution, the United States Congress passed the Resource Conservation and Recovery Act (RCRA) in 1976. Under section 6002 of this legislative act, the Environmental Protection Agency is empowered to encourage the utilization of by-product materials by mandating the use of these materials in federal procurement contracts wherever possible and at the highest practical levels. One such by-product is coal ash produced from the burning of pulverized coal to generate electricity and process metals. The United States produces over 66 million tons of coal ash annually and the world produces over 200 million tons per annum[1].

Coal ash is collected and typically buried in landfills in an effort to reduce air pollution. There are principally two types of coal ash: fly ash and bottom ash. Fly ash is the finely divided residue which is filtered from the flue gases before the gases escape into the atmosphere, whereas bottom ash is the coarser and heavier particles collected from the bottom of the furnace. Fly ash is comprised of calcium oxide, alumina, silica, and iron oxide compounds, the same chemical compounds that make up portland cement. This was first recognized in 1937 when Davis et al. reported on the properties of concrete containing fly ash [13].

Over the past fifty years, laboratory and field studies have found that it is both technically beneficial and economical to use fly ash in concrete as an addition or replacement for portland cement[7,11,13,46,99]. Since the federal government directly or indirectly purchases over $1 billion worth of cement annually, the purchasing power of federal agencies is formidable. Section 6002 of the RCRA provides the country with the means to lessen an immense solid waste disposal problem as well as reduce the cost of quality concrete in the open market. The RCRA mandated the gradual use of fly ash in public works projects over the 10 year time period from 1976 to 1986. That time period has expired and the concrete industry is embracing the change with some reservations. Reluctance to accept the use of fly ash is based on the lack of field experience of its long-term effects on concrete.

The construction of buildings, bridges, highways, and other structures is taking place at an ever increasing rate. Many such structures are suffering distress as a result of the environment, rather than from the loads they sustain. These structures will subsequently have to be replaced or repaired before their design life is reached. As a result, design engineers are beginning to understand the importance of concrete durability. Structures have often been designed for strength without regard for the long-term effects of physical and chemical surroundings. While compressive strength is often used as the measure of concrete quality in specifications, concrete must also be designed to be durable in service. If the structural elements are allowed to weaken from physical or chemical attack, the integrity of a building, foundation, or bridge may be compromised.

The demand of owners and taxpayers for more durable structures requiring less maintenance and having longer design lives is well justified. It is the responsibility of design engineers to make use of the available information on concrete durability in an effort to improve the long term integrity of modern concrete structures. This is not an easy task. There are a multitude of "new" and "improved" materials on the market, which must be considered when specifying the materials to be used in a concrete structure. The engineer must first determine what is needed to ensure the long-term durability of the concrete and then he/she must specify its use to prevent structural degradation.

One source of chemical degradation of concrete is referred to as sulfate attack. This term refers to a corrosion process that occurs in portland cement concrete when it is exposed to sulfate environments. The concrete industry, long ago, developed portland cements which are resistant to sulfate exposure. ASTM Types II and V cements provide moderate and high sulfate resistance, respectively. The effects of fly ash in concrete exposed to sulfate environments is not thoroughly understood. There is strong evidence suggesting that fly ashes resulting from the combustion of bituminous coal increase the resistance of concrete to sulfate attack[19,87], while ashes which result from the combustion of subbituminous and lignite coals show contradictory evidence as to their effect on the sulfate resistance of concrete. Some of these ashes may improve sulfate resistance, whereas others encourage the deterioration process[19,25,64].

There are several studies currently being performed in the United States and Canada to determine the effects of fly ash composition on the sulfate resistance of concrete. The study at The University of Texas at Austin involves the largest catalogue of concrete specimens and variables, while other studies are concentrating on the chemical and mineralogical effects of fly ash on concrete exposed to sulfates[14,50]. The cooperative interaction among these studies will lead to a better understanding of the mechanism and variables that affect the sulfate resistance of concrete containing fly ash.

1.2 Justification of Research

The placement of strong durable concrete benefits both the user and the owner by providing a low maintenance structure with an extended service life. The data developed to date indicate that the high calcium fly ash with a chemical composition typical of those found in Texas, has a detrimental effect on the sulfate resistance of concrete. If this is true, guidelines must be developed to prevent damage and cracking of concrete exposed to sulfate environments. Such concrete includes that used in coastal and marine structures, piers, cooling towers, foundations, pavements, tanks, canals and pipes exposed to sulfate rich solutions and high sulfate soil and groundwater.

The incentive from the Resource Conservation and Recovery Act is a secondary, yet important, reason to provide the Texas State Department of Highways and Public Transportation with guidelines for the use of fly ash in state highway projects. The reuse of industrial by-products benefits the general public by reducing the burden on landfills and recycling our nations resources. When the use of by-products such as fly ash are incorporated properly to improve the quality of the state highway infrastructure, the public receives an added bonus.

1.3 Problem Statement

The chemical and mineralogical composition of fly ash is a complex array of aluminosilicate glasses and crystalline phases. The precise structure of these minerals and glasses depends upon the composition of the coal, the condition of the burning process, and the fly ash collection device. Crystalline phases in fly ash are rich in alumina, silica, calcium oxide, iron oxide and magnesia. Some of these phases are inert when surrounded by the moist alkaline environment within concrete, while other phases are reactive and hydrate over a period of time. The stability of the hydrated aluminate and calcium phases of fly ash and portland cement can be upset by the presence of sulfate concentrations in the surrounding pore water solution. This instability results in the formation of gypsum and ettringite and an associated increase in volume within the hardened concrete. When the volumetric increase exceeds the tensile strain capacity of the concrete, cracks form and the concrete begins to deteriorate. The degradation of concrete due to sulfate attack is also affected by the ability or inability of sulfate ions to permeate into the paste structure of the concrete. Inasmuch as fly ash may reduce the permeability of concrete, concrete containing fly ash may become more resistant to sulfate attack by reducing the migration of sulfate ions into the concrete. The problem is determining which sources of fly ash have the potential to improve the the sulfate resistance of concrete and which possess the potential to decrease the sulfate resistance of concrete.

1.4 Research Objectives

The main objective of this study is to investigate and report on the performance of Texas fly ashes in concrete exposed to sulfates and to develop guidelines for the use of these fly ashes in areas where the concrete is exposed to a sulfate environment under service. These guidelines will supplement those already available to the resident engineer in the form of mix design procedures and material specifications to ensure the long term performance of quality concrete containing fly ash.

In addition, this study will investigate the permeability of concrete containing fly ash and the characterization of fly ash by chemical, physical and mineralogical means. The permeability of concrete affects many properties of concrete including chloride penetration and freeze-thaw resistance. The characterization of fly ash by different means brings about a better understanding of the mechanism by which fly ash affects the properties of concrete.

1.5 Research Plan

The research plan reported herein concentrated in four areas:

(1) Exposure Testing of Concrete Containing Fly Ash;

(2) Characterization of Fly Ashes;

(3) Permeability of Concrete Containing Fly Ash; and

(4) Review of Past Research Results.

Exposure testing of concrete containing fly ash was performed by submerging concrete cylinders in a sulfate solution and monitoring the expansion, mass change and degradation over a period up to two years. Characterization of fly ashes was done through chemical and physical analysis and semi-quantitative and qualitative X-ray diffraction. The permeability of concrete containing fly ash was studied through the use of an apparatus which measures the permeability in terms of charged ion movement. The review of other research includes past studies, as well as on-going investigations on the long term durability of concrete containing fly ash.

The entire research program was conducted in cooperation with the Materials and Test Division of the Texas State Department of Highways and Public Transportation, the Federal Highway Administration, and private industry. These agencies have provided valued information and input into the research program.

1.6 Format

The format of this document consists of a description in Chapter 2 of the mechanism of sulfate attack as it is presently understood. Chapter 3 contains a review of the research that has been conducted in the areas of sulfate resistance and chloride ion permeability of concrete containing fly ash. In Chapter 4, a descrition of the materials and test procedures used in this study is given. Chapter 5 contains an analysis of the chemical, physical and mineralogical properties of the fly ashes used in this study. In Chapter 6, the data from the chloride ion permeability testing of concrete containing fly ash are presented and discussed. In Chapters 7 and 8, the results of tests on the sulfate resistance of concrete containing pozzolans are presented and discussed. Correlations between the sulfate exposure test results and the chemical and mineralogical characteristics of the fly ash are also presented in Chapter 8. Alternative solutions to the problem of sulfate resistance of concrete containing fly ash are discussed in Chapter 9. Chapter 10 is devoted to a summary of the work and a list of conclusions and recommendations that can be made from the information presented.

CHAPTER II
REVIEW OF SULFATE MECHANISM

2.1 Sulfate Attack

The chemistry and properties of portland cement, fly ash and concrete are the subject of many books; three of the most detailed are by Troxell, Davis and Kelly[101], Lea[43], and Helmuth[35]. The material presented in this section is a synopsis of information relevant to the understanding of the mechanism of "sulfate attack" in concrete. Sulfate attack is a term used to describe a series of reactions which may occur in hardened concrete in the presence of sulfate ions. The resultant compounds of these reactions are more voluminous than the reactants, therefore causing an expansion of the concrete. Tensile stresses induced in the hardened concrete from the paste expansion cause the concrete to crack and deteriorate over a period of time.

Approximately ten percent of all concrete in the United States is exposed to sulfate ions for some time during its service life[19]. A somewhat smaller percentage of concrete is exposed to a sulfate environment which is conducive to the degradation from sulfate attack. Since it is difficult to distinguish between minimal and moderate exposure conditions, concrete exposed to sulfate ions should be designed having a moderate resistance to sulfate attack. A moderate level of resistance is seldom expensive, but must be consciously provided by the engineer through job specifications. The following sections provide the essential criteria and details to evaluate the potential for sulfate attack in concrete. It remains the designer's decision whether or not a potentially detrimental sulfate environment exists and if preventive measures should be specified.

The abbreviated notation used in this text is that common to portland cement chemistry. The complete chemical composition of the compounds described herein is presented in Appendix A, Table A-1.

2.1.1 Chemistry of Cement. Portland cement consists of five major crystalline compounds: tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF), belite (C_2S), alite (C_3S), and gypsum ($C\overline{S}H_2$). All five of these crystalline phases ionize in solution with water and precipitate as hydrated compounds.

The hydrated form of alite and belite, calcium silicate hydrate (C-S-H), becomes the primary binding component of the hardened portland cement paste. The reactions are indicated in to equations 2.1 and 2.2, with alite reacting at a faster rate than the belite. The C-S-H crystalline structure will continue to refine itself as long as unreacted alite or belite is present in the high pH pore water solution of the concrete.

$$\begin{array}{ccccccc} 2C_3S & + & 6H & \longrightarrow & C_3S_2H_3 & + & 3CH \\ \text{alite} & & \text{water} & & \text{C-S-H} & & \text{calcium hydroxide} \end{array} \tag{2.1}$$

$$\begin{array}{ccccccc} 2C_2S & + & 4H & \longrightarrow & C_3S_2H_3 & + & CH \\ \text{belite} & & \text{water} & & \text{C-S-H} & & \text{calcium hydroxide} \end{array} \tag{2.2}$$

The reactions described in equations 2.1 and 2.2 produce calcium hydroxide, a soluble by-product with no cementitious value. A mass balance of these equations reveals that nearly 40 percent of the calcium is contained in the soluble by-product.

A secondary binding component forms from the hydration of C_3A and gypsum which combine to form ettringite ($C_6A\overline{S}_3H_{32}$), monosulfoaluminate ($C_4A\overline{S}H_{12}$), and calcium aluminate hydrate (C-A-H) according to equations 2.3 through 2.5.

$$\begin{array}{ccccccc} C_3A & + & 3C\overline{S}H_2 & + & 26H & \longrightarrow & C_6A\overline{S}_3H_{32} \\ \text{tricalcium aluminate} & & \text{gypsum} & & \text{water} & & \text{ettringite} \end{array} \tag{2.3}$$

$$\begin{array}{ccccccc} 2C_3A & + & C_6A\overline{S}_3H_{32} & + & 4H & \longrightarrow & 3C_4A\overline{S}H_{12} \\ \text{tricalcium aluminate} & & \text{ettringite} & & \text{water} & & \text{monosulfoaluminate} \end{array} \tag{2.4}$$

$$\begin{array}{ccccccc} C_3A & + & CH & + & 18H & \longrightarrow & C_4AH_{19} \\ \text{tricalcium aluminate} & & \text{calcium hydroxide} & & \text{water} & & \text{C-A-H} \end{array} \tag{2.5}$$

The calcium aluminate sulfate hydrates are the first to form when water is added to portland cement and provide most of the strength in concrete at very early ages. The formation of C-A-H occurs late in the hydration process because the reaction requires the calcium hydroxide by-product produced in the reactions described in equations 2.1 and 2.2. The hydration of the C_4AF produces the iron equivalent of ettringite ($C_6F\overline{S}_3H_{32}$), monosulfoferrite ($C_4F\overline{S}H_{12}$), and calcium ferrite hydrate (C_4FH_{19}). These ferrite hydrates are generally contribute little to concrete strength.

The aluminate and silicate hydrates occupy between 60-65 percent of the hardened cement paste. The CH occupies approximately 20 percent of the hardened cement paste, while the remainder of the cement paste is composed of alumina and ferrite compounds and water.

The stability of the calcium aluminate sulfate hydrate phases, monosulfoaluminate and ettringite, is dependent upon the concentration of sulfates in the pore water surrounding the compounds. As shown in Figure 2.1, the ettringite phase will dominate during the early stages of hydration while there is an abundant supply of sulfate ions from the dissolution of gypsum. As the concentration of sulfate ions in solution is lowered, the trisulfate phase ettringite becomes unstable and converts to the monosulfate phase monosulfoaluminate. The monosulfoaluminate and calcium aluminate hydrate will dominate the aluminate crystalline phases in the hardened concrete when the sulfate concentrations are low, whereas the ettringite is only stable at higher concentrations of sulfates.

The ferrite form of ettringite is formed early in the hydration process and is transformed into the monosulfoferrite hydrate as the sulfate from the gypsum is depleted by both aluminate and ferrite reactions. The monosulfoferrite is a stable phase which cannot revert back to its ettringite form regardless of the future sulfate concentration of the pore water. The calcium ferrite hydrate phase is combined in solid solution with silica to form a phase called a "hydrogarnet". The hydrogarnet structure has an extremely low solubility and is stable in both lime and sulfate solutions.

Under certain conditions of the hydration process of portland cement, ettringite can be formed twice. Once when the sulfate from the ionized gypsum is consumed by the C_3A during the early hydration period and a second time from

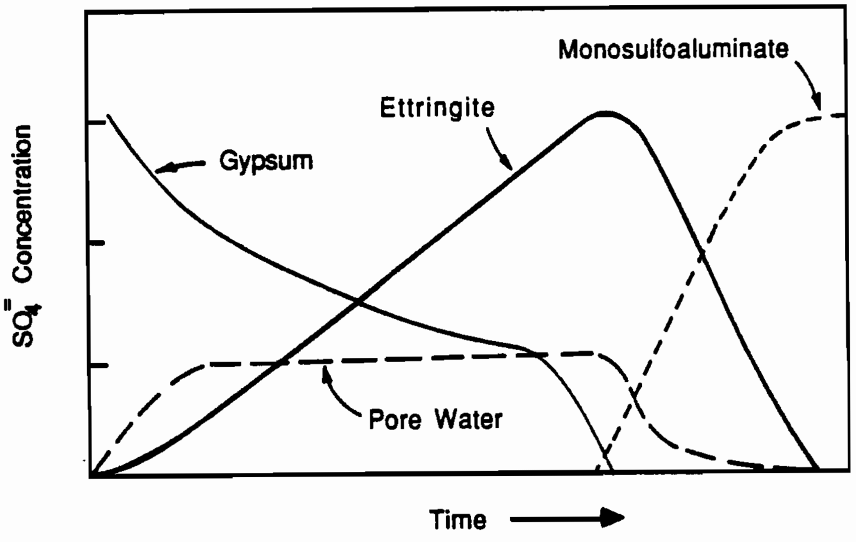


Figure 2.1 Sulfate consumption during portland cement hydration.

the monosulfoaluminate when the concrete is exposed to an aggressive sulfate environment. The first series of these crystalline phase transformations occurs while the cement paste is in its plastic state, which allows any volumetric changes associated with the reactants to occur without causing internal stress. At the completion of the normal hydration process, monosulfoaluminate remains as the only stable form of sulfoaluminate.

Hardened concrete may be exposed to an aggressive sulfate environment such as, seawater, groundwater with sulfates or clay soils with sulfates. Under such conditions, the sulfate concentration in the pore water of the cement paste increases causing gypsum to form and the monosulfoaluminate phase to become unstable. As shown in equation 2.6, the monosulfoaluminate reverts to the ettringite phase and leads to an approximate volumetric increase of twice that of the reactant compounds. This large volumetric increase cannot be accommodated by the internal voids alone and therefore causes excessive internal strains in the hardened concrete.

$$C_4A\overline{S}H_{12} \quad + \quad 2C\overline{S}H_2 \quad + \quad 16H \longleftrightarrow C_6A\overline{S}_3H_{32} \qquad (2.6)$$

monosulfoaluminate gypsum water ettringite

The precise mechanism of the this reaction is not fully understood, however it is probably a through solution reaction forming small rod-like ettringite crystals which are 1-2 μm long and 0.1 μm thick. There are two essential portions of this postulated mechanism which may be conducive to large volumetric expansions. The first is that the reaction is through solution rather than a solid solution reaction. The monosulfoaluminate crystal is a plate crystal with one sulfate ion and twelve molecules of water in its anion portion. In contrast, ettringite is a prismatic crystal with three sulfate ions and two molecules of water in its anion. The large structural differences between the monosulfoaluminate and ettringite crystals would indicate that a solid solution reaction is not probable[61]. Additionally, the through solution reaction would favor large volumetric expansions by allowing the formation of many small dispersed crystals which may grow over an extended period of time. A solid solution-reaction, as was suggested by Oberholster[71], would dictate a dispersion of crystals related to that of the monosulfoaluminate in the hardened concrete.

The second portion of the postulated mechanism is the presence of rod-like crystals rather than lath crystal structures. The lath-like ettringite crystals are long needle shaped structures 10-100 μm in length and 1-4 μm thick. Lath- like ettringite crystals are commonly observed in low pH environments such as supersulfated and rapid setting cements composed of $C_4A_3\overline{S}$, C_2S, C_4AF, and $C\overline{S}$, where the ettringite is a primary source of strength. The rod-like crystals are typically present in high pH environments such as that of normal portland cements[16]. The presence of many small rod-like crystals, rather than fewer large lath structures, provides a wide dispersion of nucleation sites for the observed expansion of ettringite crystals over long periods of time.

Whether the internal strains from ettringite and gypsum formation are sufficient to cause cracking and degradation is dependent upon several factors. The most important of these factors, and the parameter which is used by ASTM to distinguish sulfate resistant cements from other cements, is the amount of C_3A in the portland cement. The C_3A is the major source of reactive alumina and controls the total amount of monosulfoaluminate that can be formed according to equation 2.6. ASTM Type II and V portland cements have maximum limits on C_3A and are considered moderate and high sulfate resistant cements, respectively. Field studies have shown that this level of protection is adequate in most moderate and severe sulfate environments[40]. The conversion of calcium aluminate hydrates to ettringite may also contribute an expansive reaction but at a slower rate. Other factors which affect the formation of expansive compounds are the presence of calcium hydroxide and water and the permeability of the concrete to sulfate intrusion.

Expansion is not the only means of deterioration due to sulfate intrusion. Strength loss and "mushiness" are also observed forms of deterioration in concrete exposed to sulfates. Mehta theorizes that the formation of rod-like ettringite crystals deplete the paste of reactive A^{+3} ions, causing gypsum to precipitate until all the calcium from the calcium hydroxide is depleted[61]. The remaining hydroxyl ions are then leached out over time, leaving the concrete at a lower pH. The combination of a low pH and high sulfate concentration environment may cause the C-S-H to lose strength and stiffness allowing the rod-like ettringite crystals to expand. Mehta's postulated mechanism remains unproven but is a reasonable description of the observed behavior.

2.1.2 Type of Portland Cement. The type of portland cement used in concrete exposed to sulfate environments is one of the primary consideration in determining the resistance of concrete to sulfate attack. Since sulfate expansion is caused by the formation of alumina hydrates, the reduction of C_3A in the cement may lead directly to a more sulfate resistant portland cement, as shown in Figure 2.2.

The American Society for Testing and Materials, ASTM, classifies portland cement into five types. The standard chemical and physical requirements of these classes are shown in Table 2.1. ASTM Type I portland cement is the most common cement used in the concrete industry. Type I cement is widely available throughout the United States and is generally the least expensive of the five types of portland cement. The ASTM Standard Specification C 150 places no direct limit on the amount of C_3A in Type I portland cement. Typical C_3A contents for Type I portland

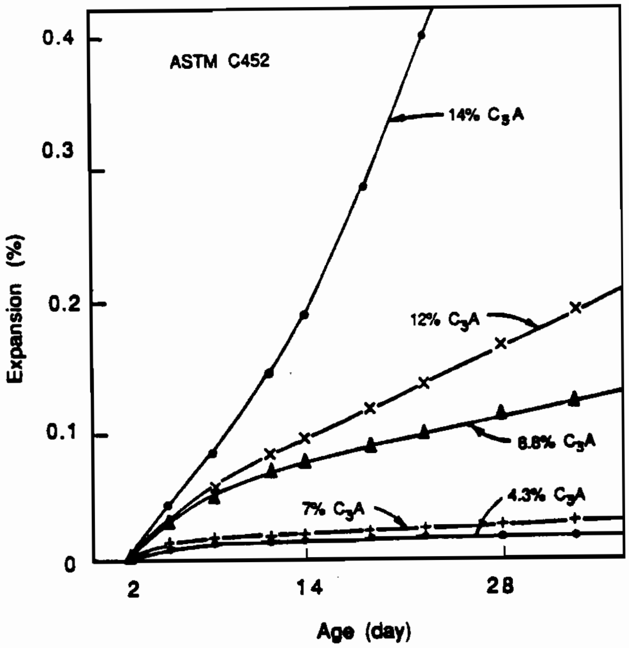


Figure 2.2 Effect of C_3A content on sulfate resistance [74].

cements range between 10 and 13 percent. Cements with C_3A contents in this range will perform at an unacceptable level in moderate to severe sulfate environments.

ASTM Type II portland cements are considered moderate exposure portland cements. A maximum C_3A content of 8 percent is specified for Type II cements. The C_3A limitation provides the cement with moderate sulfate resistance. This type of cement is used widely throughout Texas and is the most common solution to potential sulfate attack problems. ASTM Type V portland cement has a specified 5 percent maximum C_3A content and is considered highly resistant to sulfate attack. The use of Type V portland cement is often restricted to severe sulfate environments because of its limited availability and high cost.

ASTM Type III portland cement is high early strength cement. The specified C_3A limitation in this cement is a maximum of 15 percent. This type of cement is not typically used in sulfate exposures because of the high C_3A content. ASTM Type IV portland cement is low heat of hydration cement with a maximum specified C_3A content of 7 percent. Although this type of cement is resistant to sulfate attack, its limited availability keeps its use in sulfate exposures to a minimum.

Table 2.1 ASTM C 150-87 Cement Requirements[3]

ASTM Type[a]	I	II	III	IV	V
Si Oxide, min %	–	20.0	–	–	–
Al Oxide, max %	–	6.0	–	–	–
Fe Oxide, max %	–	6.0	–	6.5	–
Mg Oxide, max %	6.0	6.0	6.0	6.0	6.0
SO_3, max %	3.5[b]	3.0	4.5[b]	2.3	2.3
LOI, max %	3.0	3.0	3.0	2.5	3.0
Insol. Res., max %	0.75	0.75	0.75	0.75	0.75
C_3S, max %	–	–	–	35	–
C_2S, min %	–	–	–	40	–
C_3A, max %	–	8	15	7	5
C_4AF+C_2F, max %	–	–	–	–	25
Aval. Alk., max %[c],	0.60	0.60	0.60	0.60	0.60
Physical Data					
Specific Surface					
Blaine (cm^2/g), min	2800	2800	–	2800	2800
Comp. Str.(psi), min					
1 Day	–	–	1800	–	–
3 Day	1800	1500	3500	–	1200
7 Day	2800	2500	–	1000	2200
Set Time, minutes					
Vicat Test					
Initial Set, min	45	45	45	45	45
Initial Set, max	375	375	375	375	375

[a] See notes in ASTM C150-87 for further clarification.

[b] Reduced when C_3A content is below 8 percent.

[c] Applicable only when used with reactive aggregates.

2.1.3 Types of Sulfate Attack. Sulfates may be found in several forms in the environment surrounding concrete. They can be divided into two categories, soluble sulfates and sulfates in seawater. Sulfates in either category may contribute to sulfate attack.

Soluble sulfates are sulfates which are present as a result of the dissolution of salts, such as sodium sulfate, potassium sulfate, magnesium sulfate or calcium sulfate. The sulfate ions in solution are available to combine with aluminate compounds in hydrated portland cement to form expansive compounds containing sulfate. Magnesium sulfate is a special group among the soluble sulfates. As the magnesium ionizes along with the sulfate into solution it reacts according to equation 2.7, with the calcium hydroxide in the pore water solution to form crystalline magnesium hydroxide, brucite. Depletion of the hydroxyl ions within the pore water solution causes the pH of the concrete to decrease. The calcium silicate hydrate binder becomes less stable in the lower pH environment and is thereby susceptible to damage from the expansive pressures of sulfate attack.

$$\underset{\substack{\text{magnesium}\\ \text{sulfate}}}{2M\overline{S}} \quad + \quad \underset{\substack{\text{calcium}\\ \text{hydroxide}}}{CH} \quad + \quad \underset{\text{water}}{2H} \quad \longrightarrow \quad \underset{\text{brucite}}{MH_2} \quad + \quad \underset{\text{gypsum}}{C\overline{S}H_2} \qquad (2.7)$$

There is a mitigating effect to this reaction which occurs over long periods of exposure. The brucite will form an impermeable layer over the hydrated cement compounds preventing further sulfate intrusion and protecting the concrete from sulfate attack. This protective coating may or may not form before the concrete is deemed unserviceable.

Seawater contains high concentrations of soluble sulfates, however seawater also contains many other salts which are not sulfate based. For reasons which are not clearly understood, the presence of ions from other salts slow the formation of expansive compounds containing sulfates. The combined effects of these salts lessen the severity of sulfate attack.

2.1.4 Sources of Sulfate Attack. A major problem in providing protection against sulfate attack is determining where the problem areas lie. Much of the concrete placed in the United States is not exposed to sulfate ions. Determining the location of the less than 10 percent of concrete which is exposed to sulfate attack is a difficult task. Sulfates are always present in seawater and in saline lakes, but frequently sulfates occur in high concentrations in the soil and groundwater of small localized geographic zones. These local zones of sulfate are formed from ions leaching from the pore water of alkali soils and from groundwater movement over rocks and sediments containing gypsum.

The coastal environments can be readily identified as areas of possible sulfate attack with a standard chemical analysis of the soil and water. However localized areas of sulfate concentrations must be identified for the engineer. There are primarily three alternatives open to the engineer to combat possible sulfate exposure if local zones of sulfate pose a problem to the concrete at or below grade[33]:

1) extensive soil and groundwater testing,
2) use Type V cement throughout the project, or
3) use Type II cement and replace damaged sections at a later date, if sulfate attack is detected.

All three options can be expensive. Extensive testing for sulfates may lead to no assurance that sulfates will not be present in the subsurface environment several years after the completion of the project. The use of Type V cement is expensive, as shown in Table 2.2 and may be unnecessary. Lastly, Type II cement will provide adequate sulfate resistance in most cases, but if necessary repairs of underground structures are needed they can be both expensive and inconvenient. The United States Bureau of Reclamation chooses the alternate for sulfate exposure on the basis of usage. Extensive soil and groundwater testing is used in projects with a relatively fixed local area, such as dams, powerplants and bridges. However, for projects which cover broad expanses of land such as canals and transmission line structures, the USBR uses moderate to high sulfate resistant cements throughout the projects.

Seawater and saline lake water contains relatively large amounts of magnesium and calcium sulfates. For reasons already cited, seawater is not considered

Table 2.2 Delivered Cost of Portland Cement in Corpus Christi, Texas.

ASTM Cement Type	Cost per Ton
I	\$45.50
II	\$48.70
V	\$78.20

as a severe condition but rather as a moderate sulfate environment. Coastal and offshore structures should always be designed with at least moderate sulfate resistant cement. The mitigating effect of seawater on the sulfate attack of concrete should not be confused with the presence of chloride salts in the pore water, which may accelerate sulfate deterioration[102].

2.1.5 Concentrations of Sulfates. The relative degree of sulfate attack on concrete depends on the sulfate ion concentration in the environment. Table 2.3 indicates the level of sulfate attack that should be expected under exposure to different sulfate concentrations. Typical concentrations in soils and groundwater are less than 0.1 percent, however canals, cooling towers and waste water treatment facilities may experience much higher concentrations. The highest concentrations reported by the USBR were in the White Wood Creek Bridge in South Dakota, where a concentration of 9900 ppm was reported shortly before the bridge piers were replaced because of severe sulfate damage[33].

Table 2.3 Severity of Sulfate Concentrations[2].

Severity of Attack	Soluble Sulfate in Soil, wt. percent	Concentration in Water, ppm
Mild	0.00 - 0.10	0 to 150
Moderate	0.10 - 0.20	150 to 1500
Severe	0.20 - 2.00	1500 to 10,000
Very Severe	2.00 - More	10,000 or More

Table 2.4 Effect of Concrete Exposure on Sulfate Attack

Environmental Exposure Condition	Severity of Attack
Always Dry	Negligible
Almost Always Dry	Mild Surface Damage
Always Wet	Continual Degradation
Wet - Dry - Wet Cycling	Accelerated Degradation

2.1.6 Exposure Conditions of Concrete. In addition to the concentration of sulfates, the exposure conditions of the concrete environment are important in determining the severity of the concrete degradation. Table 2.4 lists four major physical exposure conditions and the severity associated with each.

Sulfate attack will not occur in areas of arid concrete conditions. The sulfates in the soils of continually dry areas do not migrate into the concrete and therefore are not available to cause sulfate deterioration. Concrete in areas of low relative humidity, but occasionally exposed to sulfates in solution, develops a white powder on the surface. T.J. Reading reports this powder sulfate salt is in anhydrous form and is confined to a harmless layer on the surface[84]. Nevertheless, one must consider that in dry areas the naturally occurring sulfates are not leached from the soil and remain to form alkali soils. If development and irrigation of the land takes place, the sulfates may be extracted in high concentrations leading to severe sulfate exposure.

Continual sources of sulfate ions, like that in a submerged environment, provide a constant concentration of sulfate ions to the concrete. The sulfate expansion reactions occur over a period of time until the concrete is no longer serviceable. The Wet-Dry-Wet cycling category results from concrete which is occasionally dried but spends most of the time submerged in a sulfate rich environment. The drying allows sulfate rich crystals to form under the surface of the concrete as the water is evaporated from the concrete pore structure. As the concrete is rewetted with sulfate water, the sulfate ion concentration increases as the crystals dissolve into solution again.

Submerged and Wet-Dry-Wet cycling are the most commonly observed sulfate attack environments. However damage above the water line is sometimes present in bridge piers and marine structures. Capillary action draws sulfates into the concrete just above the water line. As the water evaporates, the sulfate concentration continues to increase until the crystals progressively cause the concrete cover to flake off.

2.1.7 Permeability. The intrusion of sulfate ions into the concrete is necessary for sulfate attack to occur. There are four factors that directly affect the ability of sulfate ions to enter the hydrated cement paste matrix:

1) the water to cement ratio,
2) the cementitious content,
3) entrained air, and
4) the maturity of the concrete.

Concrete which is impermeable does not suffer distress from sulfate attack. Factors such as low water to cement ratio, high cement content, a good entrained air structure and properly cured concrete all contribute to concrete which is less permeable to capillary flow. The combination of all these factors provide the concrete with a compact matrix of disconnected voids and the reduced presence of bleed water channels. The improvement in mortar matrix properties reduces the amount of water carrying sulfate ions through the concrete.

2.1.8 Pozzolans. There are several common types of pozzolans: natural pozzolans, silica fume, blast furnace slag, and fly ash. The later three are the by-products of furnace operations, while natural pozzolans are volcanic ashes and soils. Silica fume is a very finely divided material which is composed of ninety percent or more of reactive silica. It has been recognized that silica fume improves concrete by increasing the silica to calcium ratio, depleting the calcium hydroxide in the hardened concrete and greatly refining the pore structure of the cement paste[49]. All three of these mechanisms will improve the sulfate resistance of concrete.

Blast furnace slag is a high calcium glassy pozzolan which is finely divided and may increase or decrease the sulfate resistance of concrete depending upon its SO_3 and reactive alumina contents. The effect of fly ash on the sulfate resistance of concrete is the subject of this study. There is evidence that some fly ashes improve the sulfate resistance of concrete while other fly ashes may decrease the sulfate resistance of concrete. The succeeding section will summarize the present state of knowledge of the role of pozzolans on the sulfate resistance of concrete.

2.2 Role of Fly Ash and Pozzolans on Sulfate Resistance

The addition of pozzolans such as fly ash, blast furnace slag and silica fume alter both the chemistry and properties of concrete. Typical composition and known effects of these pozzolans on the sulfate resistance of concrete are described in this section.

2.2.1 Fly Ash Composition and Sulfate Resistance. No definitive answer has yet been found to the question of how does the composition of fly ash affect the sulfate resistance of concrete. Each fly ash performs differently in combination with different portland cements to form the binding matrix of compounds in concrete. Whether the combination of a particular fly ash and portland cement is resistant to sulfate environments is dependent on the hydration products in the hardened concrete.

There are two types of fly ash reactions which contribute to the strength of concrete. The first type of reaction is a "cementitious" reaction between the constituents of high calcium fly ash and water. The C_3A, C_2S and reactive calcium aluminosilicate glass in these fly ashes react with calcium sulfate and calcium hydroxide to form calcium silicate hydrate, monosulfoaluminate and calcium aluminate hydrate according to equations 2.8 and 2.9. These reactions give the high calcium fly ash a "self-cementing" property independent of the availability of external sources of reactive calcium.

$$\underset{\text{glass}}{C_nA_mS_l} \quad + \quad \underset{\substack{\text{calcium}\\\text{hydroxide}}}{CH} \quad + \quad \underset{\text{water}}{H} \quad \longrightarrow \quad \underset{\substack{\text{calcium silicate}\\\text{(aluminate) hydrate}}}{C-S-H(C-A-H)} \qquad (2.8)$$

$$\begin{array}{ccccccccc} C_3A & + & 3C\overline{S} & \longrightarrow & C_6A\overline{S}_3H_{32} & + & 2C_3A & \longrightarrow & 3C_4A\overline{S}H_{12} \\ \text{tricalcium} & & \text{anhydrite} & & \text{ettringite} & & \text{tricalcium} & & \text{monosulfo-} \\ \text{aluminate} & & & & & & \text{aluminate} & & \text{aluminate} \end{array} \qquad (2.9)$$

The second type of reaction which contributes to the strength of concrete is the "pozzolanic" reaction. A pozzolanic reaction is a reaction of silica, alumina, water and an external source of calcium to form calcium silicate hydrate and calcium aluminate hydrate binder compounds. Fly ash is a pozzolan because it is largely comprised of soluble aluminosilicate or calcium aluminosilicate glasses, and the hydration of portland cement provides a source of calcium in the form of calcium hydroxide. The pozzolanic reaction occurs over a longer period of time than the cementitious reaction because of the slow rate of glass solubility. For this reason, pozzolans do not generally contribute to the early strength of concrete, but add substantially to the long term strength. Fly ashes generally classified into two catagories in the United States. The first is low calcium fly ash which is largely pozzolanic in nature. This type of fly ash is classified as ASTM Class F or Texas SDHPT Type A fly ash. The second type of fly ash is high calcium fly ash which possesses some cementitious properties. This type of fly ash is referred to as ASTM Class C or Texas SDHPT Type B fly ash. A review of these specifications is presented in Chapter 5.

Sulfate attack can be prevented by eliminating or controlling one or all of the components needed to form ettringite from monosulfoaluminate in hardened concrete. The components needed for ettringite formation are calcium hydroxide, reactive alumina, sulfate and water. The physical properties of fly ash affect the sulfate resistance of concrete to the extent that the fly ash provides greater pore refinement in the concrete. Fly ashes with a high fineness can be expected to make the concrete less permeable over time, therefore the concrete may be less susceptible to sulfate attack by keeping the influx of sulfate ions to a minimum.

As for the chemical and mineralogical constituents of fly ash which affect the sulfate resistance of concrete, there are five which need to be considered: calcium, alumina, iron oxide, silica, and sulfate.

Calcium is present throughout the concrete in many forms. Calcium hydroxide in the hardened concrete reacts with sulfates to form gypsum and start an expansive series of reactions. The calcium hydroxide produced by the initial hydration of the portland cement is the main source of the calcium for the formation of ettringite. Fly ash, as a result of its pozzolanic characteristic, binds the calcium from the calcium hydroxide in a stable C-S-H phase, thereby decreasing the amount of reactive calcium remaining in the hardened concrete. Low calcium fly ash, i.e. fly ash containing less than 10 percent analytic CaO, is more efficient at binding the calcium than high calcium fly ash because of a dilution effect. The low calcium fly ash replaces the calcium rich portland cement and consumes large quantities of calcium as it hydrates, whereas high calcium fly ash both contributes and consumes calcium from the hydrating paste.

Alumina is the second compound to be considered. Alumina may be present in fly ash as part of the glassy phases or in several crystalline phases. The amount of alumina in the glassy phases of fly ash is proportional to the amount of analytic calcium in the fly ash[24]. The hydration of the glassy alumina with calcium hydroxide leads to a C-A-H crystalline structure. The C- A-H structure may react in a sulfate environment to form ettringite thus contributing to sulfate attack. However, the alumina in low calcium fly ash is often present as the crystalline phase mullite. Mullite, a stable alumina rich mineral, is not reactive in sulfate solutions and the alumina in this form makes no contribution to the formation of ettringite in hardened concrete. Crystalline alumina in high calcium fly ashes may be present as melilite, C_3A and $C_4A_3\overline{S}$. The melilite phase is nonhydraulic and does not contribute to the sulfate attack mechanism. However the C_3A and $C_4A_3\overline{S}$ in some high calcium fly ash are possible sources of alumina for the formation of ettringite in concrete exposed to sulfates. Mehta proposed that the sulfate resistance of concrete containing fly ash is related to the state of reactivity of the alumina bearing phases in the fly ash[64]. If reactive alumina in fly ash leads to the formation of substantial amounts of monosulfoaluminate and C-A-H in the hardened concrete before sulfate exposure, then the fly ash should be expected to decrease the sulfate resistance of the concrete.

The third compound in fly ash that may affect the sulfate resistance of concrete is iron oxide, Fe_2O_3. The iron oxide in fly ash is present in the reactive glassy phases and in the hematite and ferrite spinel nonreactive crystalline phases. Several researchers have proposed that the total analytic iron oxide content in fly ash is beneficial to the sulfate resistance of concrete[23,34]. However, other studies have found that concrete containing fly ash with a high total analytic iron oxide content showed no improved sulfate resistance[32,64]. Kalousek found that these apparent opposing views are not incongruent[40]. Reactive iron oxide compounds have a positive influence on the sulfate resistance of concrete because they add a stabilizing effect through the formation of nonexpansive iron-rich ettringite, while the presence of iron oxide in one of its crystalline phases can be assumed to have no effect. When Fe_2O_3 is present in quantities of over 10 percent of the glassy phases, calcium ferrite hydrate may form outside of the stable hydrogarnet and iron-rich ettringite phases. This ferrite hydrate may be susceptible to sulfate attack as a ferrite ettringite without alumina.

The fourth compound of interest in fly ash is silica. Silica is the main building block of the binder which results from the pozzolanic reaction of fly ash. Reactive silica in the glassy phase of the fly ash consumes calcium hydroxide and water from the mortar matrix to form a stronger and less permeable concrete. In addition, the formation of C-S-H at later ages, or secondary C-S-H, may form a protective coating over crystalline phases containing reactive alumina such as monosulfoaluminate and calcium aluminate hydrates. Each of these effects contributes to greater sulfate resistance.

The final component of fly ash to be considered is the various sulfates in fly ash. The total sulfates are measured as sulfur trioxide. The crystalline phases of fly ash containing sulfate are anhydrite, $C_4A_3\overline{S}$, and alkali sulfates. Large quantities of sulfates in the fly ash may be beneficial to the sulfate resistance of concrete because they reduce the amount of calcium hydroxide in the hardened concrete, and promote the formation of ettringite while the concrete is still in the plastic state, effectively supersulfating the concrete. Moderate to low quantities of sulfates would have little effect on the sulfate resistance of concrete.

2.2.2 Silica Fume Composition and Sulfate Resistance. Silica fume reacts in a purely pozzolanic nature. The amorphous silica in the silica fume reacts with the calcium hydroxide from the portland cement hydration according to equation 2.10.

$$\begin{array}{ccccc} 3CH & + & 2S & \longrightarrow & C_3S_2H_3 \\ \text{calcium} & & \text{silica} & & \text{C-S-H} \\ \text{hydroxide} & & & & \end{array} \tag{2.10}$$

Silica fume increases the sulfate resistance of concrete in two ways. The first is by consuming nearly all the available calcium hydroxide in the cement paste matrix, thereby preventing the expansive transformation of monosulfoaluminate into ettringite. The second manner in which the silica fume increases the sulfate resistance of concrete is by reducing the permeability of the concrete. Silica fume is composed of fine particles which act as discrete nuclei for C-S-H hydration, impeding the movement of pore water and ions within the paste structure.

2.2.3 Blast Furnace Slag Composition and Sulfate Resistance. Blast furnace slag is largely composed of calcium aluminosilicate glass. This glass reacts according to the pozzolanic reaction described in equation 2.11. The binding hydrate contains some alumina in its structure, similar to the calcium silicate hydrate of hydrated portland cement.

$$\begin{array}{ccccc} C_nA_mS_l & + & CH & \longrightarrow & C-S(A)-H \\ \text{glass} & & \text{calcium} & & \text{calcium silicate} \\ & & \text{hydroxide} & & \text{(aluminate) hydrate} \end{array} \tag{2.11}$$

The calcium hydroxide for this reaction is the by-product from the hydration of portland cement. Blast furnace slag may also result in the formation of monosulfoaluminate as alumina is released during the glass dissolution.

Blast furnace slag has the potential to increase the sulfate resistance of concrete when used at portland cement replacement levels above 55 percent. As shown in Figure 2.3, the calcium hydroxide in cement paste is consumed at an increasing rate when slag is used at high replacement levels. The consumption of

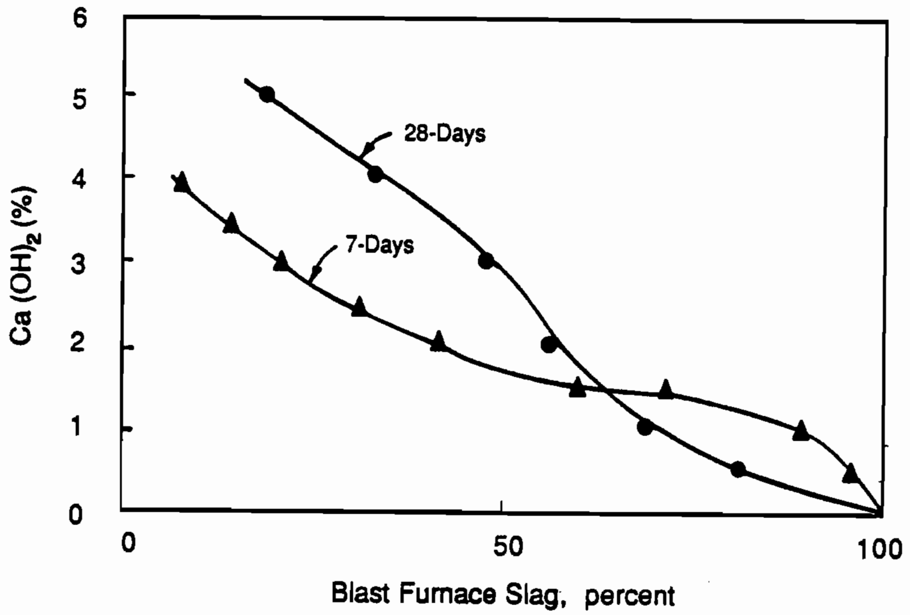


Figure 2.3 Calcium hydroxide content of hardened blast furance slag cements[43].

calcium hydroxide will control the formation of ettringite in the hardened concrete and lessen the expansion caused by sulfate attack.

The use of blast furnace slag and calcium sulfate has been used in Great Britain to provide sulfate resistance to concrete by means of supersulfating the paste and causing ettringite to remain stable throughout the hydration process and in the hardened concrete. This type of cement is typically 80 percent blast furnace slag, 15 percent anhydrite or hard-burnt gypsum and 5 percent portland cement.

2.3 Present Recommendations for Sulfate Resistant Concrete

The United States Bureau of Reclamation, the American Concrete Institute and the Texas State Department of Highways and Public Transportation each provide the design engineer with different recommendations for providing sulfate resisting concrete.

The USBR quantifies the potential of fly ashes to improve the sulfate resistance of concrete by computing an empirically derived R factor for each fly ash.

Using the R factor the USBR recommends the alternative cementitious combinations for defined levels of sulfate concentrations[81]. These recommendations are shown in Table 2.5.

The American Concrete Institute has less comprehensive guidelines but includes restrictive W/C ratios in its recommendations[2]. The ACI recommendations are presented in Table 2.6.

The Texas State Department of Highways and Public Transportation has a generalized specification for concrete which may be exposed to sulfate environments. The present recommendation is to use either Type II cement or Type II cement with Texas SDHPT Type A fly ash in areas where sulfate exposure is probable.

Table 2.5 **U.S. Bureau of Reclamation guidelines for sulfate resistant cementitious material.***

1) Negligible (less than 0.10 percent or 150 ppm SO_4). No precautions necessary for sulfate resistance.
2) Positive (0.1 + 0.2 percent or 150-1500 ppm SO_4)
   a. Type II cement
   b. Type II cement + Class N, F, C, Pozzolan ($R < 2.5$)
   c. Type IP cement with Pozzolan ($R < 2.5$)
3) Severe (0.2 - 2.0 percent or 1500-10,000 ppm SO_4)
   a. Type V cement
   b. Type V cement + Class N, F, C, Pozzolan ($R < 2.5$)
   c. Type II cement + Class N, F, C, Pozzolan ($R < 1.5$)
   d. Type IP cement with $C_3A < 5.0$ percent and Pozzolan ($R < 2.5$)
   e. Type IP cement with $C_3A < 8.0$ percent and Pozzolan ($R < 1.5$)
4) Very Severe (> 2.0 percent or 10,000 ppm SO_4)
   c. Type II cement + Class N, F, C Pozzolan ($R < 0.75$)
   d. Type IP cement with $C_3A < 5.0$ percent and Pozzolan (< 1.5)
   e. Type IP cement with $C_3A < 8.0$ percent and Pozzolan (< 0.75)

*Using the bulk chemical composition of the pozzolan the R factor = $(CaO(\%) - 5)/Fe_2O_3(\%)$

Table 2.6 **American Concrete Institute guidelines for sulfate resistant cementitious material.***

1) Mild (less than 0.10 percent or 150 ppm SO_4). No precautions necessary for sulfate resistance.
2) Moderate* (0.1 - 0.2 percent or 150 - 1500 ppm SO_4)
   a. Type II cement with $w/c < 0.50$
   b. Type IP (MS) cement with $w/c < 0.50$
   c. Type IS (MS) cement with $w/c < 0.50$
3) Severe (0.2 - 2.0 percent or 1500 - 10,000 ppm SO_4)
   a. Type V cement with $w/c < 0.45$
4) Very Severe (> 2.0 percent or 10,000 ppm SO_4)
   a. Type V cement + Pozzolan** which has proven to improve sulfate resistance with Type V cement, with $w/c < 0.40$

* Seawater also falls in this category.

** Use a pozzolan which has been determined by tests to improve sulfate resistance when used in concrete containing Type V cement.

CHAPTER III
REVIEW OF PREVIOUS RESEARCH

3.1 Background on Sulfate Attack

Smeaton, in 1756, first recognized the effects of sulfates on portland cement concrete when he reported the deterioration of coastal structures in England[92]. While documenting the problem was important, little else could be done for the degrading structures without a better understanding of the mechanisms involved. In 1890, Candlot isolated the ettringite compound as the harmful substance in concrete exposed to sulfates[10]. Michaelis later confirmed the presence of ettringite and accurately reported its complex composition, with the exception of reporting 30 instead of 32 mols of hydrated water in the compound[66]. Le Chatelier discovered by 1905 that C_3A was the controlling phase of portland cement that led to sulfate corrosion and that the substitution of iron oxide for alumina reduced the level of sulfate attack[42]. Between 1915 and 1920, the first sulfate resistant portland cements were produced in Germany and Italy by reducing the alumina:iron oxide ratio to unity. This is the predecessor of the modern day high sulfate resistance ASTM Type V portland cement.

The use of fly ash in concrete to prevent sulfate attack has largely been based on the observed improvement of sulfate durability in concrete containing pozzolans, rather than on an analytic understanding of the relationship between sulfate attack and fly ash composition. Davis et al. reported in 1937 that pozzolans could be used in concrete to prevent sulfate attack[13]. They showed that pozzolans combine with the calcium hydroxide in the concrete to somehow prevent sulfate attack. This behavior was true for low calcium fly ashes but has not been observed in the "new" type of fly ash, high calcium fly ash. The research review presented in this chapter is the basis for the direction and experimental design of the research study reported herein.

3.2 Sulfate Resistance of Concrete Containing Fly Ash

There have been numerous studies conducted on the sulfate resistance of concrete containing fly ash[8,14,19,22,24,28,33,34,40,50,55,64,76,81,85,86,100]. Each of these studies consisted of exposing concrete or mortar to some form of sulfate solution for an extended period of time and reported on the performance of the specimens. Most of the past investigations have included only low calcium ASTM Class F fly ashes because that is the type of fly ash most commonly produced in Europe, Australia and from the burning of eastern United States coals. But in the past fifteen years, western coals from Wyoming and Montana have been used to generate electrical power throughout the midwestern and western United States. These coals typically produce fly ashes with higher calcium and lower silica contents than the eastern coals and are categorized as ASTM Class C fly ash. There is coexisting evidence that fly ash can increase sulfate resistance, decrease sulfate resistance and has no effect on the sulfate resistance of concrete. The summation of all the studies on the sulfate resistance of concrete containing fly ash brings forth the conclusion that the effect of fly ash on the sulfate resistance of concrete it is not fully understood.

The previous studies summarized in this chapter were a starting point for the present research program. The test procedures, material selection and characterization, and data analysis of the reviewed research were used to guide the present research study so as to better quantify, analyze and understand the mechanism of sulfate attack in concrete containing fly ash.

3.2.1 Dikeou [1967][19]. J. T. Dikeou published the results of a 27 year study on the sulfate resistance of concrete containing fly ash. The study was performed at the United States Bureau of Reclamation, USBR, and was conducted because the bureau had measured sulfate concentrations of 5 to 6 percent in soils, and groundwater concentrations in excess of 150,000 ppm in areas where concrete drain pipe was to be installed.

The test procedure used by the USBR consisted of soaking three 3 in. x 6 in. cylindrical concrete specimens with end gage studs in a 2.1 percent solution of Na_2SO_4. The specimens were periodically measured for expansion using a length comparator. The specimens were moist cured for 14 days and dried at 50 percent relative humidity for 14 more days before starting the sulfate exposure. An accelerated procedure was developed 5 years after the study began and one of the original three specimens was moved to the accelerated test. The accelerated test consisted of soaking in a 2.1 percent solution of Na_2SO_4 for 16 hours and drying under a forced draft at 130°F for 8 hours. This test procedure was found to cause failure in 1/10 the time of the 2.1 percent Na_2SO_4 soaking test and at a slightly faster rate than a 10 percent Na_2SO_4 soaking test[26].

Dikeou used eight different portland cements: two Type I cements, four Type II cements, and two Type V cements. In combination with these cements, twelve low calcium ASTM Class F fly ashes from the Chicago area were used at volumetric replacements ranging from 15 to 35 percent of portland cement. The failure criteria used in this test was 0.2 percent expansion, indicating practical failure because internal disruption of the concrete was evident and 0.5 percent expansion indicating total failure.

There were 4 major conclusions from this study.

1) All fly ashes tested greatly improved the resistance of concrete to sulfate attack, regardless of cement used, or whether the fly ash met material specifications.

2) The addition of fly ash increased the relative sulfate resistance of Type I cement the most followed by Type V and Type II, respectively. However the Type I + fly ash concrete was not as resistant as concrete containing Type II or V cement.

3) The order of greatest sulfate resistance to least sulfate resistance was,

   Type V Cement + Fly Ash,

   Type II Cement + Fly Ash,

   Type V Cement,

   Type II Cement,

   Type I Cement + Fly Ash, and

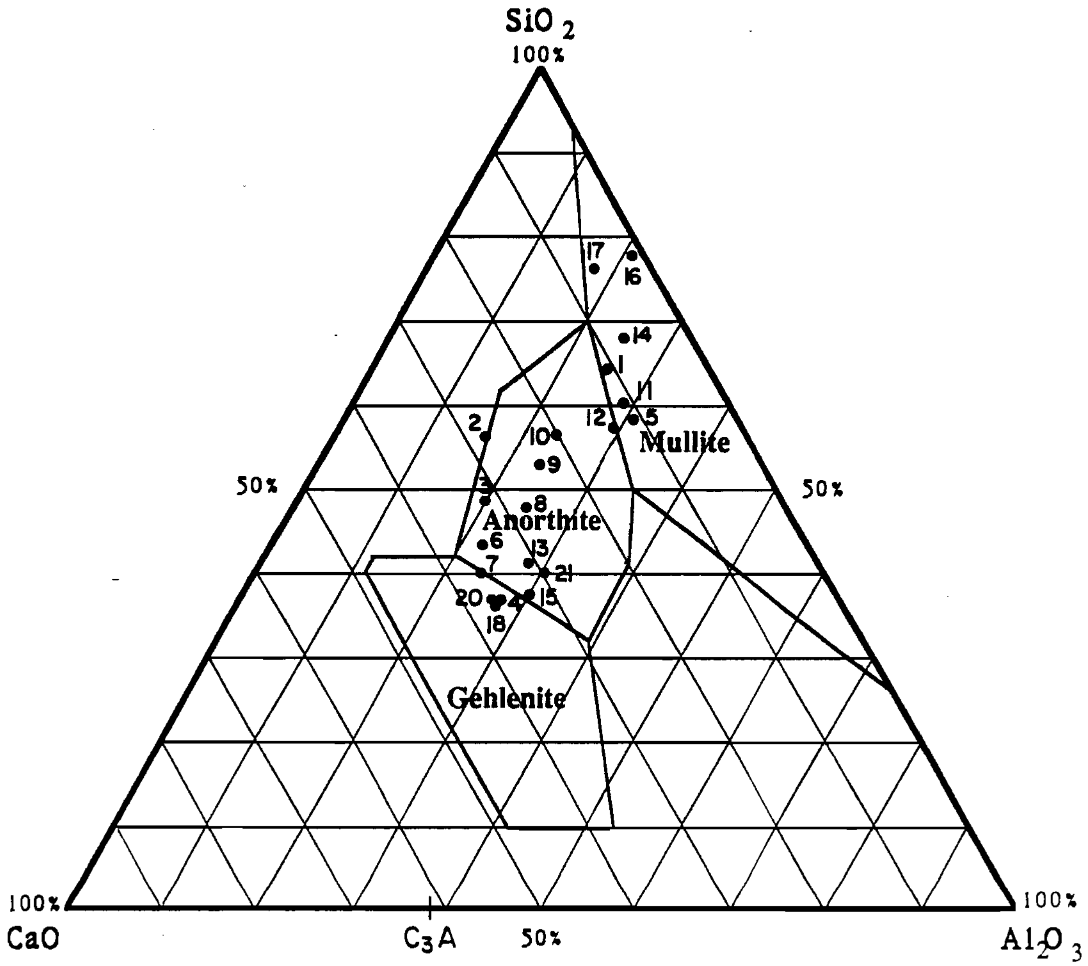
   Type I Cement.

4) Sulfate resistance was most dependent on cement type and to a lesser extent dependent on air content, cement content and differences in chemical composition of the same type cement.

3.2.2 Dunstan [1976,1980,1984,1987][24,25,26,27]. Dunstan studied the sulfate resistance of concrete containing fly ash for a decade while at the United States Bureau of Reclamation and in private practice. His research results and postulates are the basis for the USBR's specification for concrete exposed to sulfates and the only comprehensive view that addresses fly ash in concrete. Although other researchers have contested his assumptions and sulfate resistance prediction equation, his work has stimulated research in both the characterization of fly ash particles and their effect on the sulfate resistance of concrete.

Dunstan's main study consisted of 3 in. x 6 in. air entrained concrete cylinders subjected to two different exposure tests. One test used the USBR accelerated wetting and drying sulfate test described in section 3.2.1. A second slightly less severe test consisted of continuous submersion in a 10 percent solution of Na_2SO_4. The tests were performed with specimens from the same concrete mixtures. The specimens were moist cured 14 days and then air cured for 14 days at 50 percent relative humidity. Failure was defined as 0.5 percent expansion. The main study contained a Type II cement having 7.96 percent C_3A and 6 fly ashes: a bituminous coal fly ash blended from several Chicago area ashes, three lignite based fly ashes from North Dakota, and two subbituminous coal fly ashes from Colorado and Arizona.

The results of the study showed that concrete containing fly ash with a low calcium was more resistant to sulfate attack than concrete containing other fly ashes or no fly ash. In this research study, both X-ray diffraction and chemical analysis were conducted on the fly ashes. Through the use of these characterization techniques, Dunstan found that fly ashes from lignite and subbituminous sources have calcium rich glass and crystalline phases. In order to make better use of the particle characterization data, Dunstan presented the chemical composition of the fly ashes on a ternary phase diagram, as shown in Figure 3.1. The diagram shows the presence of low calcium fly ashes in the mullite field, i.e. largely aluminosilicate composition, whereas the high calcium fly ashes lie nearer the gehlenite field, calcium aluminosilicate composition. Fly ashes with gehlenite-like compositions were less



CaO • Al2O3 • SiO2 ternary oxide system diagram.

Figure 3.1 Dunstan's study of fly ash composition[25].

sulfate resistant than those with mullite field compositions. The primary difference between coumpounds from the two regions of the CaO-SiO_2-Al_2O_3 ternary diagram is that mullite is nonreactive, and gehlenite is reactive in the presence of calcium hydroxide and sulfate solutions[44].

Combining the glass characterization information and the sulfate resistance test results, Dunstan proposed a method of predicting the sulfate resistance of concrete containing fly ash. His method is referred to as the R factor method. The R factor can be simply stated as

$$R = \frac{CaO(\%) - 5}{Fe_2O_3(\%)} \tag{3.1}$$

The R factor was developed to predict the amount of reactive alumina in fly ash and to use it as an indication of the sulfate resistance of fly ash concrete. Dunstan reasoned that the best indication of reactive alumina in fly ash was the CaO content because it is relatively easy to measure and his research indicated that glasses containing increasing amounts of reactive alumina also contained increasing amounts of calcium oxide. In addition, as the calcium oxide content of fly ash increases so does the potential for the presence of the reactive crystalline aluminate phases C_3A and $C_4A_3\overline{S}$. The reason 5 percent is subtracted from the CaO content in the R factor is that Dunstan assumed that there is some calcium in nonreactive phases as well as in anhydrite. The calcium in anhydrite is consumed in the initial hydration much like gypsum is consumed in portland cement hydration and nonreactive phases containing calcium do not contribute to the sulfate mechanism. The denominator of the equation is the iron oxide content of the fly ash. Kalousek found that reactive iron oxide improves the sulfate resistance of concrete by forming iron rich ettringite, which is nonexpansive [40]. The R factor uses the total iron oxide content because it is easier to determine than the noncrystalline iron.

The level of sulfate resistance predicted by the R factor is presented in Table 3.1. The 3.0 limit in Table 3.1 is a subjective value proposed in 1980 from the results shown in Figure 3.2. Since then, Dunstan has reported that 3.35 is a more realistic value and 3.70 may even be acceptable[27]. There are two limitations to the R factor concept. The first is that the equation was developed for a water to cement plus fly ash ratio, W/(C+P), of 0.45 and is probable not valid for W/(C+P) ratios

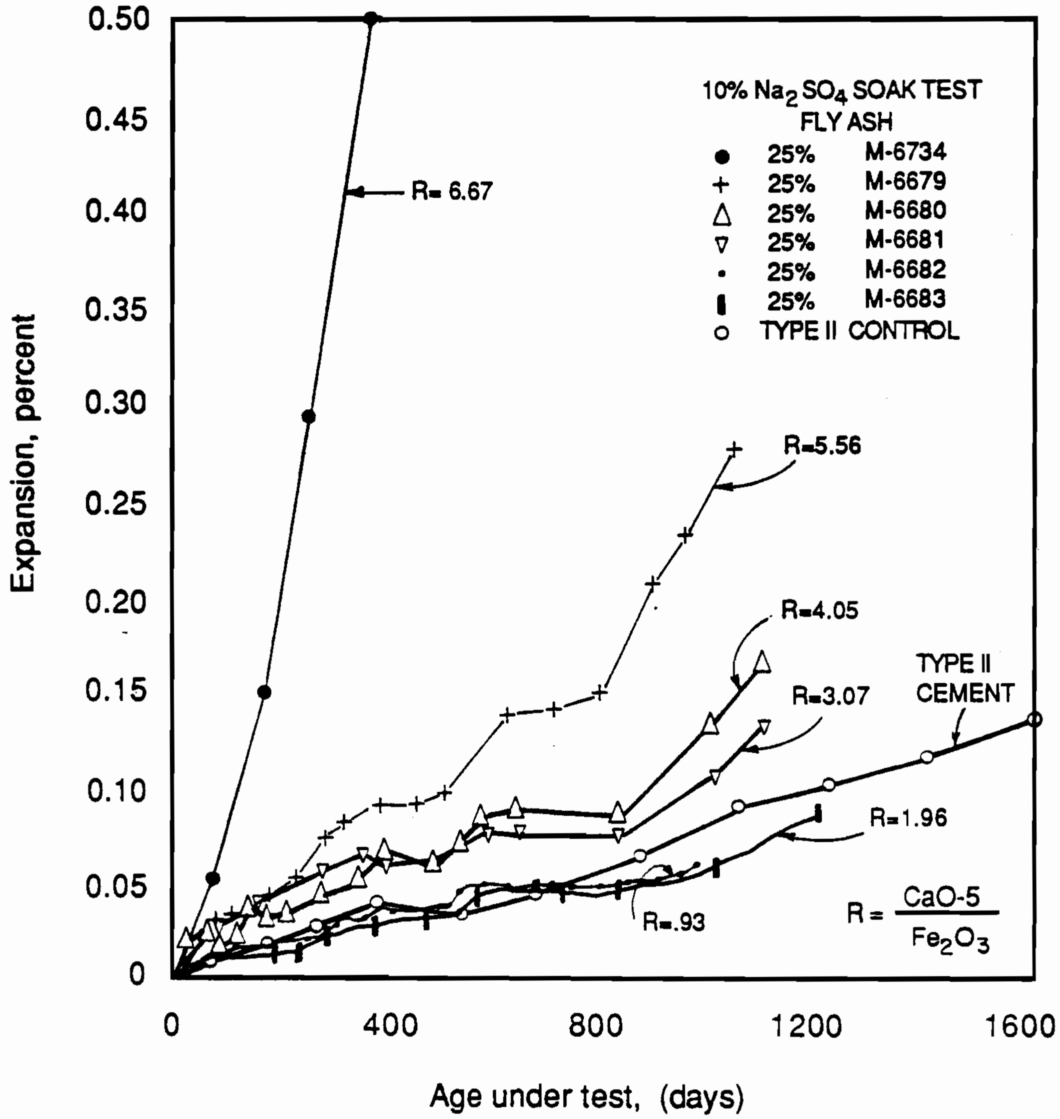


Figure 3.2 Dunstan's sulfate expansion results for concrete containing fly ash.

greatly exceeding 0.50. The second is that low Fe_2O_3 contents will cause the value of R to be artificially high. In such cases, a value of 2.0 percent should be imposed. The equation was developed for 25 percent volumetric replacement and with Type II cement. While these two parameters are important, their effect is unknown. Dunstan states that the R factor may change for different replacements and other cements but only in a minor way. Two important points of the R factor development should be emphasized. The first is that the R factor is based on the bulk chemical composition of fly ash. It does not directly account for the difference between glassy and crystalline phases in fly ashes. Secondly, the R factor assumes that iron oxide compounds in the fly ash will react in a favorable manner to prevent sulfate attack. There is evidence that the iron oxide in fly ash is mostly nonreactive[58].

Table 3.1 Sulfate resistance of concrete containing fly ash on the basis of the R factor criterion[25].

R Limit[a]	Sulfate Resistance[b]
< 0.75	Greatly Improved
0.75 to 1.5	Moderately Improved
1.5 to 3.0	No Significant Change[c]
> 3.0	Reduced Resistance

[a] $R=(CaO-5)/Fe_2O_3$ percentage from fly ash oxide analysis; for severe cyclic conditions of wetting and drying or $MgSO_4$ exposure reduce the R value by 0.50.

[b] Compared to Type II cement control at 0.45 w/c ratio.

[c] Slightly improved to slightly reduced.

In a separate research study, Dunstan investigated the sulfate resistance of fly ash cements containing 90 percent fly ash and 10 percent anhydrite. The sulfate resistance of these cements was inversely related to the 28 day compressive strength. The lowest compressive strength giving the greatest sulfate resistance. In each case, the sulfate resistance of the fly ash cement was greater than that of Type II cement.

The three conclusions related to sulfate attack from his decade of study were,

1) the sulfate resistance of concrete containing fly ash can be predicted using the R factor,
2) the sulfate resistance of concrete containing 90 percent fly ash is very good, and
3) mortar made from fly ash and anhydrite can be used to predict sulfate resistance of fly ash cements.

The conclusion with the broadest implications is the first of these. The R factor is the first equation based on the standard chemical analysis to be used to predict the behavior of fly ash in concrete exposed to sulfate environments. The development of a reliable predicting method which does not require long term exposure testing would save time and costly laboratory testing. In addition, such a factor would be easily included into present specifications for concrete exposed to sulfates.

The distinctive point in this discussion is the reliability of the R factor. The factor showed strong correlation for six fly ashes, but there are literally hundreds of fly ashes in the United States and an even a larger number of possible chemical compositions. The R factor must be proven reliable for a broader base of fly ash compositions.

3.2.3 Kalousek [1972, 1976][40,41]. G. L. Kalousek, at the USBR, conducted tests to understand the effects of pozzolans and porosity on the sulfate resistance of concrete pipe. The primary use of concrete pipe by the USBR is for the transmission of water for irrigation or drainage. These pipes are buried in soils which typically contain less than 0.2 percent sulfate. However these soils may contain up to 0.8 percent sulfate in locallized zones. Using Type I, II, V and 0 percent C_3A cements Kalousek found the predicted life of concrete pipes to be less than 50 years, the minimum expected design life of USBR projects. These tests on concrete without pozzolans also showed that the sulfate resistance of 0 percent C_3A cement was not greater than that of Type V cement. In determining the effect of both magnesium and sodium sulfate salts, a separate USBR study found that $MgSO_4$ caused more rapid expansions at the beginning of tests but Na_2SO_4 led to greater and gradually accelerating expansions over a long period of time[37].

Using the USBR's continuous soaking and accelerated testing procedure of wet and dry cycling in 2.1 percent Na_2SO_4 solution (1.4 percent total SO_4), Kalousek studied the use of fly ash, blast furnace slag, shale, bentonite, volcanic ash, and pumicite in combination with both Type II and V portland cements. While the laboratory sulfate concentrations were greater than those of typical field concentrations, conditions such as freeze-thaw cycling, shrinkage and other cracking may act to accelerate the sulfate attack mechanism in actual field applications. Furthermore, concrete which rests in wet sulfate bearing soil, and which is occasionally subjected to surface drying has been known to accumulate total sulfate concentrations as high as 4.0 percent.

The pozzolans were used as a volumetric replacement for between 15 to 35 percent of portland cement. Failure was defined as 0.5 percent expansion of the 3 in. x 6 in. concrete specimens. Three classes of concrete performance were defined in this study:

1) less than 50 year predicted life,
2) 50 to 100 year predicted life, and
3) greater than 100 year predicted life.

The predicted life is defined as the time to failure in the 2.1 percent soaking test or 8 times the time to failure in the accelerated wetting and drying test. This multiplier was determined by comparing Type II and V portland cement concrete in the soaking test after 15 years to that of concrete tested with the accelerated test.

Tests of portland cement concrete showed that 16 of 19 mixtures had a predicted life of less than 50 years. Portland cements containing less than 6.5 percent C_3A and less than 12 percent C_4AF exhibited moderate sulfate resistance, regardless of whether Type II, Type V or 0 percent C_3A cements were used. Additionally, the use of pozzolans which increased the water demand of a mix by more than 40 percent resulted in concrete that was not resistant to sulfate attack. Such pozzolanic material are diatomaceous earth, kaolin, bentonite and some shales.

The performance of concrete containing 35 percent granulated blast furnace slag was very poor, causing premature failure and a predicted life of less than 2 years. The use of 35 percent ground blast furnace slag showed a mixed performance with one of three mixtures failing at a predicted life of 14 years and the other two having a predicted life in excess of 100 years. Concrete containing 35 percent pozzolan such as volcanic ash, shales, clays, pumicite and bentonite showed a marginal increase in sulfate resistance having a typical predicted life between 45 and 80 years. The use of fly ash in concrete showed the greatest improvement in sulfate resistance. Of the 11 mixtures using 35 percent fly ash, eight had predicted lives in excess of 130 years and all mixtures had predicted lives greater than the control cements. Additionally, fly ash was found to be extremely effective in improving the sulfate resistance of high slump concrete. In a separate mixture series using air entrained concrete, the use of 30 percent fly ash was found to be more effective than 15 percent replacement in combating sulfate attack.

Kalousek's study of sulfate resistance of concrete with different porosities was conducted to study the effect of sulfate intrusion on the sulfate resistance of concrete. Six concrete pipes were cast and measured for porosity following a 5 hour boiling water test. The absorption of the pipes ranged from 6.2 percent to 12.9 percent. Concrete with a low absorption had a high sulfate resistance, however concrete with greater than 8.5 percent absorption had the effect of reducing sulfate resistance.

Table 3.2 Predicted life of concrete with varying absorptions.

Absorption, %	6.2	8.5	10.6	11.2	12.6	12.9
Predicted Life, yrs.	1240	140	30	115	75	40

The conclusions of Kalousek's studies on the sulfate resistance of concrete include the following:

1) concrete cannot be made totally sulfateresistant by altering the chemical composition of Type II or V portland cements or reducing the W/C ratio,

2) bituminous based fly ashes meeting ASTM Class F material specifications at least doubled the life expectancy of concrete subjected to sulfates when Type II or V cement was used,

3) the replacement of Type II or V cement with a high quality pozzolan which does not drastically increase the water demand will provide concrete sulfate resistance equal to or greater than that of the Type II or V cement alone, and

4) $MgSO_4$ is a harsher sulfate salt in short term testing but Na_2SO_4 will lead to larger long-term expansions.

3.2.4 Mather [1980][65]. In a research study performed at the structures laboratory of the U.S. Army Engineer Waterways Experiment Station, Katherine Mather investigated the effects of 26 different cements, 8 fly ashes, a calcined volcanic ash and a silica fume on the sulfate resistance of concrete. Through the use of X-ray diffraction, several different crystalline structures of C_3A in portland cement were identified, namely: cubic, orthorhombic, and tetragonal.

Mather's specimens consisted of 1 in. x 1 in. x 11 in. mortar bars soaked in a 0.352 molar solution of Na_2SO_4 for up to 365 days. The volume of solution to volume of specimens was 3.9 and the solution was replaced with a fresh solution every 30 days. Specimens were measured for expansion and changes in the fundamental transverse frequency. The failure criteria was 0.10 percent expansion.

In a study of 26 different cements, Mather found five that contained no C_3A and seven that contained only cubic C_3A crystalline structures; coincidentally, these seven cements also contained the largest quantities of C_3A. The other 14 portland cements contained a combination of orthorhombic, tetragonal and cubic C_3A crystalline structures. Six of the seven cements containing only cubic C_3A expanded to failure in the test period, while none of the 0 percent C_3A cements reached failure. The cements containing more than one C_3A crystalline structure expanded to failure but at a slower rate than the cements containing only cubic C_3A structures. When a low calcium Class F fly ash was added as a 15 to 25 percent replacement, by volume for portland cements containing the cubic C_3A, the resulting Type IP cements were resistant to sulfate attack. Similarly, when the same fly ash was added to other cements containing more than one C_3A crystalline structure the result was sulfate resistant Type IP cement.

Mather also studied the effect of a calcined volcanic ash, a silica fume, one bituminous, three subbituminous, and four lignite fly ashes on the sulfate resistance of concrete. When either silica fume or the calcined volcanic ash was used as 30 percent replacement, by volume for portland cement, high sulfate resistance was observed regardless of the type of cement used. Poor sulfate resistance was observed in concrete containing fly ash or containing only portland cements when the C_3A content of the cement was in excess of 13 percent. Three subbituminous coal fly ashes substantially increased the sulfate resistance of concrete when used as a 30 percent volumetric replacement for a portland cement with 9.4 percent C_3A. The replacement of this same cement with bituminous and lignite coal fly ashes did not show the same improvement in sulfate resistance. Two of the lignite fly ashes reducing the sulfate resistance of the concrete.

The conclusions from this study were,

1) it is possible to distinguish between cubic C_3A and solid solution C_3A with mixed structures,

2) silica fume and calcined volcanic ash improve the sulfate resistance of concrete, and

3) fly ash may or may not improve the sulfate resistance of concrete.

Correlating the sulfate exposure results of this study with Dunstan's R factor index of sulfate performance, the predicted and actual results are compared in Table 3.3. The results show that the R factor does not adequately predict the performance of concrete containing fly ash in sulfate environments, especially those with R factors greater than 1.9.

3.2.5 Eustache [1970][28]. Research conducted at the Lafarge Corporation in Vivier-sur-Rhone, France by Eustache and Magnan investigated the sulfate attack mechanism with respect to the changing levels of sulfate water in tidal zones. The test procedure used 20 mm x 20 mm x 100 mm mortar bars half immersed in 50 g/l $MgSO_4 \bullet 7H_2O$ solution for 10 months. Companion specimens were totally immersed in distilled water. Both solutions were replaced with fresh solutions each month. The specimens were periodically tested for compressive strength and visually inspected for signs of physical deterioration. A summary of the results is presented in Figure 3.3.

Table 3.3 Comparison of R factor prediction and actual performance of concrete exposed to sulfates.

R Factor	-0.15	-0.01	0.56	1.29	1.99	2.74	3.48	3.52
Predicted[a]	1	1	1	2	3	3	4	4
Actual[b]	2	1	1	2	1	4	3	2

1 = greatly improved, 2=improved, 3=no effect, 4=reduced

[a] Level of sulfate resistance predicted by R factor criterion.

[b] Level of sulfate resistance in laboratory test.

Using 4 portland cements ground to finenesses of 3000 and 6000 cm^2/g, and using W/C ratios of 0.4, 0.5, and 0.6, Eustache repeated each mix several times and statistically correlated the factors related to sulfate attack. The conclusions of his tests are stated below.

1) The time to apparent sulfate attack is long, but once begun the deterioration is very rapid.

2) Zones between the high and low water level are most susceptible to sulfate attack.

3) Chemical characteristics of portland cements alone are not sufficient to predict sulfate resistance on the basis that high alumina cements were found to be sulfate resistant.

4) Sulfate attack occurs in two apparent stages:

    a) slow diffusion of sulfate ions into the paste structure, and

    b) rapid chemical attack of the hydration compounds.

5) There are two kinetic stages to sulfate attack:

    a) dormant period where reactive compounds are protected, and

    b) nucleation like phenomenon which is accelerated with time.

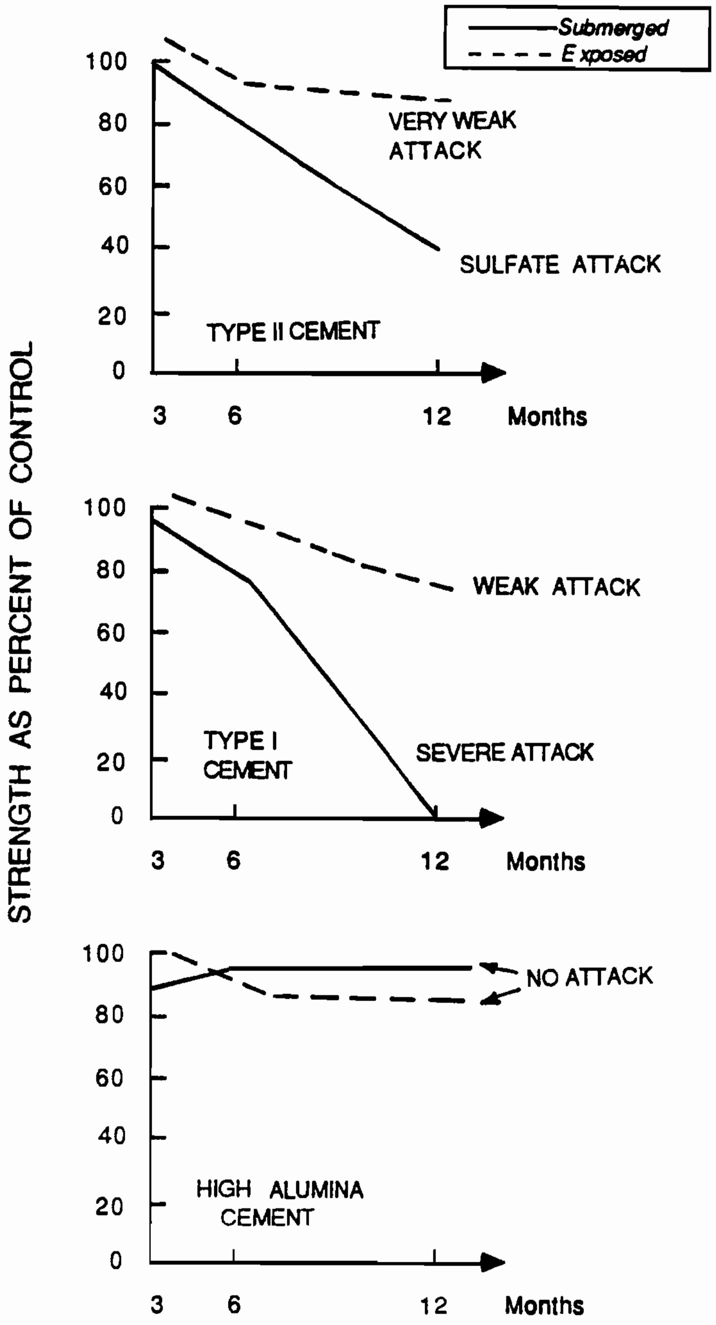


Figure 3.3 Sulfate resistance of mortar partially immersed in sulfate solution[28].

3.2.6 M. Ben-Yair [1974][8]. Ben-Yair studied the effects of chlorides on the sulfate resistance of concrete. Several investigators have indicated that chlorides have a detrimental or no effect on the sulfate resistance of concrete, while others like Russian Specification GAST 4797 recognize that chlorides enhance the sulfate resistance of concrete based on the reduction of the severity of attack in seawater despite high concentrations of sulfate salts[25,111].

Chlorides may be present in concrete from accelerating admixtures, road salts, or chloride ions in the soil and groundwater. Through the use of scanning electron microscopy, Ben-Yair determined that the addition of chloride ions promote larger ettringite crystal and calcium aluminate chloride hydrate. The chloride addition increased the average size of the ettringite crystal from 60 microns to 300 microns. Furthermore, the chlorides are thought to follow the typical reactions shown in equations 3.2 and 3.3.

$$Ca(OH)_2 \quad + \quad 2NaCl \quad \longrightarrow \quad CaCl_2 \quad + \quad 2Na(OH) \qquad (3.2)$$

$$CaCl_2 + 3CaO \bullet Al_2O_3 + 10H_2O \quad \longrightarrow \quad 3CaO \bullet Al_2O_3 \bullet CaCl_2 \bullet 10H_2O \quad (3.3)$$

The resultant calcium aluminate chloride hydrate has a molecular volume of 297 cm^3, much larger than gypsum at 74 cm^3 but considerably smaller than ettringite at 714 cm^3. The combination of calcium aluminate chloride hydrate, gypsum, and ettringite simultaneously forming in hardened concrete exposed to a sulfate environment leads to a more rapid deterioration.

Ben-Yair showed this effect by conducting mortar bar tests on 1 in. x 1 in. x 11 in. specimens soaking in solutions of sulfates and chlorides and measuring the expansions of the specimens over eight years. In a comparison of clinker cement and a normal portland cement with clinker plus gypsum, the results show that when exposed to a 3.5 percent chloride salt solution the normal portland cement expanded twice as much as the clinker cement. The reason for this is that chlorides encouraged the formation of ettringite from the sulfate within the gypsum. These same two cements were also used to study the effect of 3.5 percent sulfate salt solutions and several different seawaters. In these mortar bar tests the clinker cement and the normal portland cement expanded in approximately the same manner and ultimately to failure when exposed to sulfate solutions. The explanation for this is that sulfates migrating into hardened concrete are more harmful than sulfates found in hydrated compounds that form in the plastic stage of paste hardening. Seawater from the Mediterranean and Red seas led to moderate expansions, but not to failure during the eight year test.

In separate investigations, it was found that wet-dry cycling, such as those in coastal regions and areas with alternate rainy and arid seasons, was the harshest environment for chemical attack. Ben-Yair also found large swings in daily temperatures crack the concrete and accelerate chemical attack.

The conclusions from this study were,

1) climatic factors influence the magnitude of sulfate corrosion in the field,
2) leaching of $CaCl_2$ and its derivatives increases permeability,
3) seawater corrosion is different from chloride-sulfate corrosion in arid regions, and
4) $CaCl_2$ accelerators may increase sulfate attack.

3.2.7 Rosner [1980][86]. Research conducted at Western Technology Laboratory by Rosner, Chehovits and Warburton studied the effects of one ASTM Class C and three Class F fly ashes as a 4:3 fly ash to cement weight replacement for Type II portland cement. The test procedure continuously soaked 1 in. x 1 in. x 11 in. mortar bars in a combined solution of 0.176 molar Na_2SO_4 and 0.176 molar $MgSO_4$ (3.4 percent total SO_4) for one year. Specimens were cured to a compressive strength of 3000 psi before being exposed to the sulfate solution. The mortar bars were monitored for linear expansion, weight changes, dynamic modulus and porosity. Porosity was measured using ethyl acetate and a vacuum saturation procedure. Rosner's preliminary investigations showed that the use of accelerated testing by a heated forced draft is overly severe and that the aggregates used in sulfate testing should be independently tested rather than coupled with the effects of paste variables under sulfate attack. In addition, Rosner noted that typical field concentrations of sulfates are lower than those used in laboratory testing and therefore accelerated tests should be used only as indices and predictors for performance and not for life expectancy estimations.

After a year of sulfate exposure the sulfate expansion performance of mortar containing the 3 ASTM Class F fly ashes was excellent and the ASTM Class C fly ash was marginal when compared to the sulfate resistance of mortar with Type II cement. The amount of cement replaced, 10, 15 and 20 percent, had no effect on the performance of the concrete. The changes in weight of the specimens were determined to be due to the absorption of water, the formation of calcium sulfate, scaling and abrasion. The mortars made with Class F fly ashes displayed a greater weight loss than the Class C fly ash.

Rosner postulated that the sulfate expansion was due to the formation of gypsum products and not ettringite. He also reported, that fly ash reacted in a pozzolanic manner to form insoluble complex calcium aluminosilicates hydrates which reduced the availability of reactive alumina in the concrete. The porosity tests showed that there was no difference in the porosity of concrete containing fly ash and concrete without fly ash at early ages. However after one year of sulfate exposure concrete with 10 or 15 percent cement replacement by fly ash at a 4:3 weight ratio had lower porosity than that of concrete containing no fly ash or 20 percent cement replacement. The conclusions from this study were,

1) some fly ashes improve sulfate resistance,
2) the level of sulfate resistance is not dependent upon the percent replacement,
3) fly ash which causes greater sulfate resistance may reduce scaling and abrasion resistance, and
4) fly ash can reduce the porosity of concrete.

During the course of the investigation, Rosner determined using ANOVA analysis that relatively small differences in total expansion or days to failure are statistically insignificant. These differences were caused by the variability between individual specimens within the same mixture. Furthermore, the use of dynamic modulus testing was determined to be unreliable because of surface scaling. In studying the usefulness of Dunstan's R factor as a performance index, the effect of four fly ashes with R factors of 0.18, 0.29, 2.71 and 5.30 were used. Rosner found, based on expansion data, that the three Class F fly ashes provided excellent sulfate resistance, while the Class C fly ash (R factor = 5.3) provided marginal sulfate resistance when compared to the control cement, as shown in Figure 3.4. The performance of the two fly ashes with highest R factors was adequate, contrary to the premise of the R factor prediction method.

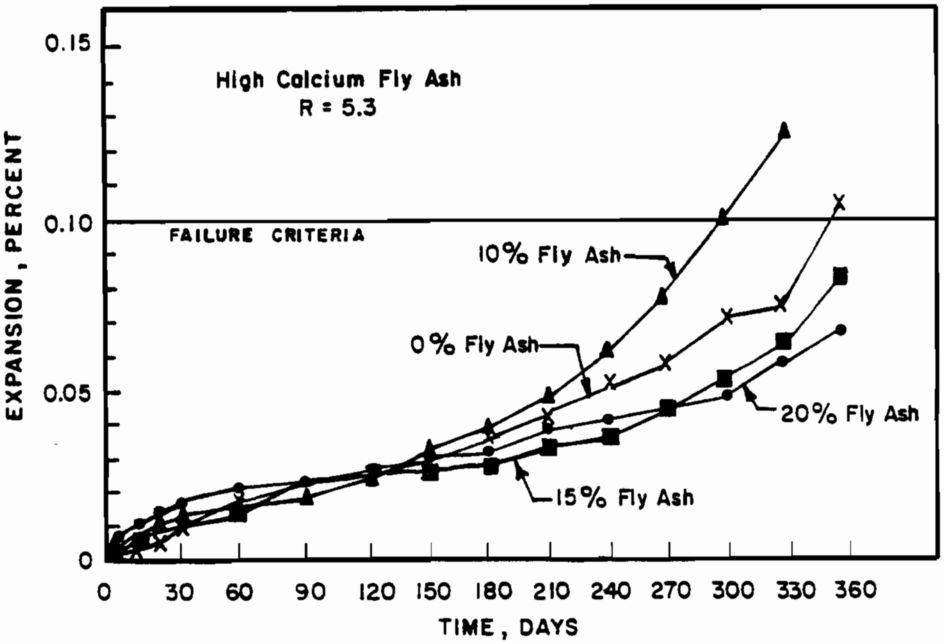


Figure 3.4 Sulfate resistance of concrete containing high calcium fly ash[86].

3.2.8 Hartmann, Mangotich [1987][84]. A research study was conducted at the Western Institute of Technology on the sulfate resistance of concrete containing ASTM Class C fly ash to develop a method more reliable than the R factor method of predicting the sulfate resistance of concrete containing fly ash. The researchers point out that the R factor has three major limitations:

1) it cannot be used to predict the sulfate resistance of concrete containing portland cement alone,

2) it does not account for the sulfate resistance of any high calcium fly ashes, and

3) the observed level of resistance does not always correspond with the magnitude of the R factor.

However, Hartmann and Mangotich agree with Dunstan's premise that a desirable sulfate resistance prediction method should be based on the bulk chemical analysis which is relatively inexpensive and uncomplicated.

Their study consisted of measuring mass loss, expansion and permeability of concrete containing fly ash as a direct weight replacement for Type II cement. Three fly ashes were used: Comanche, Tolk Station, and Navajo. Comanche and Tolk Station fly ashes were high calcium ASTM Class C fly ashes, whereas Navajo was a low calcium Class F fly ash. Comanche and Navajo fly ashes were used at a replacement level of 20 percent and Tolk Station fly ash was used at 20, 25, 30, and 35 percent. From each mixture, 3 in. x 6 in. cylinders and 2 in. cubes of concrete and 1 in. x 1 in. x 11 in. mortar bars were cast. The specimens were air cured for 14 days before being exposed to a 10 percent Na_2SO_4 solution. The solution pH was controlled using sulfuric acid and constantly circulated. The cubes and cylinders were air dried 2 hours and brushed with a steel brush before measuring mass changes weekly. Mortar bars were measured in a saturated surface dry condition. In an attempt to accelerate the test, after 28 weeks of continuous soaking the specimens were subjected to wetting and drying cycles daily.

The permeability of the concrete was tested using the Vonn Method of water flow. According to this test method, concrete containing fly ash was slightly more permeable at early ages, but no measurable permeability was detected in any specimens after 7 days of curing.

The results of the sulfate exposure testing were that all concrete mixtures containing fly ash and without fly ash were resistant to sulfate attack. Expansions for the concrete ranged from 0.03 to 0.04 percent at one year and 0.04 to 0.07 percent at two years. The researcher found that the mass loss of the concrete may be related to the compressive strength at the time of exposure and that expansion is related to the composition of the cementitious material. From these results and those published by Dunstan[25,26], Hartmann and Mangotich proposed the following factor to predict the sulfate resistance of concrete:

$$\text{Oxide Durability Factor (OD)} = \frac{C(\%) * \text{Freelime}(\%)}{S(\%) + A(\%) + F(\%)}$$

Each variable is defined by the chemical composition of the total cementitious material, i.e. cement + fly ash. The oxide durability factor (OD factor) correlated well with both this study's data and that of Dunstan's study. The major advantages to this approach were that it accounted for the sulfate resistance of the cement, includes silica and alumina contents in the equation and recognized the importance of a crystalline compound.

The conclusions of this study were,

1) sulfate durability varies with the OD factor, and the OD factor can be used to predict the sulfate resistance of the concrete,
2) if fly ash addition decreases the OD factor there will be a corresponding increase in the sulfate resistance, and
3) mass loss is not a reliable means of measuring sulfate resistance.

As a final note, the researchers also noted that the use of sulfuric acid may have induced mild acid attack on concrete having high absorptions.

3.2.9 Mehta [1986][64]. A study performed at the University of California at Berkeley on the sulfate resistance of concrete containing fly ash used 1/2 in. paste cubes to document the effect of a 4 percent Na_2SO_4 solution on the compressive strength of concrete. Twenty specimens from each mix were moist cured for 14 days at 104°F. Ten cubes were tested before exposure and the other 10 after sulfate exposure over a fixed period of time. In addition, X-ray diffraction analyses of the pastes were performed before the exposure to sulfate solution.

Mehta conducted this study because he found evidence that ASTM Class C fly ashes with relatively high R factors had improved the resistance of a Type I cement with 10 percent C_3A, and other high calcium fly ashes had no effect on the sulfate resistance of concrete. He postulated that the R factor is flawed by not accounting for the crystalline form of reactive alumina.

Mehta's study included five Class F fly ashes from bituminous coal sources, three Class C fly ashes from lignites, and eight Class C fly ashes from subbituminous coal sources. These fly ashes were used as 25 and 40 percent weight replacement for a Type I cement with 11 percent C_3A. The results of this study, shown in Table 3.4, suggest that pastes that contained ettringite as the major hydrated aluminate phase before sulfate exposure had only small reductions in compressive strength when exposed to sulfates. However, hardened pastes containing monosulfoaluminate or calcium aluminate hydrate rather than ettringite, suffered from sulfate attack and had large reductions in compressive strength.

The data from this study showed that two of the five bituminous coal fly ashes reduced the sulfate resistance of concrete. One of these fly ashes had 39 percent iron oxide and only 12 percent alumina. The second bituminous fly ash which performed poorly had only 2 percent nonreactive alumina, as mullite. These chemical and mineralogical contents were atypical of fly ashes produced from bituminous coal sources. As was discussed in the previous chapter, the reactive alumina is essential in the formation of ettringite and the subsequent deterioration of concrete from sulfate attack.

Cement pastes containing the lignite coal fly ashes showed improved sulfate resistance, despite having R factors near 4.0. These fly ashes contained between 7.8 and 16.6 percent SO_3 which is above the ASTM limit of 5.0 percent and were atypical of most lignite coal fly ashes.

Two of the eight pastes containing subbituminous coal fly ashes showed improved sulfate resistance. Both of these fly ashes had R factors less than 1.5 and one had 20.6 percent iron oxide. The six subbituminous fly ashes that reduced the sulfate resistance had R factors between 1.2 and 4.5.

Through the use of atypical fly ashes Mehta was able to demonstrate the importance of the mineralogical composition of the fly ash and hydrated paste. The conclusions of this study were,

1) the R factor is not a reliable means of predicting sulfate attack of cement mixtures containing fly ash,

Table 3.4 Influence of fly ash composition on sulfate resistance of blended cements

Ash number	R-factor	Principal alumina-bearing phases in the fly ash	Alumina-bearing hydration products of the blended cement (containing 40% fly ash)	Performance of the cement paste in the sulfate resistance test
1	-0.9	mullite, A-S glass	ettringite	satisfactory
2	-0.1	> 90% A-S glass	M$\bar{S}$H	poor
3	-0.01	A (F)-S glass	M$\bar{S}$H	very poor
4	0.3	A-S glass	ettringite	satisfactory
5	1.1	A-S glass	ettringite, a little M$\bar{S}$H	satisfactory
6	4.0	N-C-A-S glass, C, A, $\bar{S}$	ettringite	excellent
7	4.0	N-C-A-S glass, C, A, $\bar{S}$	ettringite	satisfactory
8	4.0	N-C-A-S glass, C, A, $\bar{S}$	ettringite	satisfactory
9	4.5	C, A; C, A, $\bar{S}$; C-A-S glass	M$\bar{S}$H and C-A-H	very poor
10	3.5	C, A; C, A, $\bar{S}$; C-A-S glass	M$\bar{S}$H and C-A-H	very poor
11	3.0	C, A; C, A, $\bar{S}$; C-A-S glass	M$\bar{S}$H and C-A-H	very poor
12	2.6	C, A; C-A-S glass	M$\bar{S}$H and C-A-H	very poor
13	1.8	C, A; C-A-S glass	M$\bar{S}$H	poor
14	1.5	A-S; C-A-S glass	ettrignite, a little M$\bar{S}$H	satisfactory
15	1.2	C, A; C, A, $\bar{S}$; C-A-S glass	M$\bar{S}$H and C-A-H	poor
16	0.5	A-S; C-A-S glass	ettrignite	excellent

2) sulfate resistance is dependent upon the stable hydrated aluminate phase at the time of exposure,

3) concrete containing monosulfoaluminate or calcium aluminate hydrate is susceptible to sulfate attack, and

4) the reactive Al_2O_3/SO_3 ratio is a true measure of aluminate reaction in sulfate environments.

3.2.10 Manz et al.[50]. Research has been conducted at the University of North Dakota and North Dakota State University over the last five years on the sulfate resistance of concrete containing fly ash and on the characterization of fly ash particles. Eight fly ashes at weight replacement levels of 0 to 90 percent were studied in combination with Type I cement. Fly ashes from subbituminous and northern lignite sources were used in a test procedure that is the same as the USBR's 10 percent Na_2SO_4 soaking test with the exception of the specimen size. The North Dakota tests used 3 in. x 3 in. x 12 in. concrete beams whereas the USBR test used 3 in. x 6 in. concrete cylinders.

The R factors of the fly ashes used in this study ranged from 1.6 to 4.1. After as much as 4 years of exposure the concrete containing fly ash exhibited minimal expansions in comparison to the Type I control cement. This led to Manz's conclusion that the R factor is inadequate as a prediction method for sulfate resistance. Manz et al. used bulk analytic chemistry and crystallography to propose a revised prediction method based on the reactive oxide phases. By subtracting out the crystalline phases that are nonreactive, a better picture of the glass composition can be formed and used to predict the stability of aluminate phases in hardened concrete and the potential for sulfate expansion.

The calcium aluminate potential (CAP) is the first of two factors being developed by Manz and McCarthy. This factor treats the glassy calcium, alumina and iron as detrimental to sulfate resistance and glassy silica as beneficial to sulfate resistance.

$$\mathrm{CAP} = \frac{C' + A' + F'}{S'}$$

C'(%) = Bulk CaO - Reactive Crystalline CaO(lime, anhydrite, C_2S) - Inert Crystalline CaO(melilite, merwinite)

A'(%) = Bulk Al_2O_3 - Inert Al_2O_3(mullite)

F'(%) = Bulk Fe_2O_3 - Inert Crystalline Fe_2O_3(hematite, spinel)

S'(%) = Bulk SiO_2 - Inert Crystalline SiO_2(quartz, mullite)

The CAP factor subtracts weight percentage of the inert crystalline compounds and the crystalline compounds which do not participate in the sulfate expansion reactions. This reduces the quantity of each chemical compound to that present in the glassy phases and to the reactive crystalline calcium aluminates.

A second factor proposed by Manz and McCarthy was the Calculated Sulfate Equivalent ($C\overline{S}E$). This factor assumes that the presence of SO_3 in fly ash is desirable because it favors the early ettringite formation and reduces the calcium hydroxide in the hydrated paste.

$$C\overline{S}E = \text{Anhydrite} + 1.70 \bullet \overline{S}$$

In this equation, the 1.70 is a gravimetric factor for the formation of additional anhydrite from other sources of SO_3 in fly ash. Like the CAP factor this factor is in the initial stages of development. The proposed relationship between the CAP and $C\overline{S}E$ factors and the sulfate resistance of concrete is given in Figure 3.5.

3.2.11 Other Studies. There have been other studies conducted around the world in the area of sulfate attack on concrete containing fly ash. Some of these studies are included herein to further the discussion of the effect of fly ash on concrete exposed to sulfate.

The Electric Power Research Institute (EPRI) conducted a research study to evaluate the applicability of ASTM C 1012 test procedure for predicting the sulfate resistance of portland cement mortar bars. In this study, the participating laboratories performed mortar bar expansion tests on 16 fly ashes from five regions of the United States. The ashes were collected at both base load conditions and during an upset furnace condition to verify the validity of the test procedure. The conclusion of this study was that mortars with low calcium fly ash were sulfate resistant

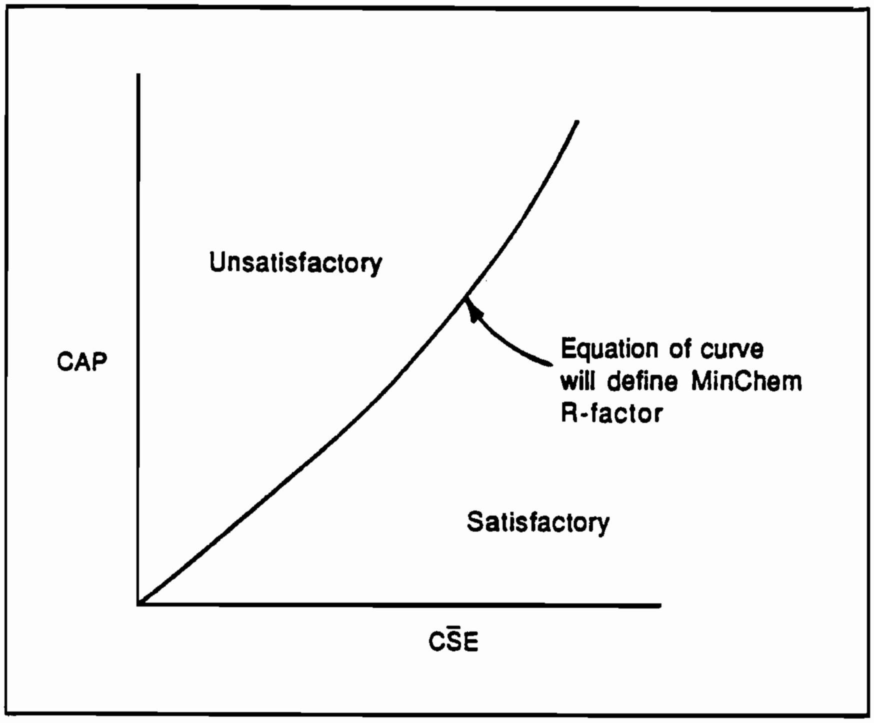


Figure 3.5 Proposed relationship between CAP and $C\bar{S}E$ factors and sulfate resistance[50].

and mortars with high calcium fly ash were typically not sulfate resistant. Patzias presented a discussion of this work in 1987, stating the following conclusions[76]:

1) an expansion of less than 0.05 percent at 180 days constitutes high sulfate resistance,
2) an expansion between 0.05 and 0.10 percent at 180 days constitutes moderate sulfate resistance, and
3) an expansion greater than 0.10 percent at 180 days constitutes poor suflate resistance, and
4) the ASTM C 1012 test is a suitable test for sulfate resistance for both portland cement and blended cements.

Similar results were obtained by Day in Canada[14]. Day tested four fly ashes using a mortar bar expansion test. He used both a concentrated solution of 5 percent Na_2SO_4 and a dilute solution of 0.9 percent Na_2SO_4. The results, summarized in Figure 3.6, show that the mortar containing high calcium fly ash failed in expansion before the Type II or Type V cement control. The three low calcium fly ashes resulted in mortar which had a greater sulfate resistance than either Type II or Type V portland cement.

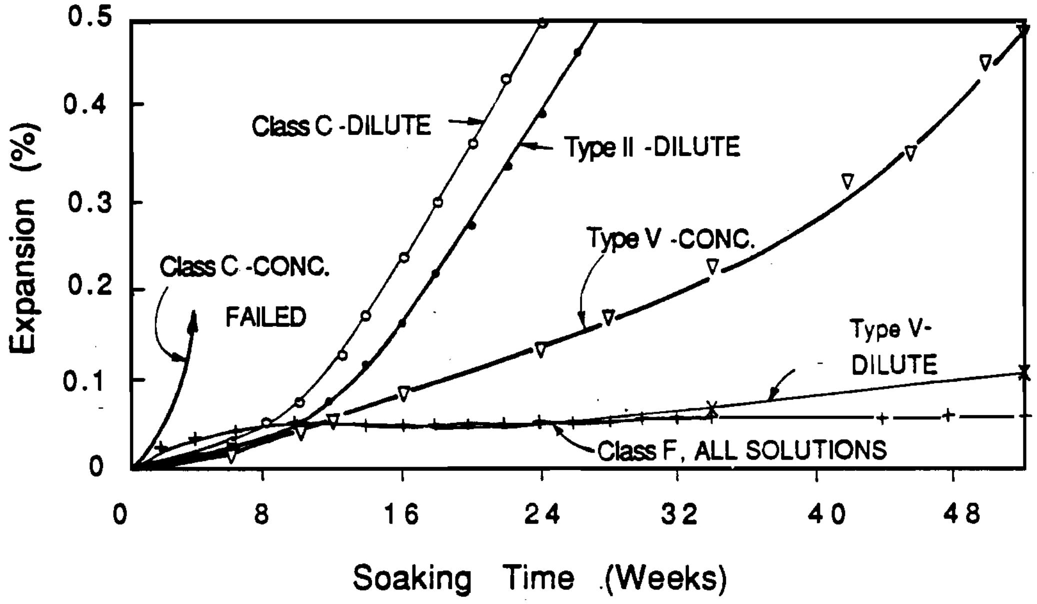
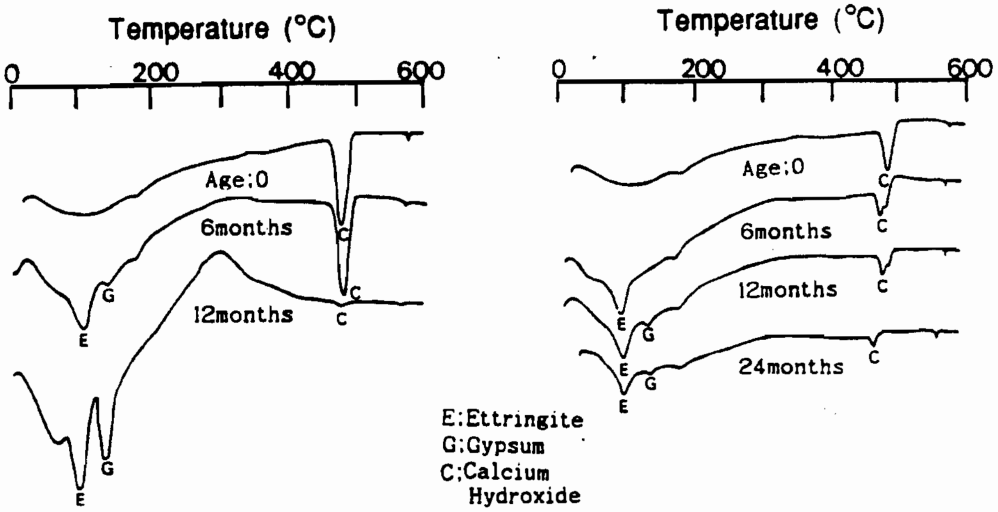


Figure 3.6 Mortar bar testing for sulfate resistance.

A study completed by Fraay at Delft University in the Netherlands came to two conclusions which could be construed as contradictory to other research studies[30]. The first of these is that the chemical composition of fly ash has no apparent influence on the sulfate resistance of concrete and the second is that the porosity of the concrete has a greater effect on the sulfate resistance than either C_3A content of the cement or the CaO content of the fly ash. The point Fraay projects is that the benefit of using fly ash in concrete exposed to sulfates is derived from the reduction in porosity, not from chemical processes which can limit ettringite and gypsum formation. Furthermore, this study found that the use of sulfuric acid to control the pH of the sulfate solution in the testing environment increases the rate of degradation.

A research program conducted by Torii et al. at Kanazawa University in Japan found that the sulfate resistance of concrete increased with increasing fly ash replacement for portland cement[100]. This study used a 10 percent Na_2SO_4 solution; measured compressive strength, dynamic modulus, volumetric changes; and examining specimens with DSC-TG analysis, X-Ray diffraction and for SO_3 content. From these analyses, Torii determined that the sulfate intrusion and the presence of ettringite and gypsum were greatly reduced when fly ash was used, as shown in Figure 3.7. He also found the sulfate resistance of concrete, as measured by the compressive strength in Figure 3.8, was increased with the use of fly ash. This study used two ASTM Class F fly ashes at replacement levels of up to 50 percent by weight. Torii et al. found that the microstructural changes caused by the pozzolanic reaction of the fly ash decreased the permeability of the concrete and decreased the calcium hydroxide content of the hardened cement paste.



(C=300 kg/m^3)

(C+F=400 kg/m^3, F/C+F=50%)

Figure 3.7 DSC-TG analysis of concrete[100].

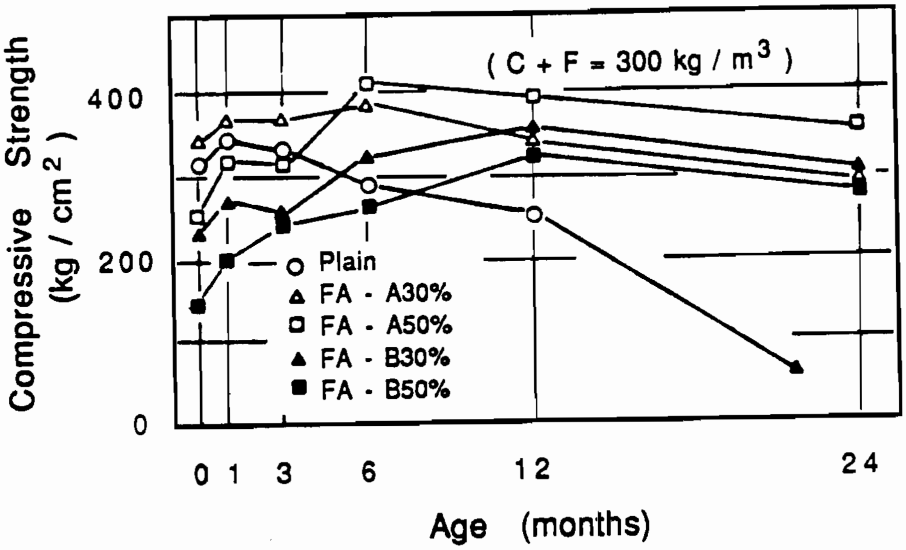


Figure 3.8 Compressive strength of concrete submerged in sodium sulfate[100].

Lastly, mortar bar tests were conducted by Texas Industries according to ASTM C1012 to observe the effect of intergrinding low calcium fly ash with Type I and Type II portland cement[95]. The interground cements had expansions less than that of the Type II control as shown in Figure 3.9.

3.3 Sulfate Resistance of Concrete Containing Other Pozzolans

3.3.1 Silica Fume. Research in Norway has shown that concrete containing silica fume in the range of 10 to 15 percent, by weight of portland cement was resistant to sulfate attack in 10 percent Na_2SO_4 solution[29] and when exposed to groundwaters containing up to 4 g/l of SO_3. The improved sulfate resistance was observed despite the increase in W/C ratio from 0.50 to 0.62 to accommodate increased fineness of the silica fume. The reasons silica fume increases the sulfate resistance of concrete are,

1) silica fume promotes a refined pore structure which reduces the transport of sulfate ions,

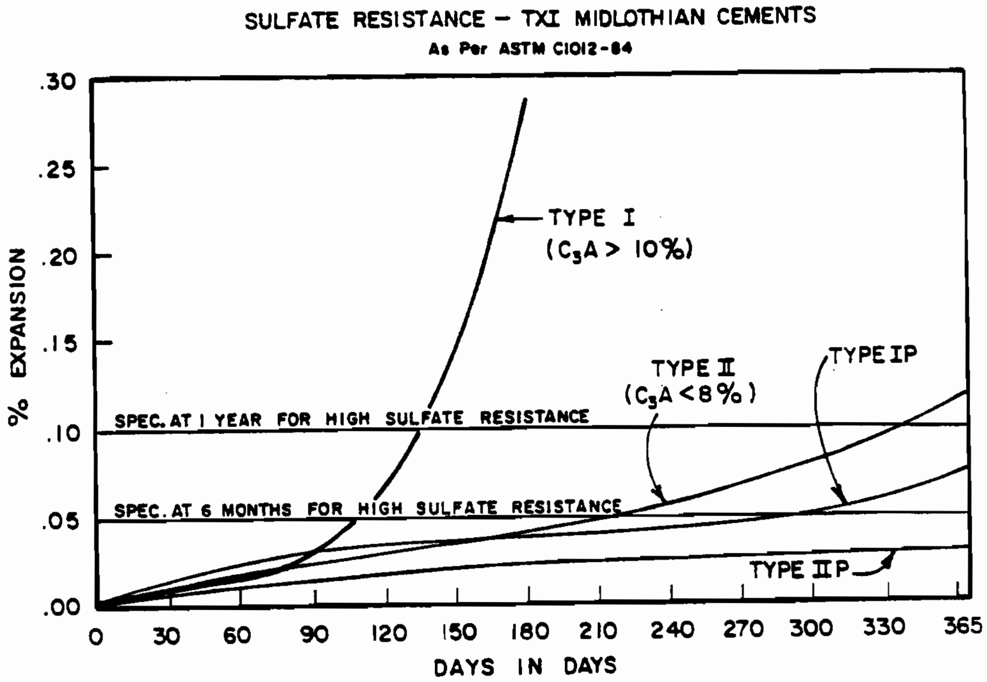


Figure 3.9 Sulfate resistance of blended cements[95].

2) a reduced calcium hydroxide content within the concrete, and

3) an increased amount of alumina incorporated in the silicate hydrate structures, thus reducing the amount of alumina available for ettringite formation [91].

3.3.2 Blast Furnace Slag. The use of blast furnace slag in concrete is common in most European countries, but its use is not as extensive in the United States. Blast furnace slag can be used to improve the sulfate resistance of concrete, especially when used as a replacement for large quantities of portland cement. Recent studies conducted in the Soviet Union[22] and Great Britain[31] document the benefits of slag cements.

Ducic found that the cements consisting of 30 percent interground granulated blast furnace slag improved the sulfate resistance of the cement provided the portland cement does not contain more than 10 percent C_3A[22]. In addition, this study found that neither 30 or 60 percent granulated blast furnace slag improved the sulfate resistance of a portland cement with a C_3A content of 11.8 percent.

Frearson used a portland cement with a C_3A content of 9.9 percent and found the intergrinding of granulated blast furnace slag improved the sulfate resistance of concrete[31]. Furthermore, the data from this study, summarized in Figure 3.10, showed that the use of 70 percent slag provided consistently higher sulfate resistance than either 30 or 50 percent, and that the percentage of slag is much more important than a reduction in the W/(C+P) ratio in reducing the effect of sulfate attack.

3.4 Permeability of Concrete

The permeability of concrete is a physical property representing the ease by which fluids, gases and ions pass through the hardened concrete. There are three principle mechanisms of transport through concrete: capillary attraction, vapor transmission, and ionic diffusion. Capillary attraction is the mechanism which transports water and other fluids through concrete. Along with these fluids, aggressive agents such as acids, chlorides and sulfates may be carried through the concrete. Vapor transmission is the mechanism by which gases are transported into and out of concrete. Carbon dioxide and sulfur gases may enter, or steam from intense fires may escape the concrete in this manner. Flow from capillary attraction of fluids and vapor transmission of gases are both governed by D'Arcy's law, expressed in equation 6.1.

$$Q = \left(\frac{k}{\mu}\right) A \left(\frac{dp}{ds}\right) \tag{6.1}$$

k = permeability coefficient

μ = viscosity

A = area

$\frac{dp}{ds}$ = pressure gradient

Ionic diffusion is governed by equation 6.2, Fick's law, and is the mechanism of transport which allows ions to move from areas of high concentration to areas of low concentration, irrespective of fluid or gas transport. Chloride and sulfate ions can be transported by this means within the mortar matrix of concrete.

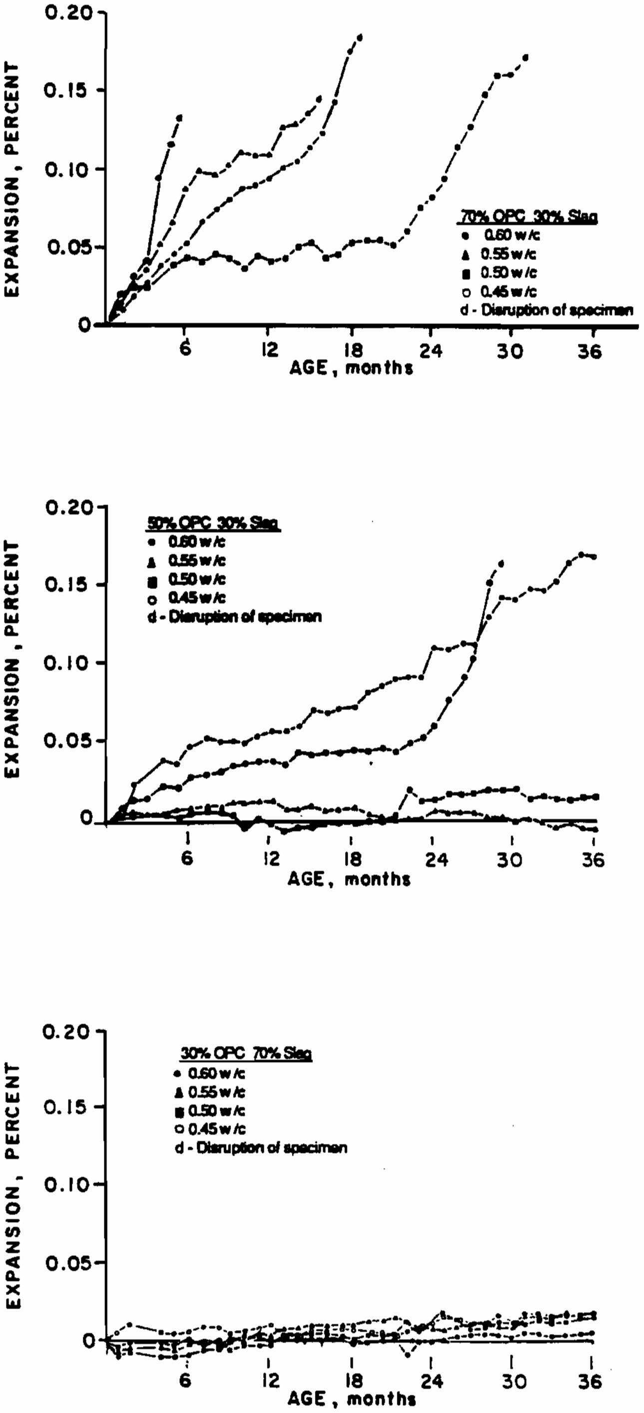


Figure 3.10 Sulfate resistance of concrete containing blast furnace slag.

$$D = \frac{\left(\frac{\delta C}{\delta t}\right)}{\left(\frac{\delta^2 C}{\delta x^2}\right)} \tag{6.2}$$

C = ionic concentration

x = distance from surface

t = time

Permeability is an important factor in the long-term durability of concrete. Impermeable concrete can resist the intrusion of aggressive agents, thereby preventing degradation. The effect of sulfate ions has been discussed in detail in the preceding chapters. Chloride ions enhance the mechanism by which steel reinforcement corrodes. Acids leaching through the concrete will deteriorate the silicate binding structures. All of these durability considerations are dependent upon the concrete permeability.

3.4.1 Permeability Measurement. There are a many ways to measure the permeability of concrete. The term measure is used loosely in this context because of the different means by which a transport mechanism can be formed. Each concrete permeability testing procedure quantifies the property differently and none of the standardized tests consider both flow and diffusion. Concrete permeability testing results should be compared to the results of well consolidated normal strength concrete, latex modified concrete or polymer concrete.

Mercury intrusion porosimetry (MIP) is a method of determining the volume and size of voids in concrete. This test uses pressure to force mercury into the concrete voids. As the pressure increases a greater amount of smaller voids are saturated. Allowing the test to quantify the size distribution and volume of voids in the concrete. Similarly, there are also various constant head tests for determining the hydraulic permeability due to capillary attraction[69,77]. These methods are most effective when transmission of fluids is through the macropores in the concrete, but are not effective in low permeability concrete. In addition, hydraulic pressure test procedures may damage the internal structure of the concrete.

Vapor transmission tests or gas permeability tests have been developed by several researchers[78,90]. These permeability tests are not well standardized and are highly dependent upon the moisture condition of the specimen at the time of testing. Neither MIP nor gas permeability testing measures the permeability of concrete in the saturated condition.

An ionic diffusion test has been developed in recent years by Whiting at the Construction Technology Laboratory for the Federal Highway Administration[103]. This test measures the flow of dc current through saturated concrete surrounded by electrolytes over a period of time. The system uses a concrete slice saturated with water as the major resistance in a circuit. Many investigators have already published results using this method with good correlation among independent laboratories [68,75,78,104]. This test method is the preferred means of measuring ion permeability because it tests the concrete in a saturated condition without duress to the internal pore structure of the concrete. The test method is not overly sensitive to the method of saturation, although a standardized procedure of saturation is used in the test[47]. Furthermore, the test is rapid and can be simultaneously performed on several specimens. This test procedure is most effective at quantifying concrete with low to moderate permeability. If capillary attraction is the major source of transport in the concrete, the test apparatus will overheat and result in a large value for chloride ion permeability. The standardization and acceptance of this test method is taking place rapidly.

The importance of concrete permeability should not be overlooked because of the difficulty in quantifying it numerically. The permeability of concrete can play an important role in the sulfate resistance of concrete. Of the several means by which the sulfate reaction can be controlled, permeability is the least complicated and offers the most benefits. Concrete which is resistant to the migration of sulfate ions will exhibit increased sulfate resistance. In addition, low ion permeable concrete may be more resistance to freeze-thaw cycling, chloride exposure and is a formidable moisture barrier.

3.4.2 Previous Ion Permeability Research. There have been a limited amount of testing of the chloride ion permeability of concrete using AASHTO T277. Most of these results were published in ACI SP-108 in 1988[77]. The effect of fly ash, silica fume, and blast furnace slag on the chloride ion permeability of concrete are reviewed herein.

In developing the test procedure for the chloride ion permeability Whiting observed that both W/C ratio and time of moist curing affect the permeability of concrete. This is true of water, gas, and ion permeability. In portland cement concrete low W/C ratios and long curing times reduce the permeability of concrete, as shown in Figure 3.11.

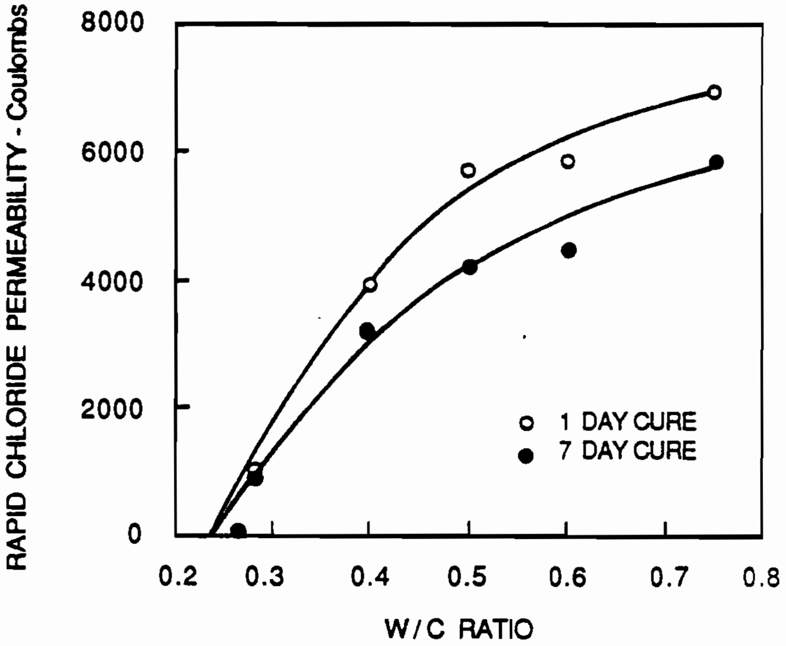


Figure 3.11 Effect of W/C ratio on chloride ion permeability.

Malek, Roy, and Licastro conducted chloride ion permeability tests on cement pastes containing three different fly ashes[48]. The fly ash was used at contents of between 20 and 35 percent replacement by weight for portland cement. The test results for paste with a W/(C+P) ratio of 0.53 are presented in Figure 3.12. The test results showed that paste containing fly ash had a lower chloride ion permeability than plain portland cement paste. The low calcium ASTM Class F fly ash reduced the chloride ion permeability of the paste more effectively than the high calcium ASTM Class C fly ash. In addition, their results showed that the chloride ion permeability of paste containing fly ash was greatly reduced by heat curing the specimens.

Scalli, Chin, and Berke investigated the effect of fly ash and silica fume on the permeability and electrical resistivity of concrete[88]. Using the AASHTO T277 rapid chloride ion permeability test and measuring the electrical resistivity of concrete, the investigators found that high calcium ASTM Class C fly ash had no significant effect on the diffusion of chlorides in concrete. However the use of silica fume in concrete greatly reduced the chloride ion permeability and increased the electrical resistivity over that of plain concrete.

Ozyildirim and Halstead conducted chloride ion permeability tests on plain concrete and concrete containing fly ash, silica fume, and blast furnace slag[75]. Their results show no significant difference between the chloride ion permeability of Type I portland cement and Type II portland cement concrete. Similarly, concrete containing 15 and 25 percent replacement of fly ash by weight of portland cement, at a ratio of 1.2:1.0 fly ash to cement, had 28 day chloride ion permeabilities approximately equal to the control. However the 90 day chloride ion permeability of concrete containing fly ash was reduced from the 28 day result by a greater amount than the control concrete. Figure 3.13 shows the 90 day test results and also the effect of the water to cement (W/C) ratio. As the W/C ratio increases, so does the chloride ion permeability of the concrete.

The addition of silica fume to concrete reduced the 28 day chloride ion permeability to very low levels compared to plain portland cement concrete. The use of blast furnace slag as a 50 percent replacement by weight for portland cement marginally reduced the chloride ion permeability of concrete at 28 days and resulted in low chloride ion permeabilities at 91 days as compared to plain portland cement concrete.

In addition to the chloride ion permeability test, AASHTO T277, several other tests provide insight into the intrusion of ions into concrete. On such test

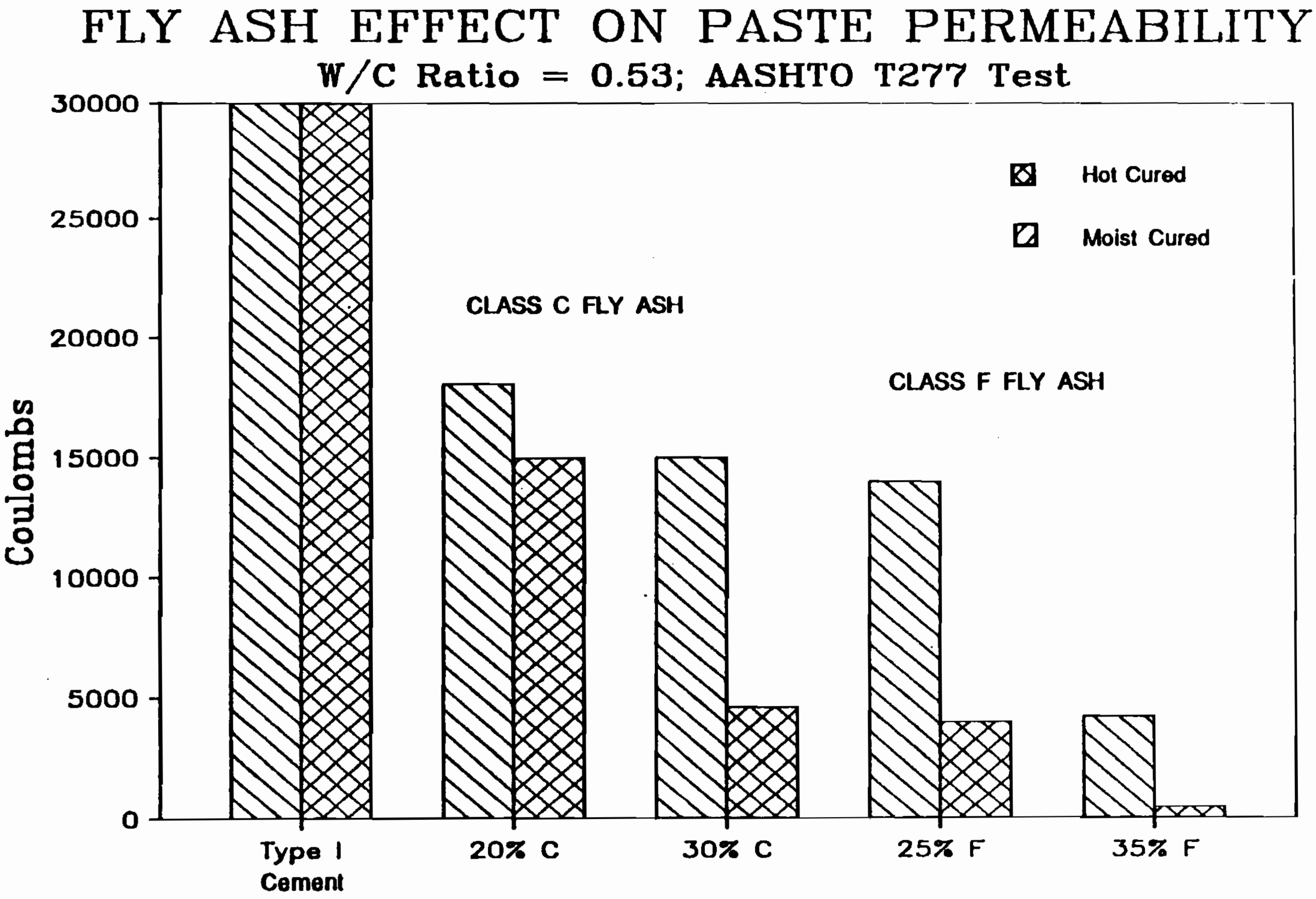


Figure 3.12 Effect of fly ash on chloride ion permeability.

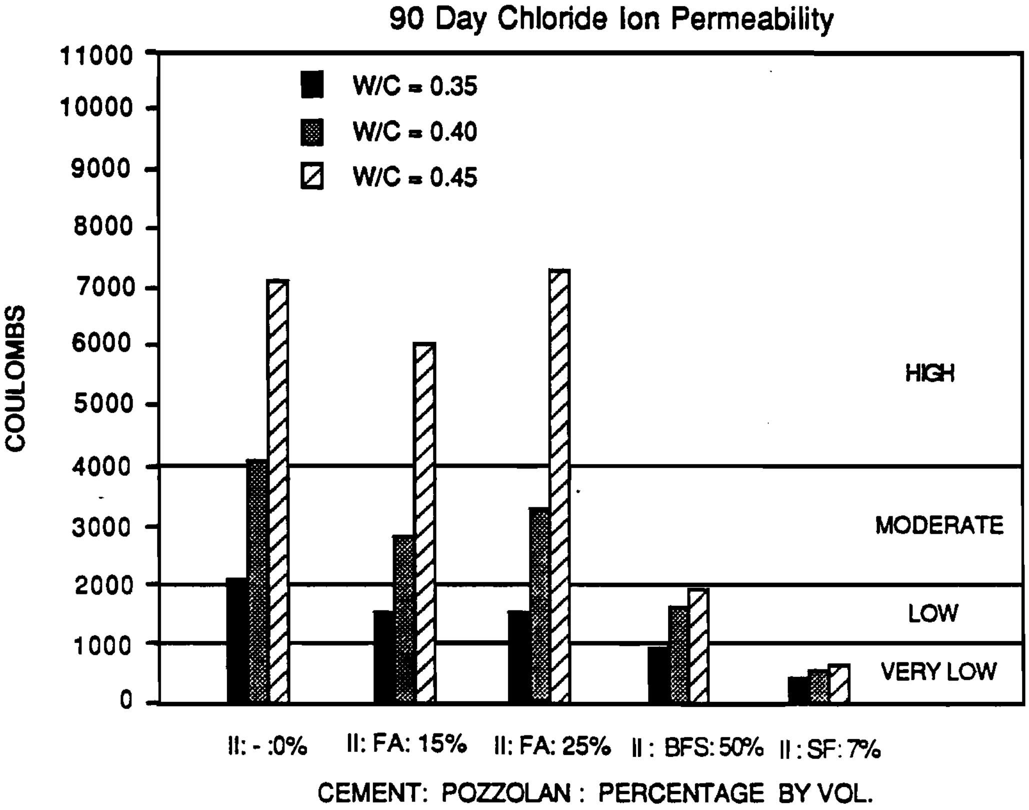


Figure 3.13 Effect of pozzolans on chloride ion permeability.

ponds water containing calcium chloride on concrete specimens subjected to freeze-thaw cycling. The chloride ion concentrations are then measured at varying depths to determine the extent of chloride ion intrusion. Water and gas permeability tests also preovide a measure of permeability.

Ponding tests (AASHTO T259) showed that portland cement concrete and concrete containing fly ash or blast furnace slag had Cl^- concentrations above the corrosion threshold of 1.32 lbs per cubic yard in the top 0.75 in. However none of the concrete mixtures in this study exceeded the corrosion threshold at greater depths. This same effect was observed by Marusin using silica fume, as shown in Figure 3.14[54].

Day and Konecny performed a study on the relationship between the chloride ion permeability, water permeability, and oxygen permeability of concrete[15]. Their results show no direct relationship between the three types of permeability testing at 7 and 28 days. However the tests showed a close correlation after 160 days of moist curing. A suggested scale for evaluating test results was presented by Day and Konecny and is shown in Table 3.5. These indices are applicable only at later ages and for the test procedures described by Day and Konecny.

Table 3.5 Revised permeability categories

Chloride Permeability	Charge Passed coulombs (T277)	Water Index suggested	Oxygen Index suggested
High	> 4000	> -12	> -6.75
Moderate	2000-4000	-12 to -12.75	-6.75 to -7.0
Low	1000-2000	-12.75 to -13.0	-7.0 to -7.1
Very Low	100-1000	-13.0 to -13.5	< -7.1
Negligible	< 100	< -13.5	—

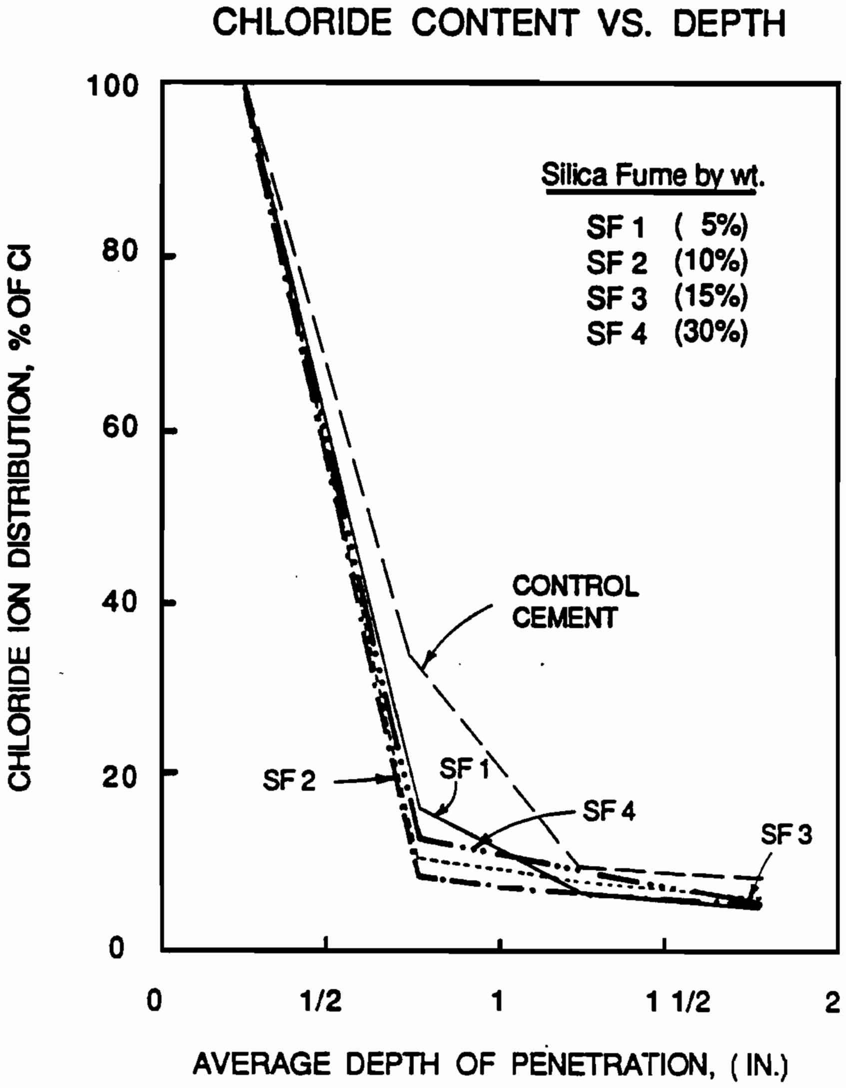


Figure 3.14 Chloride ion intrusion of concrete containing silica fume.

In summary, the chloride ion permeability of concrete is reduced by low W/(C+P) ratios, longer moist curing times, and through the use of heat curing. Silica fume may be added to concrete to reduce the chloride ion permeability of concrete at early ages and silica fume, blast furnace slag and low calcium fly ash may be used in concrete to further reduce the chloride ion permeability of concrete at later ages. The effect of high calcium fly ash on the chloride ion permeability of concrete has not been clearly determined, however high calcium fly ash will provide concrete with equal or reduced chloride ion permeability at later ages.

CHAPTER IV
MATERIALS AND TEST PROCEDURES

4.1 Introduction

The materials and standard testing procedures described herein correspond to approved Texas State Department of Highways and Public Transportation (SDHPT) procedures. The testing procedures and material standards are those described in the Texas SDHPT Manual of Testing Procedures Physical Section 400-A Series, the American Society for Testing and Materials 1988 Annual Book of ASTM Standards, Volume 04.01, "Cement; Lime; Gypsum," and Volume 04.02, "Concrete and Aggregates," and the AASHTO Manual of Standardized Testing. In addition, the sulfate exposure testing procedure was developed in the laboratory from guidelines published by the United States Bureau of Reclamation and approved for this study by the Texas SDHPT Materials and Test Division. This testing procedure has been widely used for long term testing of concrete exposed to sulfate environments. The USBR procedure was chosen over the standardized ASTM C 1012 mortar bar test because it better represents the materials found under service conditions.

4.2 Materials

The materials used in this study are those typically used in the commercial production of portland cement concrete. Except where specifically noted, these materials are approved for use in the state of Texas by the Texas SDHPT Materials and Test Division. The materials include portland cement, fly ash, crushed limestone coarse aggregate, natural sand, air-entraining admixture, water reducing-retarding admixture, and water. Other materials included silica fume and blast furnace slag.

4.2.1 Portland Cement. Five portland cements are being used in this study. All portland cements conformed to ASTM C 150-86, "Standard Specification for Portland Cement". The chemical and physical properties of the five portland cements are given in Table 4.1. The portland cements included an ASTM Type I, Type II, Type V and two 0 percent C_3A portland cements. The ASTM Type I cement was produced at a plant near Buda, Texas. The Type II cement was produced at a plant near New Braunfelds, Texas. The Type V cement and one of the 0 percent C_3A cements, hereafter referred to as "01" cement were obtained from Dallas, Texas. The second source of 0 percent C_3A cement, hereafter referred to as "02" cement, was produced in Hermosillo, SON., Mexico.

Table 4.1 Mill Test Analysis For Project 481

ASTM Type	I	II	V	01	02
Si Oxide	20.6	21.8	22.0	21.3	21.8
Al Oxide	5.3	4.2	3.4	2.8	2.5
Fe Oxide	3.3	3.2	3.2	4.8	3.8
Ca Oxide	64.2	64.7	64.9	64.4	64.8
Mg Oxide	0.9	0.6	3.3	3.9	1.3
SO_3	3.5	2.9	2.5	3.0	2.3
LOI	0.5	0.9	0.6	0.7	1.3
Insol. Res.	0.4	0.3	0.2	0.2	0.4
C_3S	51.5	54.0	62.2	66.2	70.0
C_2S	20.1	21.8	16.2	11.3	9.6
C_3A	9.9	6.0	3.6	0.0	0.0
C_4AF+C_2F	10.0	14.3	3.8	14.6	11.6
Total Alk.	0.7	0.6	0.5	0.3	0.5
Physical Data					
Specific Surface					
Blaine (cm^2/g)	3283	3350	-	-	3625
Comp. Str.(psi)					
1 Day	-	2030	-	-	1850
3 Day	-	3670	-	-	3960
7 Day	-	4670	-	-	5069
Set Time					
Vicat Test					
Initial Set	-	132 min.	-	-	140 min.
Final Set	-	244 min.	-	-	305 min.

Both of the 0 percent C_3A portland cements, 01 and 02, meet the ASTM C 150-86 standard specification for Type II portland cement. For mixture design purposes the specific gravity of all five portland cements was assumed to be 3.10

as recommended by the Texas SDHPT Construction Bulletin C-11 mixture design procedure.

4.2.2 Coarse Aggregate. The coarse aggregate used in this study is a 5/8 inch nominal maximum size crushed limestone, Texas Highway Department Grade No. 5 coarse aggregate from Georgetown, TX. This aggregate was chosen because it is nonreactive to alkali-aggregate reaction and is locally available. The aggregate has a specific gravity of 2.50, an absorption of 3.5 percent and a percent solids of 54.7 percent.

4.2.3 Fine Aggregate. The fine aggregate is a natural siliceous sand from the Colorado River Basin, and was obtained from a local source in Austin, TX. The sand has a specific gravity of 2.64 and an absorption of 1.19 percent. Table 4.2 shows the results of the sieve analysis which resulted in a fineness modulus of 2.58.

Table 4.2 Sieve Analysis of Colorado River Sand

Sieve Size	Percent Retained	ASTM C33 Limits
#4	0.2	0-5
#8	3.8	0-20
#16	26.5	15-50
#30	53.7	40-75
#50	77.8	70-90
#100	96.2	90-98
#200	99.6	—

4.2.4 Fly Ash. Twenty four fly ashes and two other pozzolans were used in this experimental program. A summary of the sources and locations is given in Table 4.3. Eleven of the fly ashes are from Texas, thirteen fly ashes are produced from subbituminous coals, six from lignite coals and five from bituminous coal sources.

Table 4.3 Summary of Pozzolans in Project 481[A]

Fly Ash	Location	Coal Source	Coal Type	TSDHPT Type	ASTM Class	Tons/yr 10^3
Baldwin	Chicago, IL	Illinois	Bituminous	A	F	-
Big Brown	Fairfield, TX	Local	Lignite	A	F	630
Bonanza	Vernal, UT	Rio Blanco, CO	Bituminous	A	F	-
Boundary Dam	Sask. Can.	Local	Lignite	A	F	420
Celonese	Pampa, TX	New Mexico	Lignite	A	F	-
Coal Creek	Underwood, ND	Local	Lignite	A	F	340
Coleto Creek	Fannin, TX	Axial, CO	Subbituminous	A	F	83
Columbia	Portage, WI	Montana	Subbituminous	A	F	-
Commanche	Pueblo, CO		Subbituminous	B	C	-
Deely	San Antonio, TX	Belle Fouche, WY	Subbituminous	B	C	140
Fayette	LaGrange, TX	Powder R., WY	Subbituminous	B	C	170
Harrington	Amarillo, TX	Powder R., WY	Subbituminous	B	C	141
Hugo	Ft. Towson, OK	Powder R., WY	Subbituminous	B	C	60
Huntington	Utah		Bituminous	A	F	-
Kimball	Mundelein, IL		Silica Fume	-	-	-
Monticello	Mt. Pleasant, TX	Local	Lignite	A	F	1250
Nelson	Westlake, LA	Powder R., WY	Subbituminous	B	C	-
Nixon	Nixon, CO		Bituminous	A	F	-
North Omaha	Omaha, NE	Rosebud, WY	Subbituminous	B	C	-
Parish	Thompsons, TX	Powder R., WY	Subbituminous	B	C	300
Pilot			Blast Slag	-	-	-
Rodemaker	Boyce, LA	Powder R., WY	Subbituminous	A	C	91
Sandow	Rockdale, TX	Local	Lignite	A	F	600
Tolk Station	Muleshoe, TX	Powder R., WY	Subbituminous	B	C	141
Welch	Cason, TX	Powder R., WY	Subbituminous	B	C	131
Yates	Newnan, GA		Bituminous	A	F	-

[A] Data from a survey of the utilities, 1987.

The properties, composition and classification of these fly ashes will be discussed thoroughly in the Chapter 5 along with a review of fly ash standard specifications.

In order to prevent the identification of any particular fly ash source a blind study of the fly ashes is reported herein. To cloak the individual sources of fly ash, the fly ashes are hereafter designated as A-1 through A-14 and B-1 through B-10. The letter designates the Texas SDHPT fly ash type, according to the chemical composition specifications of Texas SDHPT D-9-8900, and the number indicates a unique fly ash source.

4.2.5 Silica Fume and Blast Furnace Slag. Two other pozzolans were used in this study: silica fume and blast furnace slag. The chemical and physical characteristics of these materials are given in Chapter 5. The silica fume was obtained from Mundelein, IL. The silica fume has a specific gravity of 2.20. The blast furnace slag was obtained from a private source. It had a specific gravity of 2.92 and 96 percent glass content.

4.2.6 Admixtures. Two liquid admixtures were used in this study: an air-entraining agent and a water reducing- retarding admixture. The air-entraining agent is a commercially available nuetralized vinsol resin complying with the requirements of ASTM C 260. The water reducing-retarding admixture is also commercially available and complies with the requirements of ASTM C 494 Type B and D admixtures. Both admixtures are approved by the Texas SDHPT Materials and Test Division for use in concrete according to Texas SDHPT Standard Specification Item 437.

4.2.7 Water. The mixing water utilized throughout this testing program was potable tap water in compliance with Texas SDHPT Standard Specification Item 421.2.

4.3 Mix Proportioning

The mixture designs used in this study were proportioned using Texas SDHPT Construction Bulletin C-11. Table 4.4 presents the design factors used in the mixture design and a listing of all the mixtures in this study is presented in Appendix B.

The actual mixture proportions differed slightly from the design proportions shown above because the mixing water was adjusted in each mix to obtain equal workability and a slump within 0.5 in. of the control mixture for each respective series. Fly ash was used as a volumetric replacement for portland cement in the

Table 4.4 Concrete Mixture Design

Design Factors	
Cement Factor (CF)	5.5 sacks per cu. yd.
Coarse Aggregate Factor (CAF)	0.67
Water Factor (WF)	6.0 gal. per sack
Air Factor (AF)	2.0 percent
Batch Factor (BF)	0.31
Admixtures	
Water Reducer	4.0 oz per 100# (C+P)
Air Entraining Agent	1/2-1.0 oz per 100#(C+P)
Design Mix Proportions	Lbs. per Cubic Yard
Cement*	517
Coarse Aggregate	1565
Fine Aggregate	1519
Water	274

*Fly ash was used as a 1:1 volumetric replacement.

amounts of 25, 35, and 45 percent. Silica fume was used in addition to the portland cement at a rate of 9 percent of the weight of portland cement. Blast furnace slag was used as a volumetric replacement for 65 percent of portland cement.

4.4 Mix Procedure

The concrete mixing was conducted under laboratory conditions in 3 cubic foot capacity rotary drum mixer according to ASTM C 192-81, "Standard Method of Making and Curing Concrete Test Specimens in the Laboratory" with the exceptions noted in this section. Concrete batches were between 1 and 2 cubic feet each. The moisture content of the aggregates was determined by drying the aggregate in a microwave oven. The portland cement and fly ash was stored in moisture-proof containers until batching.

Mixing was conducted as follows: five minutes of initial mixing followed by a two minute rest period and a final minute of mixing. The quantity of water was determined as that required to produce a 6 to 7 inch slump. One series of mixtures was batched at a 2 to 3 inch slump.

The concrete was placed in single use plastic molds with air tight lids. The plastic molds were 3 in. x 6 in., 4 in. x 8 in. and 6 in. x 12 in. cylinders. A modified 3 in. x 6 in. mold was used to center embedded stainless steel studs in the ends of the cylinders for later expansion measurements.

Concrete specimens were demolded 48 ± 4 hours after being cast and were placed in a saturated lime water curing bath according to ASTM C 511-80, "Standard Specification for Moist Cabinets, Moist Rooms, and Water Storage Used in the Testing of Hydaulic Cements and Concretes," until the time of testing.

4.5 Testing Procedures.

4.5.1 Fresh Concrete Testing. The fresh concrete of each mix was tested for slump according to ASTM C 143-78, "Standard Test Method fo Slump of Portland Cement Concrete," and Texas SDHPT porcedure TEX 415-A, "Slump of Portland Cement Concrete". For all mixtures containing air entraining admixture and all the control mixtures of this study, the air content of concrete was measured according to ASTM C 231-78, "Standard Test Method for Air Content of Freshly Mixed Concrete by the Volume Method". These fresh concrete tests were performed immediately after the final mixing and before the concrete was placed into molds.

4.5.2 Compressive Strength. The compressive strength of concrete was determined by testing 3 in. x 6 in. and 6 in. x 12 in. cylinders according to ASTM C39-79, "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens" and Texas SDHPT procedure TEX 418-A, "Compressive Strength of Molded Concrete Cylinders". The 3 in. diameter cylinders were used to determine compressive strength of the concrete at test ages up to 28 days. The 6 in. diameter cylinders were used to confirm the 28 day strength of the concrete mixture. Concrete cylinders were capped with unbonded neoprene caps inside a steel restraining ring. The cylinders were tested using a Forney 600 kip testing machine calibrated according to ASTM E4-79, "Standard Method of Load Verification of Test Machines".

4.5.3 Sulfate Exposure. The resistance of concrete to sulfate attack was evaluated by continuously soaking 3 in. x 6 in. concrete cylinders in a 10 percent sodium sulfate solution. The specimens had stainless steel gage studs embedded at the ends for length measurements. The specimens were first exposed to the sulfate solution when the concrete reached a compressive strength of 3500 psi or 28 days, whichever was reached first. Several of the mixtures were exposed to the sulfate solution after 3 days of moist curing, regardless of compressive strength developed at that time.

The ratio of the volume of sodium sulfate solution to the volume of specimens was 4.3. The pH of the sulfate solution was maintained by flushing the tank and replacing the solution when a pH greater than 9.75 was recorded. After changing the solution in the exposure tanks four times in the first six months of concrete exposure the pH of the solution came to an equilibrium near 9.50. The solutions were changed twice more in the first year and every six months thereafter.

The sulfate resistance of concrete was determined by monitoring three parameters at 30 to 60 day intervals: length expansion, mass change and time to first cracking. Length expansion was determined by using a length comparator with a 6.6250 inch gage length and a digital indicator to determine changes in specimen lengths. Each set of specimens consisted of four cylinders cast from the same concrete mixture and subjected to identical curing and exposure conditions.

A 6.6250 inch invar reference bar was used to calibrate the frame between each set of specimens. If the calibration deviated from the zero mark more than ± 0.0001 in. the frame was recalibrated and the measurements were retaken. The mass changes in the specimens were determined by weighing the specimens on a 6000 gram capacity scale accurate to ± 0.1 gram. The surface moisture was removed by towel drying the specimens before weighing. Time to first cracking was determined by visual inspection of the specimens for cracks. A visible crack 20 mm in length or two cracks totalling 20 mm in length, observed in two of the four specimens constituted first cracking. Smaller cracks were considered minor cracks and were noted along with the other measurements. The time to first cracking was truncated to two significant digits.

When the average concrete expansion exceeded 0.5 percent, the test was terminated and one of the failed specimens was removed and saved for petrographic examination.

4.5.4 Permeability of Concrete. The ion permeability of concrete was determined according to AASHTO T 277, "Standard Test for Rapid Chloride Ion Permeability", with the following modifications:

(1) tests were conducted on 4 in. diameter concrete cylinders, and

(2) two specimens were cut from the interior of each cylinder,

(3) specimens were kept saturated in a sealed vacuum for one hour after evacuation, in lieu of a forced vacuum. This test is a relative measure of the ease of ions to pass through concrete over a period of time.

The test consists of a concrete disk, 4 in. in diameter and 2 in. thick, placed between two conducting cells of ionic solutions. A dc voltage is placed across the system and the cummulative amount of coulombs, amp•seconds, passing through the concrete in a six hour period is measured. Figure 4.1 shows the circuit diagram for the chloride ion permeability test.

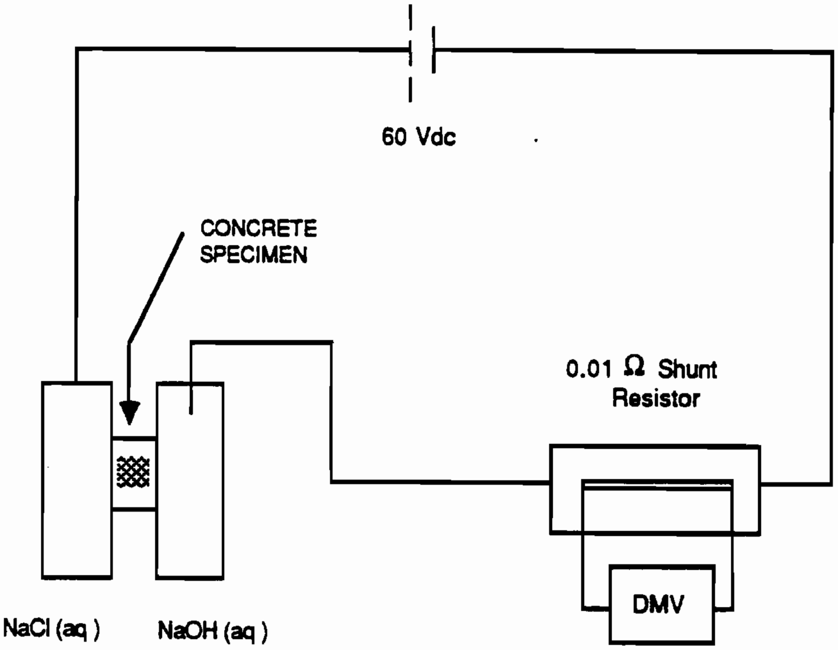


Figure 4.1 Circuit diagram of rapid chloride ion permeability test.

4.6 Overall Testing Program

The testing program described in this document was based on established procedures with the consideration of the results of many past research programs. This section provides a brief explanation of the reasoning which was used to select the experimental procedures and parameters of this study.

4.6.1 Procedures. The concrete mixing, curing and compressive strength testing procedures used in this study were those of the Texas SDHPT and the American Society of Testing and Materials. These are well defined and established procedures which need no discussion. The sulfate and the permeability testing procedures were developed from the procedures followed in other research programs.

The sulfate testing procedure was not an ASTM standardized procedure. Although ASTM has two such procedures, C 452 and C 1012, both are mortar tests and do not represent the behavior of concrete in the field. The procedure used in this study was one of three procedures developed by the United States Bureau of Reclamation. The USBR has a 2.1 percent Na_2SO_4 continuous soaking test, a 10 percent Na_2SO_4 continuous soaking test, and an accelerated wetting and drying Na_2SO_4 test for sulfate attack on concrete. The first two test procedures are identical except that the 10 percent solution accelerates the time to failure of concrete. The typical difference in time to failure between the two procedures is on the order of a factor of 10. The accelerated wetting and drying procedure of the USBR uses a 2.1 percent Na_2SO_4 solution and cycles the specimens through 8 hours of forced air drying at 130°F each day. The time to failure as measured by this procedure is similar to that of the ten percent Na_2SO_4 solution, but the effect of the wetting and harsh drying cycles is unknown. A comparison of the 10 percent and the accelerated wetting and drying methods is presented in Figure 4.2. The accelerated wet-dry test displays erratic expansions compared to the 10 percent solution testing procedure. The 10 percent Na_2SO_4 soaking procedure was chosen for this research program to isolate the chemical testing environment by eliminating other physical effects such as microcracking from drying shrinkage and large temperature changes.

The sulfate concentration had to be maintained in order to keep a constant level of sulfate ions in solution at all times. The reaction between calcium in the cement paste and the sulfate ions will precipitate gypsum both within the concrete and

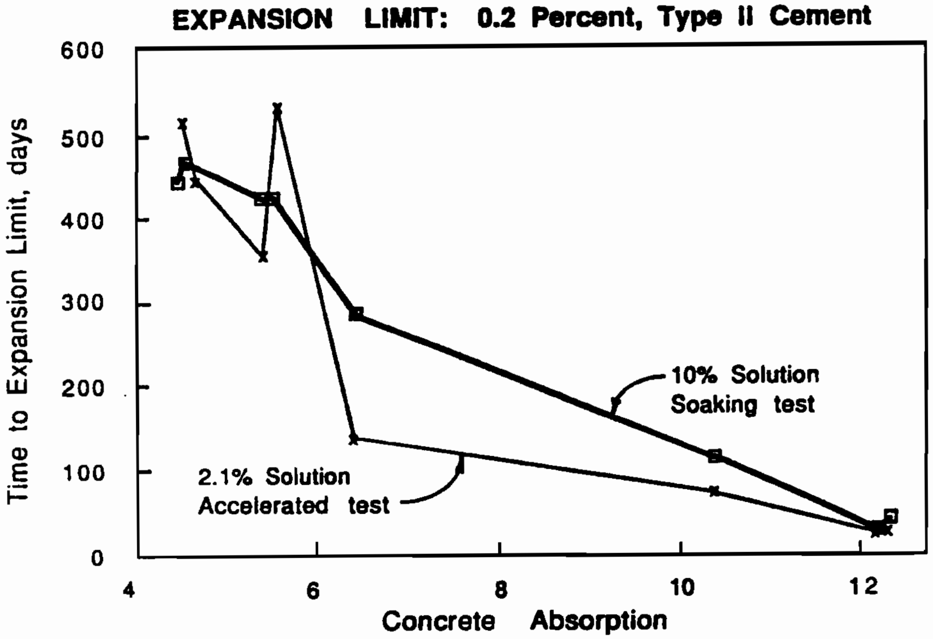


Figure 4.2 Comparison of accellerated sulfate testing methods.

in the exposure tank. This reaction diminishes the sulfate concentration surrounding the concrete and thereby lessens the effect of the chemical environment. The Na_2SO_4 solution was maintained by flushing the tanks and periodically providing a fresh solution.

The permeability testing procedure used was that of AASHTO T 277 as described in Chapter 4, with two procedural exceptions. The specimens were sealed in a vacuum while submerged in deaerated water, rather than being exposed to an active vacuum while submerged in deaerated water. This procedure was chosen to prevent water from entering the vacuum pump oil. This minor alteration had no effect on the overall chloride ion permeability results as the test is not sensitive to the method of saturation[47]. The second alteration in the AASHTO T 277 procedure was to measure the permeability at ages between 10 and 200 days, rather than just at 28 days as the AASHTO procedure requires. This was to investigate whether the ion permeability of concrete stabilizes at later ages or if the recommended 28 day test is representative of the ion permeability of concrete at later ages in service.

The AASHTO procedure is directed at the determination of chloride permeability of concrete cores from the field. The American Society of Testing and Materials is in the process of standardizing this test for laboratory testing. In a research program conducted by Mobasher and Mitchell to study the variability of this test procedure, the chloride permeability measured by this test was sensitive to concrete material such as aggregate, W/C ratio, and air content, but was not sensitive to minor inconsistencies in the specimen preparation procedure.

4.6.2 Parameters. The parameters of this study can be divided into two major categories: physical and compositional. The physical parameters include curing conditions, water content, and air content. These variables affect the strength development and physical pore structure of the cement paste within the concrete without changing the chemical or mineralogical composition of the materials used in the concrete mixtures. The compositional parameters included the chemical and mineralogical effects of combining different portland cements and fly ashes and varying the fly ash content. The coarse and fine aggregates were kept constant, as was the volume of paste and workability of the concrete.

Moist curing of the concrete until it reached a compressive strength of 3500 psi or 28 days was used as an indicator to start sulfate exposure testing. This compressive strength was chosen to give the concrete approximately equal maturity at the time of sulfate exposure. Low stiffness concrete would accommodate the accelerated sulfate expansions without damage. This would be contrary to typical field conditions of concretes exposed to sulfate environments. Concrete containing fly ash was also exposed to the sulfate environment at early ages, 3 days, to investigate the effect of sulfate exposure on concrete with low strength or at early ages. Concrete exposed to sulfate at 28 days was also investigated to observe the behavior of higher strength and more mature concrete. Air content and water content were varied to investigate their effect on the sulfate resistance of concrete. A lower water content and an entrained air structure will decrease the fluid permeability of concrete by providing the concrete with a denser paste or a paste with a nonconnected air void system. Silica fume was used for its refining effects on the pore structure of the cement paste.

The composition of cement and fly ash combinations were studied to relate the sulfate resistance of concrete to the cementitious and pozzolanic materials which make up its binding matrix. Fly ash content was varied from 25 to 45 percent replacement to investigate the effect of fly ash content as a cement replacement on concrete sulfate resistance. Eighteen different fly ashes were investigated to observe the effect of the differences in chemical and mineralogical composition of fly ash on the sulfate resistance of concrete. Blast furnace slag was used in this study to investigate the effect of a high calcium noncrystalline pozzolan as opposed to the high calcium fly ashes which may contain up to 40 percent crystalline material.

CHAPTER V
CHARACTERIZATION OF FLY ASH

5.1 General

Chapter 3 outlined the previous work conducted on the sulfate resistance of concrete containing fly ash. Each of these studies was largely empirical and assisted in defining the relationship between sulfate attack and the bulk properties of fly ash. The next step in discerning the difference between fly ashes which benefit sulfate resistance from those which detract from the concrete sulfate resistance is to gain a better understanding of the effect fly ash composition has on the sulfate attack mechanism. The mechanism of sulfate attack in portland cement concrete was discussed in Chapter 2 and in greater detail by Lea[43]. The consensus of past research is that reactive alumina in the presence of aqueous free calcium and sulfate ions will lead to sulfate attack through the formation of ettringite.

This chapter will describe the mineralogical origin and composition of fly ash particles, characterizing the fly ash used in this study according to its chemical, physical, crystalline and glassy constitution. A review of standard specifications used to classify fly ash is also presented.

5.2 Coal Classifications

The world uses over 2.4 billion metric tons of coal annually in the production of electric power[38]. This coal can be divided into four distinct categories: anthracite, bituminous, subbituminous, and lignite. Anthracite and bituminous coals, the oldest formations, are referred to as high rank coals, because they have an energy potential greater than 11,000 Btu per pound. These coals are typically obtained from deep mining operations in mountainous regions. Subbituminous and lignite coals are called low rank coals, having an energy potential of less than 9000 Btu per pound. These coals are extracted from near surface by strip mining techniques. The United States contains all four types of coal: anthracite in the northeast, bituminous in the eastern and western mountain ranges, subbituminous in Wyoming and Montana, and lignite in North Dakota, Texas and Louisiana. High rank coals are characterized by a relatively low level of mineral impurities, whereas the low rank coals may contain substantial quantities of inorganic noncombustible material such as clay, shale, quartz, carbonates, and sulfides.

5.2 Formation and Collection of Fly Ash

The process of burning coal to produce electric power creates coal ash that must be properly disposed to prevent the pollution of the environment. Figure 5.1 shows a schematic representation of a typical coal burning furnace. The pulverized coal together with any functional additives are fed from a bunker into the boiler furnace by a forced draft. The high temperature furnace first burns the volatile matter and carbon from the coal. The intense heat melts 70 to 90 percent of the mineral phases leaving fused mineral impurities to be carried out with the flue gas. The fused matter is transported from the furnace (1500°C) to a low temperature zone (200°C) in about 4 seconds where it solidifies into crystalline and spherical glassy phases. About one fifth of these particles agglomerate falling to the bottom of the furnace and are collected as bottom ash. The remainder of the particles are carried out of the furnace with the flue gas and are subsequently referred to as fly ash. A precipitator is placed between the boiler and the stack to filter out this finely divided material. After the flue gases pass through the precipitator, an additional device called a scrubber may be used to remove SO_2 gas from the flue gas before it enters the atmosphere.

Bottom ash and scrubber wastes are industrial by-products that pose unique disposal questions by themselves and are not the subject of this report. Fly ash is of concern to the cement and concrete industry and the research study reported herein.

Fly ash is most often collected in one of two ways. The first method uses an electrostatic precipitator, shown schematically in Figure 5.2, to separate the ash from the gases by passing the dust laden stack gases between two large plate electrodes. The solid material is attracted to the electrodes, accumulates on the plates and is shaken off into collection hoppers. The second type of precipitator is the bag house precipitator. This precipitator collects the fly ash on a series of tubular fabric filters in which the flue gases pass through on their way to the stack. A schematic diagram of a typical bag house precipitator is shown in Figure 5.3.

Upon the collection of the fly ash, it is stored in silos and later transported to landfills, or empty coal mineshafts. A portion of the fly ash is used as backfill, soil stabilizer, or an additive in concrete. It is this last portion which illustrates a much greater potential for the utilization of this industrial by-product. Fly ash is composed of many of the same bulk chemical compounds as portland cement with one exception. Fly ash is deficient of the large quantities of lime required to hydrate silica and alumina into a binding matrix of calcium silicate (aluminate) hydrate. However, during the hydration of portland cement, slaked lime, $Ca(OH)_2$, is produced as a precipitate. The combination of reactive fly ash particles and the slaked lime produce a calcium silicate (aluminate) hydrate which is indistinguishable from that of hydrated portland cement. This lime-fly ash reaction is commonly referred to as a pozzolanic reaction, and the fly ash is referred to as the pozzolan.

5.4 Fly Ash and Other Pozzolan Compositions

The largest fraction of fly ash consists of glassy spheres of two types: solid and hollow. The glassy phases typically make up 70 to 90 percent of the total mass of fly ash. The remaining fraction of fly ash is made up of a variety of crystalline phases. These two phases of matter are not completely separate and independent of one another. Rather, the crystalline phases may be present within a glass matrix or attached to the surface of the glassy spheres. It is this union of phases that make fly ash a complicated material to classify or characterize in specific terms.

This section presents an overview of the chemical, physical, mineralogical, and glassy compositions of fly ash. The following section presents the composition of the ashes used in this study.

5.4.1 Chemical Composition. The bulk chemical analysis of fly ash, performed to determine compliance with ASTM C 618 chemical requirements, is an analytic determination of chemical composition without regard to the nature or reactivity of the particle structure. The chemical composition of fly ash is typically made up of calcium, silicon, aluminum, iron, magnesium and sulfur oxides, carbon and various trace elements. These elements remain after combustion because of their high melting points and the short combustion time.

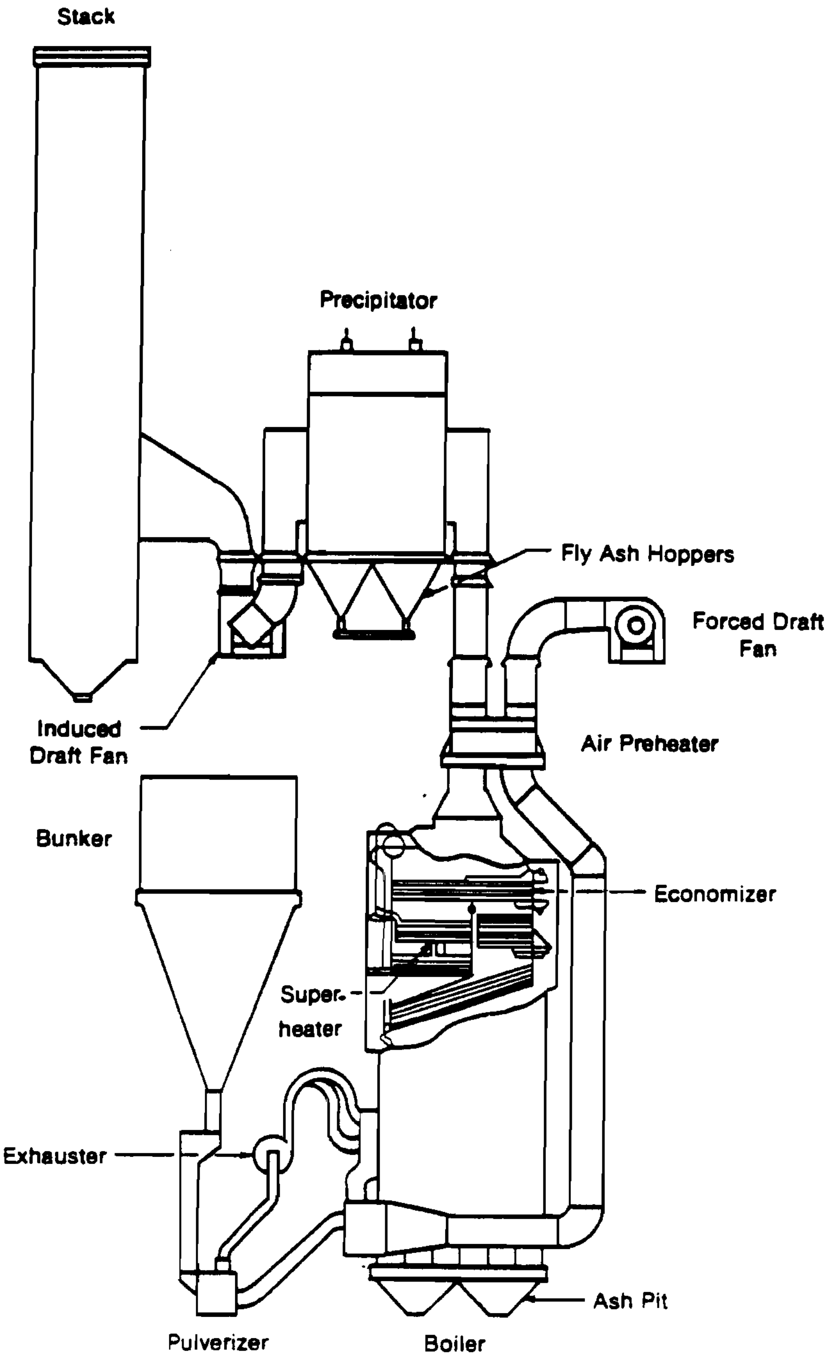


Figure 5.1 Pulverized Coal Furnace and Boiler.

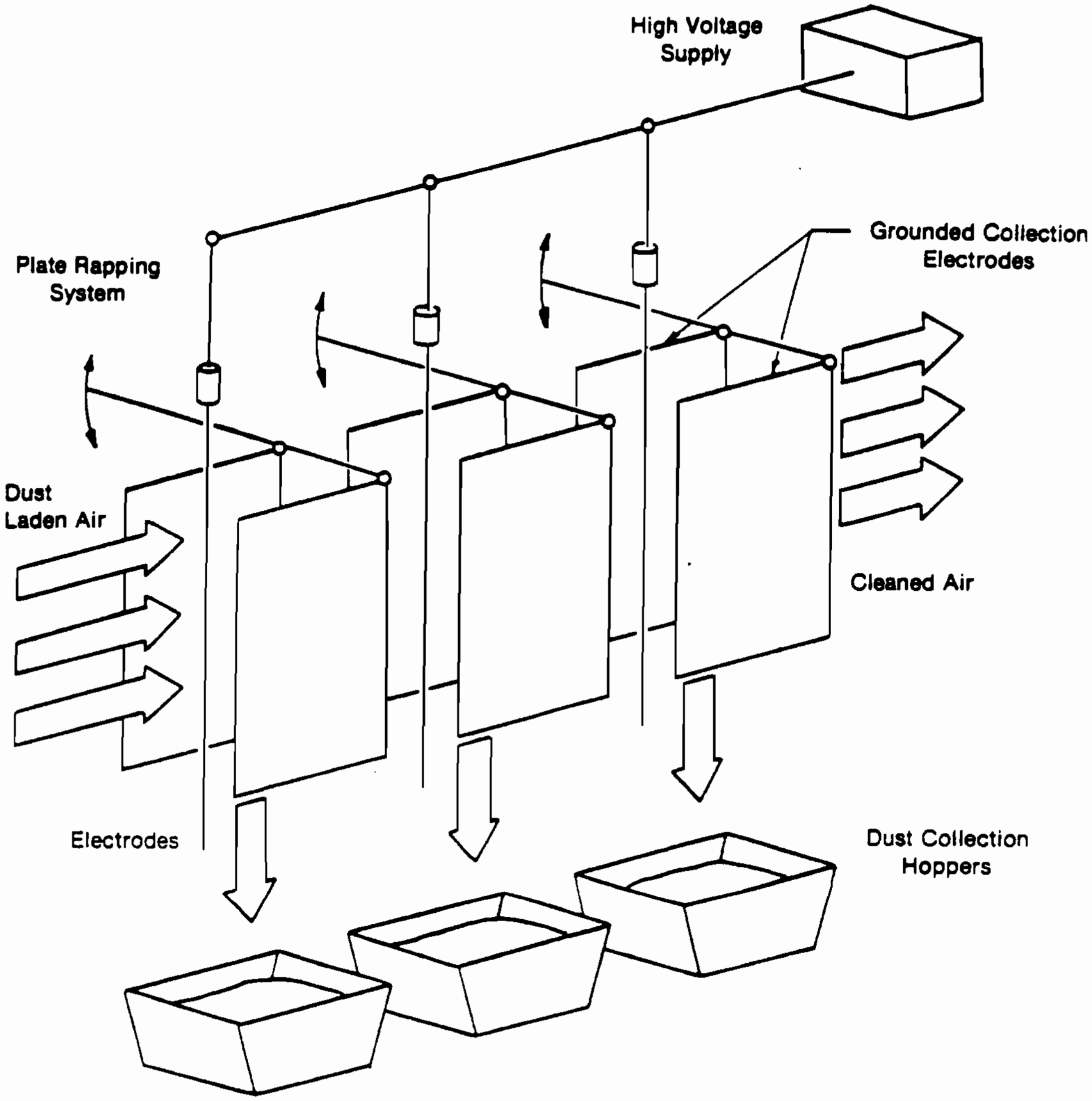


Figure 5.2 Electrostatic Precipitator.

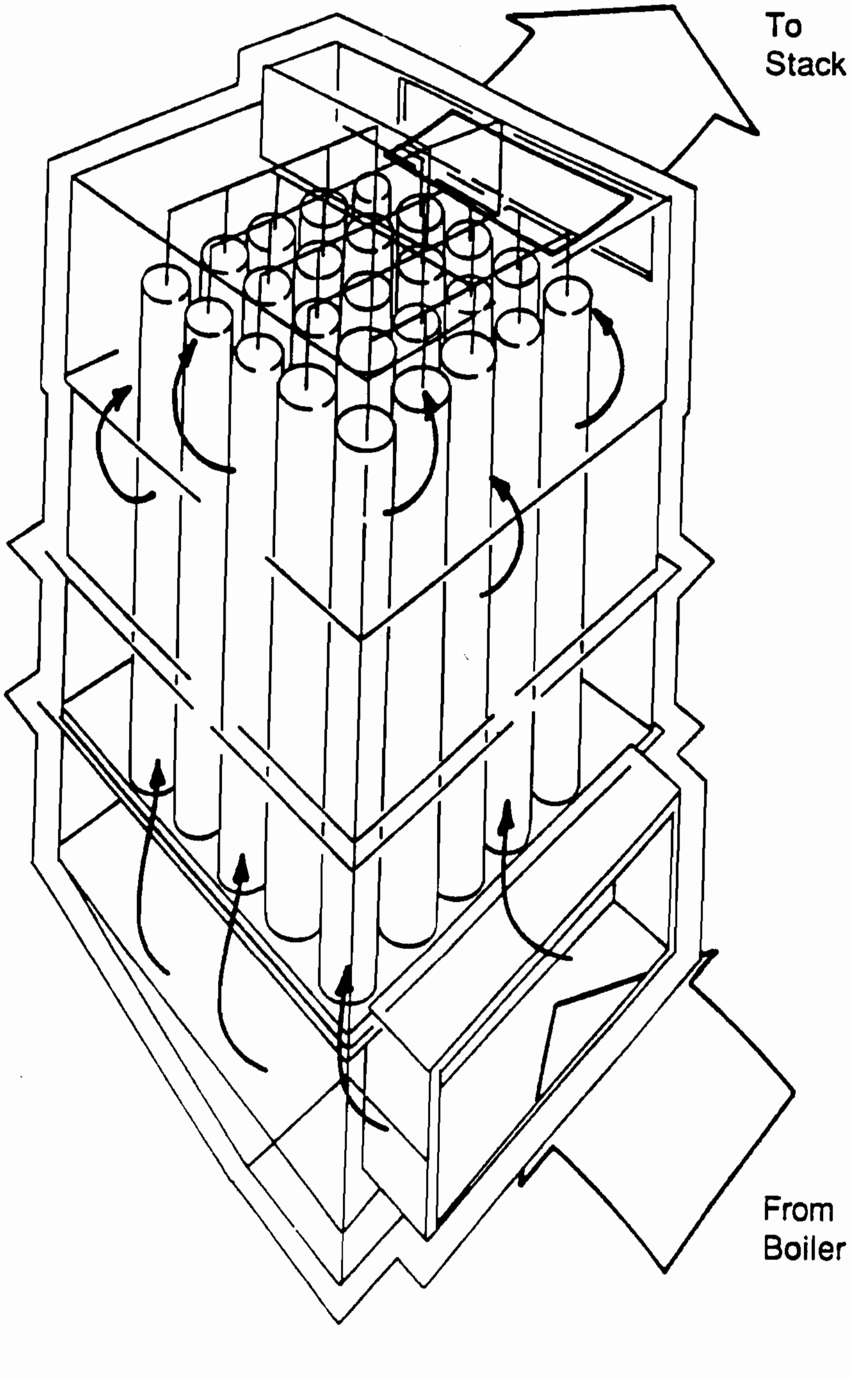


Figure 5.3 Bag House Precipitator.

The source of analytic CaO in fly ash is calcium from coal organics along with calcite and gypsum coal impurities. High rank coals, such as anthracite and bituminous coal, contain fewer mineral impurities typically leaving less than five percent analytic CaO after combustion. Low rank coals may contain substantial amounts of calcium producing fly ash with up to 35 percent analytic CaO. The southern lignite coals found in Texas and Louisiana have the least calcium impurities of the low rank coal producing analytic CaO contents near 10 percent.

The analytic MgO in fly ash is derived from coal organics, montmorillinite, ferromagnesium minerals and sometimes dolomitic coal impurities. These impurities are typically minimal in high rank coals, but may produce analytic MgO contents in excess of 7 percent in fly ashes from subbituminous and northern lignites fly ashes. Southern lignites have analytic MgO contents of less than 2 percent.

The principal source of analytic Al_2O_3 in fly ash is the clay material in the coal, with some alumina coming from the organics in low rank coal. The three types of clays found in coal are:

1) Smectite $Na(Al_5,Mg)Si_{12}O_{30}(OH)_6 \bullet nH_2O$
2) Illite $KAl_4(AlSi_7O_20)(OH)_4$
3) Kaolinite $Al_4Si_4O_{10}(OH)_8$

Northern lignites contain smectite, a sodium montmorillonite, whereas bituminous coal contains only illite and kaolinite. This difference in clay types explains the lower Al_2O_3 in low rank coal fly ash. From the alumina/silica ratios of smectite, 0.35, illite, 0.61 and kaolinite, 0.85, it is clear why lignite fly ashes typically contain 40 percent less analytic Al_2O_3 than bituminous fly ashes. McCarthy notes that analytic Al_2O_3 content is the most reliable indicator of the coal source of fly ash[57]. The correlation between Al_2O_3 content and coal source is presented in Table 5.1.

The alkalies in fly ash come from the clay minerals and other sodium and potassium impurities in the coal. Alkali sulfates form in northern lignite fly ash from the combination of sodium and potassium with oxidized pyrite, organic sulfur and gypsum in the coal. McCarthy et. al. reported that Na_2O is found in greater amounts than K_2O in lignite and subbituminous fly ash, but the reverse is true of bituminous fly ash[57].

Table 5.1 Correlation between alumina in fly ash and coal type.

COAL SOURCE OF FLY ASH	TYPICAL ANALYTIC ALUMINA CONTENT
Northern Lignite	Less than 16 percent
Southern Lignite	16 - 20 percent
Subbituminous	18 - 24 percent
Bituminous/Anthracite	Greater than 24 percent

The SiO_2 content of fly ash results from the clay minerals, mullite and quartz in the coal. Anthracite and bituminous coal contain a higher percentage of mullite and clay minerals than do subbituminous and lignite coal, therefore the fly ash from the high rank coals are richer is silica.

The Fe_2O_3 content of fly ash comes from the presence of pyrite in the coal. The highest concentration of iron rich fly ash particles are between 30 and 60 μm, with the lowest iron contents in particles less than 15 μm[17,72].

The SO_3 in fly ash is a result of pyrite and gypsum impurities in the coal. The sulfur in these minerals is released as sulfur dioxide gas and precipitated into the fly ash through a reaction with lime and alkali particles.

5.4.2 Physical Properties. The most significant physical properties of fly ash are fineness, pozzolanic activity, soundness, uniformity, and alkali reactivity. In engineering practice these properties are judged against acceptable subjective standards which provide the user with a qualitative indication of the expected performance of fly ash in concrete.

Fly ash is typically as fine or finer than the portland cement. The fineness of fly ash is determined by the nature of its formation. Hemmings and Berry found that the smallest molten droplets within the flue gases are quenched quickly into an amorphous glassy state[36]. The larger fly ash particles are the result of cooling at a slower rate, allowing nonreactive crystalline phases to form within the melt before the glassy phases are solidified. Fly ash fineness affects the properties of concrete by influencing the workability, "stickiness", permeability and strength development.

The increase in fine particles does not increase the demand for water for a specified slump as would be suggested by the greater surface area. On the contrary, the fly ash may add to the workability by providing glassy spherical particles which act as a lubricating agent, therefore reducing the water demand of the fresh concrete mixture.

Sticky concrete can be caused by the use of any material that adds too many fine particles to the concrete mix. When fly ash is used as a 1:1 weight or volume replacement for portland cement this is not usually a problem. Some specifications require 1.25 parts fly ash for 1 part cement replacement, this practice can lead to a reduction in the sand or coarse aggregate fraction of the mix and a substantial increase in the particles, smaller than 45μm. This makes the mixture more difficult to finish and handle, i.e. sticky.

Very fine particles in concrete decrease the permeability of concrete by providing a more densely packed paste structure. The finer fraction of fly ash particles will reduce the permeability of concrete, more than the coarser fraction. In addition to the improved packing density, fine fly ash particles add to greater pore refinement by adding more pozzolanic surfaces than coarse particles on an equal weight basis.

The effect of fly ash fineness on concrete strength development was studied by Joshi[39]. He found that fly ash with a greater coarse fraction (up to 38 percent retained on the #325 sieve) decreased the compressive strength at early ages but reduced the time to initial and final setting when compared to finer fly ash from the same source. However, in both cases, concrete containing fly ash had greater compressive strengths and slightly longer setting times than concrete without fly ash.

Fineness is measured by the amount retained on the #325 sieve (45μm). These particles are mostly carbon and large cenospheres of glass[15]. The #325 sieve is an adequate means of quality control, but is not a suitable method of determining particle size distribution since most particles which can be carried by flue gases are inherently small. The Blaine and Wagner surface area methods of determining fineness are based on Stokes' law. These methods are subject to the errors of the difference of specific gravity between particles but are inexpensive and reliable. Other methods based on liquid absorption are equally flawed because of the presence of carbon containing high surface areas. New methods of laser scattering of suspended samples and the Sedigraph 5000 are expensive and as of yet nonstandardized for fly ash.

The pozzolanic activity index is intended to evaluate the contribution of the mineral admixture to the long term strength development of concrete. The test is used as a minimum quality control tool, rather than a quality assurance tool because this index does not directly correlate with 7 or 28 day compressive strength tests of concrete[9,52]. There are two methods of testing for pozzolanic activity. The first combines fly ash with portland cement and the second method uses fly ash in combination with lime. Of the two methods the portland cement method is more reliable for all fly ash. The lime method is not directly applicable to high calcium fly ash which contains lime and exhibits cementitious characteristics without a lime addition[89].

The test for soundness is an autoclave expansion test based on accelerated curing techniques. The soundness test is derived from the soundness problems observed in portland cements containing over 6 percent analytic MgO and high free lime contents. Large amounts of either one of these compounds in portland cement may lead to expansion from delayed hydration. High calcium fly ashes may commonly contain more than 5 percent MgO. The crystalline form of MgO, periclase, is susceptible to the delayed formation of brucite, $Mg(OH)_2$, the compound associated with portland cement unsoundness. The reactivity and fineness of periclase is also a factor in the expansive mechanism. The periclase in fly ash is thought to be in a stable nonreactive crystalline form[60]. In addition, if reactive periclase is present in the finely divided fly ash it will hydrate at early ages because of its small particle size[43]. Therefore relatively large amounts of MgO are seldom detrimental to the soundness of concrete containing fly ash.

Crystalline lime, sometimes referred to as "free lime", is present in most high calcium fly ashes, and may be a cause of autoclave expansion. However, lime in the form of $Ca(OH)_2$ is called "slaked lime" and does not contribute to the unsoundness mechanism. Soft-burnt free lime crystals hydrate while the concrete is at early ages and has greater plasticity, therefore not contributing to the unsoundness of concrete. However hard- burnt lime crystals are the result of insufficient burning of the lime in the furnace and hydrate slowly after the concrete has hardened.

Demirel hypothesizes that the carbon dioxide rich environment of the combustion gases cause a carbonate coating to form on these poorly burnt lime particles, creating a high diffusion energy barrier[21]. This barrier retards the hydration of the lime particle and thereby increases the potential for unsoundness.

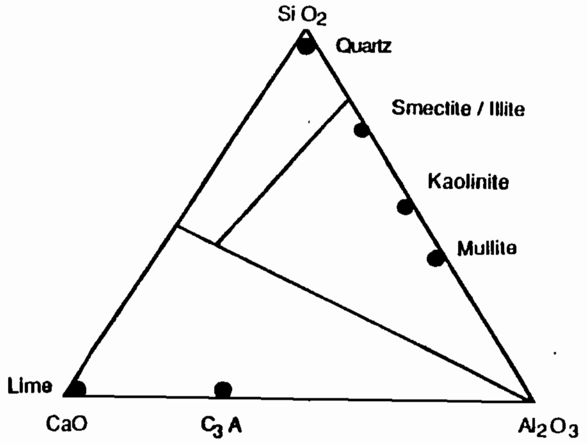
The uniformity requirements of ASTM C 618 for specific gravity and fineness are employed to ensure fly ash consistency with regard to size and composition. A 5 percent deviation limit from the previous ten samples is imposed so as to guard against drastic changes in field performance of the fly ash in concrete. Stevenson and Huber performed SEM microprobe analysis on hundreds of fly ash grains to determine their bulk chemical compositional uniformity[103]. Their results, shown in Figure 5.4, show that fly ashes from low calcium coal sources were homogeneous in nature but that fly ashes from high calcium coal sources were more heterogeneous because of their complex mineralogy. Of all the particles in fly ash, the finest fraction was found to be the most homogeneous in composition[36].

The alkali reactivity of fly ash can lead to alkali-silica reaction with reactive aggregates and eventual degradation of the concrete. ASTM C 618 has an optional 1.5 percent available alkali requirement. This requirement need only be imposed when a reactive aggregate is used.

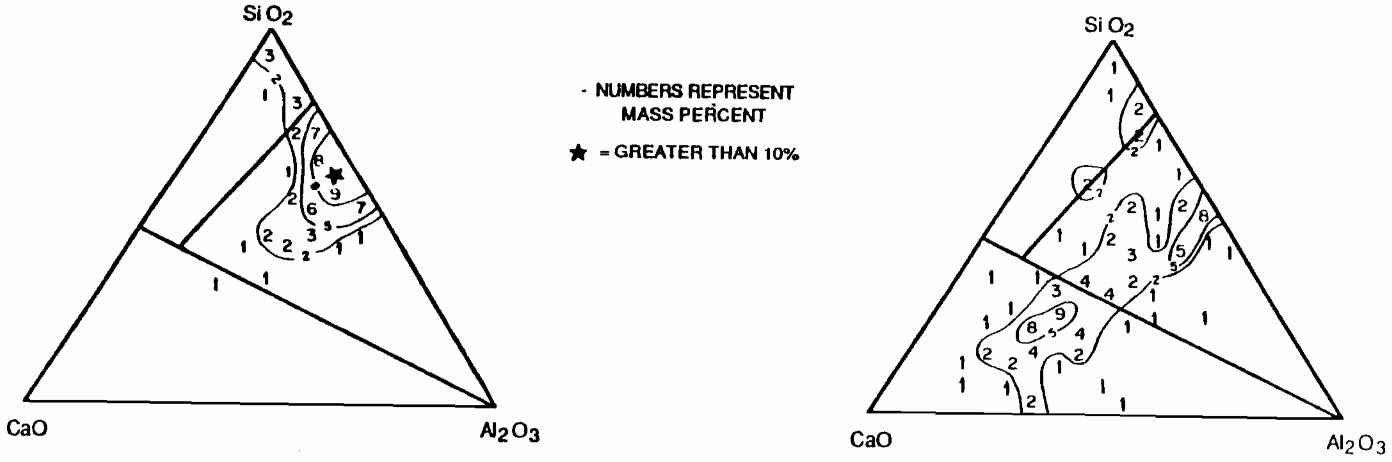
5.4.3 Crystalline Composition. The crystalline phases found in fly ash are presented in Table 5.2. Low calcium fly ashes are characterized by having only the inert crystalline phases namely, hematite, mullite, quartz, and ferrite spinel[45]. High calcium fly ashes may contain these four crystalline phases plus anhydrite, alkali sulfate, dicalcium silicate, tricalcium aluminate, lime, melilite, merwinite, periclase, and sodalite structures[56].

Alpha quartz is present in all fly ash. The quartz is a result of the impurities in the coal that failed to melt during combustion. Quartz is typically the most intense peak in the X- ray diffractogram, but this peak is also subject to the most quantitative variability. The quartz phase found in fly ash is nonreactive in the sulfate attack mechanism.

Low rank coals containing high calcium contents often contain between 1 and 3 percent anhydrite. The calcium acts as a "scrubber" for SO_2 in the combustion gases and forms anhydrite.



Mineral Compositions



Low Calcium Fly Ash

High Calcium Fly Ash

Figure 5.4 SEM particle analysis of fly ash.

Table 5.2 Mineralogical Phases in Fly Ash.

Abbreviation	Name	Composition
$A\bar{S}$	Thenardite (Aphthitilite)	$(Na,K)_2SO_4$
Ah	Anhydrite	$CaSO_4$
C_3A	Tricalcium Aluminate	$Ca_3Al_2O_6$
C_2S	Dicalcium Silicate	Ca_2SiO_4
Hm	Hematite	Fe_2O_3
Lm	Lime	CaO
Ml	Melilite	$Ca_2(Mg,Al)(Al,Si)_2O_7$
Mu	Mullite	$Al_6Si_2O_3$
Mw	Merwinite	$Ca_3MgSi_2O_8$
Pc	Periclase	MgO
Qz	Quartz	SiO_2
So	Sodalite-Structures	$Na_8Al_8Si_6O_{24}SO_4$ $Ca_2Na_6Al_6Si_6O_{24}(SO_4)_2$ $Ca_8Al_6Al_6O_{24}(SO_4)_2$
Sp	Ferrite Spinel	Fe_3O_4
Po	Portlandite	$Ca(OH)_2$

The various effects of free lime were discussed in the previous section. If free lime is present as highly sintered crystals, hard-burnt lime, there is a potential for long term expansion from its hydration. Although there is no easy way to determine soft-burnt lime from the sintered lime, McCarthy et. al. note that when hard-burnt lime is present it is often found in the larger grains of fly ash[56]. Hydrated lime, Portlandite, is also present in some high calcium fly ash that have been exposed to moisture.

Crystalline MgO, periclase, is found in fly ashes with more than two percent analytic MgO. Low rank coals may contain periclase contents equal to 80 percent of the analytic MgO content. The periclase in fly ash is not "free" MgO such as that found in some portland cements. Rather, the crystalline MgO in fly ash is similar to the phase of MgO found in granulated blast furnace slags, in that it is nonreactive in water or basic solutions at normal temperatures[43,56].

In its purest form magnetite (Fe_3O_4) is the crystalline spinel structure closest to that found in fly ash. A slight decrease in the d spacing on the diffractogram of ferrite spinel is detected through XRD. Stevenson and McCarthy used a SEM electron probe on a magnetically separated portion of the fly ash to determine that the cause of this deviation is the Mg and Al substitution into the structure of this phase as an iron replacement [58]. The ferrite spinel phase found in fly ash is inert and does not participate in the sulfate attack mechanism. Hematite, formed by the oxidation of magnetite, is also an inert phase in some fly ashes.

The crystalline compound mullite is only found in substantial quantities in low calcium fly ashes. Mullite forms within the spheres as the glass solidifies around it. It is the largest source of inert alumina in fly ash. Consequently, this phase is nonreactive in the sulfate attack mechanism.

Melilite is a mineral structure group including:

1) Gehlenite: $Ca_2Al_2SiO_7$

2) Akermanite: $Ca_2MgSi_2O_7$

3) Sodium-Melilite: $NaCaAlSi_2O_7$

Each of these phases can have an Fe substituted for Mg or Al and is nonreactive. McCarthy believes that the actual composition in fly ash is nearly 50 percent gehlenite and 50 percent akermanite[58]. The melilite phase in fly ash is also nonreactive in the sulfate attack mechanism.

The presence of C_3A in high calcium fly ash was confirmed by Diamond, Demirel, Mather, and McCarthy[17,20,26,56]. The intense peaks of this phase overlap those of the merwinite phase, making the quantitative interpretation of the diffractogram difficult. However, McCarthy reports that the C_3A phase is the dominant phase in fly ashes with subbituminous coal sources, and the merwinite phase is most prevalent in lignite fly ashes[59]. Neither phase is present in low calcium fly ashes. The cementitious value of C_3A contributes to the be self-cementing of high calcium fly ashes in many applications in which low calcium fly ashes are unsuitable. The C_3A phase is extremely reactive in the presence of calcium and sulfate ions in solution.

Merwinite is a common phase in metallurgical slags, high calcium fly ashes, and the early stages of the devitrification of Mg containing glasses. Northern lignites typically have higher MgO contents and lower Al_2O_3 contents than subbituminous coal fly ashes, allowing the merwinite phase to dominate over the C_3A phase in the northern lignite fly ash. Merwinite is nonreactive at normal temperatures and is does not participate in the sulfate attack mechanism.

The feldspathoids sodalite-structure minerals form from melts rich in alkalis, sulfate and calcium and poor in silica. The Nosean and Hauyne compounds have been identified in fly ash by McCarthy[59].

Nosean: $Na_8Al_6Si_6O_{24}SO_4$

Hauyne: $(Ca, Na)_8Al_6Si_6O_{24}(SO_4)_2$

Under this same classification Demirel, Diamond, and Mather refer to the compound tetracalcium trialuminate sulfate, also known as the Klein compound, which can be written stoichiometrically similar to the Hauyne compound but completely deficient of silica.

Klein: $Ca_8Al_6Al_6O_{24}(SO_4)_2$

In either case, this compound contains reactive alumina sulfate which reacts readily with water to form ettringite.

Among the other phases found in fly ash are alkali sulfate and dicalcium silicate. Dicalcium silicate is a crystalline phase which is present in some high calcium fly ashes and is thought to be reactive in the same manner as C_2S in portland cement. Northern lignite fly ashes often contain crystalline alkali sulfates such as thenardite and aphthitilite.

5.4.4 Glass Composition. Fly ash is largely comprised of small glassy spheres which form while the burned coal residue cools very rapidly. The composition of these glasses is dependent upon the composition of the pulverized coal and the temperature at which it is burnt. The major differences in fly ash glass composition lie in the amount of calcium present in the ash. Coal which leaves only small amounts of calcium in the fly ash e.g. anthracite and bituminous or some lignite coals, result in aluminosilicate glassy fly ash particles. Subbituminous and some lignite coals leave larger amounts of calcium in the fly ash and result in calcium aluminosilicate glassy phases[58]. This can be seen in the ternary system diagram shown in Figure 5.5. The normalized average glass composition of high calcium fly ash plot within the ranges where anorthite to gehlenite are the first phases to crystallize from a melt, whereas the low calcium fly ashes fall within the regions of the diagram where mullite is the primary crystalline phase. It is widely believed that the disordered structure of a glass resembles that of the primary crystallization phase that forms on cooling from the melt.

A schematic of the basic structure of a silica glass is compared with a vitrified crystalline silica structure in Figure 5.6. The crystalline silica is characterized by a tetrahedral network of silicon and oxygen atoms. The vitreous silica structure occurs when the molten silica is quenched rapidly locking in a level of disorder in the network. In fly ash, the molten silica is accompanied by other molten oxides. As the melt is quenched, these additional oxides create two types of added disorder in the silica glass network. In the first type, high valance cations like Al^{+3} and Fe^{+3} substitute into the structure for Si^{+4}. This substitution breaks the continuous nature and distorts the 3-D network, causing an excess negative charge which must be neutralized by an additional cation, e.g. Mg^{++}, Na^{+}. The second type of disorder is caused by the modification of the glass structure by the random presence of low valence ions such as, Na^{+}, K^{+}, Ca^{++}, or Mg^{++}, in the vitreous structure. These cations depolymerize the 3-D network[36]. The greater the disorder and depolymerization of the fly ash glass structure, the less stable the network becomes. Also, the greater the depolymerization of the silicate network the lower the viscosity of the melt. High calcium fly ashes, with their higher content of network modifiers, have a much lower viscosity than low calcium fly ash.

Glasses in fly ash with a devitrified composition furthest from the cristoballite and mullite fields are most reactive within a portland cement-fly ash system. This would indicate that fly ash containing high calcium - high alkali glasses possess a greater reactivity than low calcium - low alkali fly ashes.

The nature of the glass composition is exposed in the "diffuse scattering" of the X-ray diffraction. A specific feature of a fly ash X-ray diffractogram is a broad elevation of the diffraction response caused by the disordered structure of the glass particles. This feature is referred to a diffraction halo and is shown in Figure 5.7. Research conducted by Diamond indicates that the peak of this diffraction halo occurs at the 2Θ angle which corresponds to the major Bragg reflection peak of the compound that would be formed if the glass were devitrified[18]. This can be

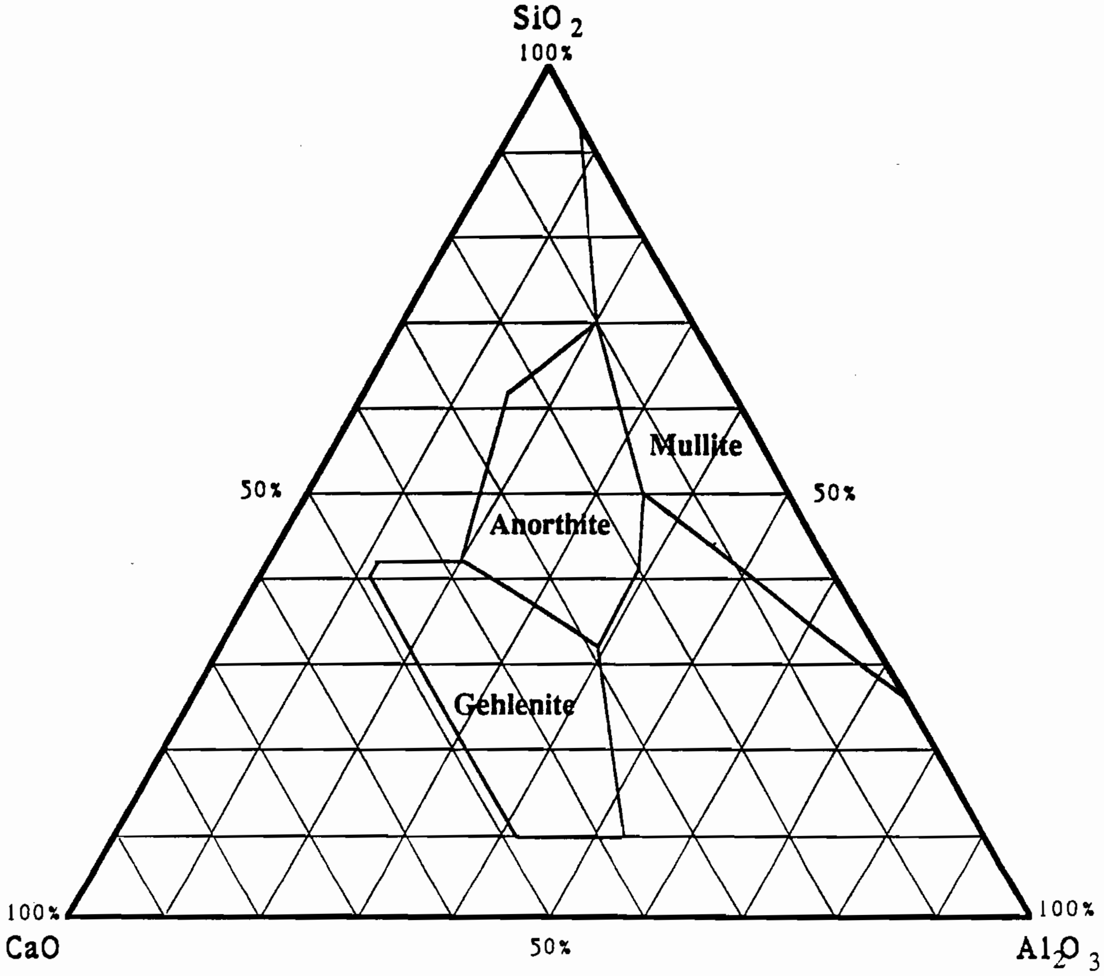


Figure 5.5 CaO - SiO_2 - Al_2O_3 Ternary System Diagram.

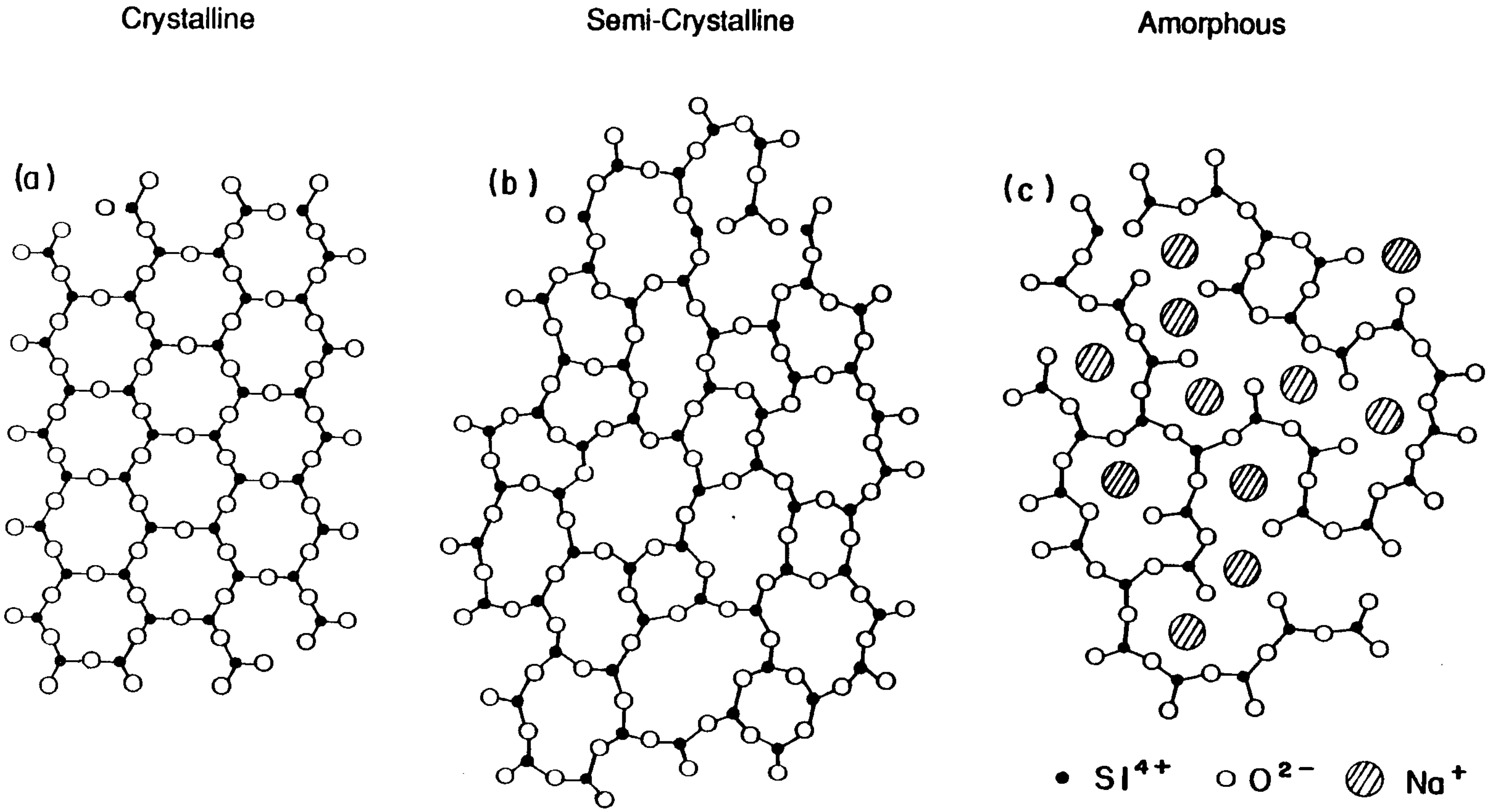


Figure 5.6 Crystalline and noncrystalline silica structures.

illustrated in Figure 5.8 which shows a nearly linear correlation between the calcium oxide content of fly ash and the observed diffraction halo peak in ashes containing less than 20 percent calcium oxide[18].

Fly ash containing little of no analytical calcium oxide showed a halo maximum near 23° 2Θ which is near the major peak for cristobalite at 22° 2Θ. Cristobalite is the first silicate to form upon cooling silica from above its melting point (1723°C). As the calcium content of the fly ash increases from 0 to 20 percent the angle of the diffraction halo increases from 23° 2Θ to slightly greater than 27° 2Θ [64]. The resulting glasses take on the alumina-silica composition of mullite and the calcium aluminosilicate composition of the feldspar mineral, anorthite, shown in Figure 5.9. Mullite has its major diffraction peak at 26.5° 2Θ and anorthite has its major diffraction peak at 27.8° 2Θ. Both form at temperatures near 1550°C. The alkalies in fly ash glasses may form a third mineral, albite, which may be present in small quantities in the vitrified form of fly ash. Albite is a sodium aluminosilicate mineral which may contain up to 10 percent calcium. The glasses of low calcium fly ashes are characterized by a continuous diffuse band between 21-34° 2Θ with a peak of the diffraction halo between 23 and 27° 2Θ [64].

High calcium fly ash contains glass which is rich in calcium and reactive in a hydrous solution. These fly ashes show calcium aluminosilicate glass with a diffraction halo peak between 31 to 34° 2Θ [64]. These types of glasses have a composition near that of gehlenite in the ternary diagram shown in Figure 5.9.

5.5 Fly Ashes and Pozzolans in Study 481

The fly ashes and pozzolans used in this study were analyzed to determine their chemical, physical, mineralogical, and glass compositions. The compositions of the 24 fly ashes, one blast furnace slag and one silica fume were determined to identify amorphous and crystalline phases which may contribute to the problem of sulfate attack of concrete containing fly ash. Eighteen of the fly ashes, the silica fume and the blast furnace slag have already been tested for sulfate exposure. The 5 additional fly ashes will be tested as the study is continued.

The bulk chemical oxide contents were determined by X-ray fluorescence and other methods according to the procedures of ASTM C 311, "Sampling and

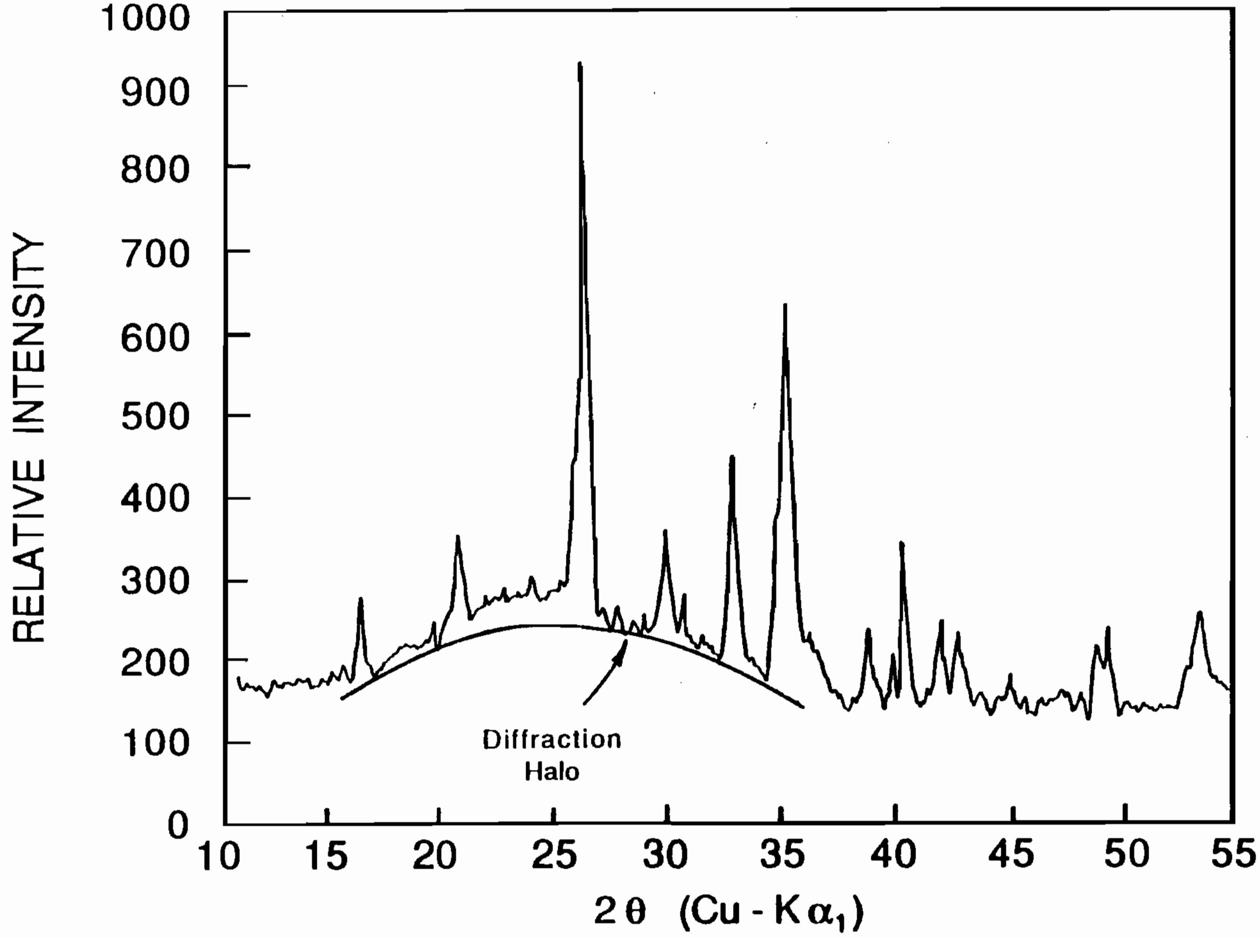


Figure 5.7 X-ray diffractogram with halo.

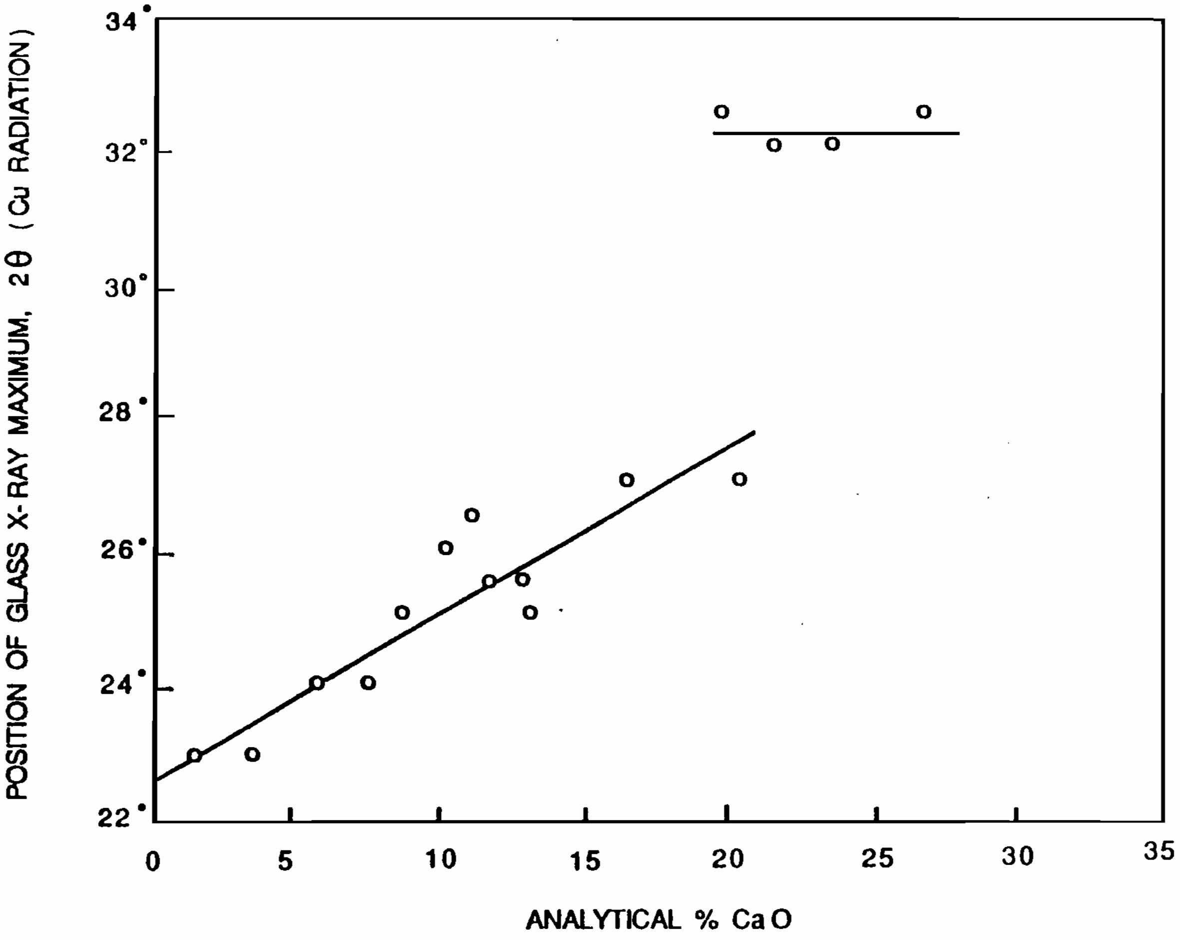


Figure 5.8 Correlation between halo peak and CaO content[45].

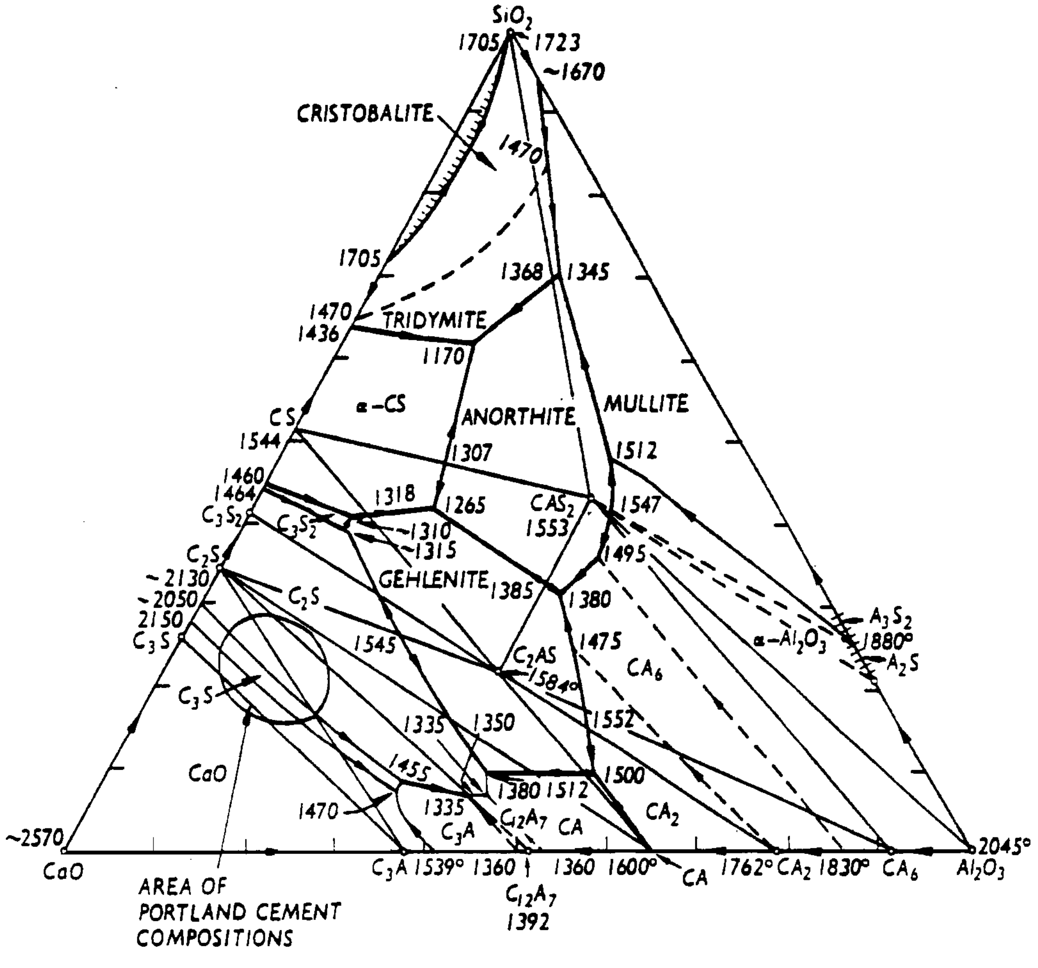


Figure 5.9 Phase Diagram of Ternary System CaO-SiO2-Al2O3.

Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland Cement Concrete" by the Texas SDHPT Materials and Testing Laboratory. The results are tabulated in Table 5.3. Fly ashes A-1 to A-9 and A-14 have CaO contents less than 11 percent. Fly ashes A-11 to A-13 have CaO contents between 11 and 22 percent. Fly ashes A-10 and B-1 to B-8 have CaO contents greater than 22 percent.

Table 5.3 Results of Chemical Analysis of Fly Ashes

I.D.	CaO	SiO_2	Al_2O_3	Fe_2O_3	Oxide Sum	MgO	SO_3	Av. Alk.
A-1	1.57	43.04	27.44	16.06	86.54	0.00	1.24	-
A-2	9.55	52.90	17.89	8.98	79.77	1.66	0.90	0.57
A-3	6.97	55.54	18.60	4.33	78.48	0.81	0.26	0.31
A-4	7.98	51.33	20.92	6.00	78.25	1.05	0.52	0.25
A-5	4.24	47.33	24.44	5.56	77.33	0.08	0.39	1.76
A-6	7.90	44.99	23.57	7.49	76.05	0.00	0.89	1.90
A-7	8.76	50.89	18.55	5.60	75.04	0.47	0.71	-
A-8	3.68	45.87	24.15	4.66	74.68	0.00	0.42	-
A-9	10.09	42.48	24.12	5.96	72.56	1.58	0.52	-
A-10	22.44	34.53	23.77	6.69	64.99	3.88	1.97	2.35
A-11	20.90	44.60	15.50	7.70	67.80	6.10	1.50	0.89
A-12	12.40	46.50	22.30	3.60	72.40	3.00	0.58	3.14
A-13	15.00	46.90	20.90	5.30	73.10	4.70	1.45	0.23
A-14	1.22	50.70	20.00	16.70	87.40	0.90	1.22	0.73
B-1	25.97	36.18	21.35	6.00	63.53	6.22	2.69	0.86
B-2	26.34	33.31	24.10	5.77	63.18	4.24	-	4.35
B-3	23.13	35.59	22.41	5.14	63.14	4.25	2.10	2.04
B-4	29.86	32.23	22.18	4.97	59.38	5.63	2.48	1.67
B-5	27.95	31.34	22.51	4.98	58.83	4.34	2.28	1.56
B-6	31.34	30.80	21.94	4.66	57.40	6.14	1.97	1.67
B-7	28.35	30.40	21.68	4.47	56.55	4.29	5.60	3.75
B-8	33.93	28.38	20.19	4.94	53.51	8.41	4.45	1.54
B-9	23.10	39.00	19.50	4.80	63.30	5.60	2.30	1.49
B-10	25.57	34.46	18.38	6.20	58.04	5.12	2.78	2.18
S-1	0.11	92.00	3.00	2.00	97.00	0.00	1.24	0.34
S-2	41.29	36.38	9.04	0.44	45.86	8.06	3.01	0.38

Table 5.4 Results of Physical Analysis of Fly Ashes

I.D.	Pozzolanic Activity	Retained #325	Blaine (cm^2/g)	Specific Gravity	Moisture Content
A-1	86	15.4	2430	2.43	0.18
A-2	91	23.8	2560	2.43	0.03
A-3	97	13.3	2520	2.32	0.07
A-4	90	30.7	3120	2.18	0.09
A-5	94	25.8	3100	2.02	0.11
A-6	78	25.8	3870	2.20	0.08
A-7	74	46.3	2880	2.23	0.19
A-8	97	18.2	4030	2.18	0.04
A-9	103	16.6	4330	2.28	0.04
A-10	100	17.3	4370	2.57	0.03
A-11	84	21.6	3290	2.54	0.01
A-12	83	28.2	2340	2.26	0.05
A-13	105	10.5	4160	2.49	0.06
A-14	91	16.5	2360	2.39	0.29
B-1	98	13.1	3370	2.64	0.11
B-2	92	14.3	4560	2.60	0.06
B-3	102	22.0	3820	2.58	0.02
B-4	92	18.9	4220	2.70	0.10
B-5	100	17.0	3930	2.70	0.01
B-6	105	15.7	3940	2.73	0.06
B-7	86	11.2	3940	2.62	0.13
B-8	91	10.4	3510	2.79	0.02
B-9	101	12.2	2620	2.47	0.04
B-10	92	17.20	3640	2.71	0.02
S-1	86	0.0	n/a	2.20	0.18
S-2	-	0.9	5645	2.92	0.10

The physical characteristics of the 24 fly ashes are given in Table 5.4. The tests were performed according to ASTM and Texas SDHPT standard test methods. Four of the fly ashes had Blaine finenesses below 2500 cm^2/gm.

The mineralogical characteristics of the 24 fly ashes used in this study are listed in Table 5.5. The mineralogy of each fly ash was determined by identifying the crystalline phases present from an X-ray diffraction pattern of each fly ash. A semi-quantitative procedure using a 10 percent rutile standard was used to determine the amount of each phase[58,59]. The X-ray diffraction of each fly ash was performed twice, using samples obtained from the same bulk supply, but sent to the laboratory at a 6 month interval. The values in Table 5.5 are an average of two analyzes. The diffractograms of all the fly ashes and pozzolans used are presented in Appendix C. The normalized average glass composition is plotted on the ternary diagram in Figure 5.10 and shown in Table 5.6.

5.5.1 Fly Ash A-1. This fly ash was derived from an eastern bituminous coal. The chemical and mineralogical composition of fly ash A-1 was that of a typical bituminous coal fly ash, i.e. calcium oxide content less than 5 percent, alumina content greater than 24 percent and a low magnesium oxide content. However, fly ash A-1 contained an unusually high amount of iron oxide in both the crystalline form and in the glassy phase. Nearly half of the iron oxide in this fly ash was present as magnetite (Fe_3O_4) and hematite (Fe_2O_3). The other major crystalline phases present were 9.9 percent mullite and 4.5 percent quartz. The silica to calcium oxide ratio (S/C) in the glassy phase of fly ash A-1 was 23.0, resulting in a glass within the mullite field. This fly ash had a Blaine fineness of 2430 cm^2/g.

5.5.2 Fly Ash A-2. This fly ash was derived from a southern lignite coal. It had the typical composition of a Texas lignite fly ash, i.e. calcium oxide content near 10 percent, silica content of 50 percent, and an alumina content between 16 and 20 percent. Quartz and mullite were the major crystalline phases at 14.3 and 5.9 percent respectively. The silica to calcium oxide ratio (S/C) in the glassy phase of fly ash A-2 was 3.9, resulting in a glass within the mullite field.

5.5.3 Fly Ash A-3. This fly ash was derived from a southern lignite coal. It had the standard composition of a Texas lignite fly ash. The major crystalline phases were quartz, 16.4 percent, and mullite, 9.5 percent. This fly ash was noticeably deficient of the crystalline iron oxides hematite and magnatite. The silica to calcium oxide ratio (S/C) in the glassy phase in fly ash A-3 was 5.3, resulting in a glass within the mullite field.

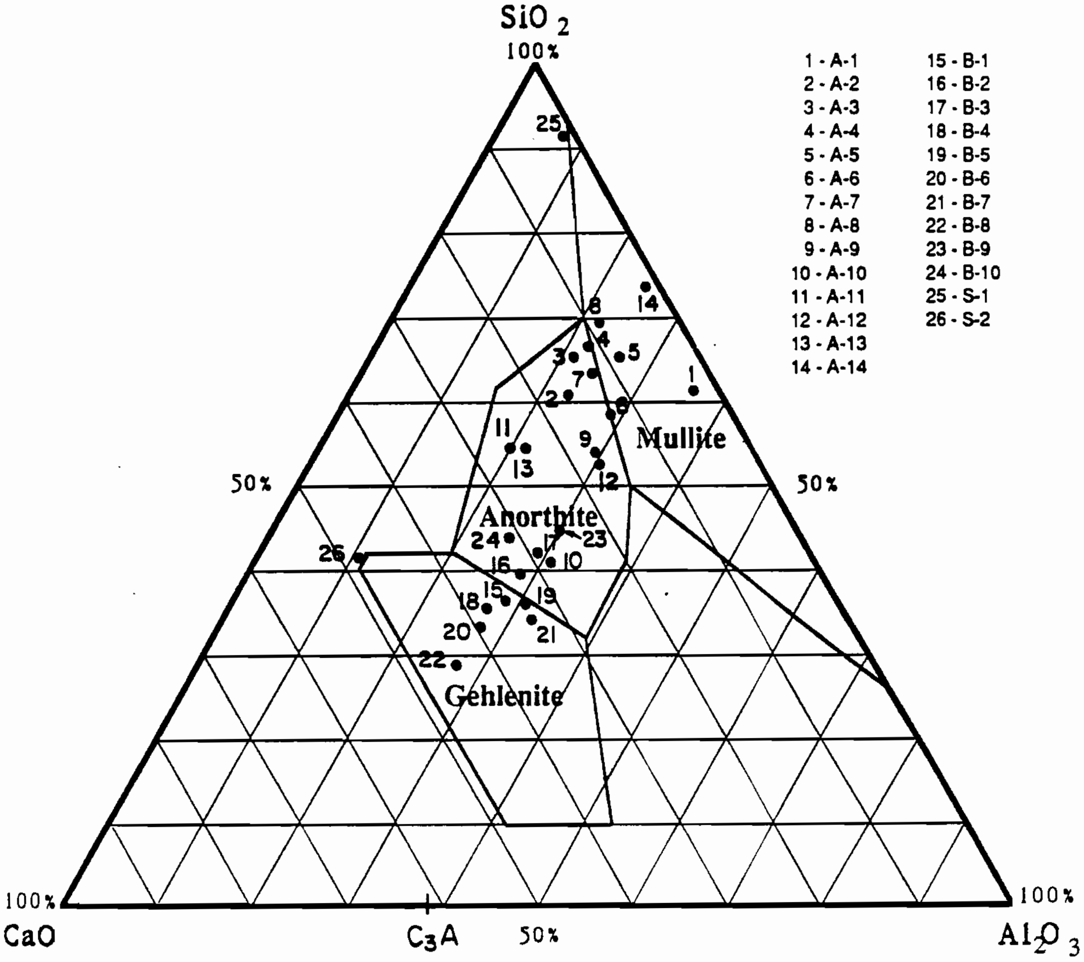
5.5.4 Fly Ash A-4. This fly ash was derived from a southern lignite coal. It had the typical composition of a Texas lignite fly ash. Mullite and quartz were the major crystalline phases at 9.9 and 5.0 percent respectively. The total silica in the

Table 5.5 Mineralogical Analysis of Fly Ashes

I.D.	Ah	Mu	Qz	Ml	Hm	C_3A	Mw	Sp	Lm	Pc	So	Pl	Sum
from XRD analysis, percent of total ash													
A-1	0.0	9.5	4.2	0.0	3.6	0.0	0.0	4.8	0.0	0.0	0.0	0.0	22.1
A-2	0.0	6.3	13.9	0.0	1.7	0.0	0.0	1.5	0.0	0.0	0.0	0.0	23.3
A-3	0.0	9.6	16.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	25.7
A-4	0.0	9.9	5.0	0.0	0.3	0.0	0.0	2.6	0.4	0.0	0.0	0.0	18.2
A-5	0.0	15.0	9.1	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	25.1
A-6	0.5	8.9	6.7	0.0	0.0	0.0	0.0	0.8	0.0	0.0	0.0	0.0	16.9
A-7	0.0	6.7	10.7	0.0	0.0	0.0	0.0	0.7	0.8	1.1	0.0	1.7	21.7
A-8	0.0	19.4	7.9	0.0	0.0	0.0	0.0	1.4	0.2	0.8	0.0	0.0	29.7
A-9	0.4	9.7	7.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	18.2
A-10	1.2	2.5	2.8	2.0	0.0	0.6	3.2	1.8	0.3	0.8	0.0	0.0	15.2
A-11	0.9	0.0	2.6	1.3	0.0	1.8	0.0	3.9	0.9	2.1	0.0	0.0	28.5
A-12	0.0	0.0	5.7	0.0	0.0	0.0	0.0	1.0	0.0	1.1	0.0	0.0	28.2
A-13	0.9	11.0	10.3	1.1	0.0	0.0	0.0	3.2	0.6	1.4	0.0	0.0	25.2
A-14	0.7	7.3	5.6	0.0	2.3	0.0	0.0	7.8	1.5	0.0	0.0	0.0	7.8
B-1	1.7	2.5	10.5	1.9	2.4	2.1	0.0	2.4	1.5	2.9	1.3	0.0	29.2
B-2	1.3	2.5	1.6	4.0	0.0	1.0	1.2	1.9	0.3	0.8	0.7	0.0	15.4
B-3	1.1	2.5	6.5	3.1	0.0	2.2	1.1	2.5	0.4	1.5	0.7	0.0	21.7
B-4	1.6	3.1	4.9	3.0	2.8	2.3	2.5	1.0	1.2	2.5	1.2	0.0	26.0
B-5	1.1	2.5	4.3	2.7	0.0	1.7	3.0	1.5	0.6	1.5	1.1	0.0	20.1
B-6	1.2	3.2	4.7	1.9	2.3	2.5	2.8	1.2	1.8	3.5	1.6	0.0	26.6
B-7	1.6	2.5	5.1	2.3	2.7	0.0	10.8	0.0	2.2	2.2	1.7	0.0	31.1
B-8	2.4	2.5	6.6	2.9	3.9	0.8	5.6	0.0	3.0	5.4	3.1	0.0	36.2
B-9	1.9	0.0	8.7	2.2	0.0	3.1	4.2	1.3	1.5	3.3	2.0	0.0	14.5
B-10	1.9	0.0	2.5	3.9	0.0	1.2	2.7	1.4	0.5	1.1	0.0	0.0	15.2
S-1	0.0	0.0	0.3	0.0	0.0	0.0	0.0	1.5	0.0	0.0	0.0	0.0	1.9
S-2	0.0	0.0	0.0	0.0	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.1

Table 5.6 Glass Composition of Fly Ashes.

I.D.	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Other	Sum
A-1	1.57	36.16	20.62	6.22	0.00	1.24	12.1	65.8
A-2	9.55	37.22	13.37	5.33	1.66	0.90	8.7	68.0
A-3	6.97	36.73	11.72	4.33	0.81	0.26	13.5	60.8
A-4	7.58	43.54	13.81	2.32	1.05	0.50	13.0	68.8
A-5	4.20	33.97	13.63	4.30	0.10	0.40	18.3	56.6
A-6	7.69	35.78	17.18	6.45	0.00	0.61	15.4	67.7
A-7	7.96	38.30	13.74	4.69	0.00	0.71	12.9	65.4
A-8	3.48	32.50	10.22	2.84	0.00	0.42	20.8	49.5
A-9	9.93	32.74	17.16	4.66	1.58	0.28	15.4	66.4
A-10	18.81	29.19	21.37	4.35	2.39	1.26	7.4	77.4
A-11	-	-	-	-	-	-	-	-
A-12	-	-	-	-	-	-	-	-
A-13	-	-	-	-	-	-	-	-
A-14	-	-	-	-	-	-	-	-
B-1	21.68	21.86	21.83	0.00	3.02	1.70	0.71	70.1
B-2	22.63	29.23	21.18	3.30	2.70	1.82	3.7	80.9
B-3	19.07	26.95	19.21	1.89	2.16	1.45	7.6	70.7
B-4	24.06	24.54	18.53	0.87	2.38	1.54	2.1	71.9
B-5	23.19	24.34	19.57	3.03	2.07	1.63	6.1	73.8
B-6	25.28	23.54	18.34	0.80	2.01	1.26	2.2	71.2
B-7	18.97	19.88	19.47	1.80	0.43	4.66	3.7	65.2
B-8	25.39	18.06	17.55	1.04	1.89	3.03	0.0	67.0
B-9	-	-	-	-	-	-	-	-
B-10	-	-	-	-	-	-	-	-
S-1	0.11	91.70	3.00	0.05	0.00	1.24	0.0	94.9
S-2	40.21	35.61	9.04	0.44	7.88	3.01	0.0	93.1



CaO • Al2O3 • SiO2 ternary oxide system diagram.

Figure 5.10 Fly ash normalized glass composition.

glassy phase of this fly ash was the highest of all the fly ashes analyzed. However this fly ash failed to meet the ASTM C 618 requirement for amount passing the #325 sieve. The silica to calcium oxide ratio (S/C) in the glassy phase of fly ash A-4 was 5.7, resulting in a glass within the mullite field.

5.5.5 Fly Ash A-5. Fly ash A-5 was derived from a western bituminous coal. It had the typical composition of bituminous coal fly ash. The major crystalline phases were mullite, 15.0 percent, and quartz, 9.1 percent. The silica to calcium oxide ratio (S/C) in the glassy phase of fly ash A-5 was 8.1, resulting in a glass within the mullite field.

5.5.6 Fly Ash A-6. This fly ash was a result of burning low calcium subbituminous coal from a Colorado basin. The fly ash had a low magnesium oxide content, a 45 percent silica content and contained 23.6 percent alumina. Mullite and quartz were the dominant crystalline phases in fly ash A-6 at 8.9 and 6.7 percent respectively. The silica to calcium oxide ratio (S/C) in the glassy phase of fly ash A-5 was 4.6, resulting in a mullite field glass.

5.5.7 Fly Ash A-7. Fly ash A-7 was derived from a western bituminous coal. For a bituminous coal fly ash, fly ash A-7 had a high calcium oxide content and a low alumina content. The chemical composition was closer to that of a southern lignite fly ash than a bituminous fly ash. The major crystalline phases were quartz and mullite at 10.5 and 6.4 percent respectively. The presence of periclase indicated that the bulk MgO content may have been incorrectly reported. The pozzolanic activity and the amount of fly ash A-7 passing the #325 sieve were below the ASTM C 618 standards. The silica to calcium oxide ratio (S/C) in the glassy phase of fly ash A-7 is 4.8, resulting in a mullite field glass.

5.5.8 Fly Ash A-8. Fly ash A-8 was derived from a western bituminous coal. It had the typical composition of bituminous coal fly ash, with the exception of small amounts of periclase and lime. The major crystalline phases were mullite, 19.5 percent, and quartz, 8.7 percent. This fly ash contained the largest amount of mullite of any of the fly ashes studied. The silica to calcium oxide ratio (S/C) in the glassy phase in fly ash A-8 was 9.3, resulting in a glass within the mullite field.

5.5.9 Fly Ash A-9. This fly ash was derived from a southern lignite coal. It had the typical composition of a Texas lignite fly ash. Mullite and quartz were the major crystalline phases at 10.1 and 7.3 percent respectively. The alumina content in this fly ash was relatively high for a Texas lignite. This was the only fly ash in this study which was not commercially available. The silica to calcium oxide ratio (S/C) in the glassy phase in fly ash A-9 was 3.3, resulting in a glass within the mullite field.

5.5.10 Fly Ash A-10. This fly ash was formed as a result of burning subbituminous coal. It had the typical composition of high calcium subbituminous coal fly ash, i.e. calcium oxide content greater than 22 percent, alumina content between 20 and 24 percent, silica content less than 38 percent, and magnesium oxide and sulfur trioxide contents greater than 2 percent. Fly ash A-10 also contained the numerous crystalline phases found in the subbituminous coal fly ash. This fly ash was the only subbituminous coal fly ash with greater than 20 percent calcium oxide to meet the chemical and physical requirements of Texas SDHPT D-9-9800 Type A fly ash. None of the crystalline phases were present in amounts greater than 4 percent of the total fly ash composition. The alumina content of the glass phase was one of the highest of the fly ashes studied. Fly ash A-10 also had a high glass content when compared to the other fly ashes. The silica to calcium oxide ratio (S/C) in the glassy phase in fly ash A-10 was 1.6, resulting in an anorthite field glass.

5.5.11 Fly Ash A-11. This fly ash was produced from a northern lignite coal. It had the typical composition of North Dakota lignite coal fly ash, i.e. calcium oxide content between 16 and 25 percent, and alumina content less than 16 percent. Its major crystalline phases were ferrite spinel and quartz at 3.9 and 2.6 percent respectively. The silica to calcium oxide ratio (S/C) in the glassy phase of fly ash A-11 was 2.2, resulting in an anorthite field glass.

5.5.12 Fly Ash A-12. This fly ash was produced from a saskatchewan lignite coal. It has the highest glass content of any fly ash in this study. Fly ash A-12 had a Blaine fineness of 2340 cm^2/g, and contained 3.14 percent available alkalis. Its major crystalline phase was quartz at 5.7 percent. The silica to calcium oxide ratio (S/C) in the glassy phase of fly ash A-12 was 3.3, resulting in an anorthite field glass.

5.5.13 Fly Ash A-13. This fly ash was formed as a result of burning Montana subbituminous coal. Fly ash A-13 had a Blaine fineness of 4160 cm^2/g. Its major crystalline phases were mullite and quartz at 11.0 and 10.3 percent respectively. The silica to calcium oxide ratio (S/C) in the glassy phase of fly ash A-13 was 2.3, resulting in an anorthite field glass.

5.5.14 Fly Ash A-14. Fly ash A-14 was derived from a bituminous coal. It had the typical composition of high iron oxide bituminous coal fly ash. Fly ash A-14 had a Blaine fineness of 2360 cm^2/g. Its major crystalline phases were mullite and ferrite spinel at 7.3 and 7.8 percent respectively. The silica to calcium oxide ratio (S/C) in the glassy phase of fly ash A-14 was 46.3, resulting in an mullite field glass.

5.5.15 Fly Ash B-1. This fly ash resulted from the burning of subbituminous coal. It had the typical composition of high calcium subbituminous coal fly ash. Fly ash B-1 also contained the numerous crystalline phases found in a subbituminous coal fly ash. The major crystalline phase was quartz at 11.4 percent. This fly ash had 29.2 percent crystalline phases. The silica to calcium oxide ratio (S/C) in the glassy phase in fly ash B-1 was 1.0, resulting in a gehlenite field glass.

5.5.16 Fly Ash B-2. This fly ash was formed as a result of burning subbituminous coal. It had the typical composition of high calcium subbituminous coal fly ash. Fly ash B-2 also contained the numerous crystalline phases found in the subbituminous coal fly ash. The major crystalline phases were quartz at 11.4 percent and melilite at 3.5 percent. This fly ash had 15 percent crystalline phases making it the least crystalline fly ash in this study. It also had the highest available alkalis of any of the fly ashes. The silica to calcium oxide ratio (S/C) in the glassy phase in fly ash B-2 was 1.3, resulting in an anorthite field glass.

5.5.17 Fly Ash B-3. This fly ash was formed as a result of burning subbituminous coal. It had the typical composition of high calcium subbituminous coal fly ash. The major crystalline phase was quartz at 6.2 percent. The silica to calcium oxide ratio (S/C) in the glassy phase in fly ash B-3 was 1.4, resulting in an anorthite field glass.

5.5.18 Fly Ash B-4. This fly ash was formed as a result of burning subbituminous coal. It had the typical composition of high calcium subbituminous coal fly ash. The major crystalline phase was quartz at 5.0 percent. The silica to calcium oxide ratio (S/C) in the glassy phase in fly ash B-4 was 1.0, resulting in a gehlenite field glass.

5.5.19 Fly Ash B-5. This fly ash was formed as a result of burning subbituminous coal. It had the typical composition of high calcium subbituminous coal fly ash. The major crystalline phase was quartz at 4.3 percent. The silica to calcium oxide ratio (S/C) in the glassy phase in fly ash B-5 was 1.0, resulting in a gehlenite field glass.

5.5.20 Fly Ash B-6. Fly ash B-6 was formed as a result of burning subbituminous coal. It had the typical composition of high calcium subbituminous coal fly ash. The major crystalline phase was quartz at 4.7 percent. The silica to calcium oxide ratio (S/C) in the glassy phase in fly ash B-6 was 0.9, resulting in a gehlenite field glass.

5.5.21 Fly Ash B-7. This fly ash was formed as a result of burning subbituminous coal. It had the typical composition of high calcium subbituminous coal fly ash, with the exceptions of containing sodium sulfate. The major crystalline phases were merwinite at 10.8 percent, and sodium sulfate at 3.7 percent. This fly ash was high in available alkalis. The silica to calcium oxide ratio (S/C) in the glassy phase in fly ash B-7 was 1.0, resulting in a gehlenite field glass.

5.5.22 Fly Ash B-8. This fly ash was formed as a result of burning subbituminous coal. It had the typical composition of high calcium subbituminous coal fly ash. The major crystalline phases were quartz, merwinite, periclase, and hematite at 6.6, 5.6, 5.4, and 3.9 percent, respectively. The silica to calcium oxide ratio (S/C) in the glassy phase in fly ash B-8 was 0.7, resulting in an gehlenite field glass.

5.5.23 Fly Ash B-9. This fly ash was formed as a result of burning subbituminous coal. It had the typical composition of high calcium subbituminous coal fly ash. The major crystalline phase was quartz at 8.7 percent. The silica to calcium oxide ratio (S/C) in the glassy phase in fly ash B-9 was 1.6, resulting in an anorthite field glass.

5.5.24 Fly Ash B-10. This fly ash was formed as a result of burning subbituminous coal. It had the typical composition of high calcium subbituminous coal fly ash. The major crystalline phase was melilite at 3.9 percent. The silica to calcium oxide ratio (S/C) in the glassy phase in fly ash B-10 was 1.4, resulting in a anorthite field glass.

5.5.25 Pozzolan S-1. Pozzolan S-1 was a silica fume from a silicon manufacturing facility. Its composition was largely reactive silica glass. This pozzolan was too fine to measure with the Blaine test. The glassy phase of pozzolan S-1 was in the cristobalite field of the ternary diagram.

5.5.26 Pozzolan S-2. Pozzolan S-2 was a blast furnace slag. It had a Blaine fineness of 5640 cm^2/g and a calcium oxide content of 41.3 percent. Pozzolan S-2 contained mostly reactive calcium silica glass.

5.6 Summary Fly Ash Characterization

The fly ashes described in the previous section can be characterized in a hierarchy with respect to the complexity of their mineralogical composition. The fly ashes having a low calcium oxide content and silica contents greater than 45 percent have relatively simple mineralogical compositions. The major crystalline phases in these fly ashes were mullite and quartz, with lesser amounts of hematite and ferrite spinel. These four phases contain no alkalis or calcium and were nonreactive. As the calcium content of the fly ash increased to about 10 percent, small amounts of anhydrite and crystalline lime were formed.

A second group of fly ashes consisted of those containing less than 22 percent calcium oxide and silica contents greater than 38 percent. These fly ashes contained greater amounts of calcium rich phases such as, anhydrite, lime, melilite, tricalcium aluminate and merwinite. Mullite and quartz remained the two major phases in these fly ashes.

The third group of fly ashes consisted of the high calcium fly ash, i.e. greater than 22 percent calcium fly ash. These fly ashes typically had silica contents less than 38 percent, sulfur trioxide contents over 2 percent, and greater quantities of magnesium oxide. The crystalline phases in these fly ashes consisted of calcium-rich phases as well as alkali phases and the phases found in low calcium fly ash.

The relative quantities of ferrite spinel and hematite depend upon the amount of iron present in the fly ash. Large quantities of iron oxide typically diluted the silica content of the fly ash.

5.7 Review of Fly Ash Specifications

Material specifications for fly ash suitable for use in portland cement concrete have been written by many private and public agencies. These specifications vary widely in limits and extent of properties covered. Presented in Table 5.7 are the chemical and physical requirements of many codes worldwide. These specifications show two distinct categories of codes: those that recognize the use of both low and high calcium fly ashes and those that recognize the use of only one type of fly ash. The codes that place a maximum limit on CaO of less than 10 percent or a minimum limit on the sum of oxides (SiO_2 + Al_2O_3 + Fe_2O_3) at or above 70 percent are only recognizing the use of low calcium fly ash. These specifications include the India I.S. 31812 Pts. 1 & 2 (1966) and Japan J.I.S. A6201 (1967). The codes which consciously recognize both common types of fly ash are the Texas SDHPT D-9-8900 (1982), U.S.S.R. GOST 6269-63 (1963), and ASTM C 618-87 (1987). The codes of Australia and Canada do not define the material specifications in enough detail to be considered in either class of specification, but provide minimum quality standards.

In characterizing fly ashes according to categories such as ASTM Class F and Class C or Texas SDHPT Type A and B, these codes are attempting to distinguish between fly ashes with mostly pozzolanic properties and those fly ashes with both cementitious and pozzolanic properties. However the arbitrary oxide limits stated in these specifications are chosen by informed committee members. A fly ash having a sum of oxides as low as 40 percent may still enhance the quality of concrete when used in the correct proportions and fly ashes containing more than 6 percent carbon, as measured by LOI, may produce excellent concrete where air entraining agents are not required. ASTM C 618 recently dropped the 5 percent maximum MgO limit because it was based on the potential periclase expansion in portland cement. Many codes retain a five percent MgO maximum limit, assuming MgO is in the form of expansive periclase. However magnesium oxide in fly ash is present in several nonreactive forms including merwinite, melilite, and hard-burnt periclase[58].

Table 5.7 Fly Ash Specifications

	ASTM		Texas	
	F	C	A	B
SiO_2, min				
Sum Oxides, min %	70	50	65	50
CaO, max %	–	–	–	–
MgO, max %	–	–	5.0	5.0
SO_3, max %	5.0	5.0	5.0	5.0
Av. Alkali, max %	1.5	1.5	1.5	1.5
LOI, max %	6.0	6.0	3.0	3.0
M.C., max %	3.0	3.0	2.0	2.0
Fineness				
R#325, max %	34	34	30	30
Blaine(cm^2/g), min %	–	–	–	–
Autoclave, max %	0.8	0.8		
Pozz. Activity, min %	75	75		
Shrinkage, max %	0.03	0.03		

	Canada	Aus.	India	U.S.S.R.	Japan
SiO_2, min %	–	–	35	–	45
Sum Oxides, min %	–	–	70	40	70
CaO, max %	–	–	–	–	6.0
MgO, max %	–	–	5.0	–	5.0
SO_3, max %	3.0	2.5	3.0	3.0	5.0
Av. Alkali, max %	1.5	–	1.5	–	–
LOI, max %	12	8.0	12	10	10
M.C., max %	3.0	1.5	–	–	3.0
Fineness R#325, max %	34	50	–	–	–
Blaine(cm^2/g), min %	–	–	3200	–	2700
Autoclave, max %	0.5	–	0.8	–	0.8
Pozz. Activity, min %	85	–	–	85	–
Shrinkage, max %	0.3	–	–	–	0.15

Specifications such as the Japanese and Indian codes use limits much like those of the ASTM C 618-84 (AASHTO M295-86) Class F fly ash. In these countries, high calcium fly ashes are not available and therefore have no need for the Class C fly ash classification. However, the existence of these codes show the arbitrary nature of some specification limits. These specifications are based on the past field performance of fly ash and exclude a broad class of high quality fly ash that exists outside of the Class F specification.

Knowing the chemical and physical properties of fly ash is important in understanding how it will perform in concrete. However, there are other characteristics to be considered such as the uniformity with which the fly ash is collected, the performance of the fly ash in the laboratory and field with different portland cements, and the mineralogical composition of the fly ash.

5.8 Revised Method of Fly Ash Classification

The present specifications for fly ash are difficult to justify on the basis of available technical knowledge. The chemical limitations are based on historic applications of bituminous coal fly ash with a recent addition of a class to include the high calcium fly ashes from western coal sources.

Often imposed are specification limitations for both MgO and SO_3 based on the premise that large quantities of either may result in unsoundness in concrete. The presence of these compounds in large quantities, as crystalline periclase (MgO) or anhydrite ($CaSO_4$), has not been shown to cause unsoundness. These limitations are based on the crystalline phases found in the portland cement. Dunstan reports fly ashes with MgO contents of 11.3, 8.1, and 6.4; Demiril reports MgO contents of 7.7, and 6.2; Manz reports MgO contents of 7.6, 7.2, and 6.1; EPRI reports a MgO content of 6.7; Mehta reports MgO contents of 7.9, and 7.6; and this author reports fly ashes with MgO contents of 8.41, and 6.1. None of these fly ashes failed an autoclave expansion test. In addition, blast furnace slags have been shown to contain 16 percent MgO before periclase forms. Similarly, the presence of SO_3 does not necessarily indicate unsoundness. Researchers have reported SO_3 contents of 16.6, 9.6, 8.8, 7.8, and 7.7 without an unsoundness problem [50,64]. In contrast, Manz and Mehta reported improved sulfate resistance from the use of these ashes.

A second point of dispute within the ASTM C618-87 is that it fails to distinguish chemically or physically between Class F and Class C. The specification has the older category for low calcium fly ashes, Class F, (standing for "fly ash"), and a newer special category for so called high calcium fly ashes, Class C (standing for "cementitious")[80]. However most low calcium fly ashes also meet the limitations of this second category. Therefore, low calcium fly ashes are contained by both classes and the high calcium fly ashes meet only the Class C category. The specific and most obvious difference between these fly ashes is the cementitious properties of higher calcium fly ashes. Some of the high calcium fly ashes are not just pozzolans, but also a class of portland cement. There is no chemical or physical test within ASTM C618 to define this difference.

The third point of discussion over many years is the written definition of Class C and Class F fly ash. The ASTM C618-87 document states:

> **Class F - Fly ash normally produced from burning anthracite or bituminous coal that meets the applicable requirements for this class as given herein. This class fly ash has pozzolanic properties.**

This definition is a paradox in that it is both too narrow and too broad. Fly ashes "normally" produced from lignite coal may also produce this class of ash, according to chemical and physical specifications. The word "normally" implies it would be unusual, uncommon, or atypical to produce Class F fly ashes from lignite coals. This is not the case. Manz studied the known lignite sources in North America and found that the lignites in Saskatchewan, Texas and Louisiana typically produced fly ashes meeting the chemical and physical requirements of ASTM Class F fly ash[52]. Only those lignites found in the Fort Union region, near the North Dakota - Montana border in the United States produce ASTM Class C fly ash from lignite coal. Furthermore, the last statement of the Class F definition is ambiguous, in that every material under this specification is to some degree pozzolanic, and adds nothing to the delineation of this class of fly ash from the other classes of pozzolans covered by this specification.

The fourth point to be addressed is that of the limits on the summation of silica, alumina and iron oxide in fly ash. The limits of 70 and 50 percent for

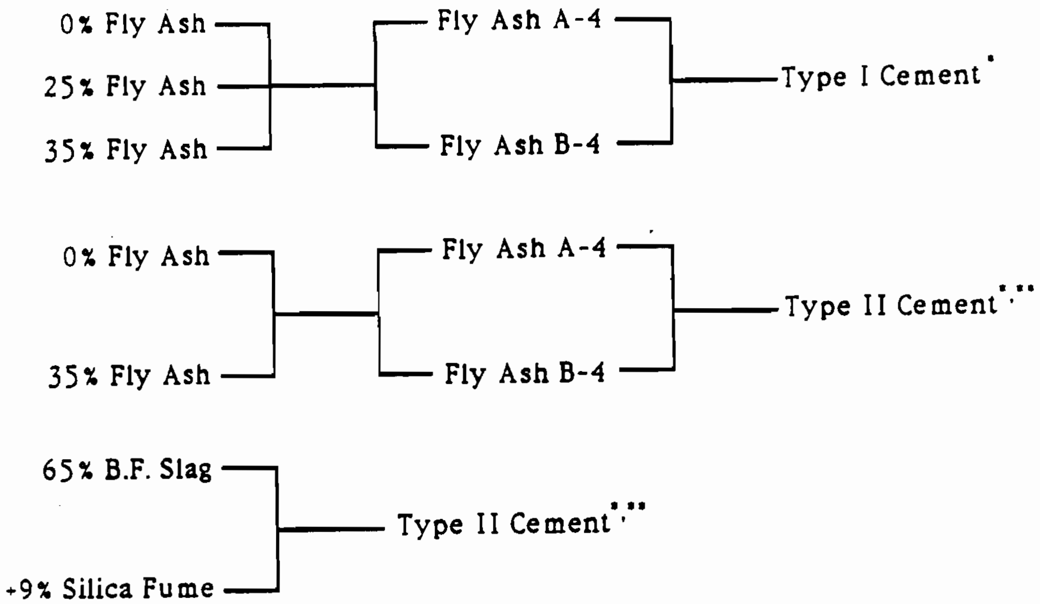
Class F and C respectively are historical but nonetheless arbitrary. The 70 percent limit has performed well over the years to ensure quality fly ash is used in concrete. In a review of the ASTM specification, Butler indicates that the ASTM chemical requirements for fly ash provides safeguards against the use of materials harmful to concrete but does not assist in developing the benefits of fly ash in concrete[9,52,53]. This same attitude is expressed by Philleo who writes, "these compositional limits could be dropped with no adverse effect on the user since all the properties intended to be controlled by these limits ... may be assured by physical tests.[80]"

The point of this discourse is that a fly ash specification would be better constructed if it relied more on the performance of the fly ash in laboratory tests, field performance records, and collection uniformity requirements. This is not to presuppose that the present chemical and physical requirements are not of value. On the contrary, these requirements are excellent measures of uniformity in fly ash composition and collection. Specifically, a 50 percent limit on the three metal oxides for both classes would better serve the industry. Similarly, a higher pozzolanic index, using portland cement rather than lime, for Class C fly ash, such as 85, or a test of initial set would aid in defining the cementitious fly ashes from those with mostly pozzolanic properties. Other possible methods of delineating cementitious properties would be to measure the pozzolanic index at 7 and 28 days or use higher fly ash contents in the test. In addition, a test for sulfate resistance could be added with a form similar to the alkali requirement, e.g. for concrete exposed to sulfates fly ashes with greater than 10 percent total CaO must pass the ASTM C1012 test for sulfate expansion. Finally, an autoclave expansion performance limit should be set and chemical limits for unsoundness set aside.

CHAPTER VI
PERMEABILITY OF CONCRETE

6.1 Permeability Testing

In this research program, the AASHTO T277 "Rapid Determination of Chloride Ion Permeability," was used to compare the permeability of normal weight concrete to similar concrete containing fly ash, silica fume and blast furnace slag. Both moist and air curing were investigated, as well as, curing time and percent replacement of cement with fly ash. Figure 6.1 shows the parameters of the permeability test program presented in this chapter.



* moist cured 10, 56, 105, 200 (± 2) Days

** air cured 28, 56, 105, 200 (± 2) Days

Figure 6.1 Permeability tests conducted using AASHTO T277.

The Type I and II cements used in this portion of the study were the same cements used in the sulfate resistance test reported herein. Fly ashes A-4 and B-4 and Pozzolan S-2, blast furnace slag, were used as volumetric replacement for the portland cement. The silica fume was used in addition to the portland cement rather than as a cement replacement and is stated as a weight percentage of the cement content. In addition to the tests listed above, fly ashes A-2, A-3, and B-8 were tested for chloride ion permeability after 100 days of moist curing. These fly ashes were used as a 25 percent volumetric replacement for portland cement.

The tests were conducted on specimens cut from 4 in. x 8 in. concrete cylinders. The top 3/4 inch was cut off to exclude the effects of concrete finishing and bleed water channels near the surface. Previous research has shown that this layer is very permeable to chloride ions[75,105]. Two specimens were then cut from the remaining cylinder. The specimens were then conditioned in a desiccator to saturate the concrete with deaerated water and sealed in acrylic cells. A solution of sodium chloride was placed in the negative cell and a sodium hydroxide solution in the positive cell before 60 volts dc potential was applied to the circuit, as per the requirements of AASHTO T277.

The data was collected as a millivolt drop across a calibrated shunt resistor using a Helios data acquisition system or 4.5 digit digital volt meter (DVM). The shunt resistor had a resistance of 10 mΩ, which can be used to calculate the amperage of the circuit using Ohm's law, expressed in equation 6.3.

$$V = I\,R \tag{6.3}$$

V = volts   I = current   R = resistance

The current integrated over time is equal to the coulombs passed through the system. As illustrated in Figure 6.2, the total number of coulombs in a six hour period is defined as the "chloride ion permeability of concrete." The results of each set of tests is presented in Appendix D.

6.1.1 Effect of Fly Ash. Fly ashes A-4 and B-4 were used as a 25 and 35 percent volumetric replacement for Type I and a 35 percent replacement for Type II portland cement in this test series. Fly ash A-4 was a low calcium-high silica fly

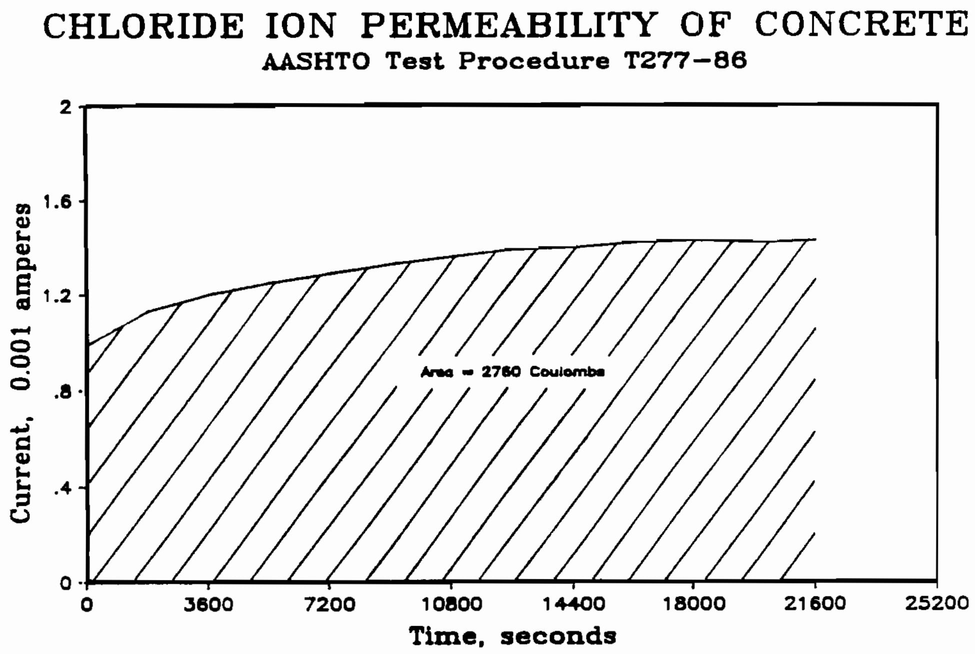


Figure 6.2 Integrated current-time function.

ash from a lignitic coal source and B-4 was a high calcium-low silica fly ash from a Wyoming subbituminous coal source. The silica to calcium oxide ratio (S/C) in the glassy portion of these ashes was 5.0 for fly ash A-4 and 1.0 for fly ash B-4.

The effect of fly ash on the chloride ion permeability of concrete was observed to be beneficial at test ages greater than 10 days. At early ages, concrete containing fly ash as well as concrete without fly ash was generally found to be highly permeable to chloride ions. Figures 6.3 and 6.4 show the behavior of the chloride ion permeability of concrete containing fly ash. The 10 day ion permeability exceeded 8000 coulombs for all the concrete tested. At this high level of permeability capillary flow will control the influx of aggressive agents. At later ages, the chloride ion permeability is greatly reduced due to the pore refinement of the hydrated paste structure. The chloride ion permeability of plain portland cement concrete decreased to half of the 10 day test value after 105 days of curing and remained relatively constant

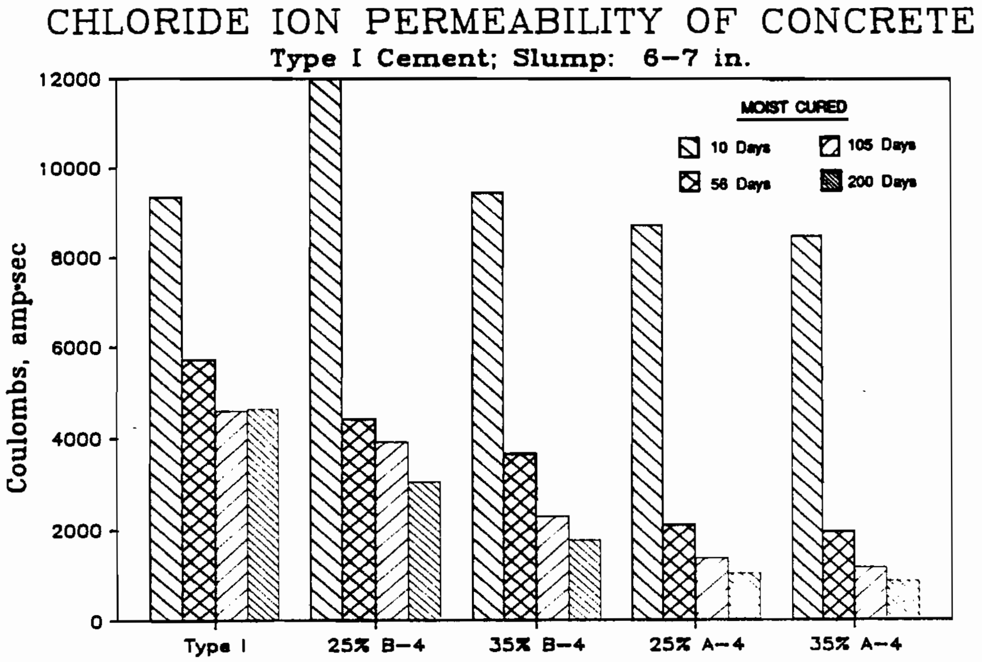


Figure 6.3 Chloride ion permeability of concrete containing Type I cement.

thereafter. This indicates that the pore structure of plain portland cement concrete was established to a large extent after 100 days of moist curing.

The chloride ion permeability of concrete containing fly ash continued to decrease throughout the first 200 days of moist curing. Concrete containing fly ash A-4 decreased in chloride ion permeability eightfold between 10 and 200 days. In addition, concrete containing fly ash A-4 had a chloride ion permeability at 200 days of 1/4 that of the portland cement control mixtures. Concrete containing fly ash B-4 decreased in chloride ion permeability fourfold between 10 and 200 days. These concrete mixtures had 200 day chloride ion permeability between 2/5 and 2/3 that of the portland cement control. For the three additional fly ashes tested at 105 days for chloride ion permeability, each concrete mixture containing fly ash had a permeability less than that of the control without fly ash, as shown in Figure 6.5.

In all cases the concrete containing fly ash was less permeable after 60, 105, and 200 days of moist curing than concrete without fly ash. The greatest reductions occurred in concrete containing low calcium-high silica fly ash at a 35 percent volumetric replacement level.

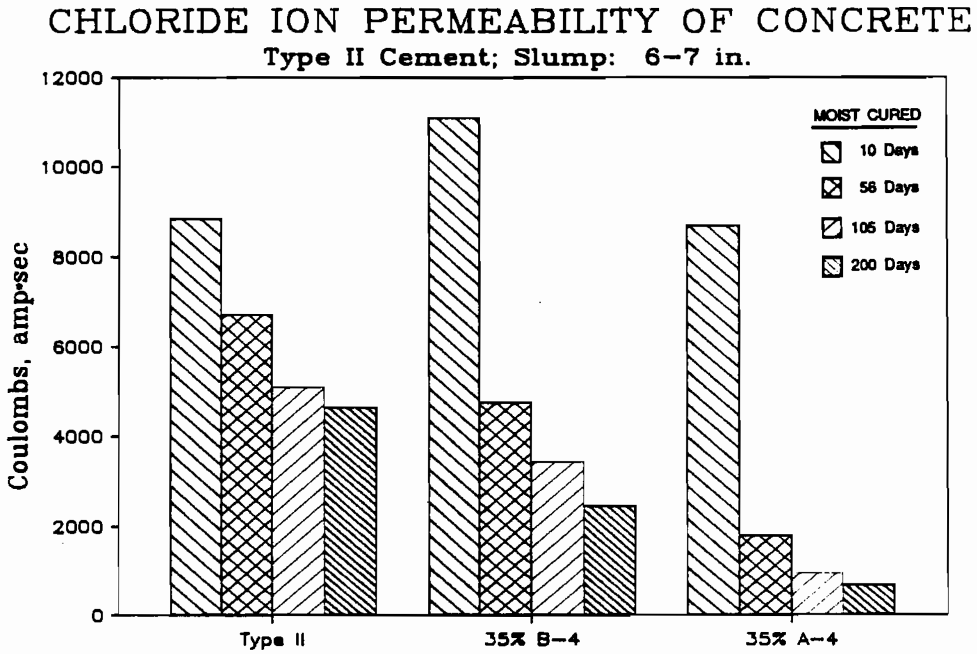


Figure 6.4 Chloride ion permeability of concrete containing Type II cement.

The cause of the reduced chloride ion permeability of the concrete containing fly ash was largely due to the pozzolanic nature of the fly ash. The slow dissolution of the silicate glasses to form calcium silicate hydrate benefited the concrete permeability in two ways:

1) the pozzolanic reaction of fly ash consumed the calcium hydroxide which resulted from the portland cement hydration process, and

2) the long term formation of calcium silicate hydrate provided the cement paste with a refined pore structure which was more resistant to the diffusion of chloride ions.

The consumption of the calcium hydroxide reduces the amount of leaching which may occur during wetting and drying cycles and reduces the damage associated with carbonation, both of which can lead to increased chloride ion permeability. The reduction in calcium hydroxide from the pozzolanic hydration within concrete is also beneficial to the sulfate resistance of the concrete, in that sulfate attack cannot occur without the availability of free calcium.

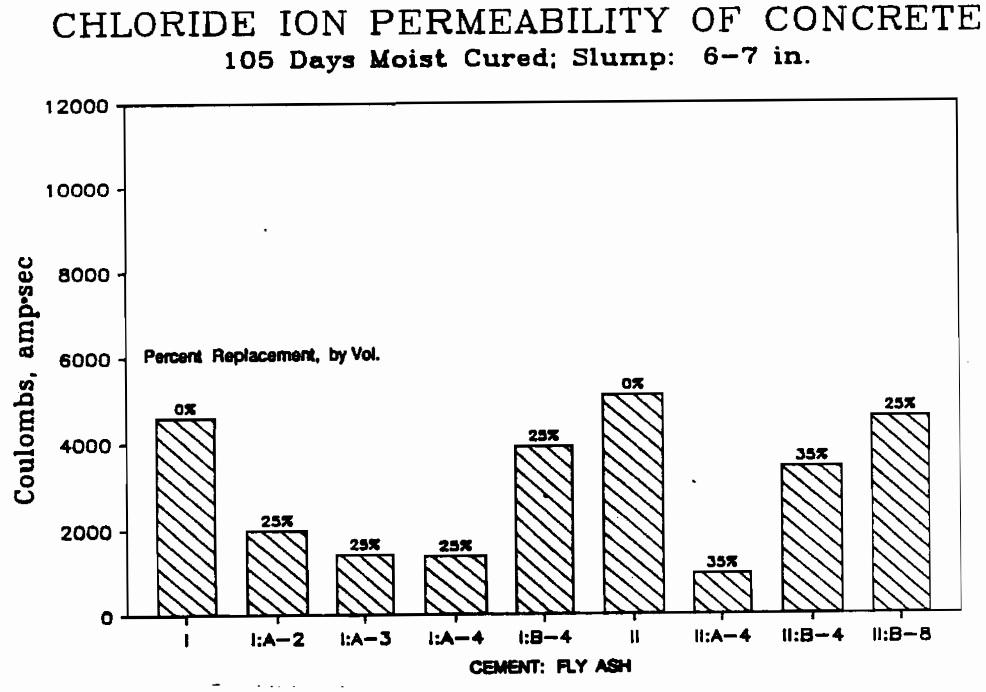


Figure 6.5 Chloride ion permeability of concrete containing fly ash.

Concretes containing silica fume, S-1, and blast furnace slag, S-2, were also investigated for their effect on chloride ion permeability. Figure 6.6 shows the relationship of these pozzolans as compared to concrete containing fly ash and concrete without fly ash. Both the silica fume and the blast furnace slag greatly reduced the chloride ion permeability at early ages as well as at later ages. The high fineness of both of these pozzolans provided additional pore refinement and nucleation sites for the C-S-H binder.

The chloride ion permeability of concrete containing silica fume did not substantially change between 60 and 200 days of moist curing. The silica fume may have consumed the available calcium hydroxide from the paste, preventing further hydration and subsequent additional pore refinement. The blast furnace slag showed a continued reduction of the chloride ion permeability through the 200 day test. Although permeability of concrete containing low calcium-high silica fly ashes deceased at a faster rate and at later ages to a lower value, the pozzolans S-1 and S-2 reduced the permeability below that of either of the high calcium-low silica fly ashes.

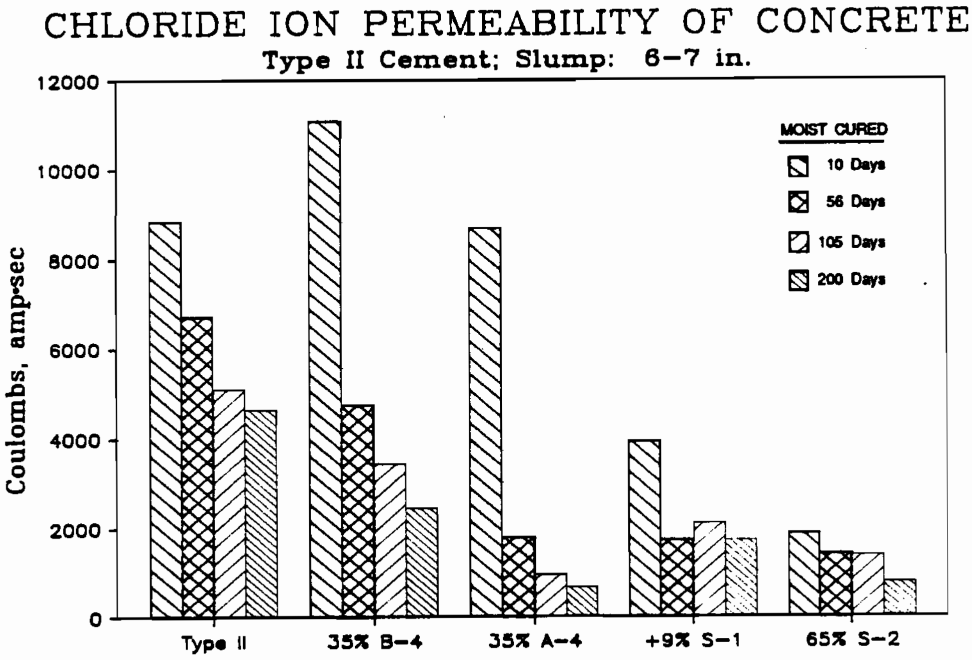


Figure 6.6 Chloride ion permeability of concrete containing pozzolans.

The silica fume will further reduce the chloride ion permeability of concrete when used with water reducing and superplasticizing admixtures. These admixtures reduce the effect of the high water demand of this extremely finely divided material. The test program reported herein proportioned concrete on an equal slump basis which required a W/C ratio of 0.62 for the concrete containing silica fume, whereas the control concrete had a W/C ratio of 0.53. On an equal water basis the silica fume concrete would consistantly produce an estimated cloride ion permeability less than 1000 coulombs at 28 days.

6.1.2 Effect of Curing. The effect of curing conditions was studied by comparing the moist cured at 100 percent relative humidity (73°F) specimens to that of specimens which were air cured at 50 percent relative humidity (73°F). The air cured specimens were stored in plastic molds with both the top and bottom surfaces exposed to simulate the conditions of an eight inch concrete slab. The typical difference in chloride ion permeability between moist and air cured specimens is

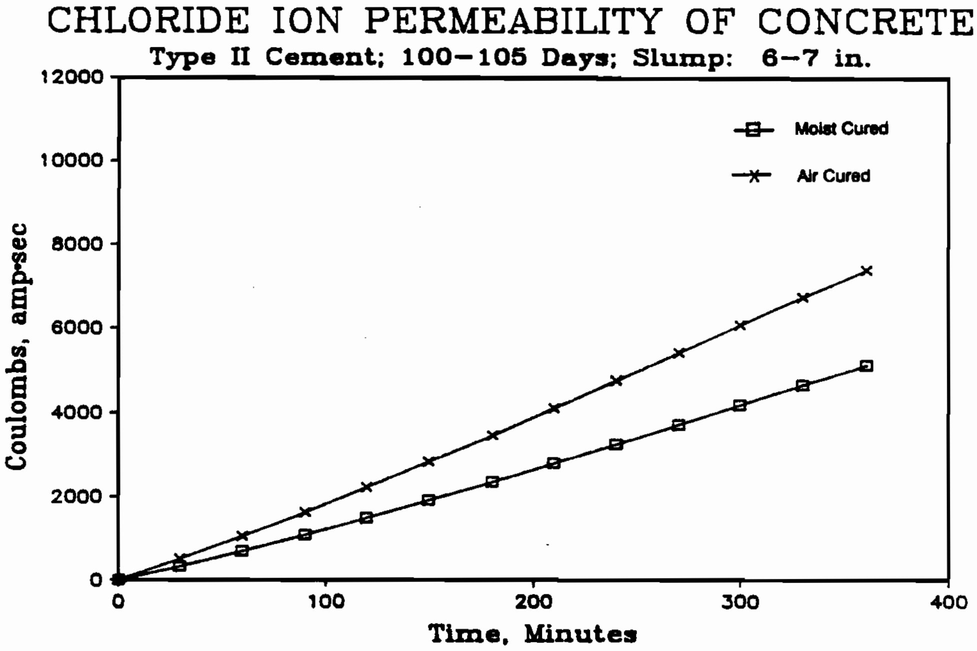


Figure 6.7 Comparison of the permeability of moist and air cured concrete.

shown in Figure 6.7. The air cured specimens had a greater chloride ion permeability than the moist cured specimens.

A summary of the chloride ion permeability of the air cured specimens is presented in Figure 6.8. Air cured concrete containing silica fume and blast furnace slag had chloride ion permeabilities less than 1/3 that of plain portland cement concrete at all test ages. Air cured concrete containing fly ash B-4 had a chloride ion permeability less than the control concrete at all test ages except 28 days. Air cured concrete containing fly ash A-4 had a chloride ion permeability lower than the control concrete at all test ages. The use of fly ash A-4 in air cured concrete decreased the chloride ion permeability to 1/2 that of the portland cement control concrete at ages of 105 and 200 days. The chloride ion permeability of air cured concrete did not substantially decrease after 56 days with the exception of concrete containing fly ash A-4. Air cured concrete containing fly ash A-4 showed a gradual decrease in chloride ion permeability between 28 and 200 days.

Figures 6.9 and 6.10 show comparisons between the air cured and moist cured specimens. The benefits of moist curing portland cement concrete were realized

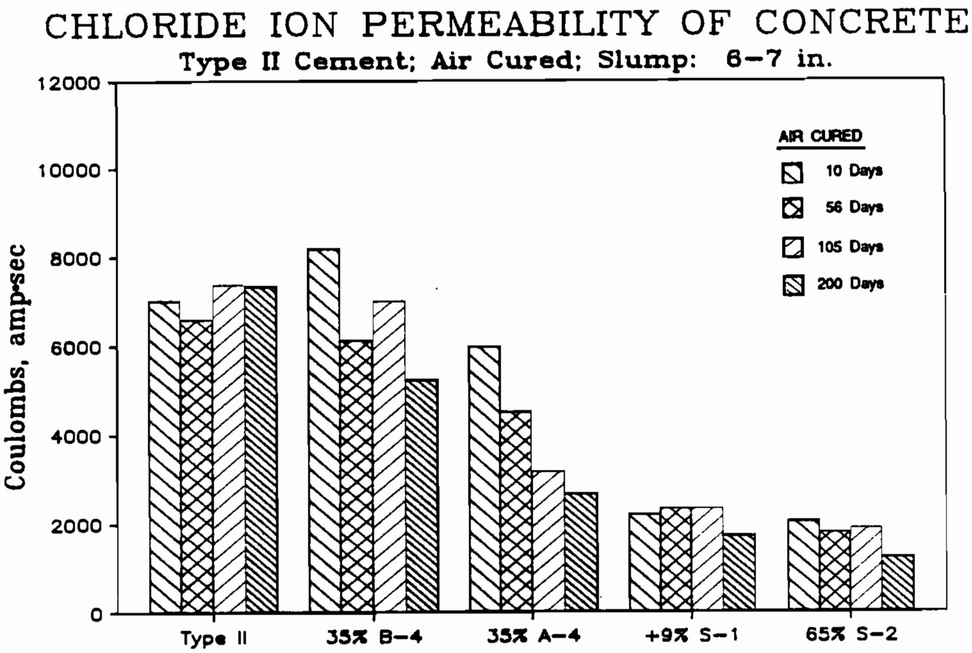


Figure 6.8 Chloride ion permeability of air cured concrete.

between 56 and 100 days, after which time the permeability remained relatively unchanged. This is not the case with concrete containing fly ash. The benefits of moist curing concrete containing fly ash were evident at 56 days and became more pronounced with time. The chloride ion permeability of concrete containing silica fume and blast furnace slag was slightly increased by moist curing at early ages. These pozzolans effectively sealed in the pore water of the air cured specimens creating a near moist cured condition.

6.2 Summary

The results presented herein were based on concrete with a cement content of 5.5 sacks per cubic yard and nominal 6 inch slump. For normal strength concrete, the low calcium-high silica fly ash was the most effective means in this study of reducing chloride ion permeability over a long period of time. The benefits of this fly ash were amplified by the use of moist curing. At ages less than 28 days, the low calcium-high silica fly ash provided a chloride ion permeability equal to that of concrete containing no fly ash.

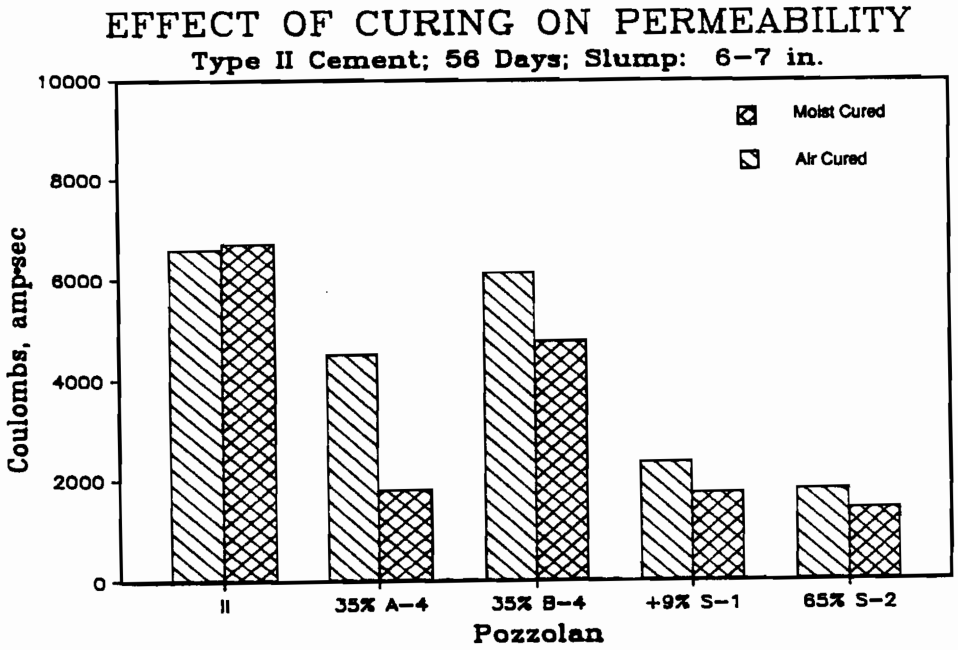


Figure 6.9 Comparison of 56-day permeability of concrete containing pozzolans.

Concrete containing high calcium-low silica fly ash exhibited high permeability at ages less than 10 days. However this is the time period when capillary flow is typically the dominant means of transport. The permeability of concrete containing high calcium-low silica fly ash can be reduced well below that of ordinary portland cement concrete by providing moist curing.

Silica fume and blast furnace slag greatly reduced the chloride ion permeability of concrete. This was primarily due to the increased fineness of the pozzolans. The silica fume and slag particles acted as nuclei for calcium silicate hydrate crystals. The increased number of nuclei provided a high degree of pore refinement throughout the paste structure. This effect and the others discussed in this section would be amplified by a reduction in water content or an increased cementitious material content[105]. Both of these factors increase the density of the cementitious paste and improve the binding structure of cement.

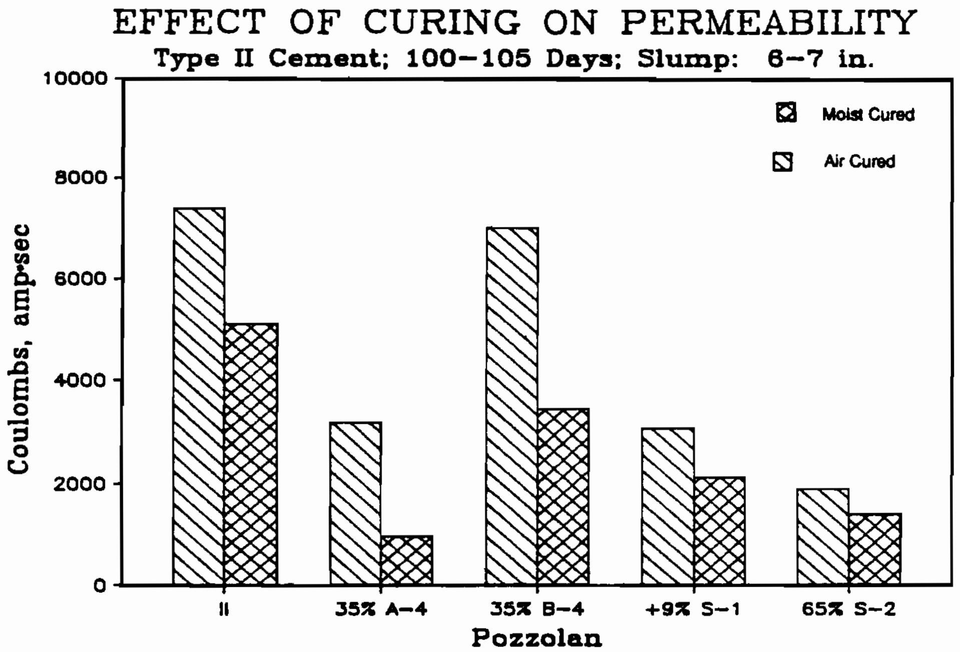


Figure 6.10 Comparison of 105-day permeability of concrete containing pozzolans.

CHAPTER VII
RESULTS OF CONCRETE TESTING

7.1 Introduction

The test results presented herein were compiled from standardized tests performed on over 2000 concrete specimens from 152 concrete mixtures over a three year period. The results presented in this chapter will be discussed in detail in Chapter 8.

The variables studied in this experimental program were fly ash content, slump, fly ash composition, cement type, air content, curing time, and admixture addition. The test data are presented in sections 7.3, and 7.4, and Appendices B and E. Section 7.3 and Appendix B present the compressive strength and fresh concrete characteristics as well as the mixture numbering system and proportions. Section 7.4 and Appendix E are devoted to presenting data on the sulfate resistance of concrete.

7.2 Experimental Outline and Overview

The experimental program has been divided in four phases, each building on the results of previous phases. Phase I was devoted to determining the effect of fly ash on the sulfate resistance of concrete. In this phase, the fly ash was used as a volumetric replacement for Type II, moderate sulfate resistant cement. Phase II investigated the effect of fly ash on the sulfate resistance of Type I cement and 0 percent C_3A portland cement; and on correlating the sulfate resistance of concrete with the chemical and mineralogical composition of the fly ash. Phase III of the program is in progress and is investigating the effectiveness of additives and blending procedures on the sulfate resistance of concrete containing fly ash. Phase IV will be a field evaluation of the sulfate resistance of concrete containing fly ash (funding under consideration). This chapter and the succeeding chapter are the presentation and discussion of the data from the first two phases of this study.

Table 7.1 outlines the concrete mixtures cast for sulfate exposure in Phases I and II. In these phases, there were 18 fly ashes and two other pozzolans used in combination with Type II cement; 10 of the 18 fly ashes and both pozzolans were

Table 7.1 Listing of sulfate exposure mixtures.

CEMENT	FLY ASH	PERCENT, vol.	SLUMP, in.	COMMENTS
TYPE II		0	6	
		0	2	
	A-2	25, 35, 45	6	
		25, 35, 45	2	
	A-3	25, 35, 45	6	
		25, 35, 45	2	
	A-10	25, 35, 45	6	
		25, 35, 45	2	
	B-1	25, 35, 45	6	
		25, 35, 45	2	
	B-3	25, 35, 45	6	
		25, 35, 45	2	
	B-5	25, 35, 45	6	
		25, 35, 45	2	
	B-6	25, 35, 45	6	
		25, 35, 45	2	
	B-8	25, 35, 45	6	
		25, 35, 45	2	
TYPE V		0	6	
		0	2	
TYPE 02		0	6	
TYPE 01		0	6	
		0	2	
TYPE II	A-1	35	6	
	A-4	35	6	
	A-5	35	6	
	A-6	35	6	
	A-7	25, 45	6	
	A-8	25, 45	6	
	A-9	25, 45	6	
	B-2	25, 35	6	

Table 7.1 Listing of sulfate exposure mixtures (continued)

CEMENT	FLY ASH	PERCENT, vol.	SLUMP, in.	COMMENTS
TYPE II	B-4	25, 35, 45	6	
	B-7	35	6	
	S-1	9[a]	6	
	S-2	65	6	
TYPE V	B-3	35	6	
TYPE II		0	6	WATERPROOF ADMIXTURE
	B-3	35	6	WATERPROOF ADMIXTURE
	B-4	25	6	SEAWATER
	B-8	35	6	SEAWATER
TYPE 02	A-1	35	6	
	A-2	35	6	
	B-3	35	6	
	B-5	35	6	
	B-6	35	6	
	B-8	35	6	
TYPE II		0	6	5 % AIR
	B-3	35	6	5 % AIR
	B-5	35	6	5 % AIR
	B-6	35	6	5 % AIR
	B-8	35	6	5 % AIR
TYPE I		0	6	
	A-2	25	6	
	A-3	25, 35	6	
	A-4	25	6	
	A-5	25	6	
	A-6	25	6	
	A-10	25, 35	6	
	B-1	25	6	
	B-3	25, 35	6	
	B-4	25, 35	6	
	B-5	25	6	
	S-1	9[a]	6	
	S-2	65	6	

[a] Used in addition to cement.

Table 7.1 Listing of sulfate exposure mixtures (continued).

CEMENT	FLY ASH	PERCENT, vol.	SLUMP, in.	COMMENTS
TYPE II		0	2	3 Day Moist Cure
	A-2	25, 35	2	3 Day Moist Cure
	A-3	25	2	3 Day Moist Cure
	A-10	25[b], 35	2	3 Day Moist Cure
	A-10	25	2	28 Day Moist Cure
	B-1	25	2	3 Day Moist Cure
	B-3	25[b], 35, 45	2	3 Day Moist Cure
	B-3	25	2	28 Day Moist Cure
	B-5	25[b], 35	2	3 Day Moist Cure
	B-5	25	2	28 Day Moist Cure
	B-5	35	6	3 Day Moist Cure
	B-6	25[b], 35	2	3 Day Moist Cure
	B-6	25	2	28 Day Moist Cure
	B-8	25[b]	2	3 Day Moist Cure
	B-8	25	2	28 Day Moist Cure
	B-8	35	6	3 Day Moist Cure
TYPE II		0	6	Repeated twice
		0	2	Repeated twice
		0	6	6 sks/yd3, twice
		0	2	6 sks/yd3, twice
		0	6	7 % Air
		0	6	9 % Air
	B-3	35	2	Repeated
	B-6	35	2	Repeated
	B-8	25	2, 6	Repeated
	B-8	35	6	Repeated

[b] Also the 3500 psi sulfate exposure mixture.

also used in combination with Type I cement; and six of the 18 fly ashes were used as volumetric replacements for the 0 percent C_3A cement 02. The parameters studied were fly ash composition, cement type, level of cement replacement, slump, air content, curing time. The Type II portland cement concrete mixture that was used as the control and standard for moderate sulfate resistance was repeated several times during the study to verify its performance. This control was repeated at both 2 and 6 inch slumps. A 5.5 sack cement factor was used throughout the study.

The effect of fly ash composition was examined using 18 fly ashes as volumetric replacements for Type II portland cement. Ten of these fly ashes were chemically classified as Texas SDHPT Type A fly ashes and eight of the fly ashes were chemically classified as Texas SDHPT Type B fly ashes. The effect of fly ash replacement percentage was investigated using 12 of the 18 fly ashes as volumetric replacements for Type II portland cement. These fly ashes included six Texas SDHPT Type A fly ashes (i.e., A-2, A-3, A-7, A-8, A-9, and A-10) and six Texas SDHPT Type B fly ashes (i.e., B-1, B-3, B-4, B-5, B-6, and B-8). The effect of slump was investigated using eight of the 18 fly ashes. Each of these fly ashes (i.e., A-2, A-3, A-10, B-1, B-3, B-5, B-6, and B-8) were used in concrete mixtures as 25, 35, and 45 percent volumetric replacements for Type II portland cement at slumps of 2 and 6 inches.

The effect of cement type on the sulfate resistance of concrete containing fly ash was examined by using 10 of the 18 fly ashes (i.e., A-2, A-3, A-4, A-5, A-6, A-10, B-1, B-3, B-4, and B-5) and both pozzolans (i.e., S-1 and S-2) as volumetric replacements for Type I and II portland cements. In addition, six of the 18 fly ashes (i.e., A-1, A-2, B-3, B-5, B-6, and B-8) were used as volumetric replacements for Type II and 0 percent C_3A cement, 02. The choice of the fly ashes to be used with the respective cements was made on the basis of their potential to combine to perform at the level of a moderate sulfate resistant cement; for example, more low calcium fly ashes were chosen to be used with Type I cement because concrete containing Type II cement and low calcium fly ash showed excellent sulfate resistance. Similarly, more high calcium fly ashes were chosen to be used with the 0 percent C_3A cement because the cement by itself was highly sulfate resistant but the high calcium fly ashes showed a tendency to reduce the sulfate resistance. Fly ashes A-2, B-3, and

B-5 were used with all three portland cements, and fly ash B-3 was also used as a volumetric replacement for Type V portland cement.

The effects of entrained air were investigated using fly ashes B-3, B-5, B-6, and B-8 as volumetric replacements for Type II cement. The concrete containing fly ash was entrained with 5 percent total air. Three Type II cement concrete mixtures containing entrained air were cast as controls. The total air contents of the controls were 5, 7, and 9 percent.

The effect of curing time was studied using eight of the 18 fly ashes (i.e., A-2, A-3, A-10, B-1, B-3, B-5, B-6, and B-8) as volumetric replacements for Type II portland cement. Concrete mixtures containing these fly ashes were cast and moist cured three days before sulfate exposure, regardless of compressive strength. Additionally, concrete mixtures containing fly ashes A-10, B-3, B-5, B-6, and B-8 were cast and moist cured 28 days before sulfate exposure testing commenced.

The effects of two other additives were surveyed to determine the potential for future research. Seawater was used as the mixing water for two concrete mixtures containing fly ash. Fly ashes B-4 and B-8 were chosen as volumetric replacements for Type II cement in these mixtures because concrete containing these fly ashes failed at early ages. A waterproofing admixture was the other additive used in concrete containing fly ash. The waterproofing admixture was used in Type II cement concrete and in concrete containing fly ash B-3 as a volumetric replacement for Type II cement.

The mixture proportions, age and compressive strength at exposure, 28 day compressive strength and sulfate exposure data of the individual concrete mixtures are catalogued in the appendices of this report according to mixture numbers 1 through 152. In the text of this chapter and in subsequent chapters of this report concrete mixtures will be identified in a descriptive notation. For example,

II:35%:A-4

denotes concrete containing fly ash A-4 as a 35 percent volumetric replacement for Type II cement. Similarly,

02:35%:B-8

denotes concrete containing fly ash B-8 as a 35 percent volumetric replacement for the 0 percent C_3A cement called 02.

7.3 Compressive Strength

The concrete used in this study was designed to have a 5.5 sack per cubic yard cement content and a minimum 28 day compressive strength of 3500 psi. The actual compressive strengths of the control mixture having a 6-7 inch slump are given in Table 7.2. Sulfate exposure testing was started when the concrete reached a minimum compressive strength of 3500 psi or at an age of 28 days, which ever was reached first. Table B-2 of Appendix B lists the age and compressive strength at which concrete specimens were first submerged in the sodium sulfate solution.

Table 7.2 28 Day Compressive Strengths of Control Mixtures.

Cement	28 day F_c[a]	Slump	W/C
Type I	4050 psi	6"	0.51
Type II	5120 psi	6"	0.53
Type II	5470 psi	2"	0.51
Type V	4520 psi	6"	0.49
Type V	4700 psi	2"	0.48
Type 01	3920 psi	6"	0.59
Type 01	4900 psi	2"	0.45
Type 02	4040 psi	6"	0.53

[a] 3 in. x6 in. compressive strength cylinders.

The compressive strength development of each concrete mixture was monitored by testing 3 in. x 6 in. moist cured concrete cylinders between the ages of 3 and 28 days. A pair of 6 in. x 12 in. concrete cylinders were cast in 47 of the concrete mixtures to verify the 28 day compressive strength. The smaller cylinders were chosen for this study because they were identical in size to the exposure specimens. There is no significant statistical difference between the two sizes of compressive

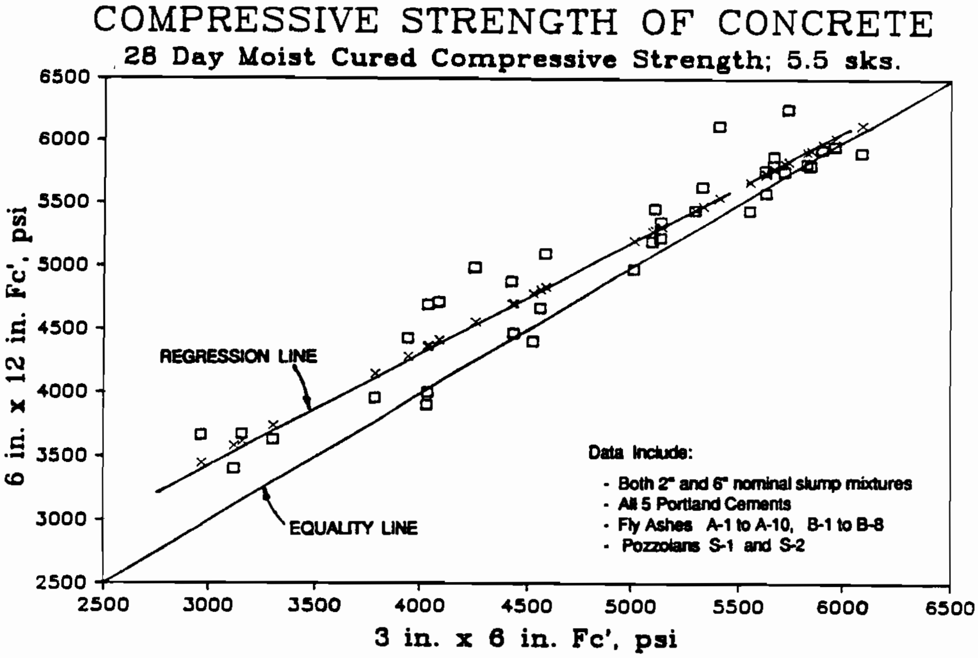


Figure 7.1 Comparison of 3 in. and 6 in. diameter compressive strength cylinders

strength cylinders[70]. The compressive strength of the 3 inch diameter cylinders in this study are shown to be a lower bound in Figure 7.1.

The remaining figures presented in this section indicate the effects of fly ash replacement on the early strength development of concrete with a nominal slump between 6 and 7 inches. The data presented are the results of compression testing 3 inch diameter cylinders. The 28 day compressive strength of all the mixtures is presented in Table B-1 of Appendix B.

There were five portland cements used in this study. The compressive strength development of these cements is presented in Figure 7.2. The Type II portland cement concrete reached the highest compressive strength of any of the control mixtures at ages between 3 and 28 days. The two 0 percent C_3A cements and the Type I cement had 28 day compressive strengths that were about 80 percent of the Type II portland cement concrete.

Figures 7.3 through 7.11 present the compressive strength development of the concrete containing low calcium fly ash. These fly ashes typically provided a

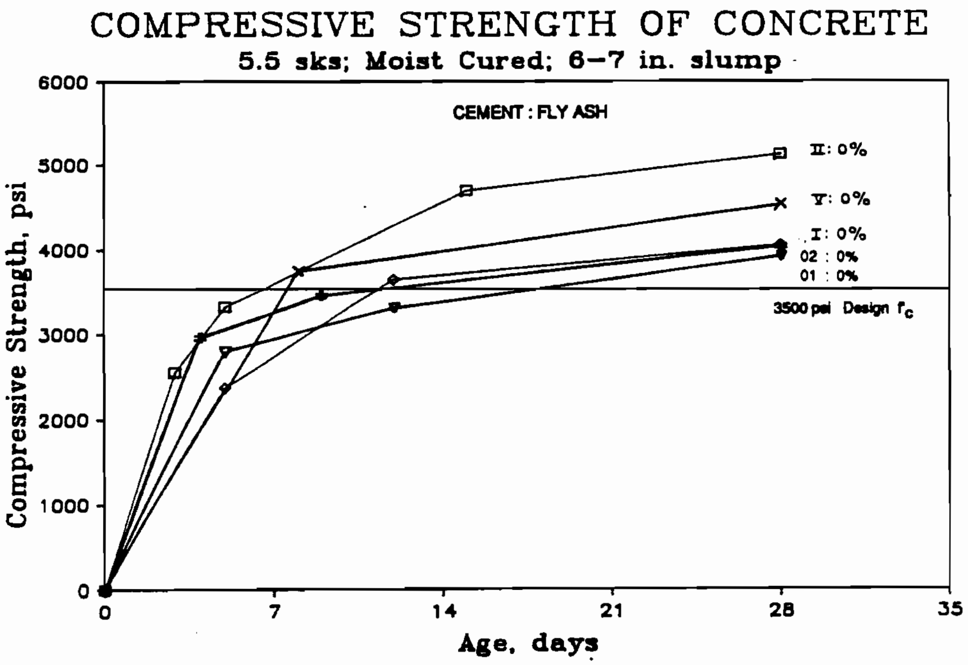


Figure 7.2 Compressive strength development of portland cement concrete.

pozzolanic contribution to the strength of concrete. The Type II cement control consistently had a higher compressive strength than any of the mixtures containing low calcium fly ash.

Figures 7.12 through 7.20 present the compressive strength development of the concrete containing high calcium fly ash. Concrete containing fly ashes A-10 and B-5 consistently had compressive strengths greater than or equal to the Type II control concrete without fly ash throughout the replacement range of 25 to 45 percent.

The compressive strength development of concrete containing pozzolans S-1 and S-2 is shown in Figures 7.21 and 7.22, respectively. The addition of silica fume, S-1, to concrete increased the compressive strength of concrete over that of the control at all ages between 3 and 28 days.

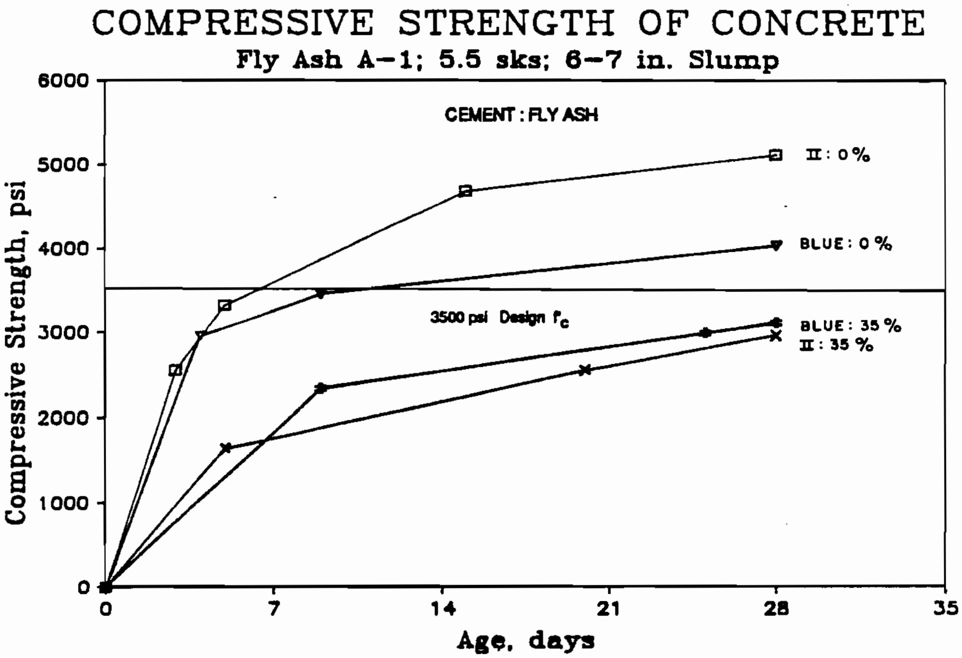


Figure 7.3 Compressive strength development of concrete containing fly ash A-1.

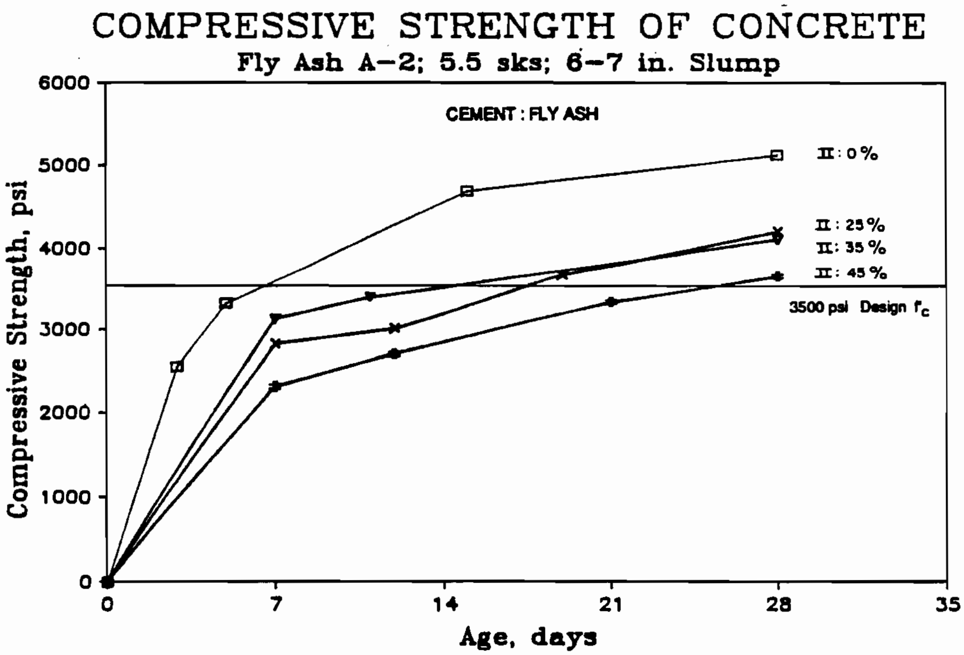


Figure 7.4 Compressive strength development of concrete containing fly ash A-2.

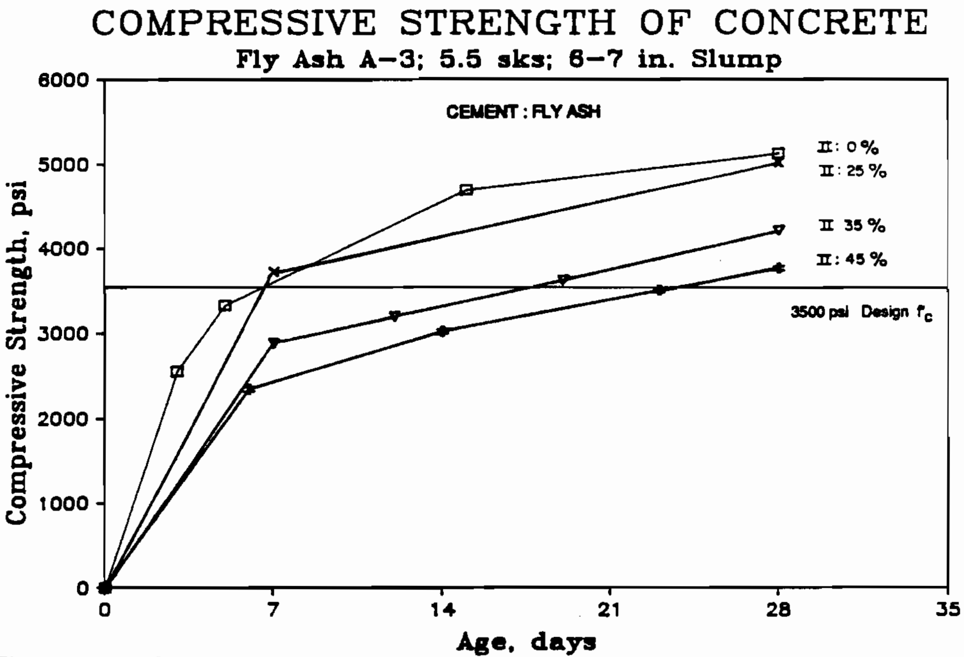


Figure 7.5 Compressive strength development of concrete containing fly ash A-3.

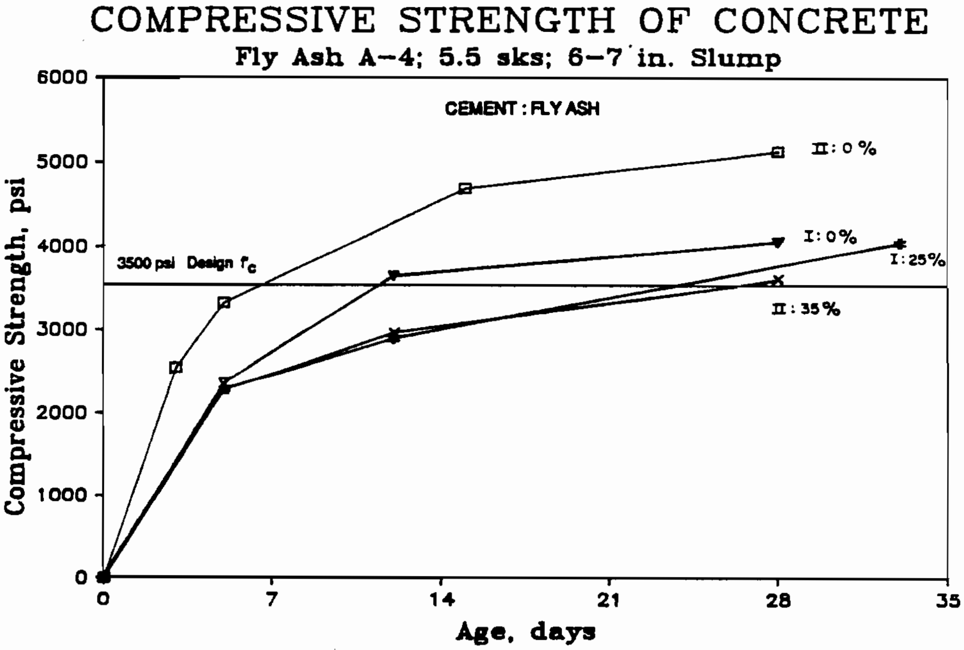


Figure 7.6 Compressive strength development of concrete containing fly ash A-4.

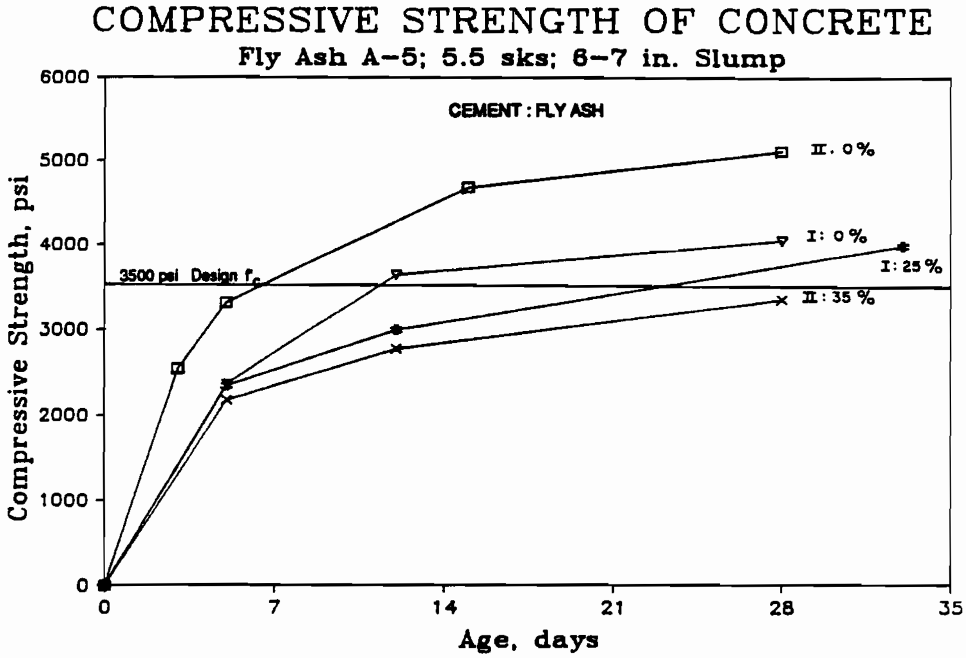


Figure 7.7 Compressive strength development of concrete containing fly ash A-5.

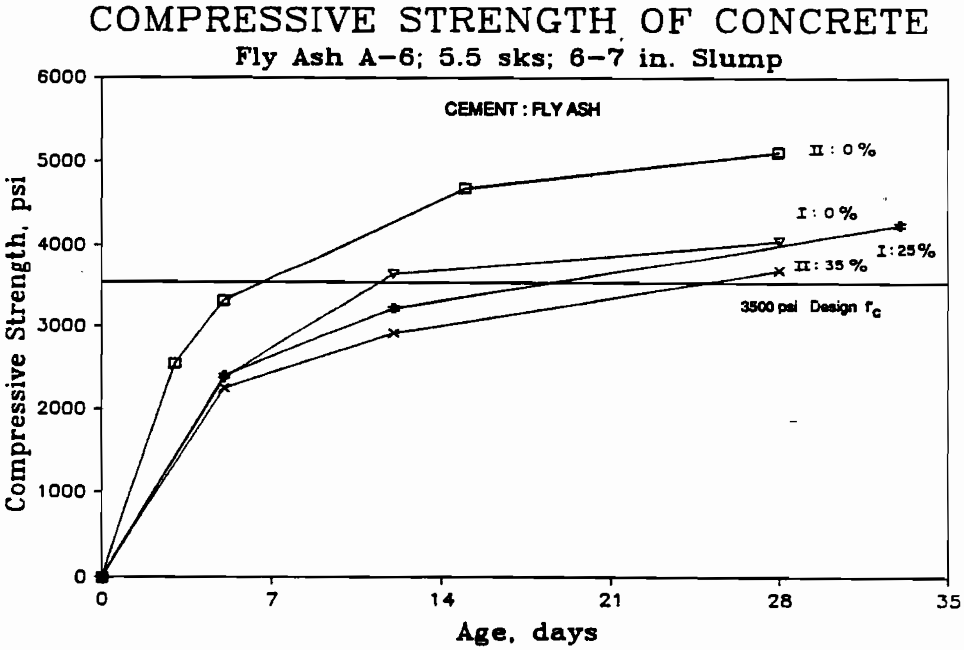


Figure 7.8 Compressive strength development of concrete containing fly ash A-6.

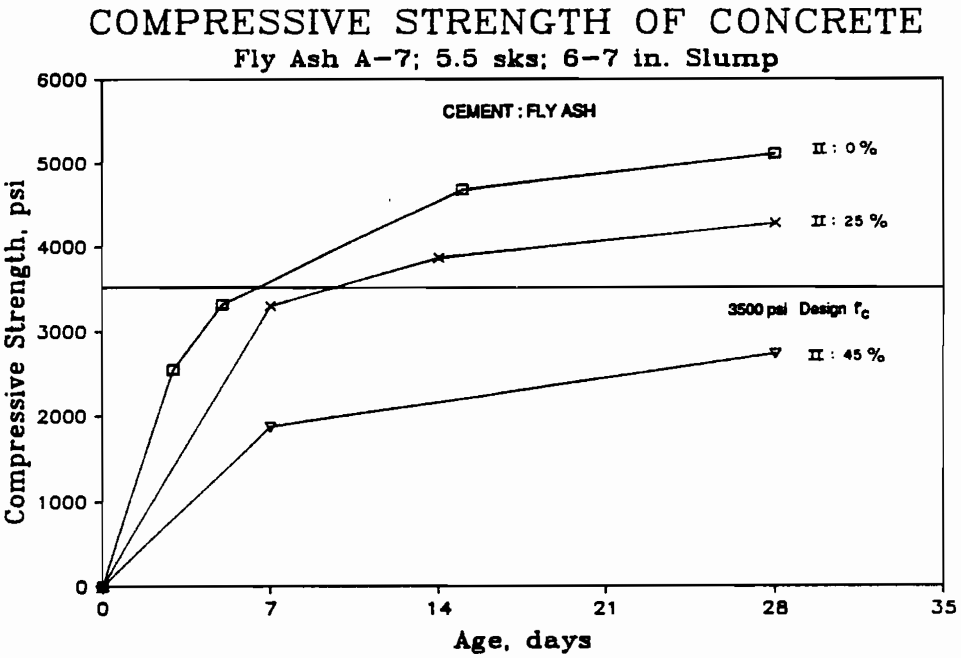


Figure 7.9 Compressive strength development of concrete containing fly ash A-7.

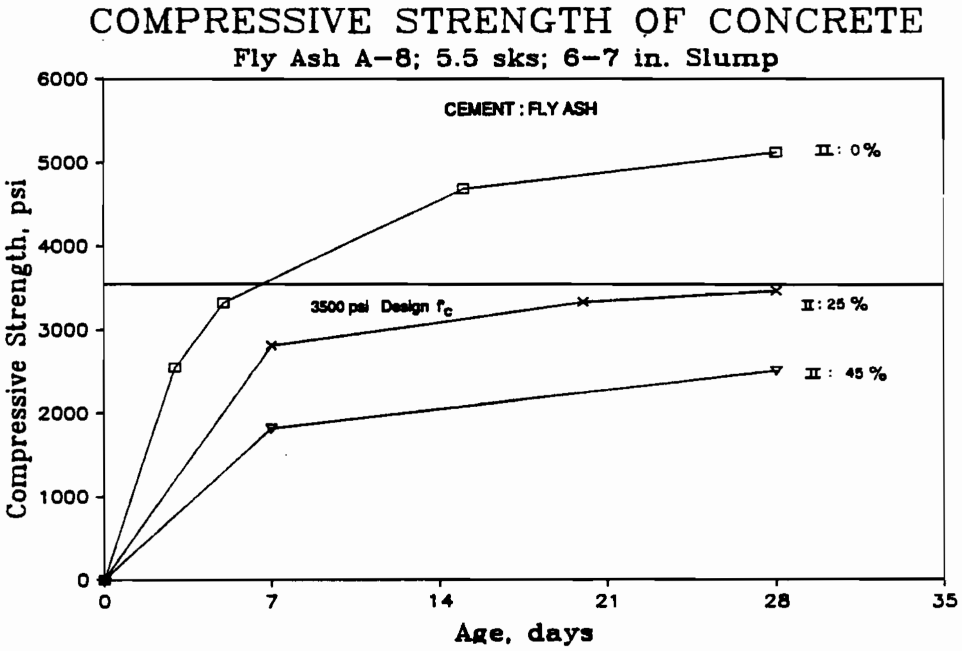


Figure 7.10 Compressive strength development of concrete containing fly ash A-8.

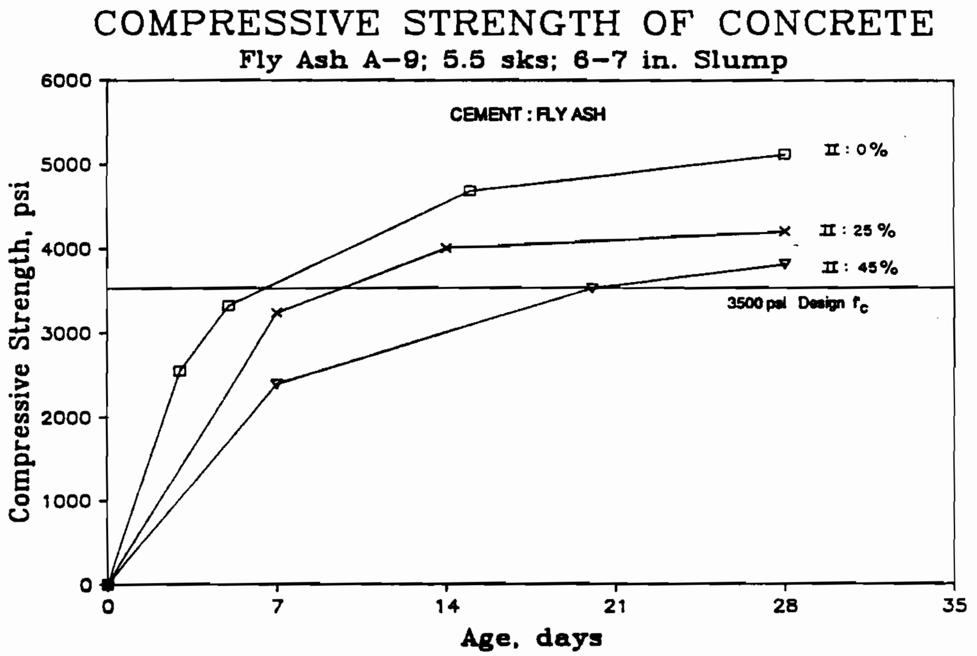


Figure 7.11 Compressive strength development of concrete containing fly ash A-9.

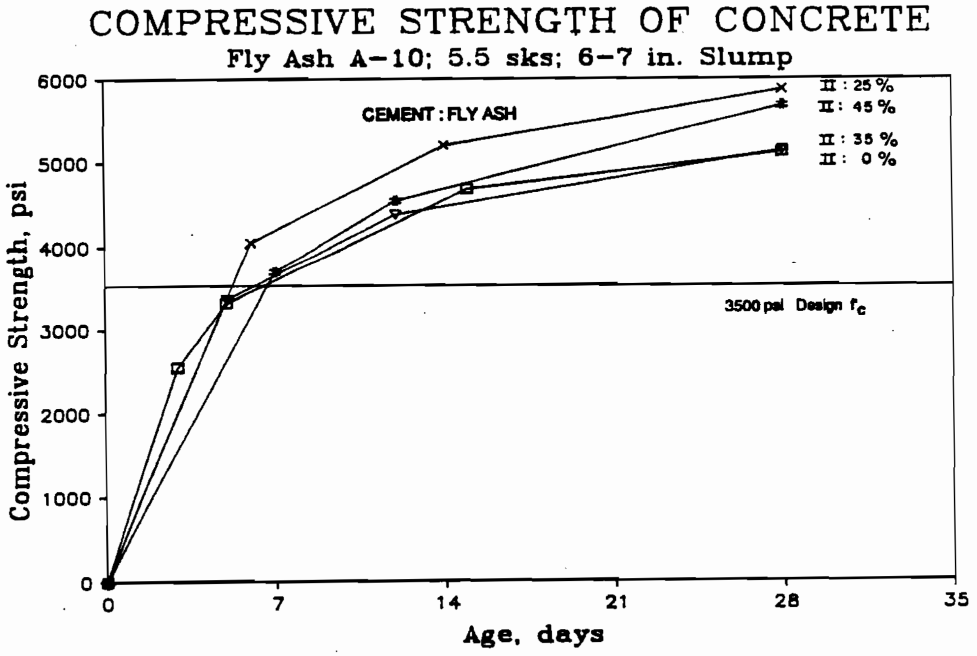


Figure 7.12 Compressive strength development of concrete containing fly ash A-10.

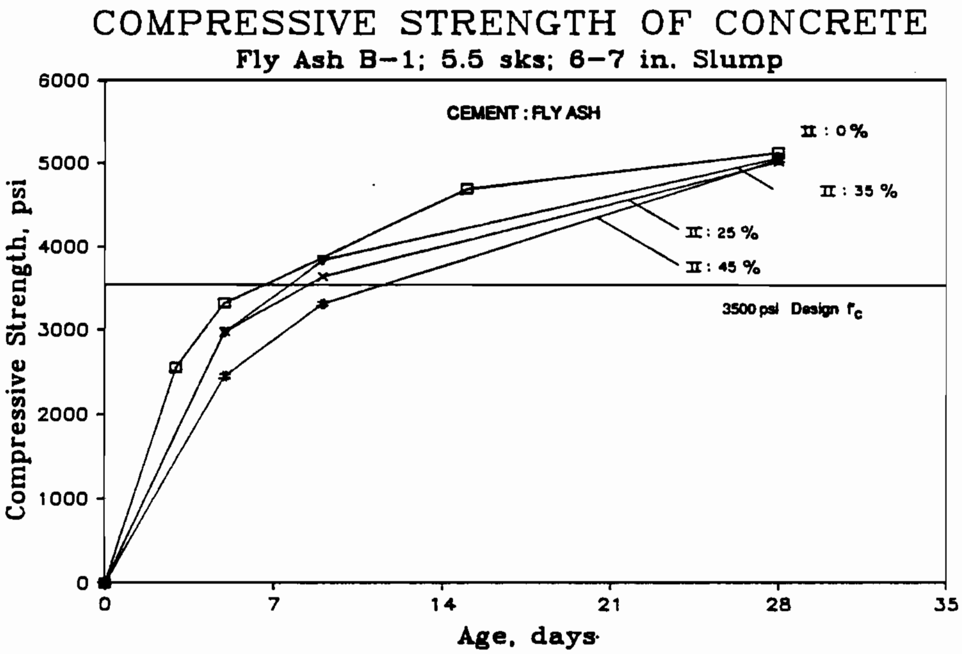


Figure 7.13 Compressive strength development of concrete containing fly ash B-1.

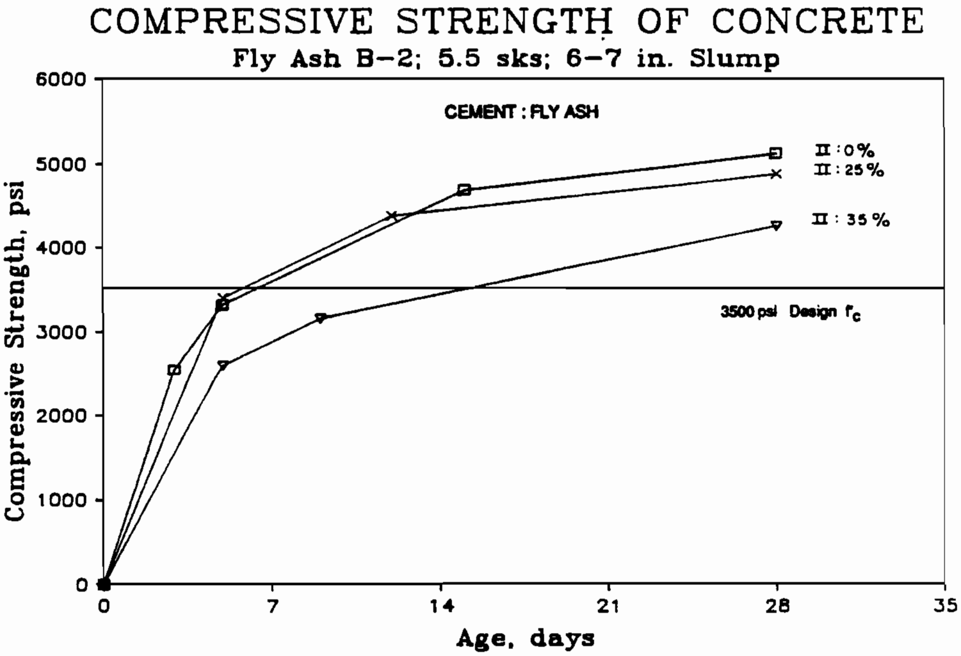


Figure 7.14 Compressive strength development of concrete containing fly ash B-2.

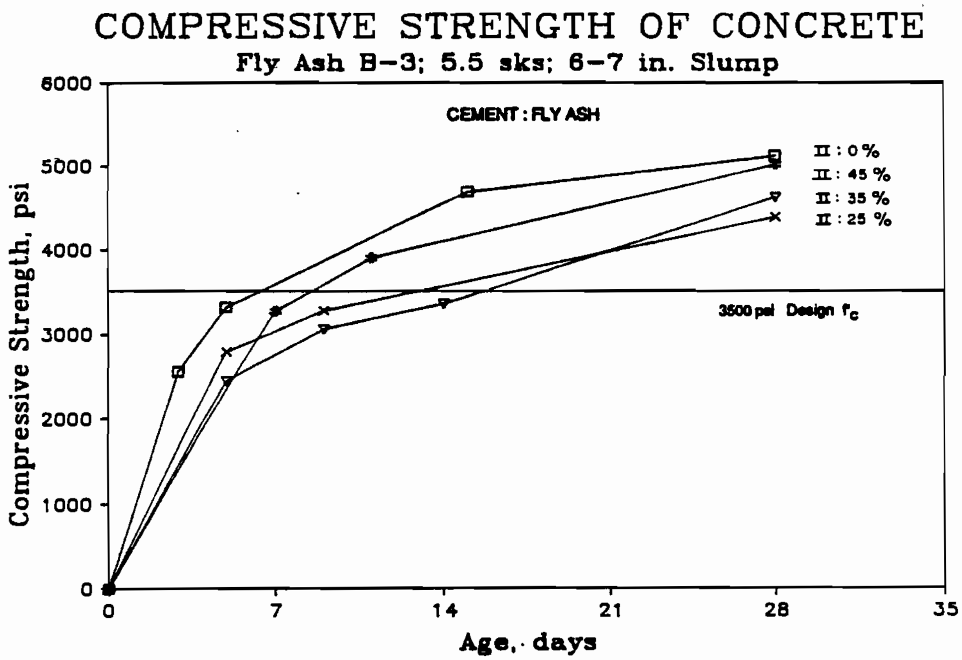


Figure 7.15 Compressive strength development of concrete containing fly ash B-3.

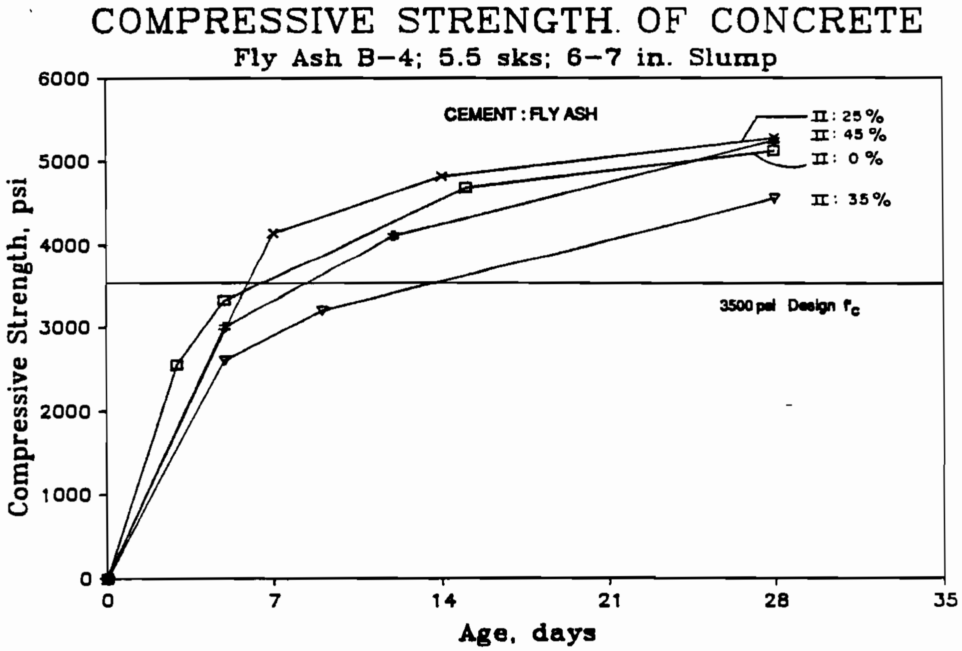


Figure 7.16 Compressive strength development of concrete containing fly ash B-4.

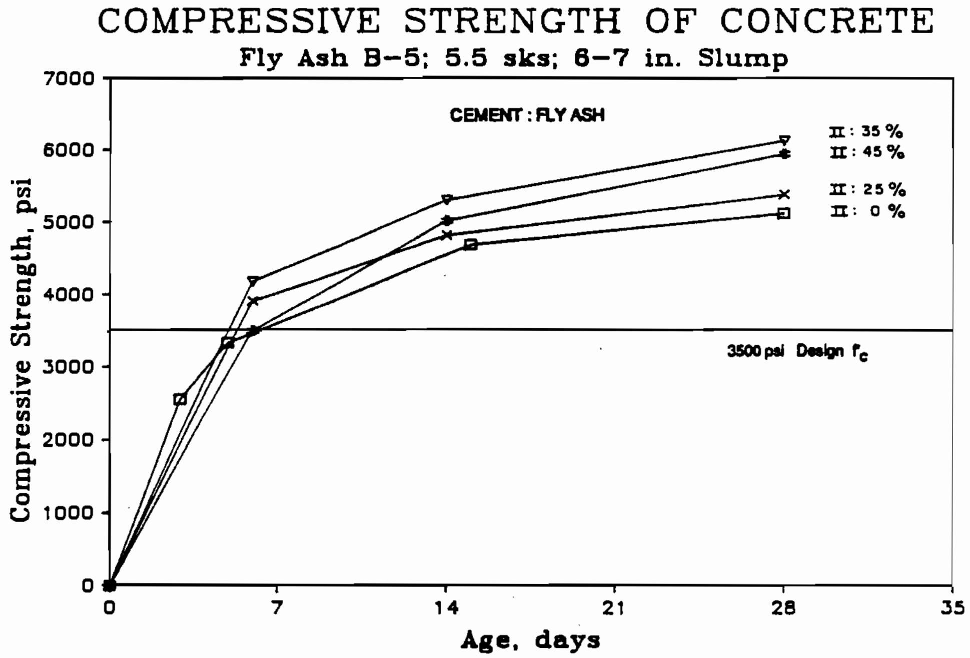


Figure 7.17 Compressive strength development of concrete containing fly ash B-5.

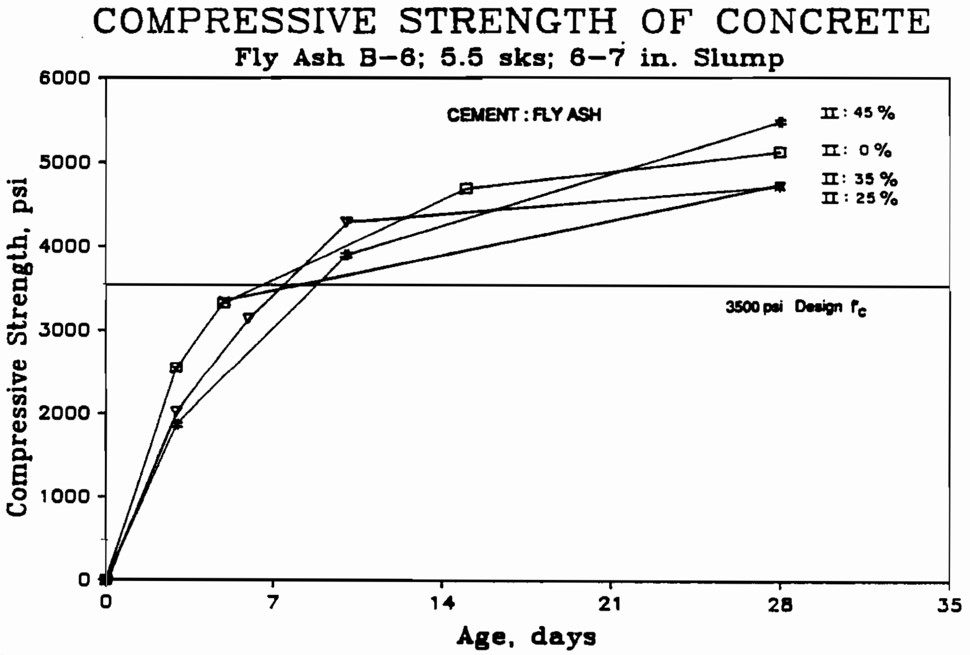


Figure 7.18 Compressive strength development of concrete containing fly ash B-6.

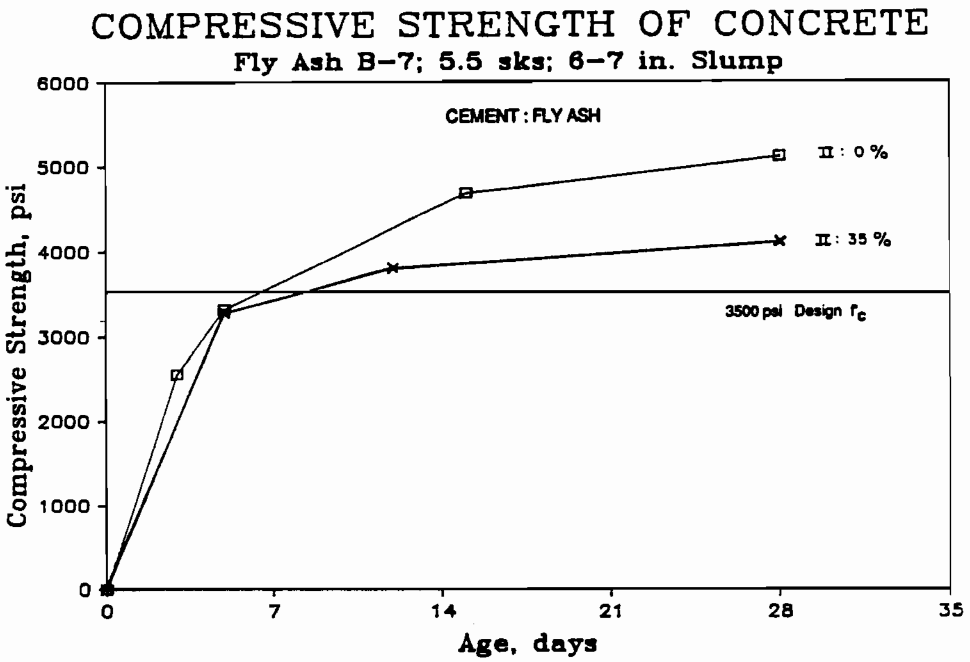


Figure 7.19 Compressive strength development of concrete containing fly ash B-7.

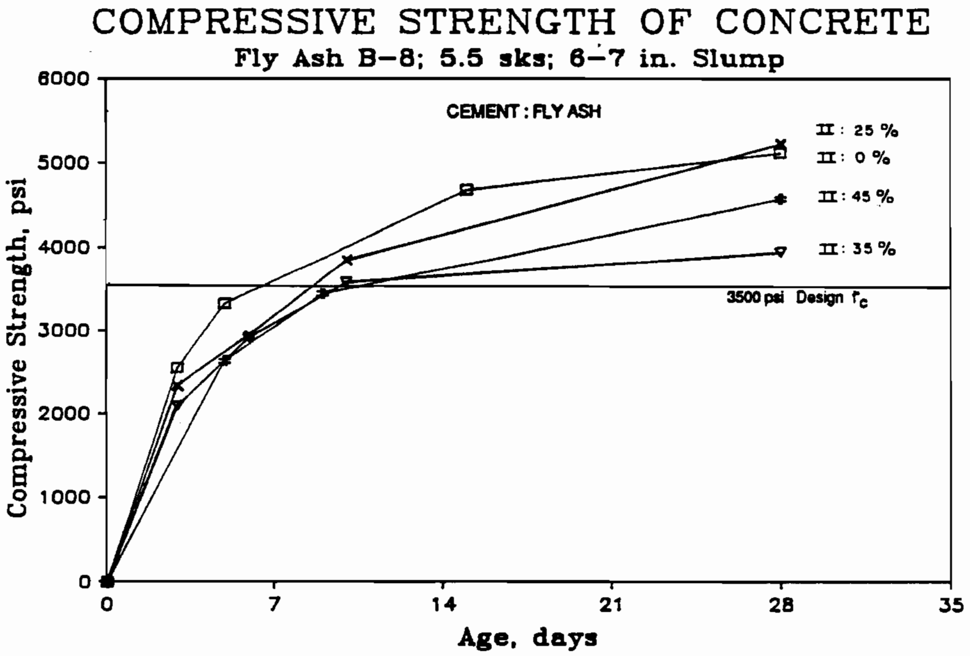


Figure 7.20 Compressive strength development of concrete containing fly ash B-8.

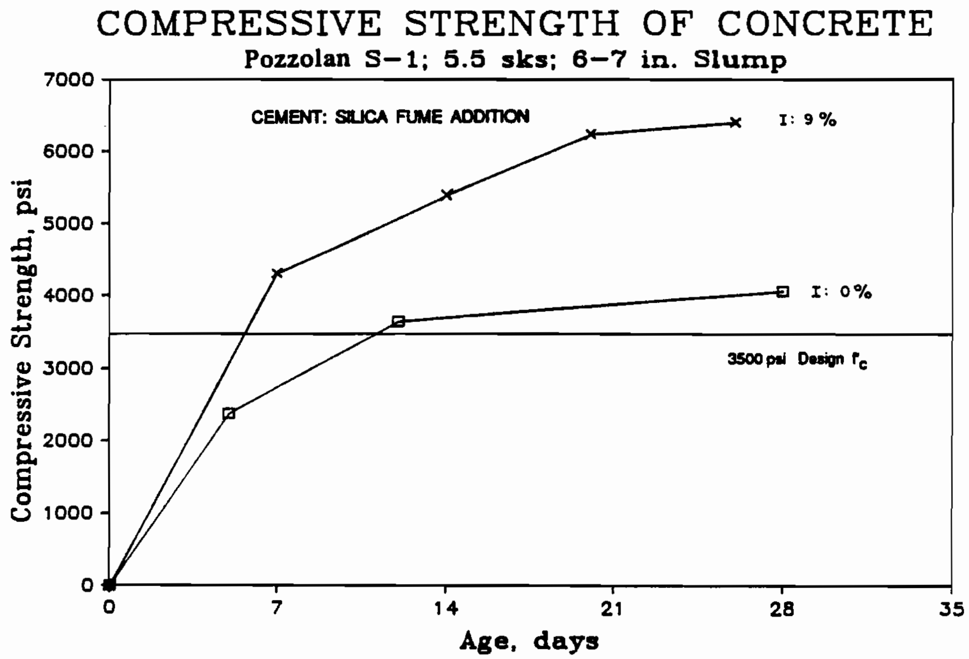


Figure 7.21 Compressive strength development of concrete containing pozzolans S-1.

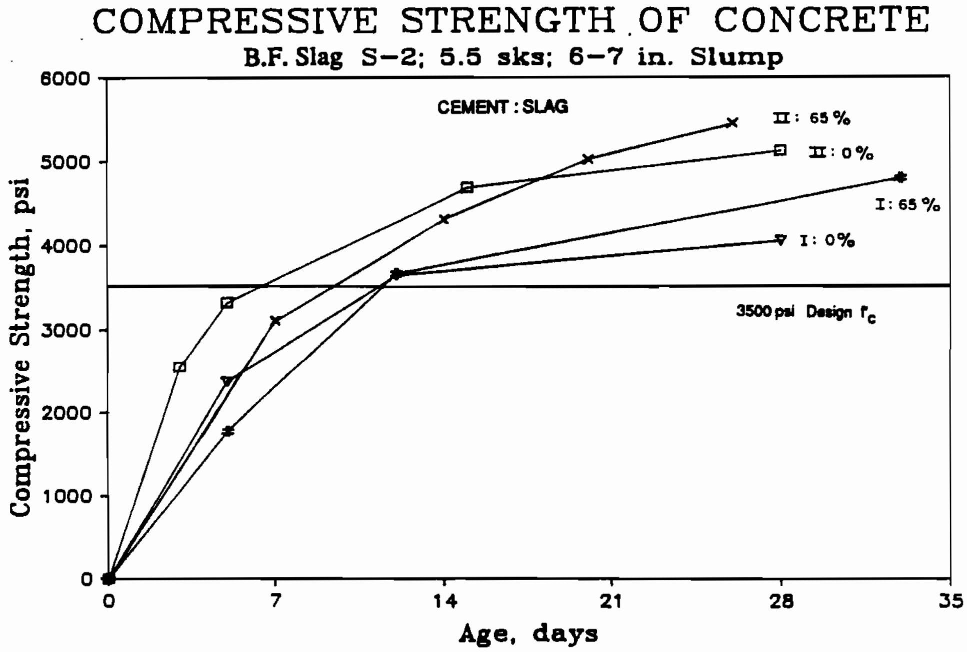


Figure 7.22 Compressive strength development of concrete containing pozzolans S-2.

7.4 Sulfate Exposure

In order to understand the effect of fly ash and pozzolans on the sulfate resistance of concrete, basic research had to be conducted to document the behavior of concrete containing each of the fly ashes and pozzolans in a standard exposure environment. The results of this basic research were then applied to investigate the effects of physical and material concrete properties. This section is focused on the presentation of the data which documents the behavior of concrete containing each of the fly ashes and pozzolans used in this study. Chapter 8 will present a discussion of the physical and material implications of the fly ashes and pozzolans on the sulfate resistance of concrete.

The exposure of concrete to a sulfate solution may cause degradation due to internal expansion. This concrete degradation was monitored in three ways in this study, time to first cracking, mass change and expansion. The first sign of sulfate attack on the concrete was cracking during the early stages of degradation, which led to spalling in severe cases of sulfate attack. External cracking of the concrete was detected by visual inspection. Mass changes in the concrete were measured by weighing the specimens. After being exposed to the sulfate solution, concrete specimens typically gained mass until cracking occurred. The mass gain was due to the formation of gypsum and ettringite within the concrete. After cracking, the specimens generally began spalling within 120 days, thereby resulting in mass losses. Expansion was measured by monitoring length changes in the specimens. The rate of increase in expansion was low until the concrete reached a length expansion level of 0.1 percent of its original length, after which expansion progressed exponentially. The complete sulfate exposure testing procedure was described in Chapter 4.

The data in this section and the succeeding chapter are presented as the average expansion, mass change and time to cracking of four cylinders cast from the same concrete mixture and cured under identical conditions. The 90, 180, 270, 360, 450, and 540 day data were linearly extrapolated from the time vs. function curve, as shown in Figure 7.23, so as to compare the behavior of all the concrete mixtures at specific time intervals after the initial sulfate exposure. Some specimens reported herein have been under test longer than the 540 days. This is reflected in the time to cracking data, but is not shown in the expansion and mass change data. Table E-1, E-2 and E-3 of Appendix E presents this information in tabular form. The actual readings of the individual specimens are presented in graphical form in Appendix E of this document.

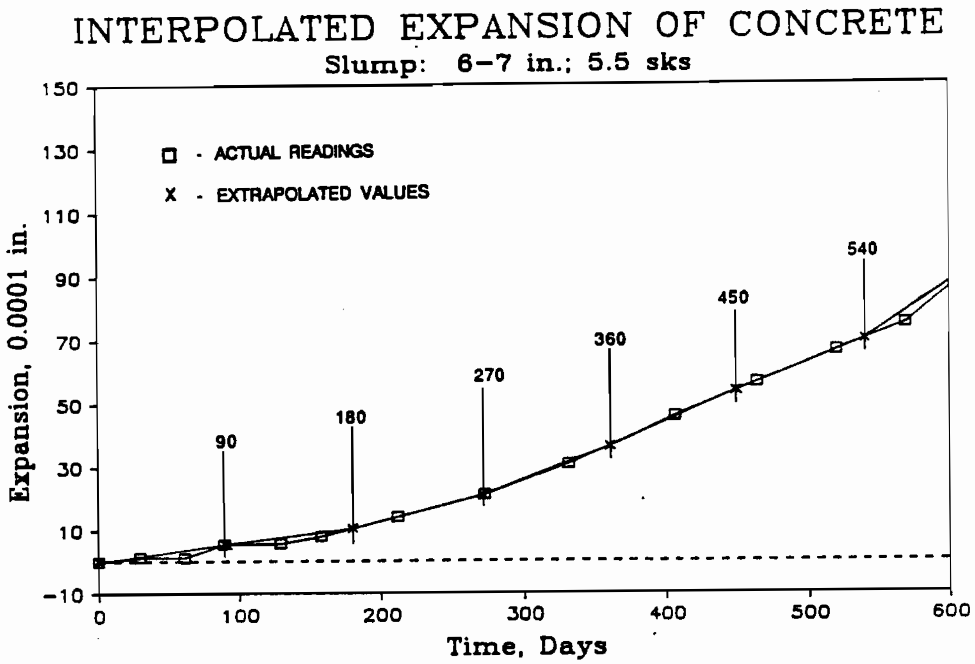


Figure 7.23 Example of linear extrapolation of sulfate expansion.

7.4.1 Portland Cement Concrete. The control concrete in this study contained 5.5 sacks per cubic yard of an ASTM Type II portland cement. This was the standard to which all other concrete mixtures were compared. The Type II cement provides a moderate level of sulfate resistance and is the cement specified by the Texas State Department of Highways and Public Transportation (SDHPT) for concrete exposed to sulfate environments.

Figures 7.24 and 7.25 show the sulfate resistance of four Type II portland cement concrete mixtures. The time to cracking of the 2 inch slump, 6 inch slump, and the 6 inch slump with 5 percent air content concrete mixtures was between 350 and 360 days after exposure to the sulfate solution. The 6 inch slump concrete containing a waterproofing admixture was only exposed to the sulfate solution 360 days at the time of this report, and showed no signs of degradation. All of these

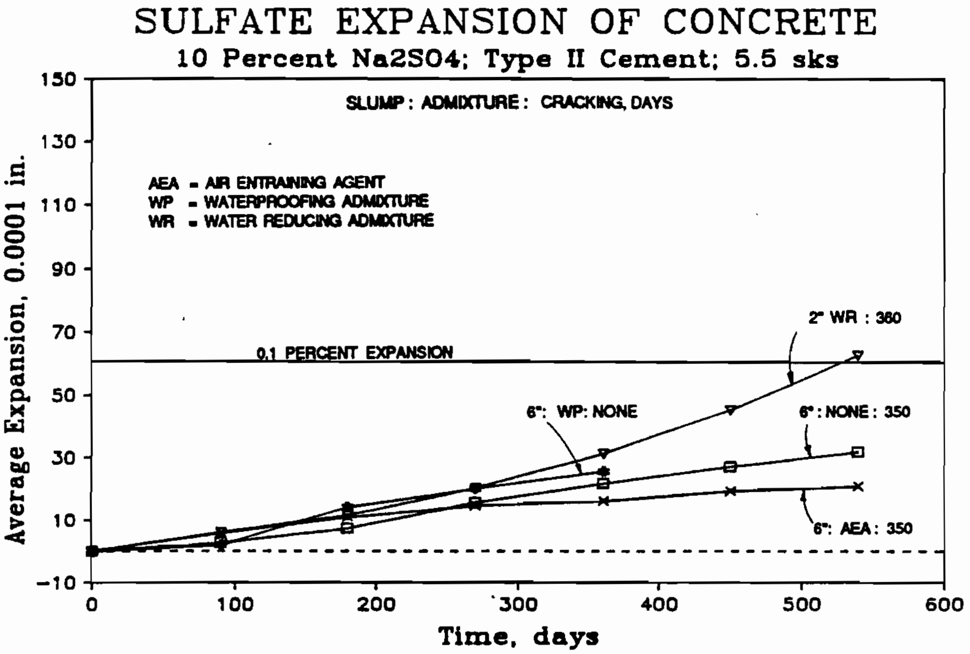


Figure 7.24 Effect of admixtures on sulfate expansion.

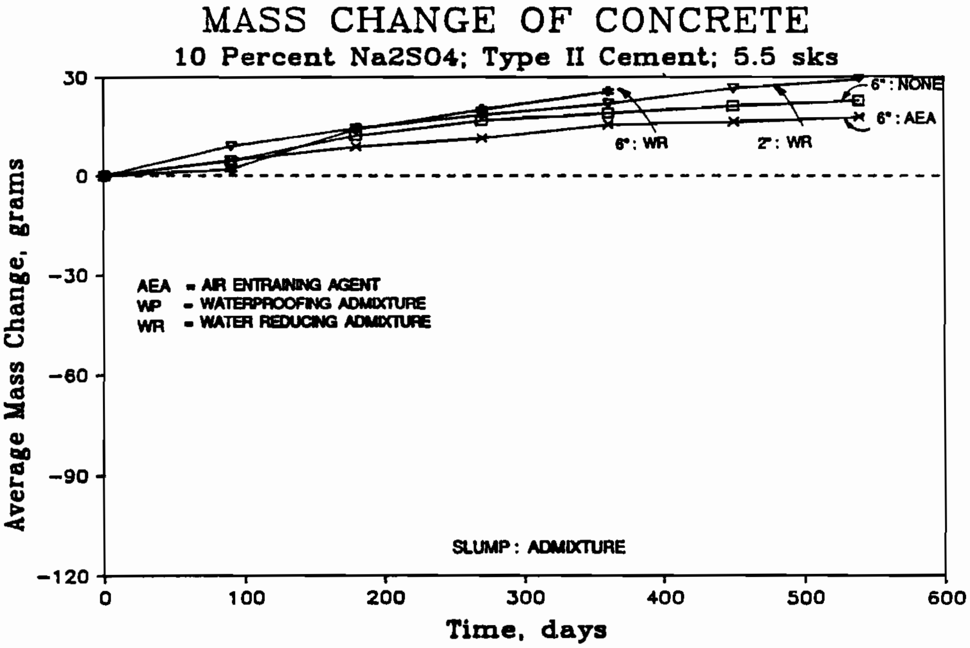


Figure 7.25 Effect of admixtures on mass loss.

concrete mixtures had expansions at or below 0.1 percent expansion. None of the portland cement concrete mixtures suffered mass losses from spalling.

Five portland cements were used in this study. The sulfate resistance of these cements are presented in Figures 7.26 and 7.27. Time to cracking for the Type I portland cement concrete was 280 days, while the time to cracking for the Type V cement and the two 0 percent C_3A portland cements were in excess of 490 days.

The Type II portland cement concrete control mixtures were repeated several times to verify their performance in the sulfate exposure test. The sulfate expansion and mass change of these mixtures are presented in Figures 7.28 and 7.29.

7.4.2 Texas SDHPT Type A Fly Ash. The chemical requirements of Texas SDHPT Type A fly ash were met by all nine of the fly ashes with less than 15 percent total calcium oxide, fly ashes A-1 through A-9. These fly ashes will be referred to hereafter as low calcium fly ashes. Fly ash A-10 was the only high calcium fly ash, containing greater than 15 percent total calcium oxide, to meet the Texas SDHPT Type A fly ash chemical requirements. All of the low calcium Texas SDHPT Type A fly ashes also met the ASTM Class F fly ash chemical requirements. However, the high calcium fly ash, A-10, was chemically classified as an ASTM Class C fly ash.

Fly ash A-1 was a fly ash from a bituminous coal source with a total silica content greater than 40 percent. This fly ash was used in two concrete mixtures, II:35%:A-1 and 02:35%:A-1. The use of this fly ash as a 35 percent replacement for Type II portland cement and the 0 percent C_3A cement produced expansions and changes in mass due to sulfate exposure less than that of concrete containing Type II portland cement and no fly ash, hereafter referred to as the Type II control. The time to first cracking was 530 days for the concrete containing Type II cement and fly ash A-1. The results of expansion and mass change are shown in Figures 7.30 and 7.31, respectively.

Fly ash A-2 was a fly ash from a Texas lignite coal source with total silica content greater than 50 percent. This fly ash was used as a volumetric replacement for portland cement in 10 mixtures. Those mixtures were as follows:

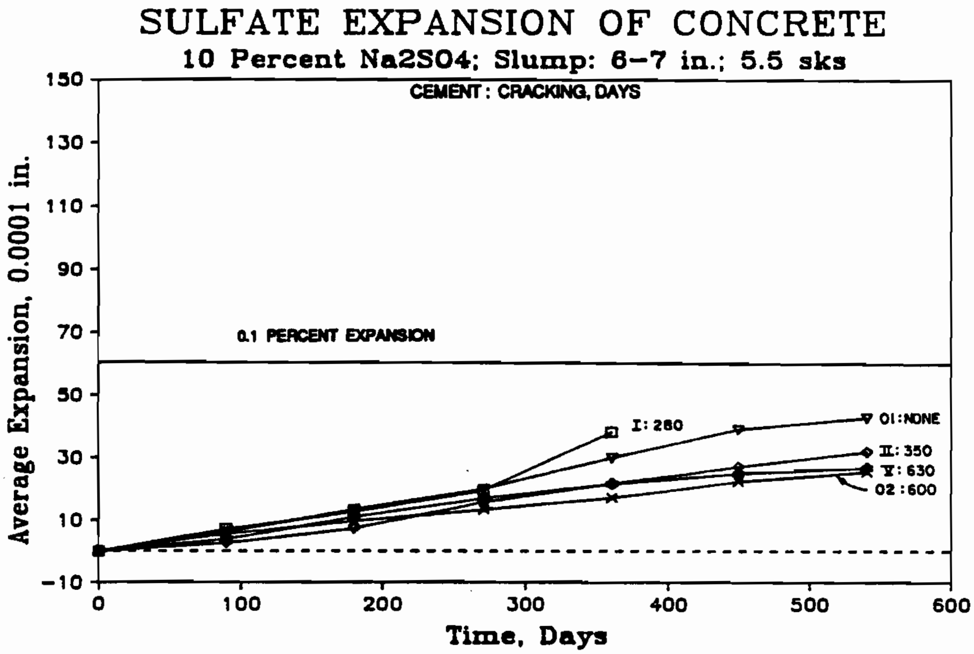


Figure 7.26 Effect of cement type on sulfate resistance.

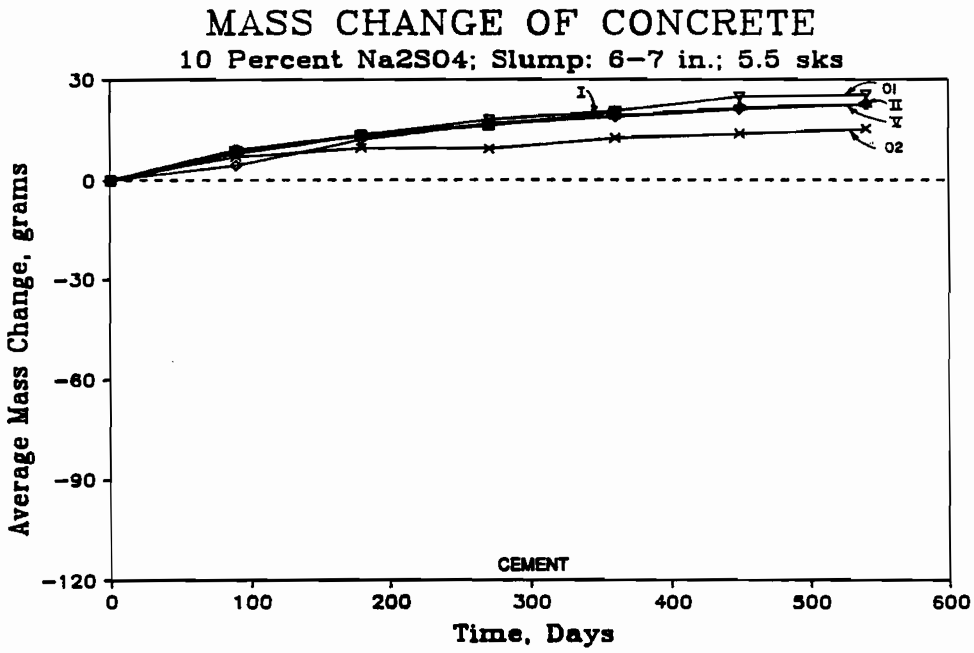


Figure 7.27 Effect of cement type on sulfate resistance.

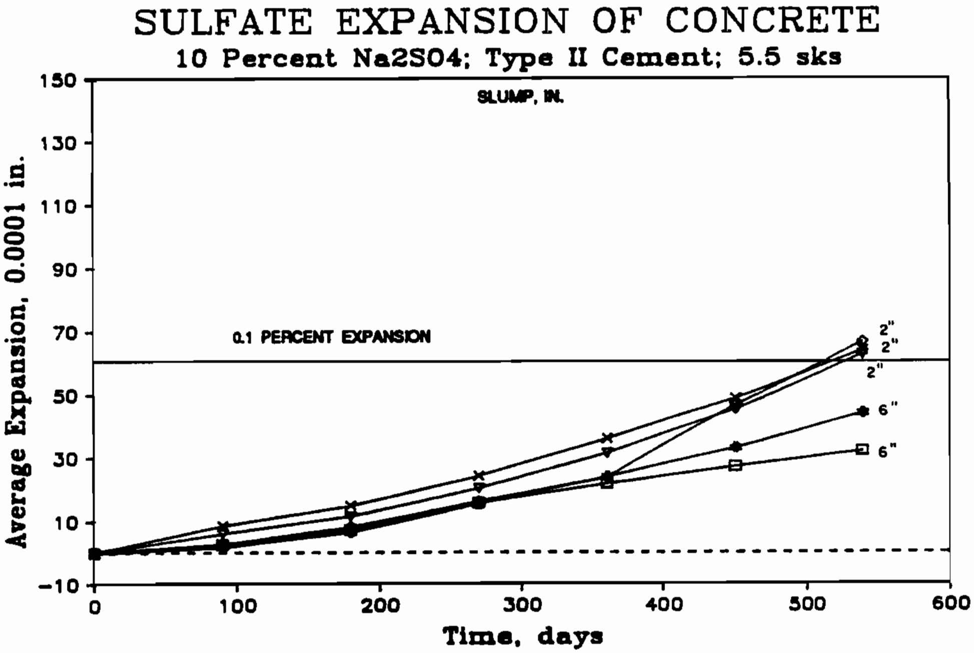


Figure 7.28 Sulfate expansion of Type II controls.

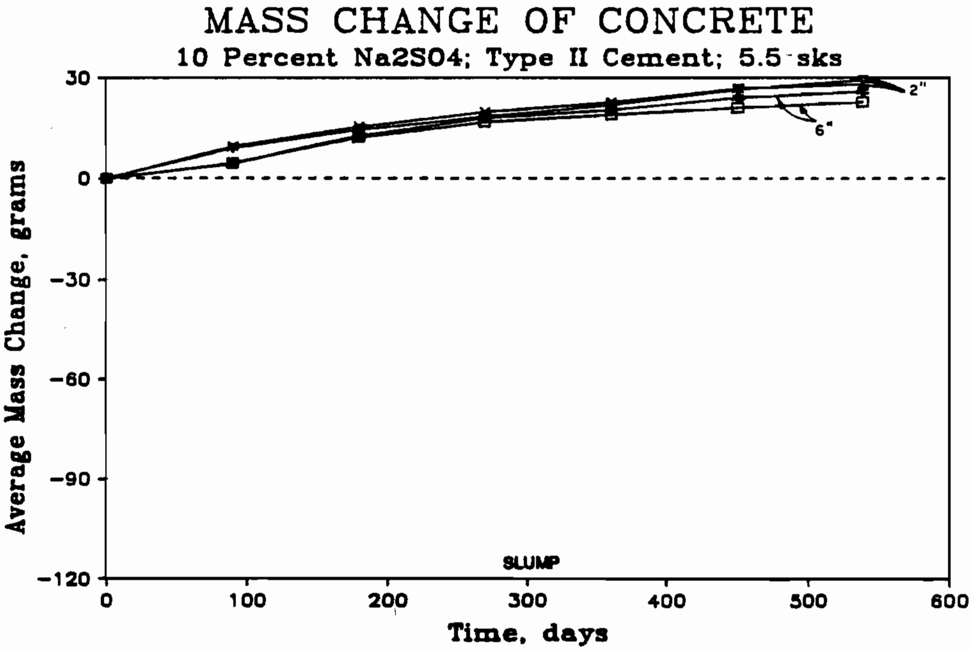


Figure 7.29 Sulfate mass change of Type II controls.

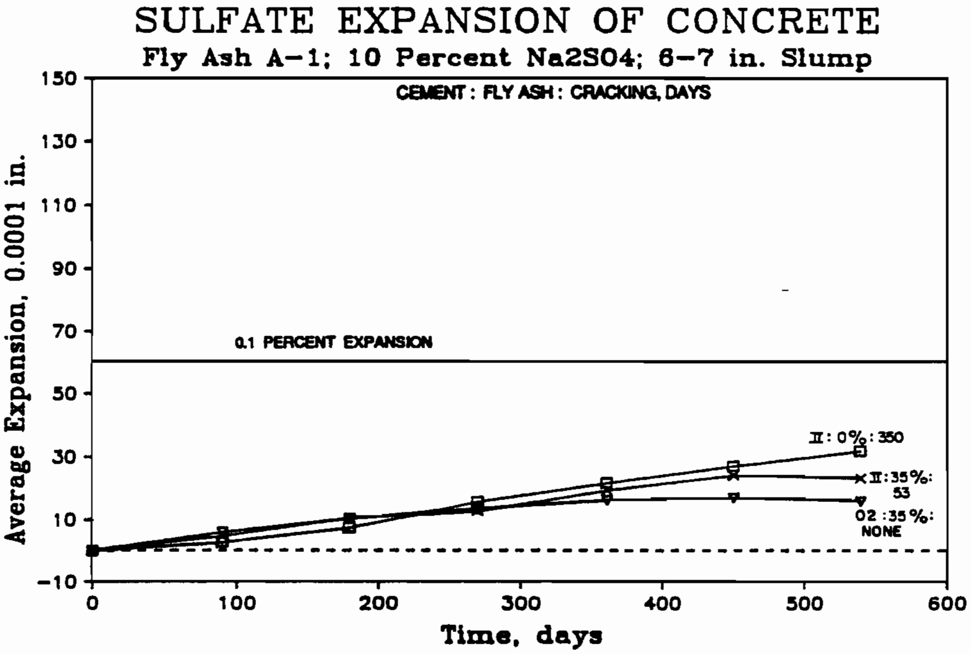


Figure 7.30 Sulfate expansion of concrete containing fly ash A-1.

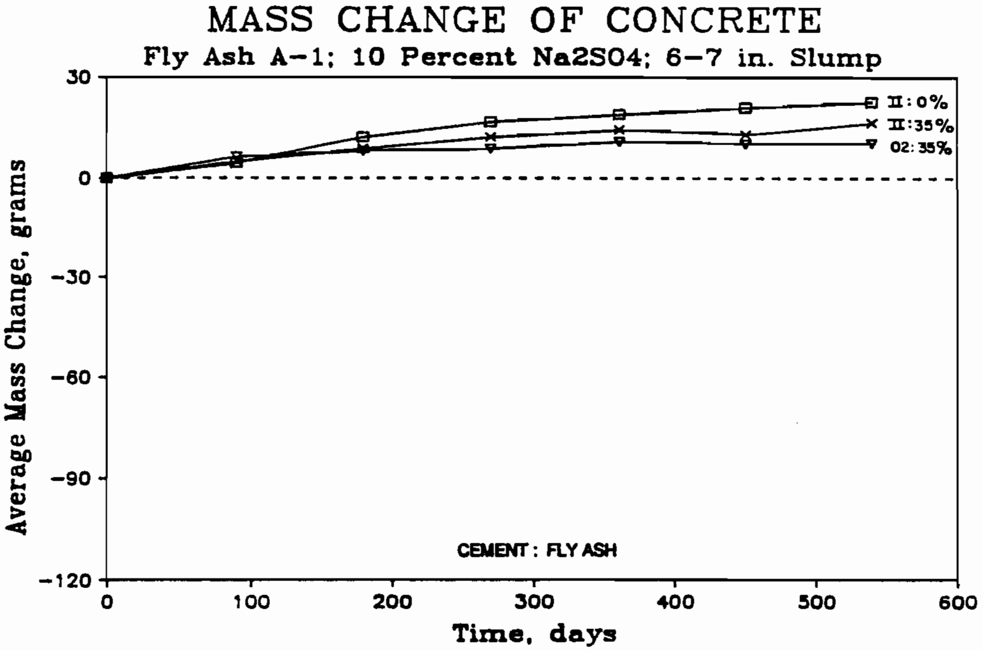


Figure 7.31 Sulfate mass change of concrete containing fly ash A-1.

6 in. slump	2 in. slump
II:25%:A-2	II:25%:A-2
II:35%:A-2	II:35%:A-2
II:45%:A-2	II:45%:A-2
I:25%:A-2	II:25%:A-2 (3 day)
02:35%:A-2	II:35%:A-2 (3 day)

M.C. refers to moist curing

The results of the sulfate resistance testing are presented in Figures 7.32 through 7.35. The sulfate expansions and changes in mass of the concrete from these mixtures were less than that of the Type II control. The concrete containing fly ash A-2 with a 2 inch slump showed no signs of cracking. The 6 inch slump mixtures II:25%:A-2, II:45%:A-2, and 02:35%:A-2 cracked at ages in excess of 500 days, whereas the 6 inch slump mixture II:35%:A-2 had a time to first cracking of 330 days, similar to that of the Type II control. The 6 inch slump mixture I:25%:A-2 did not show any cracking after 360 days of sulfate exposure.

Fly ash A-3 was a fly ash from a Texas lignite coal source with total silica content greater than 50 percent. This fly ash was used as a volumetric replacement for portland cement in nine mixtures. Those mixtures were as follows:

6 in. slump	2 in. slump
II:25%:A-3	II:25%:A-3
II:35%:A-3	II:35%:A-3
II:45%:A-3	II:45%:A-3
I:25%:A-3	II:25%:A-3 (3 day)
I:35%:A-3	

M.C. refers to moist curing

The results of the sulfate resistance testing are presented in Figures 7.36 through 7.39. The sulfate expansions and changes in mass of the concrete from these mixtures were less than that of the Type II control. The concrete containing fly ash A-3 with a 2 inch slump showed no signs of cracking. The 6 inch slump mixtures II:25%:A-2 and II:35%:A-2 cracked at ages in excess of 660 days, whereas the 6 inch slump mixtures II:45%:A-2, I:25%:A-2, and I:35%:A-3 did not show any cracking. The Type I portland cement concrete mixtures containing fly ash A-3 were only 360 days into the sulfate exposure testing at the time of this report.

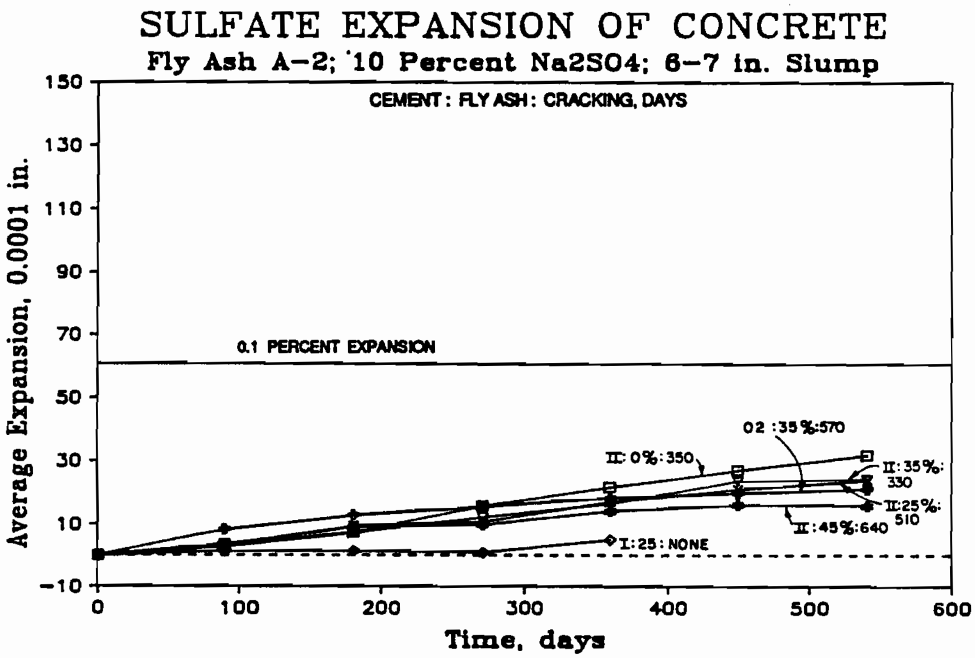


Figure 7.32 Sulfate expansion of concrete containing fly ash A-2.

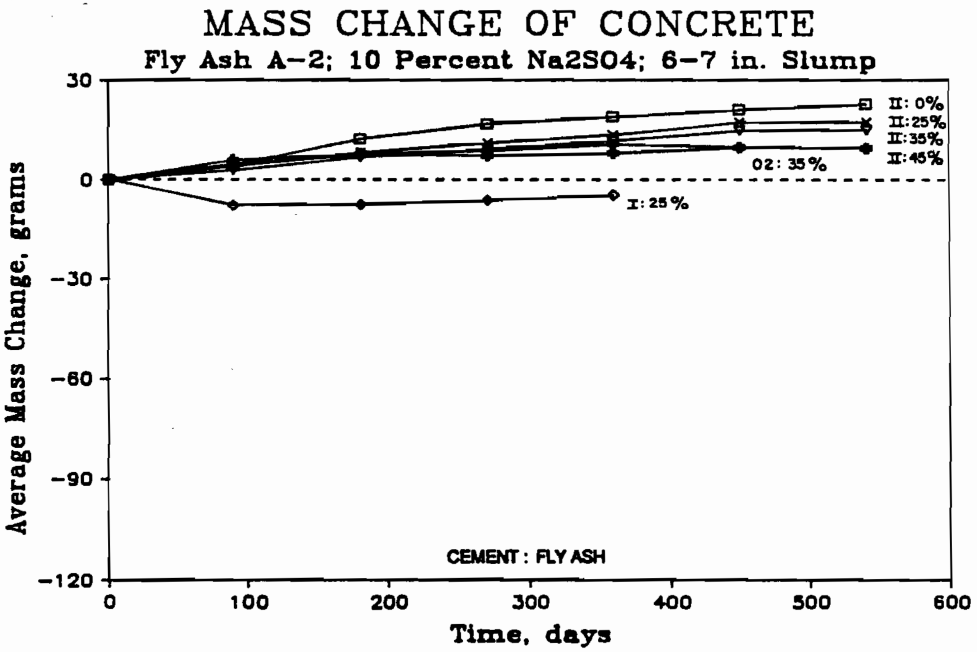


Figure 7.33 Sulfate mass loss of concrete containing fly ash A-2.

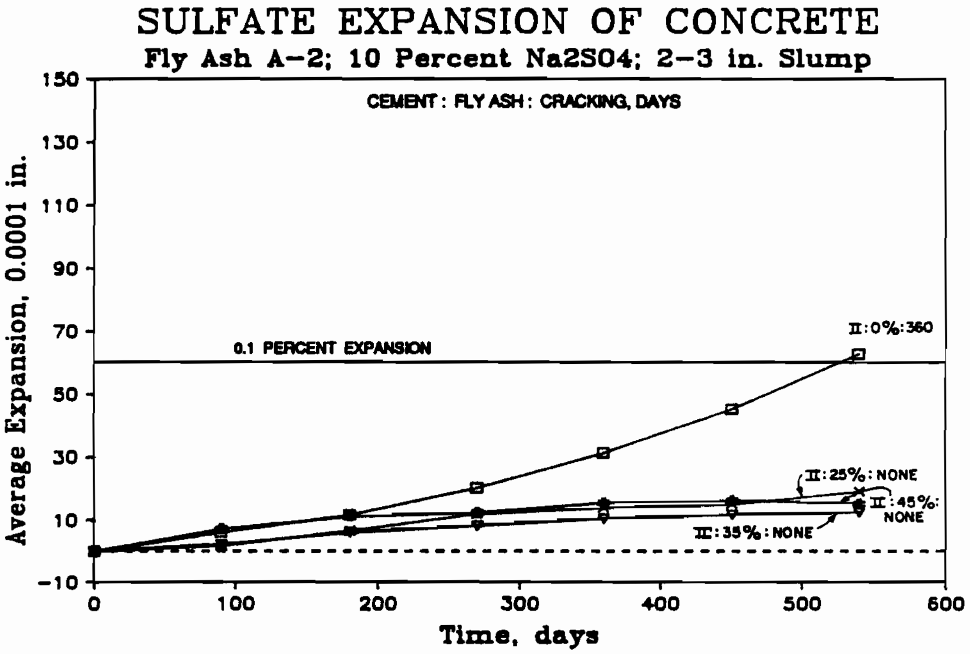


Figure 7.34 Sulfate expansion of concrete containing fly ash A-2.

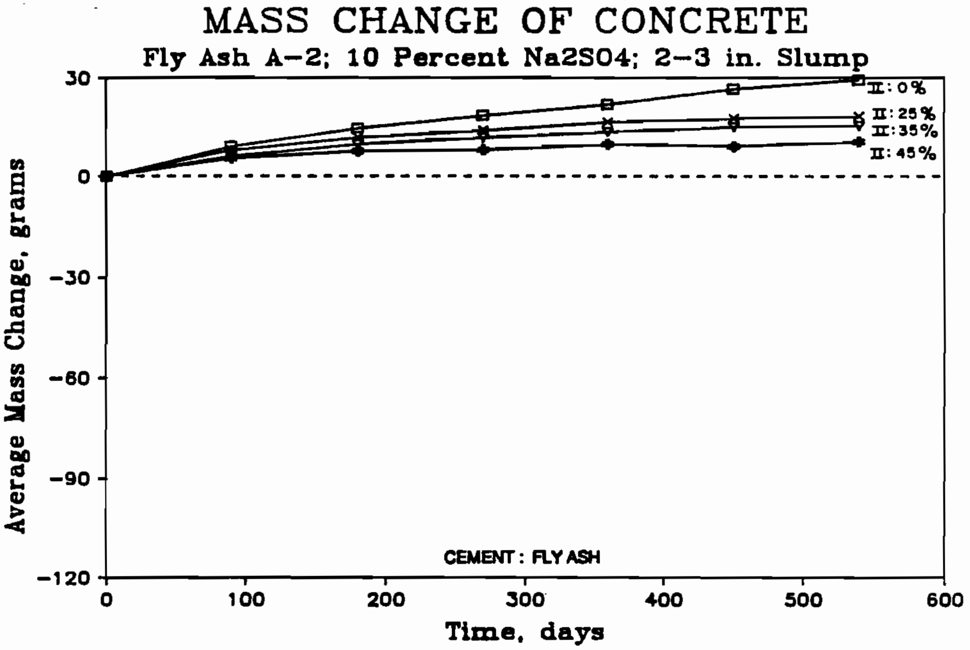


Figure 7.35 Sulfate mass loss of concrete containing fly ash A-2.

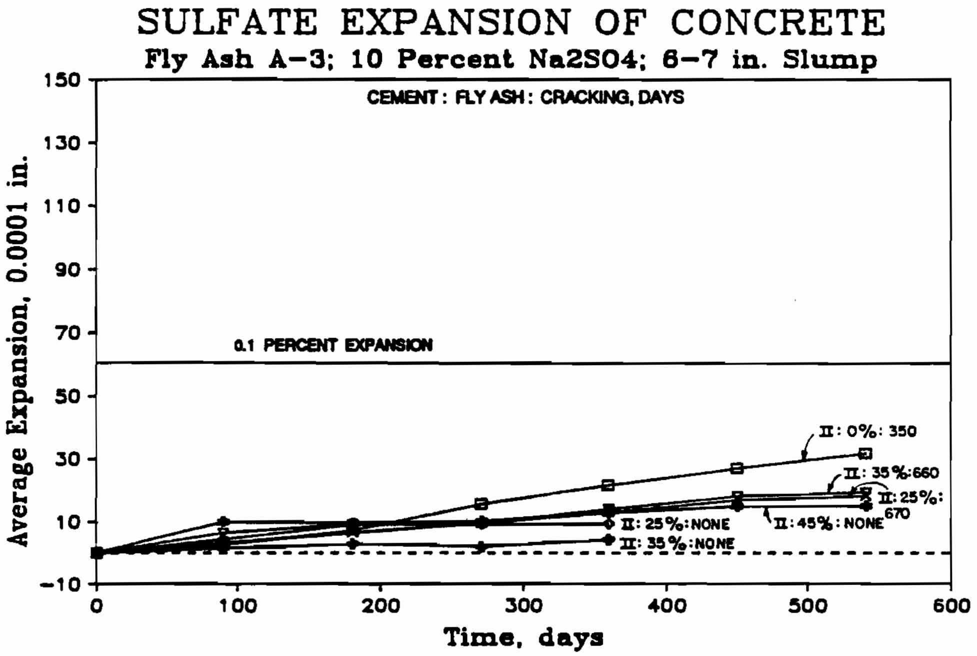


Figure 7.36 Sulfate expansion of concrete containing fly ash A-3.

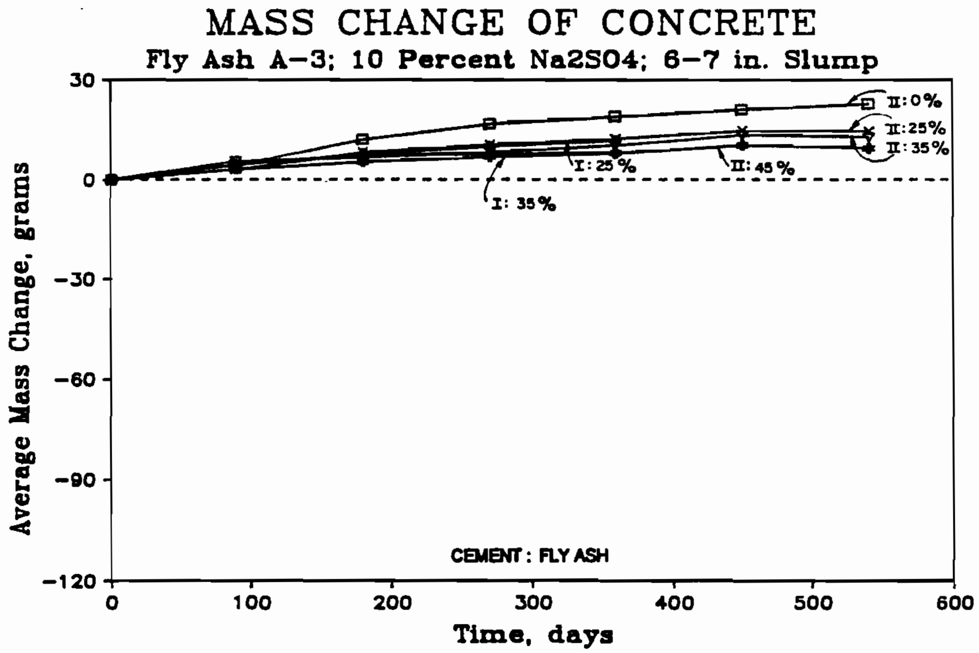


Figure 7.37 Sulfate mass loss of concrete containing fly ash A-3.

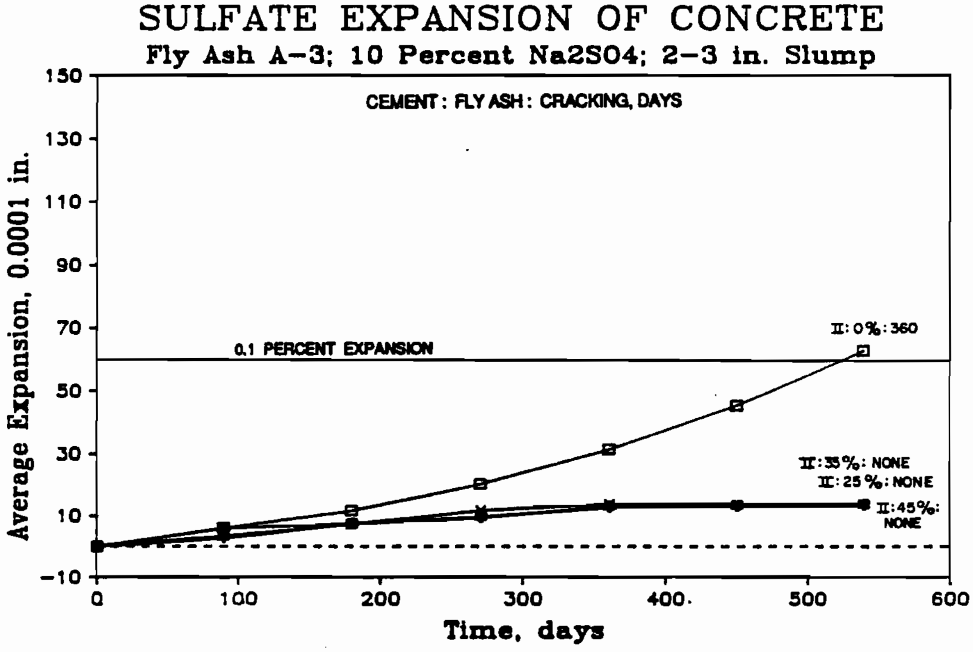


Figure 7.38 Sulfate expansion of concrete containing fly ash A-3.

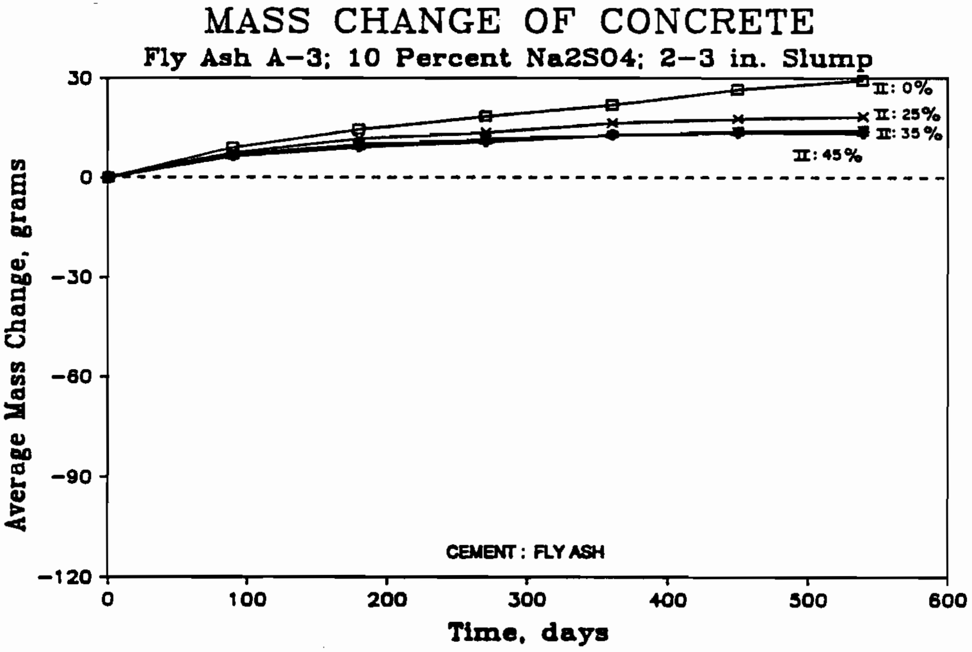


Figure 7.39 Sulfate mass loss of concrete containing fly ash A-3.

Fly ash A-4 was a fly ash from a Texas lignite coal source with total silica content greater than 50 percent. This fly ash was used as a volumetric replacement for portland cement in two 6 inch slump mixtures, II:35%:A-4 and I:25%:A-4. The results of the sulfate resistance testing are presented in Figures 7.40 and 7.41. The sulfate expansions and changes in mass of the concrete from these mixtures were less than that of the Type II control. Neither of these concrete mixtures showed signs of cracking after 360 days of sulfate exposure testing.

Fly ash A-5 was a fly ash from a bituminous coal source. This fly ash was used as a volumetric replacement for portland cement in two 6 inch slump mixtures, II:35%:A-5 and I:25%:A-5. The results of the sulfate resistance testing are presented in Figures 7.42 and 7.43. The sulfate expansions and changes in mass of the concrete from these mixtures were less than that of the Type II control. Neither of these concrete mixtures showed signs of cracking after 360 days of sulfate exposure testing.

Fly ash A-6 was a fly ash from a low calcium subbituminous coal source. This fly ash was used as a volumetric replacement for portland cement in two 6 inch slump mixtures, II:35%:A-6 and I:25%:A-6. The results of the sulfate resistance testing are presented in Figures 7.44 and 7.45. The sulfate expansions and changes in mass of the concrete from these mixtures were less than that of the Type II control. Neither of these concrete mixtures showed signs of cracking after 360 days of sulfate exposure testing.

Fly ashes A-7 was from a bituminous coal sources. This fly ash was used as a volumetric replacement for portland cement in two 6 inch slump mixtures, II:25%:A-7 and II:45%:A-7. The results of the sulfate resistance testing are presented in Figures 7.46 and 7.47. The sulfate expansions and changes in mass of the concrete from these mixtures were equal to or less than that of the Type II control. The concrete mixture II:25%:A-7 cracked after 650 days of sulfate exposure testing. The concrete mixture II:45%:A-7 showed no signs of cracking.

Fly ashes A-8 was from a bituminous coal sources. This fly ash was used as a volumetric replacement for portland cement in two 6 inch slump mixtures, II:25%:A-8 and II:45%:A-8. The results of the sulfate resistance testing are presented in Figures 7.48 and 7.49. The sulfate expansions and changes in mass of the concrete

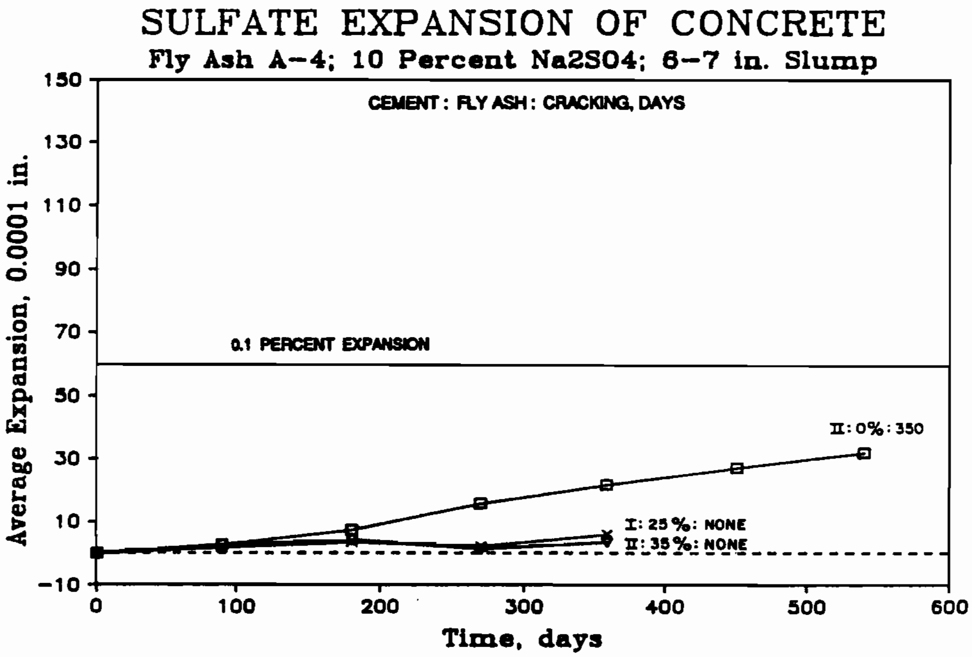


Figure 7.40 Sulfate expansion of concrete containing fly ash A-4.

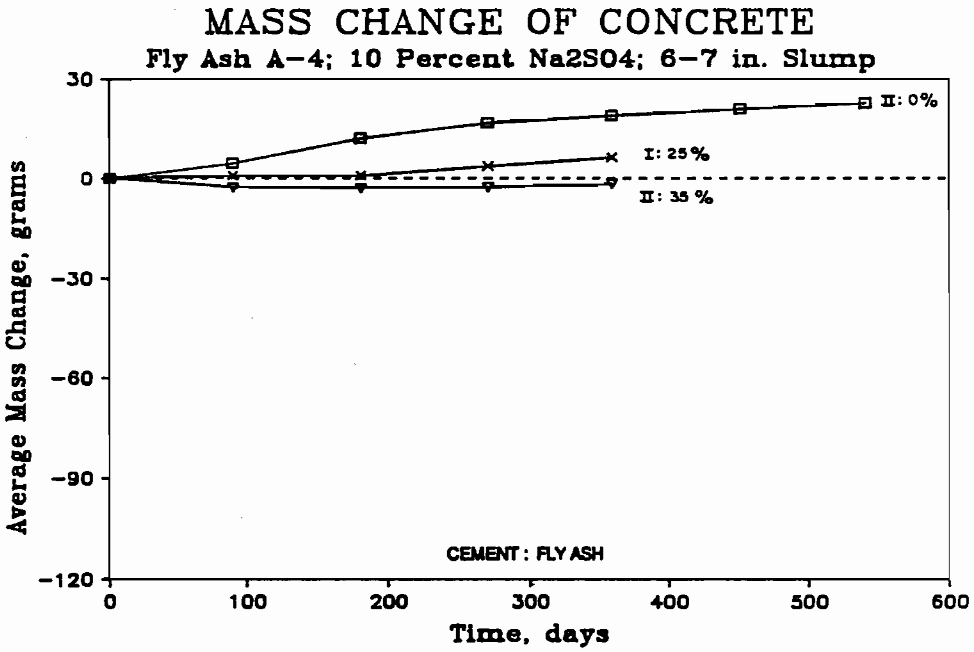


Figure 7.41 Sulfate mass loss of concrete containing fly ash A-4.

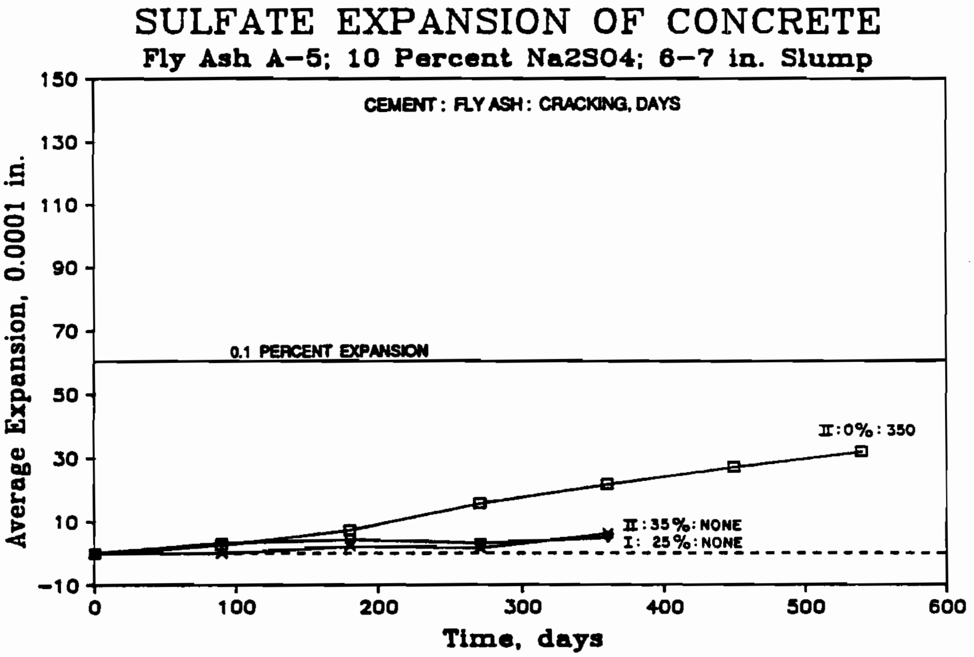


Figure 7.42 Sulfate expansion of concrete containing fly ash A-5.

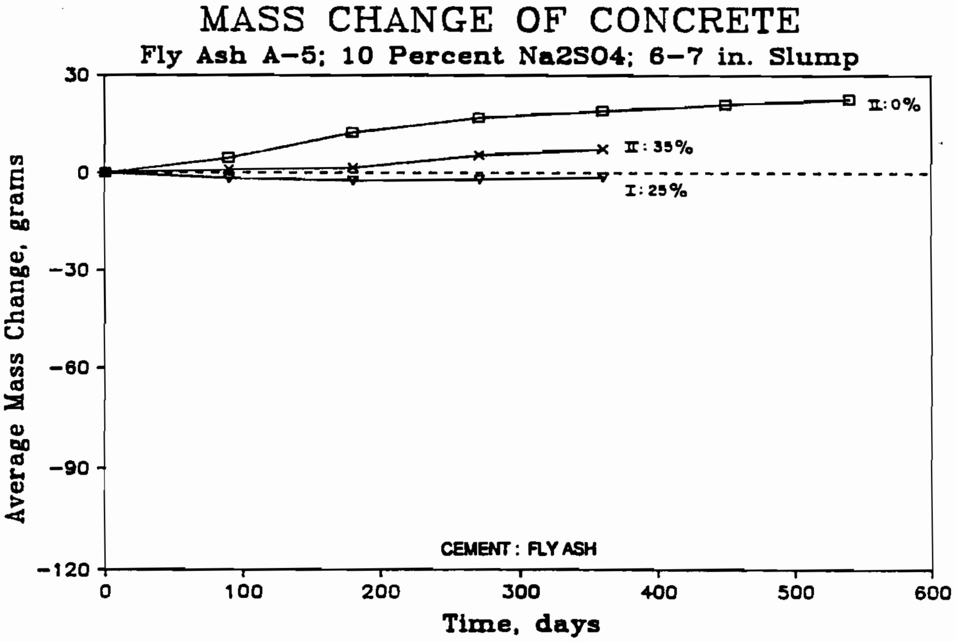


Figure 7.43 Sulfate mass loss of concrete containing fly ash A-5.

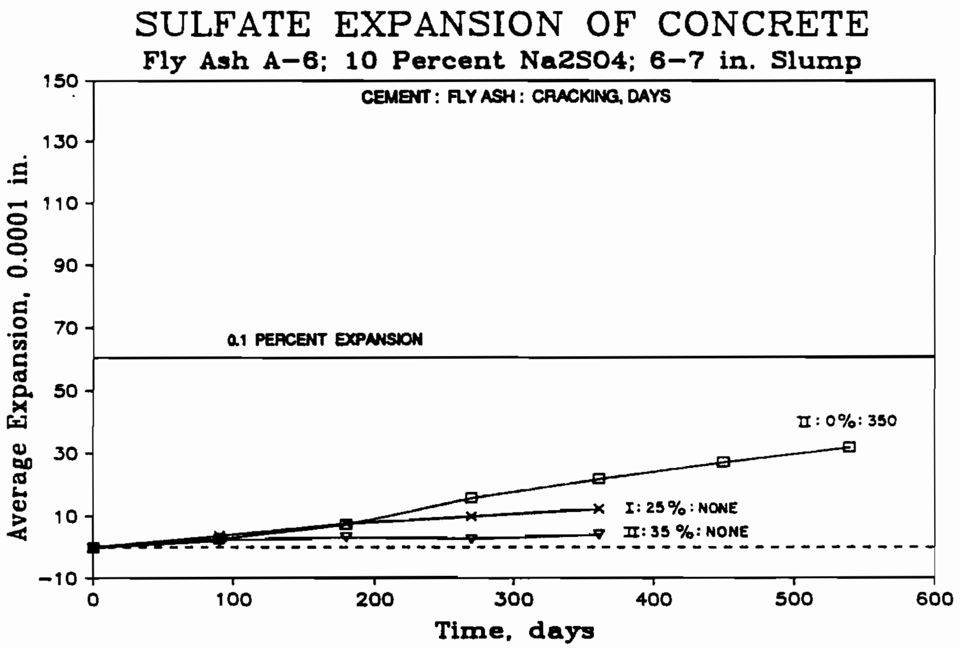


Figure 7.44 Sulfate expansion of concrete containing fly ash A-6.

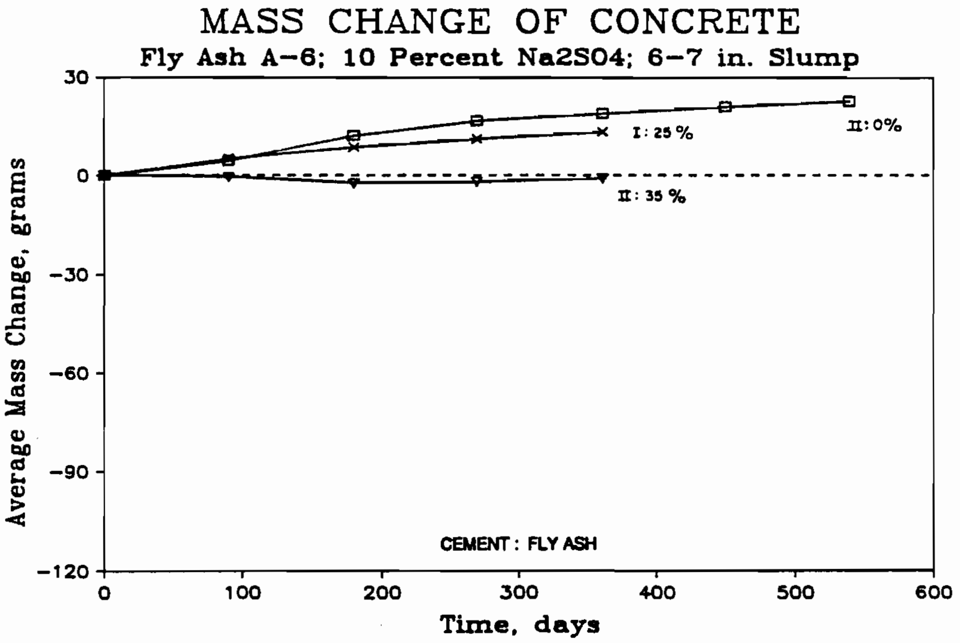


Figure 7.45 Sulfate mass loss of concrete containing fly ash A-6.

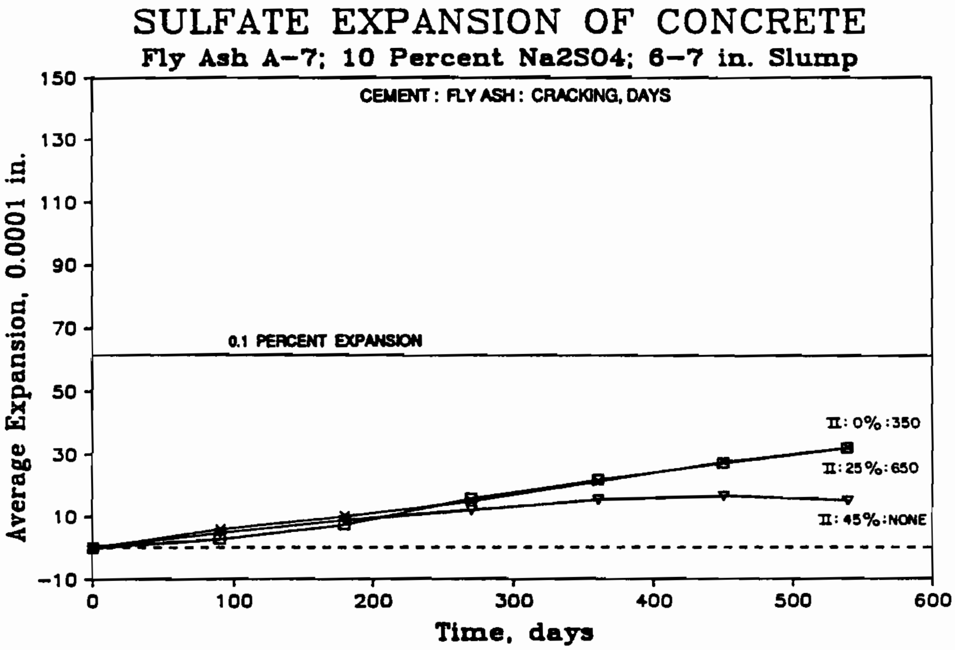


Figure 7.46 Sulfate expansion of concrete containing fly ash A-7.

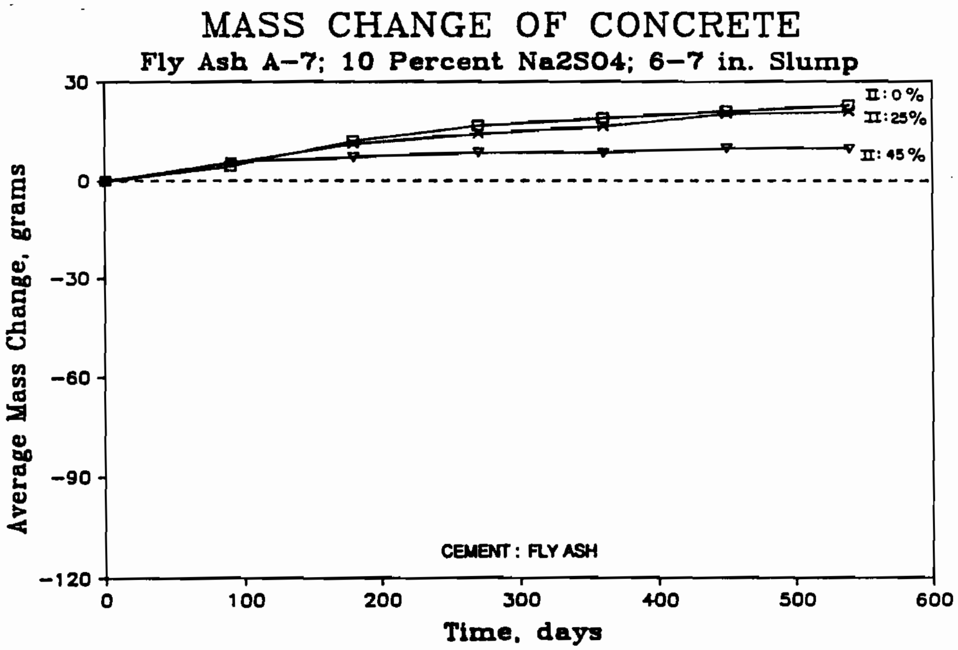


Figure 7.47 Sulfate mass loss of concrete containing fly ash A-7.

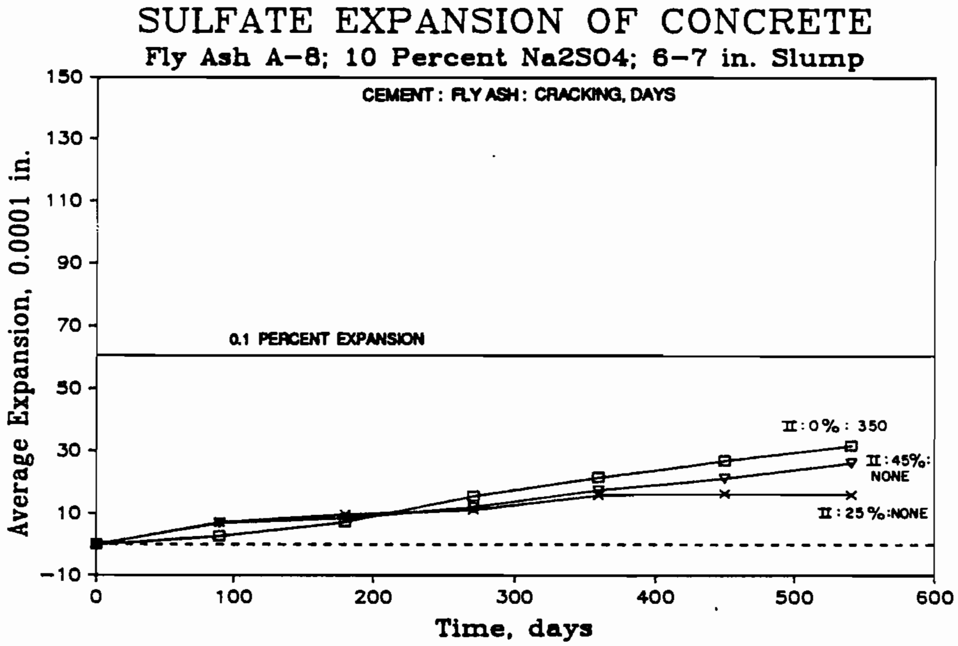


Figure 7.48 Sulfate expansion of concrete containing fly ash A-8.

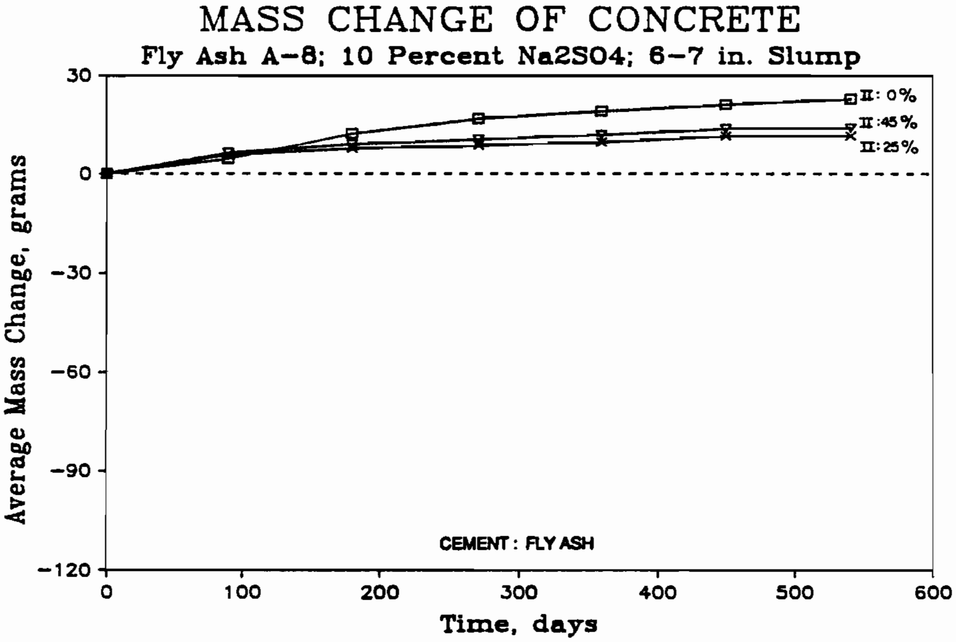


Figure 7.49 Sulfate mass loss of concrete containing fly ash A-8.

from these mixtures were less than that of the Type II control. Neither concrete mixture showed signs of cracking.

Fly ash A-9 was a fly ash from a Texas lignite coal source.

This fly ash was used as a volumetric replacement for portland cement in two 6 inch slump mixtures, II:25%:A-9 and II:45%:A-9.

The results of the sulfate resistance testing are presented in Figures 7.50 and 7.51. The expansion of mixture II:25%:A-9 was slightly greater than that of the Type II control, whereas the expansion of mixture II:45%:A-9 was less than that of the Type II control. The changes in mass of the concrete from these mixtures were equal to or less than that of the Type II control. The concrete mixture II:25%:A-9 cracked after 440 days of sulfate exposure testing. The concrete mixture II:45%:A-9 showed no signs of cracking.

Fly ash A-10 was the only high calcium fly ash among the Texas SDHPT Type A fly ashes. It was produced from a subbituminous coal source identical to several of the Type B fly ashes used in this study. This fly ash was used as a volumetric replacement for portland cement in 10 mixtures. Those mixtures were as follows:

6 in. slump	2 in. slump
II:25%:A-10	II:25%:A-10
II:35%:A-10	II:35%:A-10
II:45%:A-10	II:45%:A-10
I:25%:A-10	II:25%:A-10 (3 day)
I:35%:A-10	II:35%:A-10 (28 day)

M.C. refers to moist curing

The results of the sulfate resistance testing are presented in Figures 7.52 through 7.55. The sulfate expansions and changes in mass of the concrete from these mixtures were less than that of the Type II control, except in the 6 inch slump mixture I:35%:A-10. This mixture had a 360 day expansion greater than that of the Type II control and a mass loss from spalling. A minor mass loss was also observed in the 2 inch slump concrete mixture II:45%:A-10. Seven of the 10 concrete mixtures containing fly ash A-10 showed signs of cracking before the Type II control. The 2 inch slump mixtures II:35%:A-10 (3 day) and II:25%:A-10 (28 day) cracked at

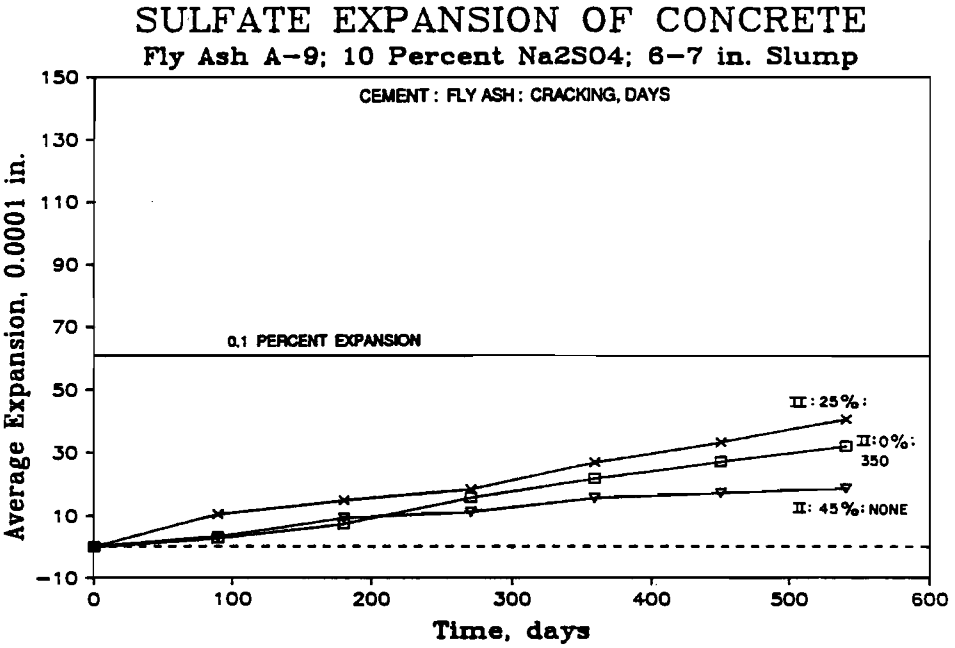


Figure 7.50 Sulfate expansion of concrete containing fly ash A-9.

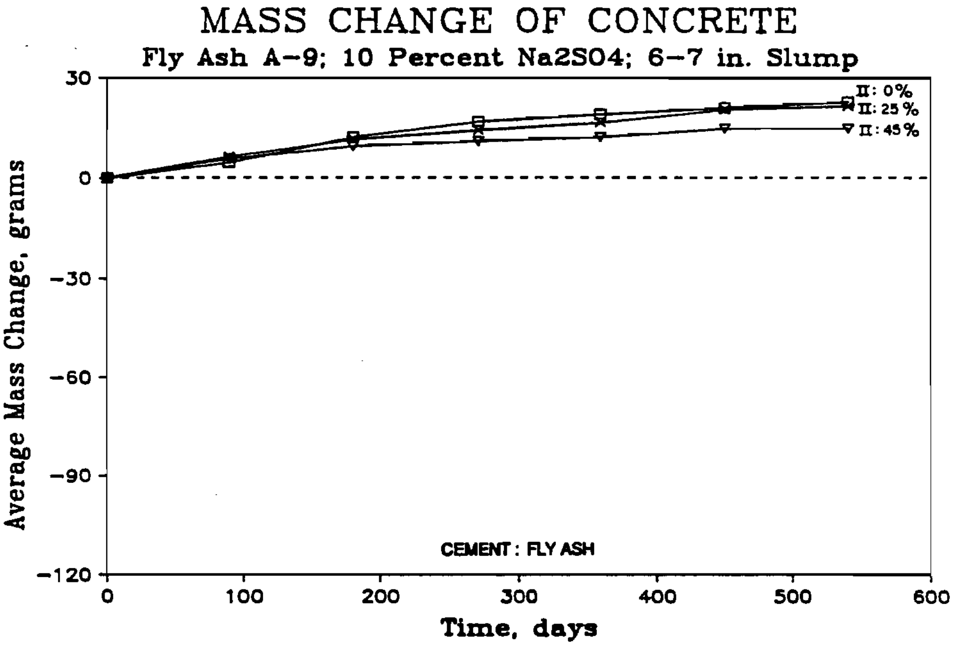


Figure 7.51 Sulfate mass loss of concrete containing fly ash A-9.

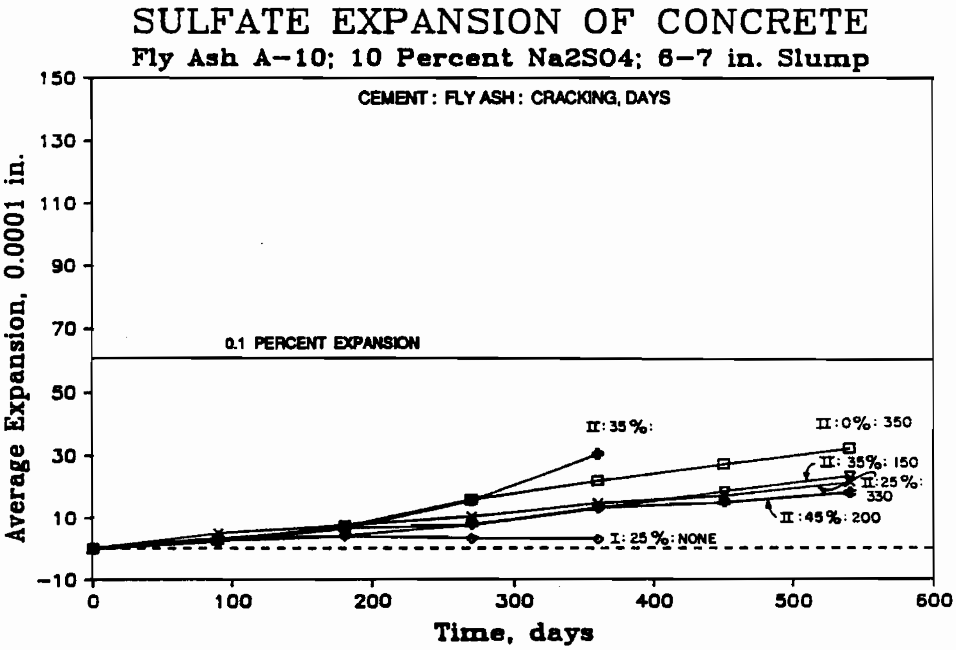


Figure 7.52 Sulfate expansion of concrete containing fly ash A-10.

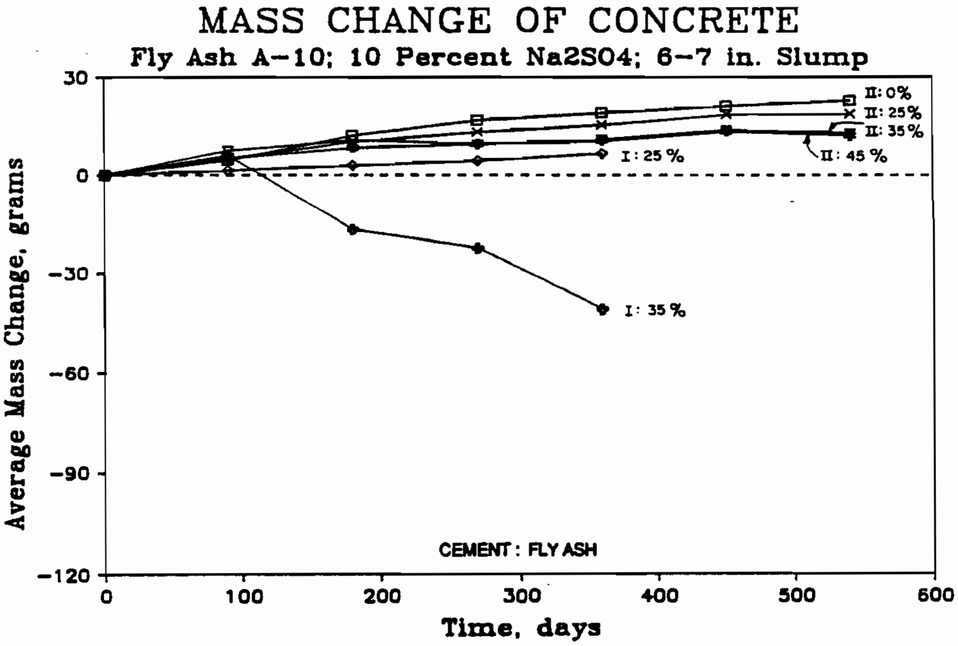


Figure 7.53 Sulfate mass loss of concrete containing fly ash A-10.

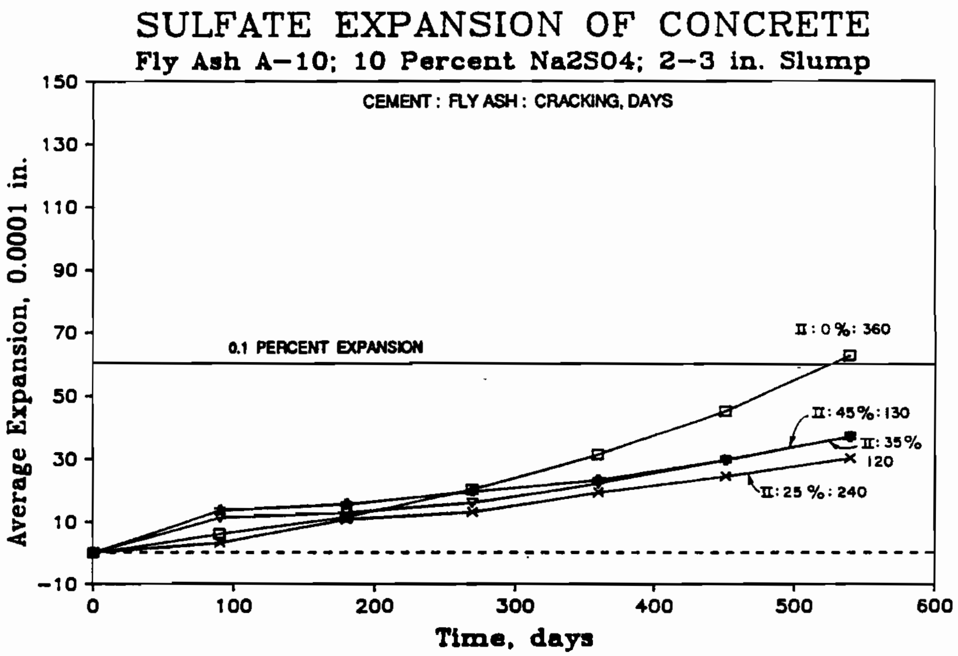


Figure 7.54 Sulfate expansion of concrete containing fly ash A-10.

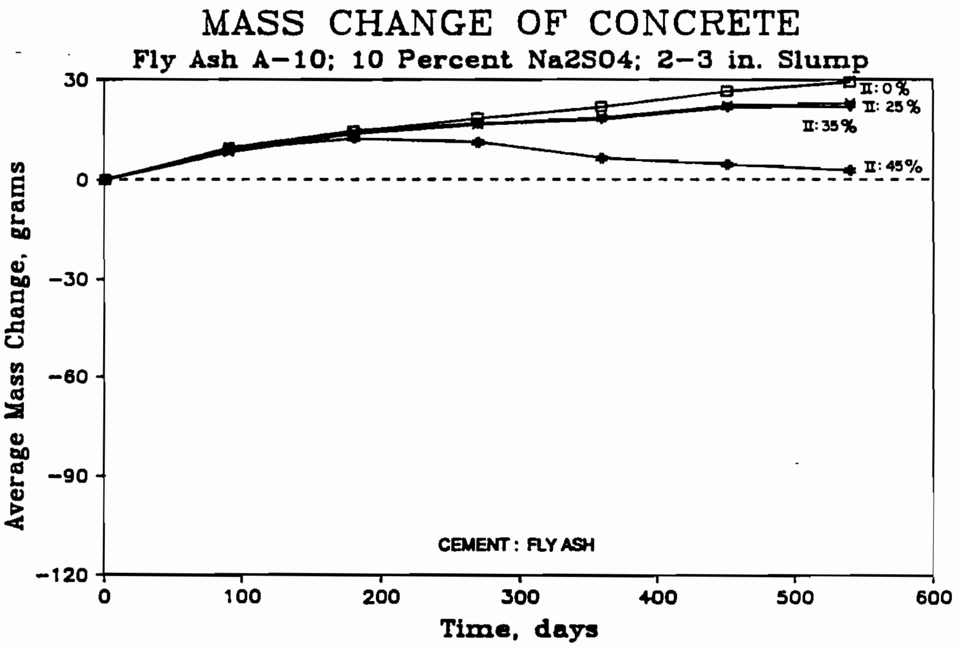


Figure 7.55 Sulfate mass loss of concrete containing fly ash A-10.

ages greater than that of the control at ages of 420 and 450 days, respectively. The concrete mixture I:25%:A-10 remained uncracked after 360 days of sulfate exposure testing.

7.4.3 Texas SDHPT Type B Fly Ash. The Texas SDHPT Type B fly ashes used in this study were all high calcium fly ashes. Fly ashes B-1 through B-8 had total silica contents less 40 percent and calcium oxide contents in excess of 20 percent. All of these Type B fly ashes met the chemical requirements of ASTM Class C fly ash.

Fly ash B-1 was produced from a subbituminous coal source. This fly ash was used as a volumetric replacement for portland cement in 8 mixtures. Those mixtures were as follows:

6 in. slump	2 in. slump
II:25%:B-1	II:25%:B-1
II:35%:B-1	II:35%:B-1
II:45%:B-1	II:45%:B-1
I:25%:B-1	II:25%:B-1 (3 day)

M.C. refers to moist curing

The results of the sulfate resistance testing are presented in Figures 7.56 through 7.59. The sulfate expansions and changes in mass of the 6 inch slump concrete containing fly ash B-1 were equal to or greater than that of the Type II control, except in the 6 inch slump mixture I:25%:B-1. This mixture had a 360 day expansion and mass change less than that of the Type II control. Spalling was observed in the 6 inch slump mixtures II:35%:B-1 and II:45%:B-1. The expansions of the 2 inch slump concrete mixtures containing fly ash B-1 were less than that of the Type II control. In the 2 inch slump concrete mixtures, only mixture II:45%:B-1 experienced a mass change greater than that of the Type II control. Spalling was observed in the specimens from this mixture. All concrete mixtures containing fly ash B-1 showed signs of cracking before or at the same age as the Type II control.

Fly ash B-2 was produced from a subbituminous coal source. This fly ash was used as a volumetric replacement for portland cement in two 6 inch slump mixtures, II:25%:B-2 and II:25%:B-2. The results of the sulfate resistance testing are presented in Figures 7.60 and 7.61. The sulfate expansion and change in mass

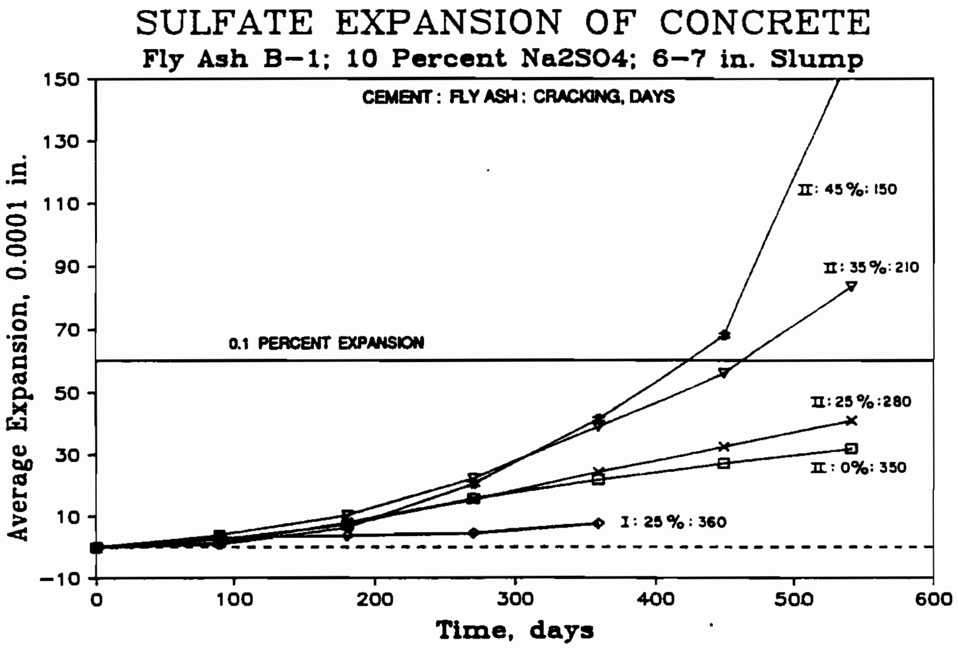


Figure 7.56 Sulfate expansion of concrete containing fly ash B-1.

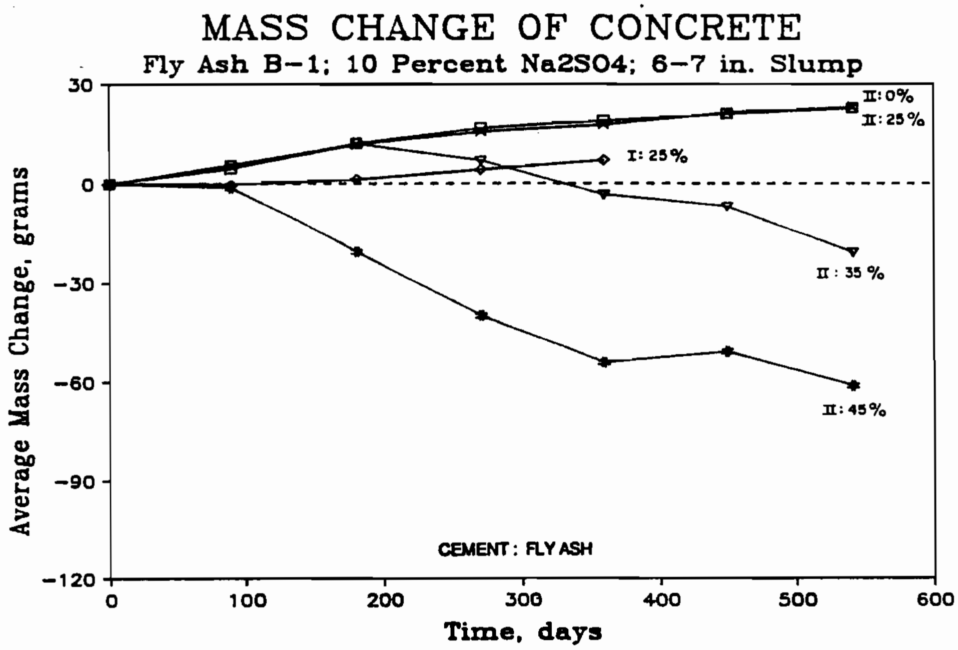


Figure 7.57 Sulfate mass loss of concrete containing fly ash B-1.

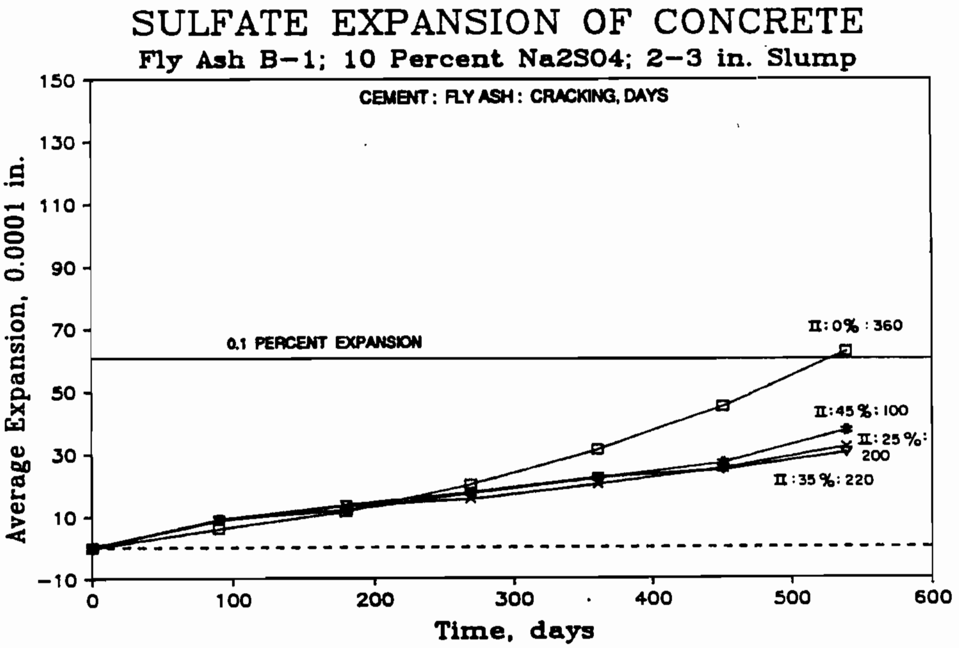


Figure 7.58 Sulfate expansion of concrete containing fly ash B-1.

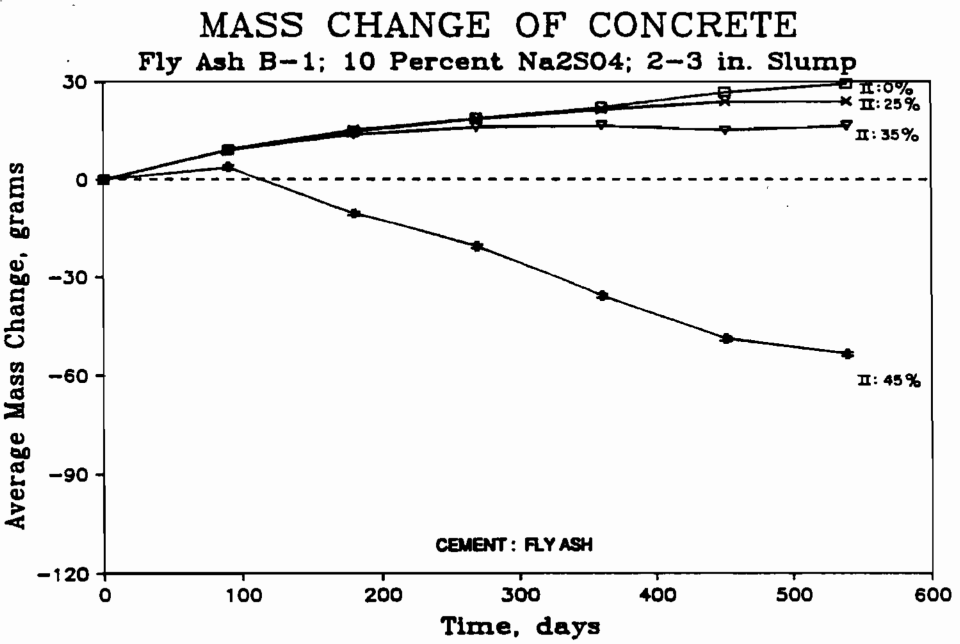


Figure 7.59 Sulfate mass loss of concrete containing fly ash B-1.

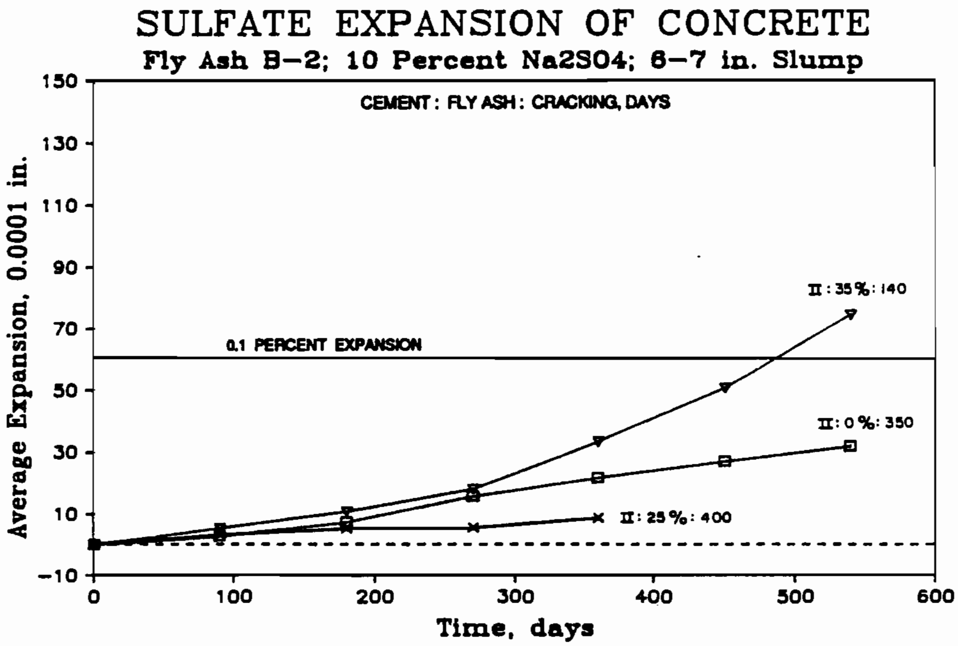


Figure 7.60 Sulfate expansion of concrete containing fly ash B-2.

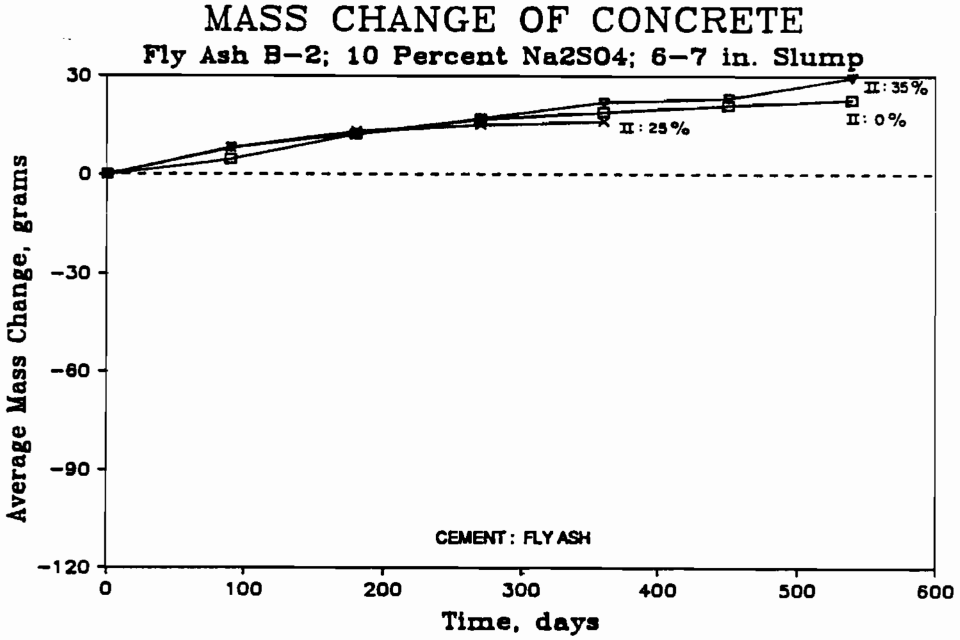


Figure 7.61 Sulfate mass loss of concrete containing fly ash B-2.

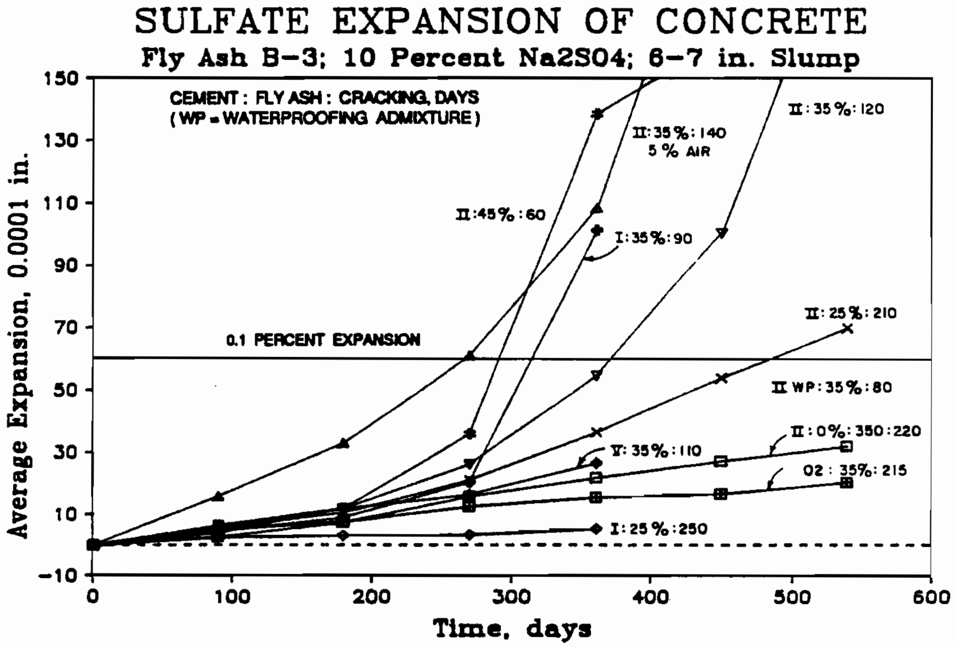
of the 6 inch slump concrete mixture II:35%:B-2 were greater than that of the Type II control. This mixture also exhibited cracking at ages earlier than the Type II control. The sulfate expansion and change in mass of the 6 inch slump concrete mixture II:25%:B-2 were less than that of the Type II control. This mixture exhibited cracking after 400 days, slightly later than the Type II control.

Fly ash B-3 was produced from a subbituminous coal source. This fly ash was used as a volumetric replacement for portland cement in 16 mixtures. Those mixtures were as follows:

6 in. slump	2 in. slump
II:25%:B-3	II:25%:B-3
II:35%:B-3	II:35%:B-3
II:45%:B-3	II:45%:B-3
I:25%:B-3	II:35%:B-3 (3 day)
I:35%:B-3	II:45%:B-3 (3 day)
II:35%:B-3 (5% Air)	II:25%:B-3 (28 day)
02:35%:B-3	II:35%:B-3 (repeat)
V:35%:B-3	
II:35%:B-3 (waterproofing)	

M.C. refers to moist curing

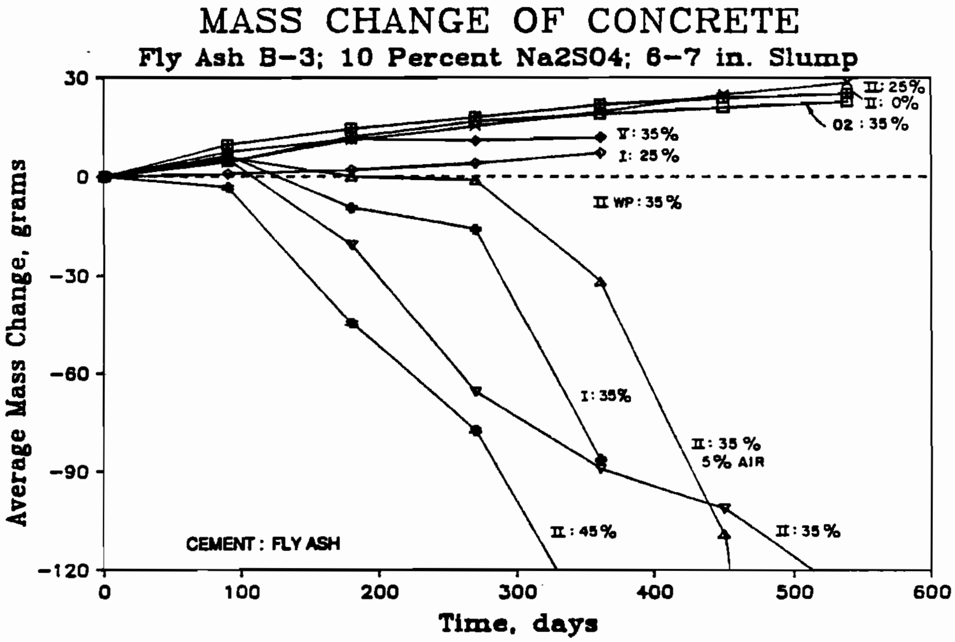
The results of the sulfate resistance testing are presented in Figures 7.62 through 7.65. The sulfate expansions and changes in mass of the Type II portland cement concrete containing fly ash B-3 were greater than that of the Type II control, with the exception of the 2 inch slump mixture II:25%:B-3 which had a sulfate expansion and mass change identical to that or the Type II control. In addition, the 6 inch concrete mixture I:35%:B-3 had a greater expansion and mass change than the Type II control. The 6 inch slump concrete mixtures V:35%:B-3, 02:35%:B-3, and I:25%:B-3 exhibited sulfate expansions and mass changes less than that of the Type II control. Spalling was observed in all the concrete mixtures containing fly ash B-3 except the 6 inch slump mixtures II:25%:B-3, V:35%:B-3, 02:35%:B-3, and I:25%:B-3; and the 2 inch slump mixture II:25%:B-3. All concrete mixtures containing fly ash B-3 showed signs of cracking at earlier ages than the Type II control.



SULFATE EXPANSION OF CONCRETE

Fly Ash B-3; 10 Percent Na2SO4; 6-7 in. Slump

Figure 7.62 Sulfate expansion of concrete containing fly ash B-3.



MASS CHANGE OF CONCRETE

Fly Ash B-3; 10 Percent Na2SO4; 6-7 in. Slump

Figure 7.63 Sulfate mass loss of concrete containing fly ash B-3.

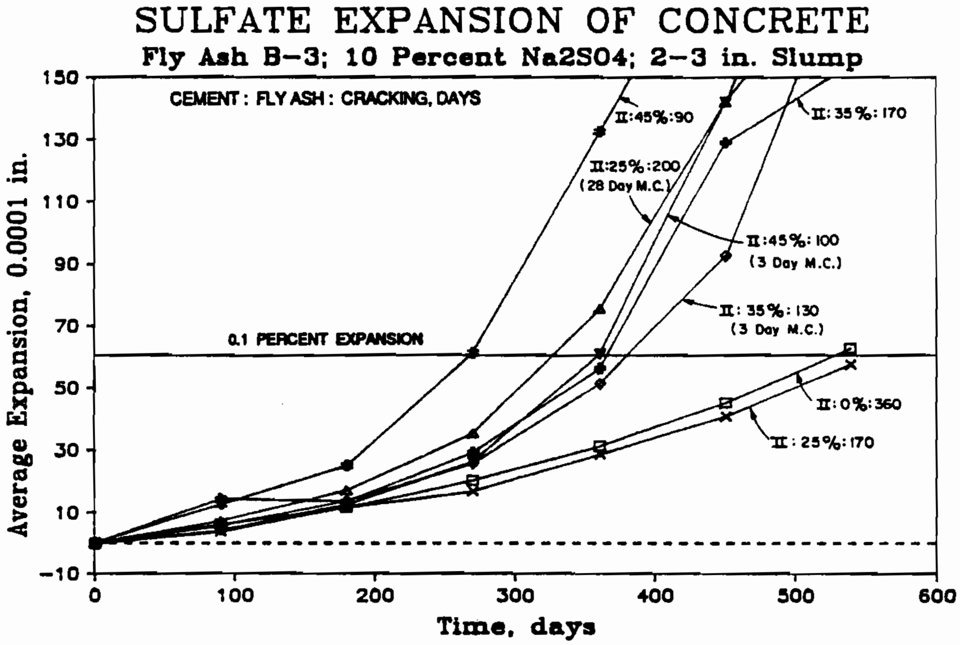


Figure 7.64 Sulfate expansion of concrete containing fly ash B-3.

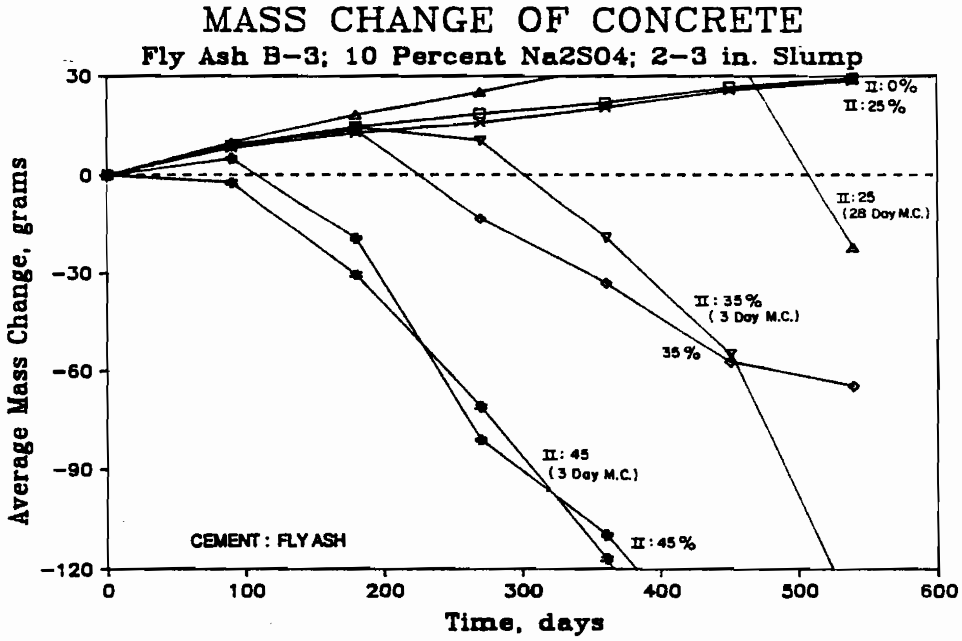


Figure 7.65 Sulfate mass loss of concrete containing fly ash B-3.

Fly ash B-4 was produced from a subbituminous coal source. This fly ash was used as a volumetric replacement for portland cement in six 6 inch slump mixtures. Those mixtures were as follows: II:25%:B-4, II:35%:B-4, II:45%:B-4, I:25%:B-4, I:35%:B-4, and II:25%:B-4 (seawater). The results of the sulfate resistance testing are presented in Figures 7.66 and 7.67. The sulfate expansions and the changes in mass of the Type II portland cement concrete containing fly ash B-3 were greater than that of the Type II control, with the exception of the concrete which contained seawater. The concrete mixture II:25%:B-4 (seawater) had a sulfate expansion and mass change less than that of the Type II control. The 6 inch concrete mixture I:25%:B-4 had an expansion less than the Type II control but exhibited a mass change greater than the Type II control. Spalling was observed in all the concrete mixtures containing fly ash B-4 except the mixture containing seawater. All concrete mixtures containing fly ash B-4 showed signs of cracking at earlier ages than the Type II control.

Fly ash B-5 was produced from a subbituminous coal source. This fly ash was used as a volumetric replacement for portland cement in 12 mixtures. Those mixtures were as follows:

6 in. slump	2 in. slump
II:25%:B-5	II:25%:B-5
II:35%:B-5	II:35%:B-5
II:45%:B-5	II:45%:B-5
I:25%:B-5	II:35%:B-5 (3 day)
II:35%:B-5 (5% Air)	II:25%:B-5 (28 day)
II:35%:B-5 (3 day)	
02:35%:B-5	

M.C. refers to moist curing

The results of the sulfate resistance testing are presented in Figures 7.68 through 7.71. The sulfate expansions and changes in mass of the Type II portland cement concrete containing fly ash B-5 were greater than that of the Type II control, with the exception of the 6 inch slump mixture II:25%:B-5. Concrete mixtures II:25%:B-5 and I:25%:B-5 had a sulfate expansions slightly less than the Type II control, but exhibited mass losses from spalling. Spalling was observed in all the concrete

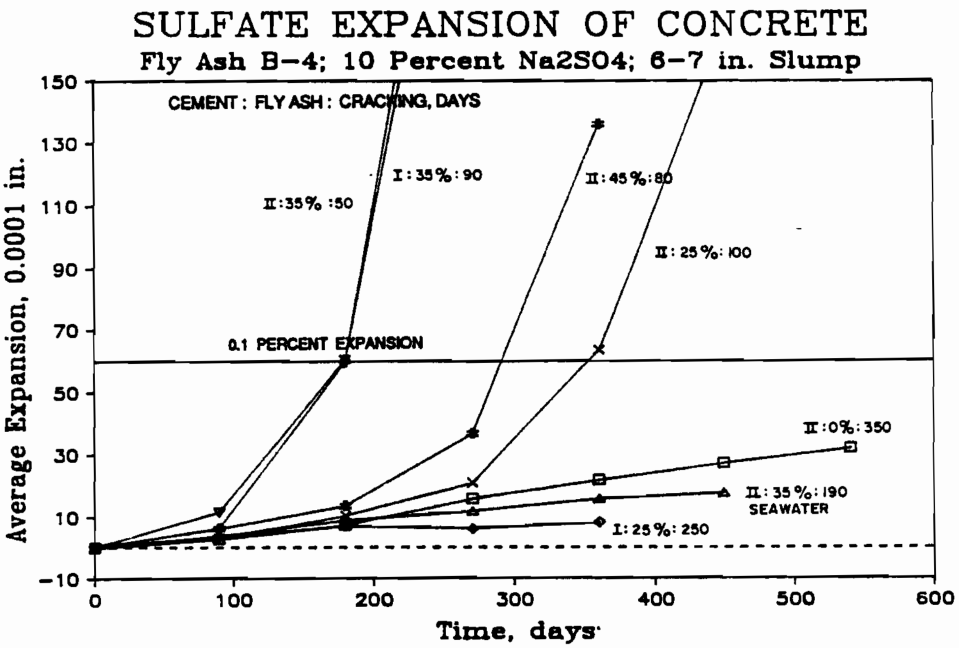


Figure 7.66 Sulfate expansion of concrete containing fly ash B-4.

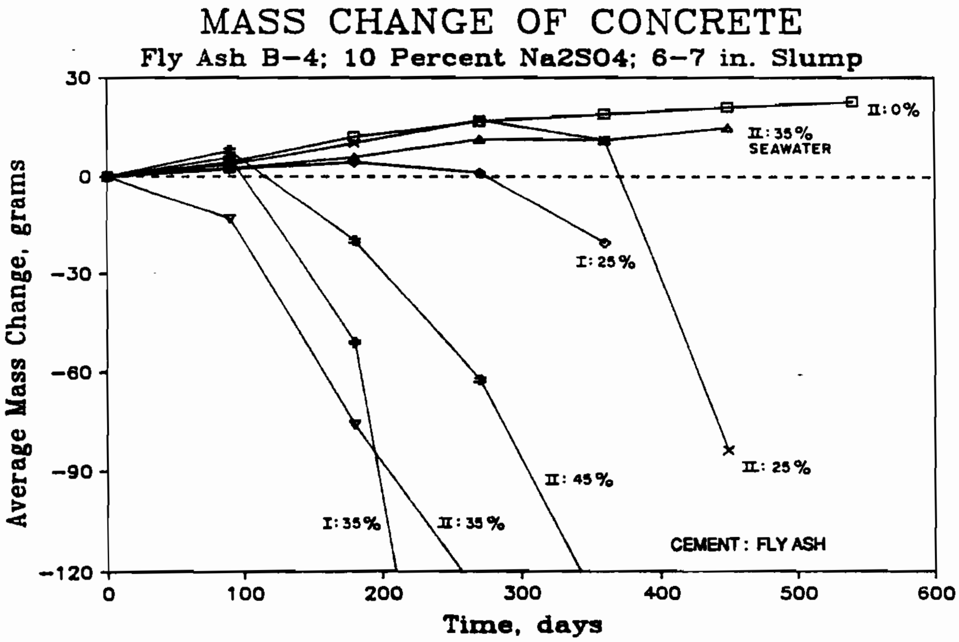


Figure 7.67 Sulfate mass loss of concrete containing fly ash B-4.

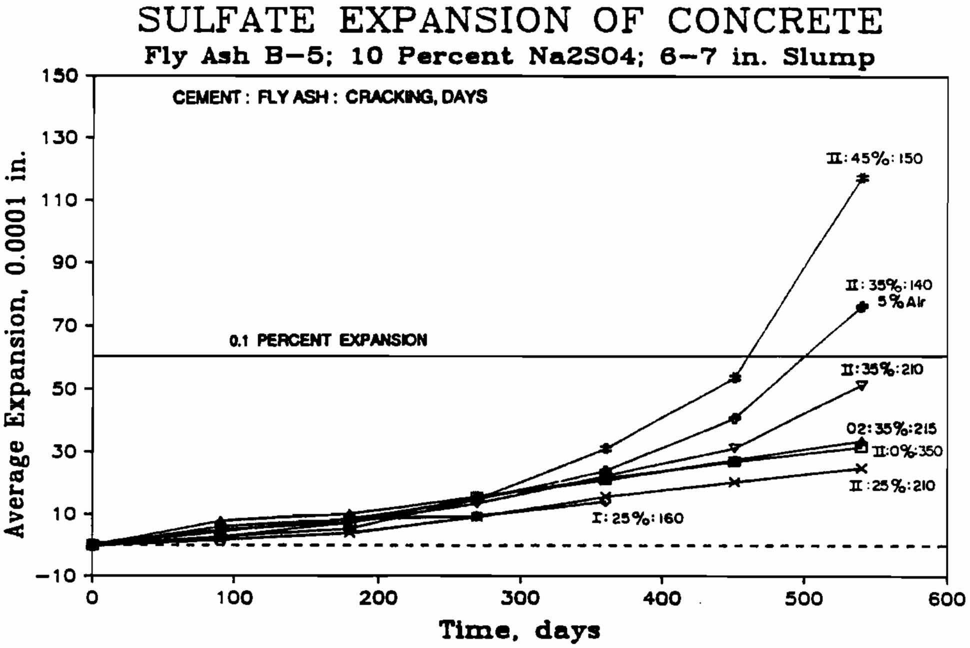


Figure 7.68 Sulfate expansion of concrete containing fly ash B-5.

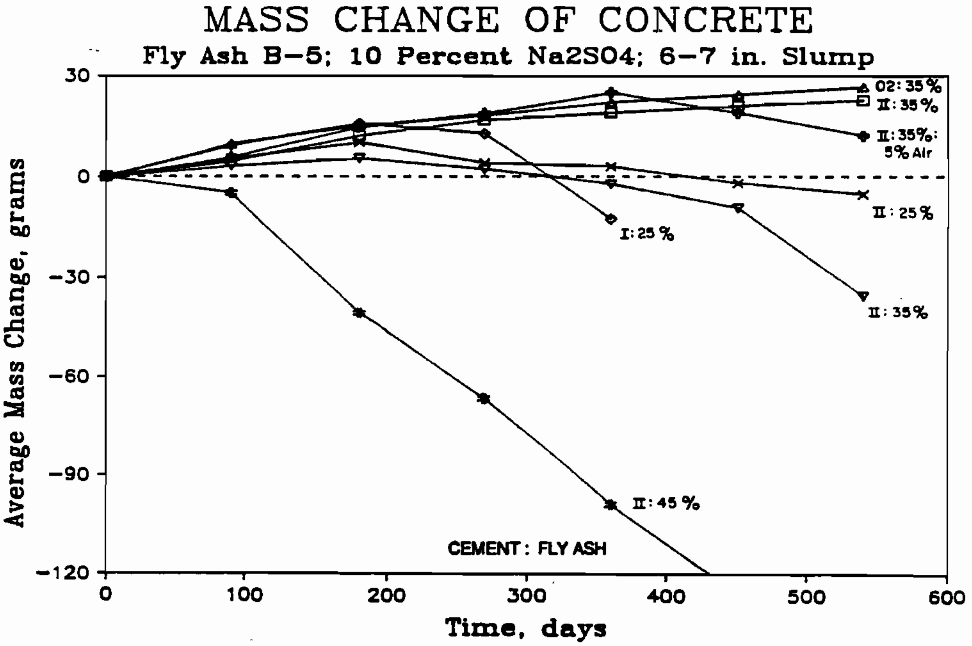


Figure 7.69 Sulfate mass loss of concrete containing fly ash B-5.

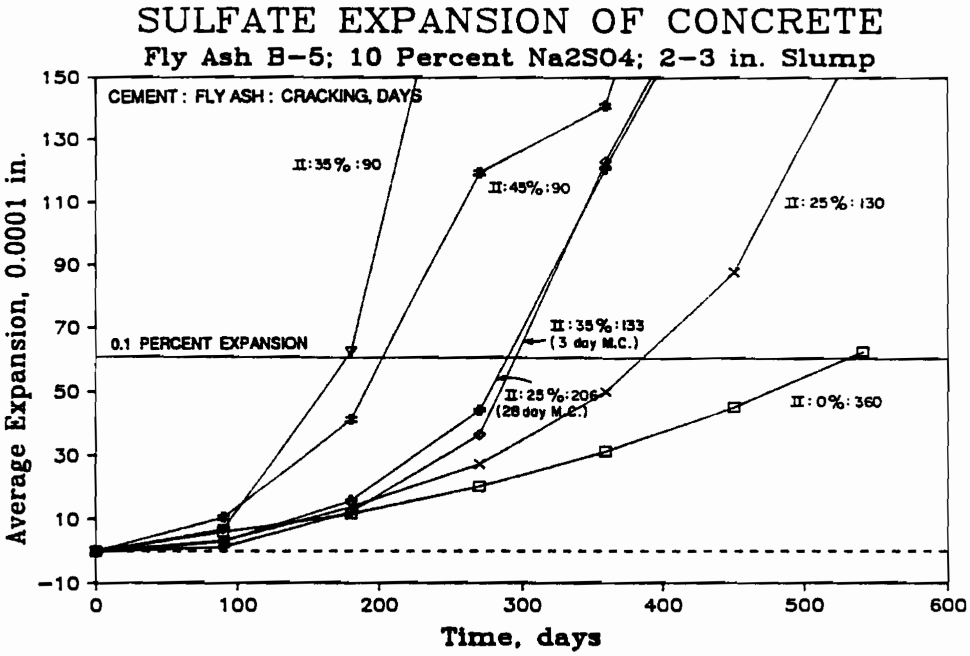


Figure 7.70 Sulfate expansion of concrete containing fly ash B-5.

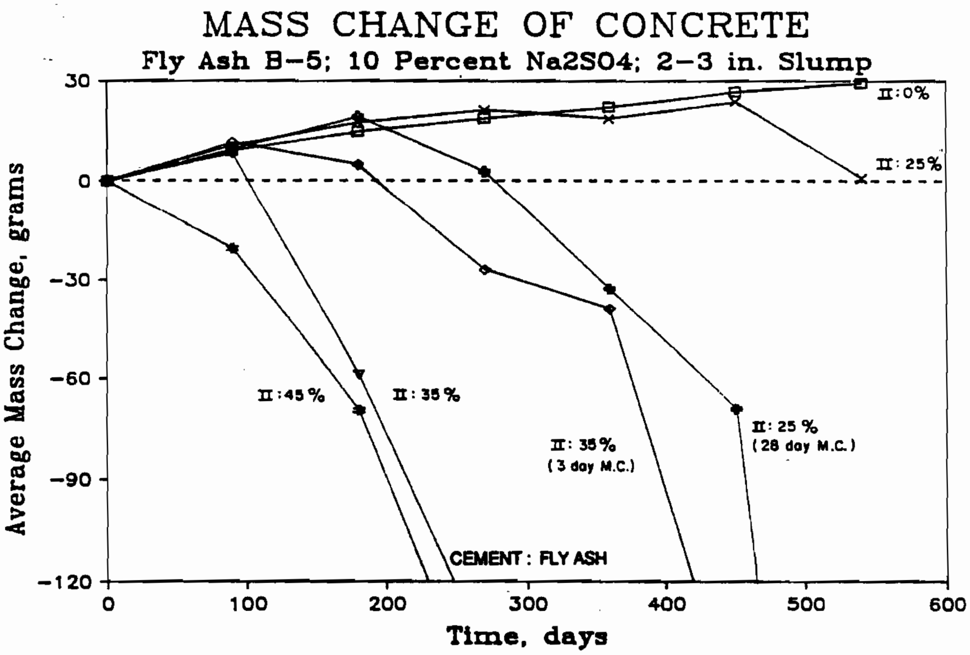


Figure 7.71 Sulfate mass loss of concrete containing fly ash B-5.

mixtures containing fly ash B-5. All concrete mixtures containing fly ash B-5 showed signs of cracking at earlier ages than the Type II control.

Fly ash B-6 was produced from a subbituminous coal source. This fly ash was used as a volumetric replacement for portland cement in 11 mixtures. Those mixtures were as follows:

6 in. slump	2 in. slump
II:25%:B-6	II:25%:B-6
II:35%:B-6	II:35%:B-6
II:45%:B-6	II:45%:B-6
02:35%:B-5	II:35%:B-6 (3 day)
II:35%:B-6 (5% Air)	II:25%:B-6 (28 day)
II:35%:B-6	

M.C. refers to moist curing

The results of the sulfate resistance testing are presented in Figures 7.72 through 7.75. The sulfate expansions and changes in mass of concrete containing fly ash B-6 were greater than that of the Type II control. Spalling was observed in all the concrete mixtures containing fly ash B-6 except the 6 inch slump concrete mixtures II:25%:B-6 and 02:35%:B-6. All concrete containing fly ash B-6 showed signs of cracking at earlier ages than the Type II control.

Fly ash B-7 was produced from a subbituminous coal source. This fly ash was used as a volumetric replacement for portland cement in one 6 inch slump mixture, II:35%:B-7. The results of the sulfate resistance testing are presented in Figures 7.76 and 7.77. The sulfate expansion and change in mass of concrete containing fly ash B-7 was greater than that of the Type II control. All concrete containing fly ash B-7 showed signs of cracking at an earlier age than the Type II control.

Fly ash B-8 was produced from a subbituminous coal source. This fly ash was used as a volumetric replacement for portland cement in 14 mixtures. Those mixtures were as follows:

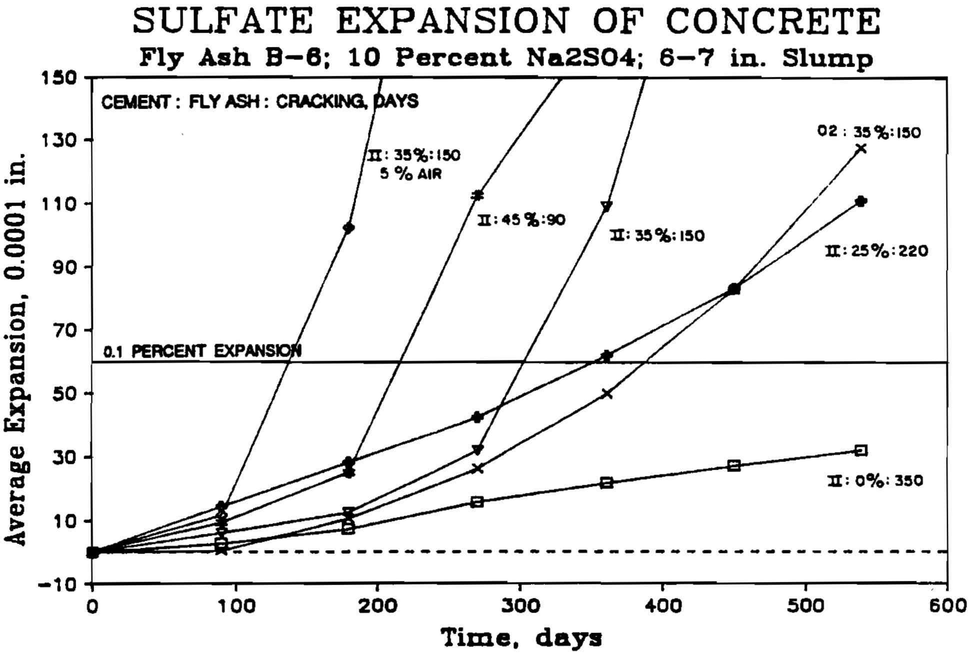


Figure 7.72 Sulfate expansion of concrete containing fly ash B-6.

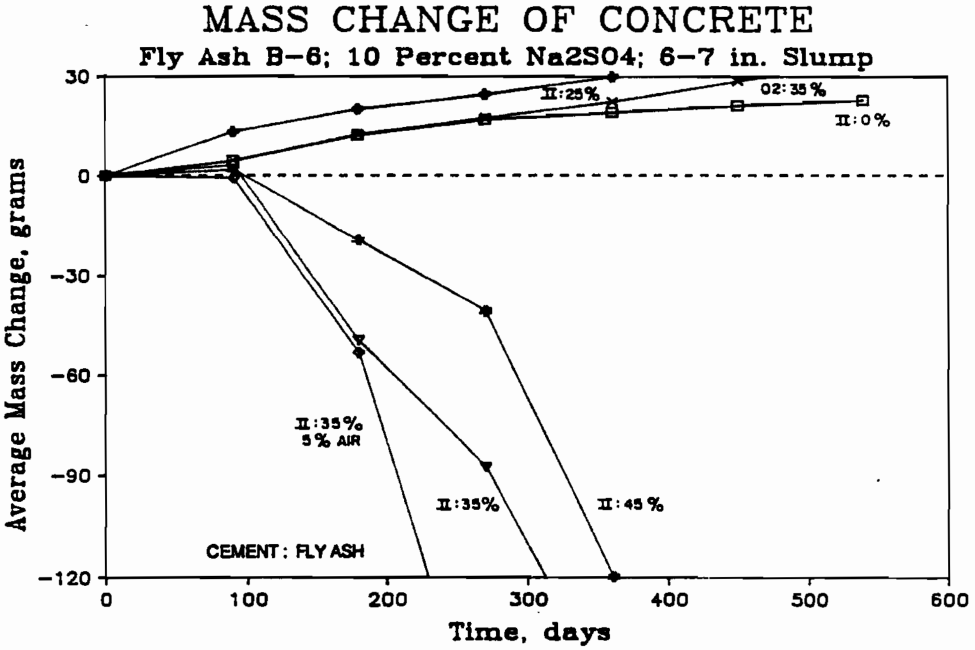


Figure 7.73 Sulfate mass loss of concrete containing fly ash B-6.

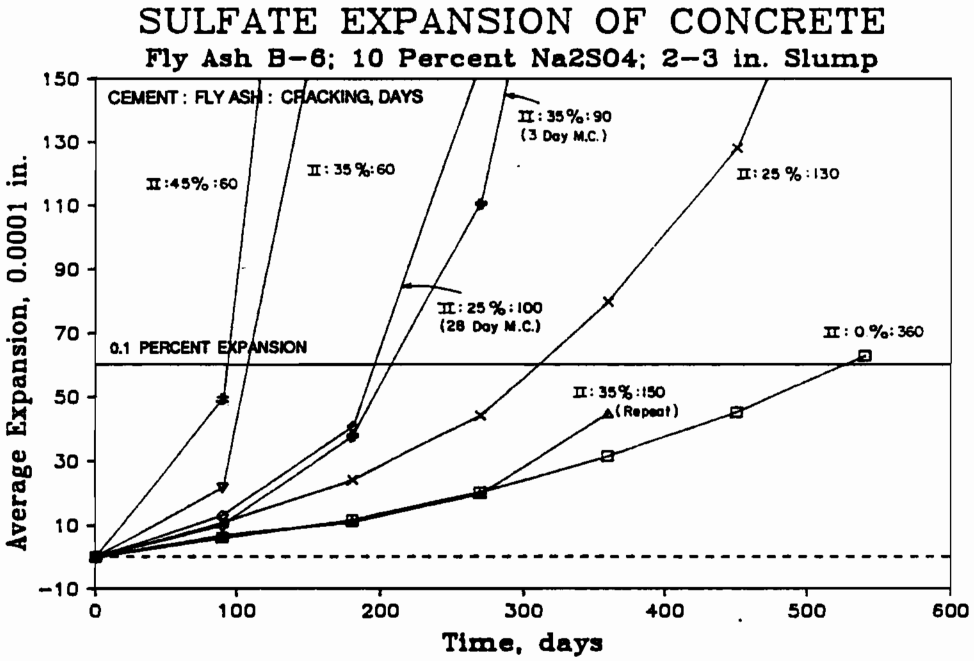


Figure 7.74 Sulfate expansion of concrete containing fly ash B-6.

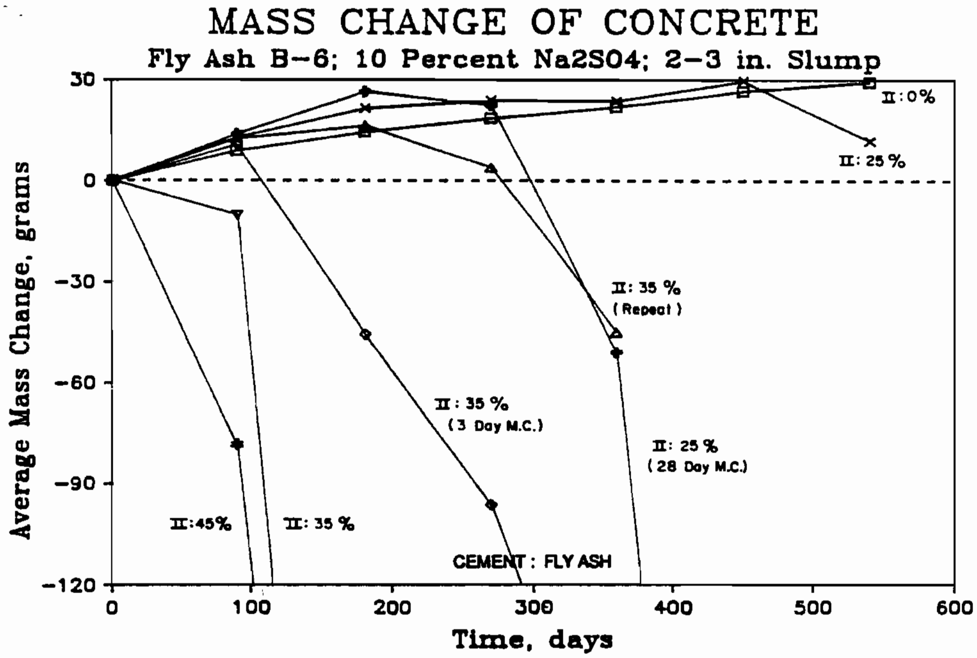


Figure 7.75 Sulfate mass loss of concrete containing fly ash B-6.

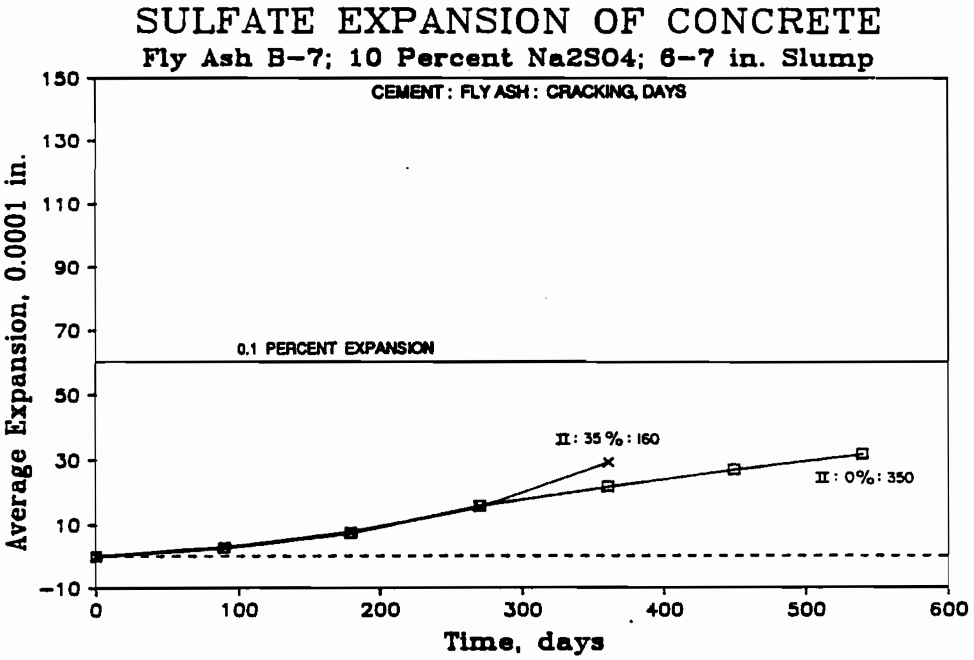


Figure 7.76 Sulfate expansion of concrete containing fly ash B-7.

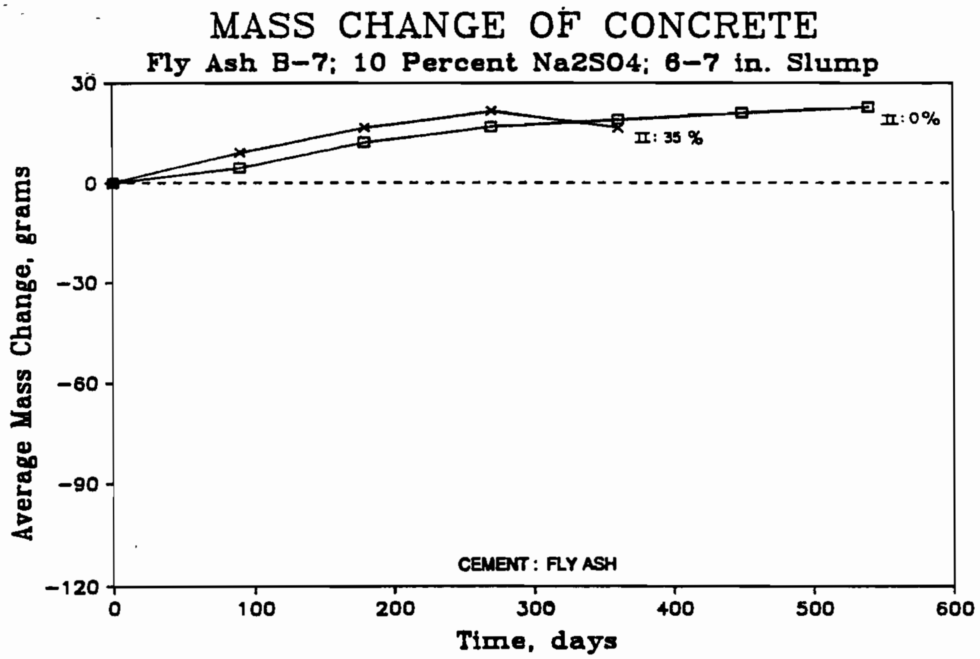


Figure 7.77 Sulfate mass loss of concrete containing fly ash B-7.

6 in. slump	2 in. slump
II:25%:B-8	II:25%:B-8
II:35%:B-8	II:35%:B-8
II:45%:B-8	II:45%:B-8
02:35%:B-8	II:25%:B-8 (repeat)
II:35%:B-8 (5% air)	II:25%:B-8 (28 day)
II:35%:B-8 (repeat)	
II:35%:B-8 (seawater)	
II:35%:B-8 (3 day)	
II:35%:B-8 (repeat)	

M.C. refers to moist curing

The results of the sulfate resistance testing are presented in Figures 7.78 through 7.81. The sulfate expansions and changes in mass of concrete containing fly ash B-8 were greater than that of the Type II control with the exception of the 6 inch slump concrete mixture II:25%:B-8 which had sulfate expansion slightly less than the Type II control. Spalling was observed in all the concrete mixtures containing fly ash B-8 except the 6 inch slump concrete mixtures 02:35%:B-8. All concrete containing fly ash B-8 showed signs of cracking at earlier ages than the Type II control.

7.4.4 Other Pozzolans. Other pozzolans used in this study, other than the fly ashes described above, were silica fume and blast furnace slag. These pozzolans were used in the typical manner in which they are used in portland cement concrete i.e. silica fume as a low percentage addition to portland cement and blast furnace slag as a high percentage replacement for portland cement.

7.1 Both pozzolans were produced as a byproduct of an industrial furnace. These pozzolans were used in four 6 inch slump concrete mixtures, II:+9%:S-1, I:+9%:S-1, II:65%:S-2, and I:65%:S-2. Concrete containing pozzolans S-1 and S-2 exhibited expansions and changes in mass less than that of the Type II control. Cracking was observed in concrete containing S-1 and S-2 at or before 400 days of exposure testing. Figures 7.82 through 7.85 show the results of sulfate exposure testing.

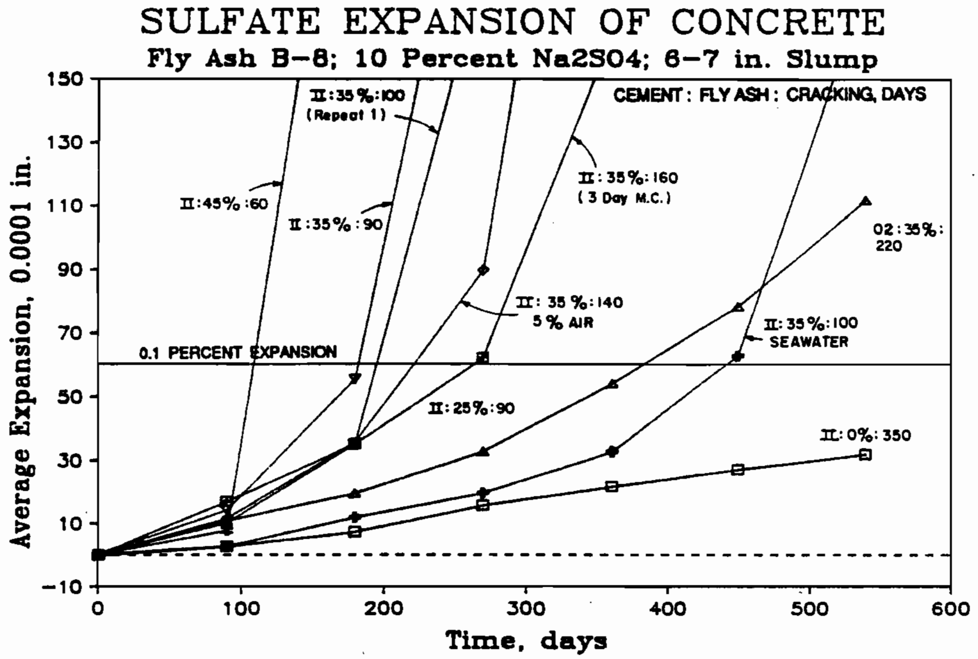


Figure 7.78 Sulfate expansion of concrete containing fly ash B-8.

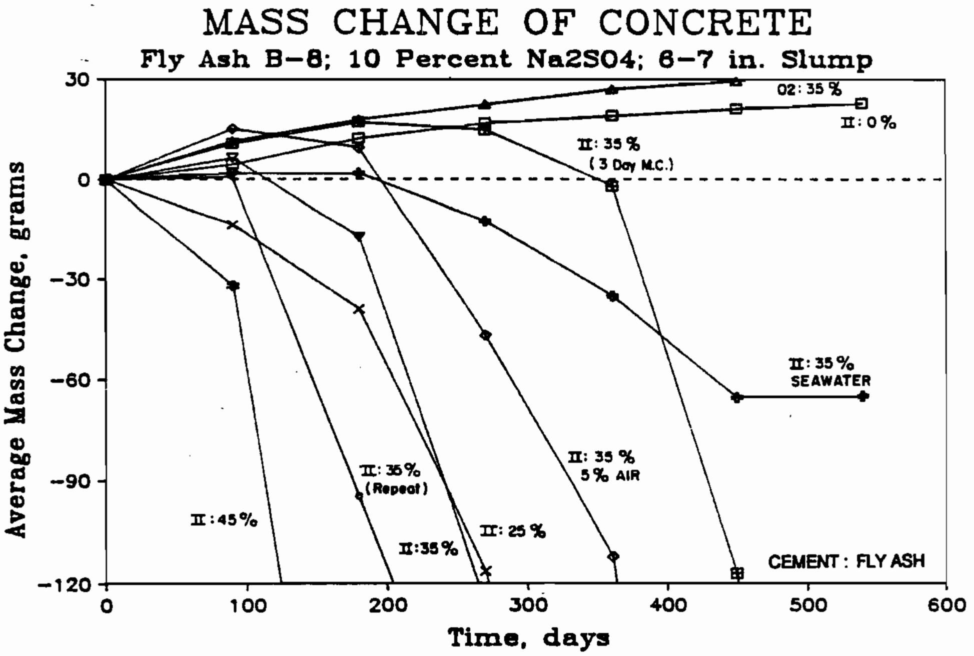


Figure 7.79 Sulfate mass loss of concrete containing fly ash B-8.

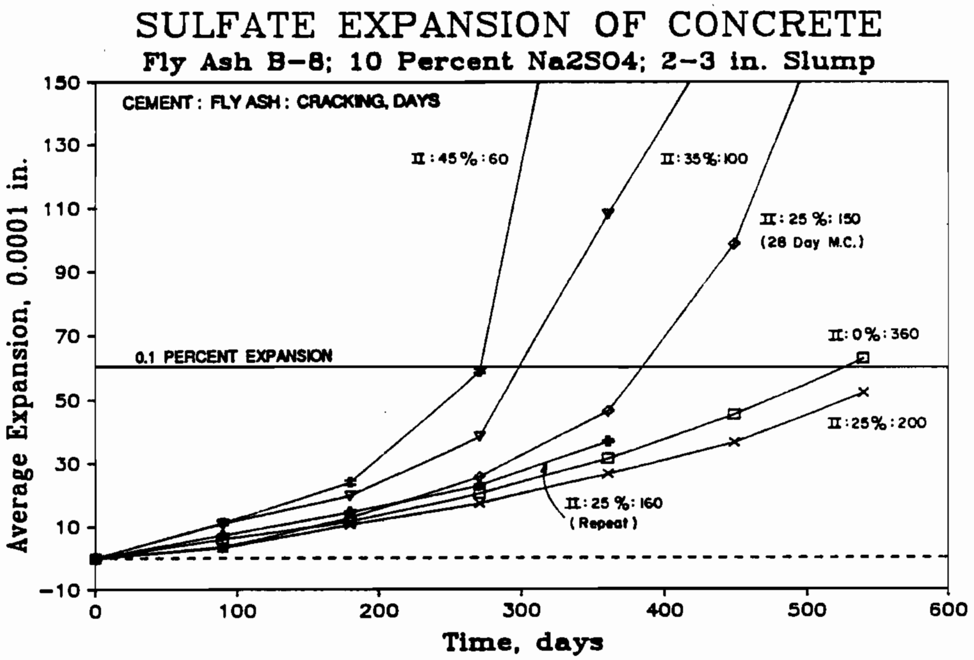


Figure 7.80 Sulfate expansion of concrete containing fly ash B-8.

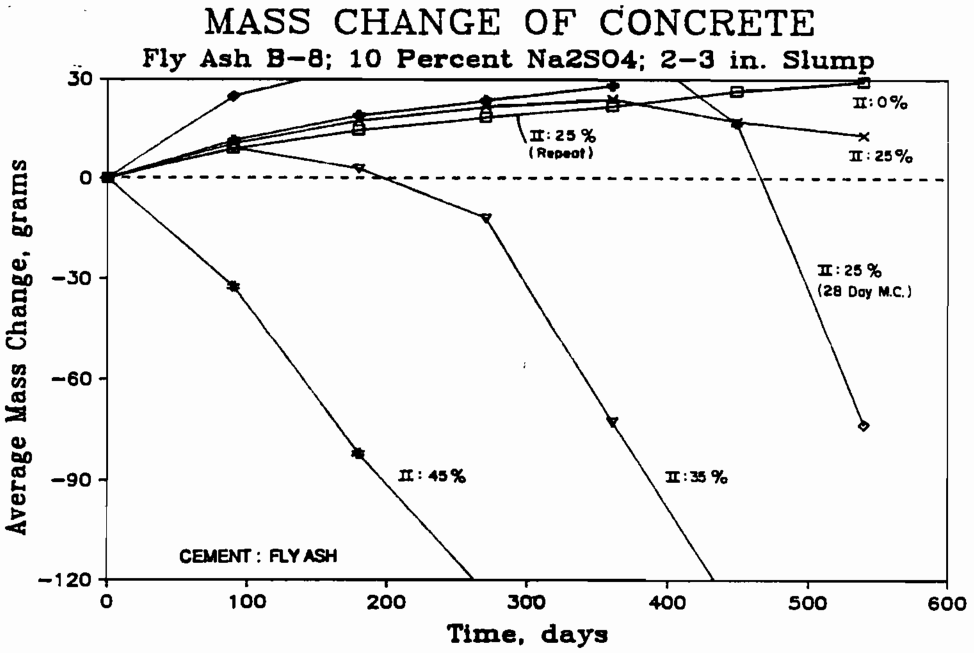


Figure 7.81 Sulfate mass loss of concrete containing fly ash B-8.

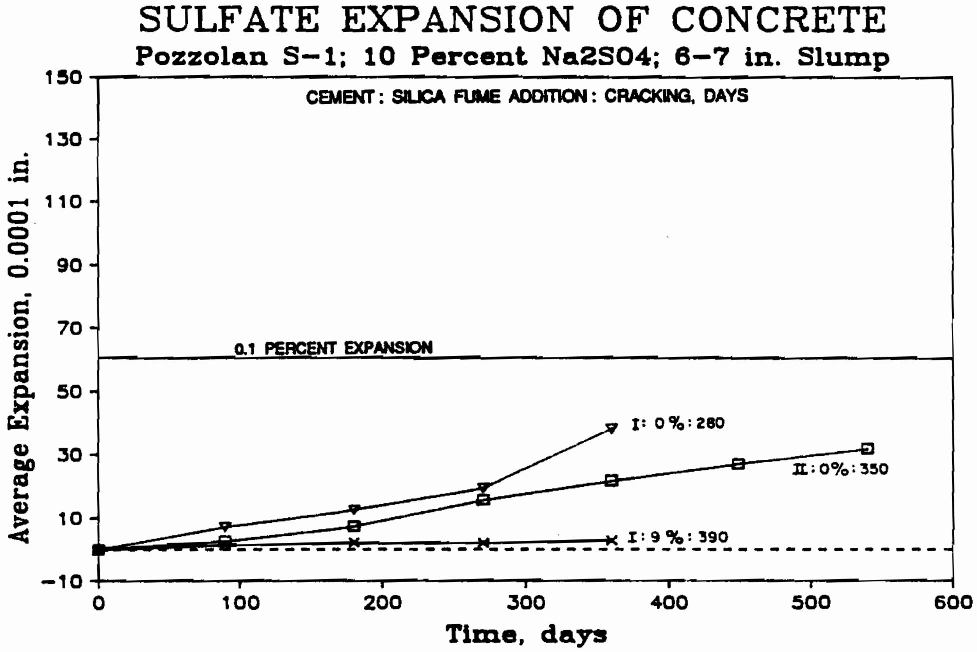


Figure 7.82 Sulfate expansion of concrete containing silica fume.

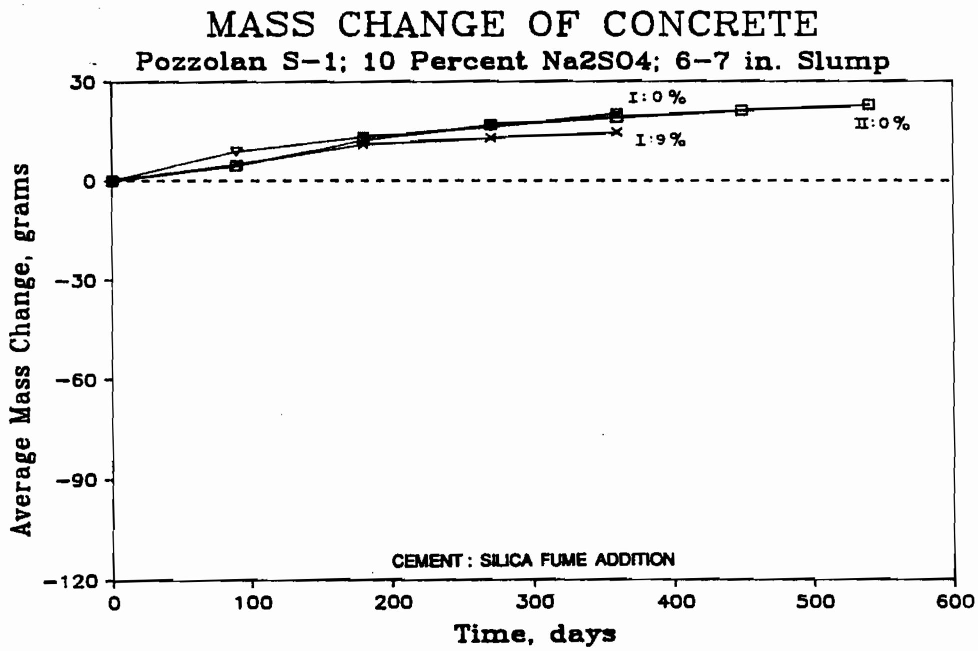


Figure 7.83 Sulfate mass loss of concrete containing silica fume.

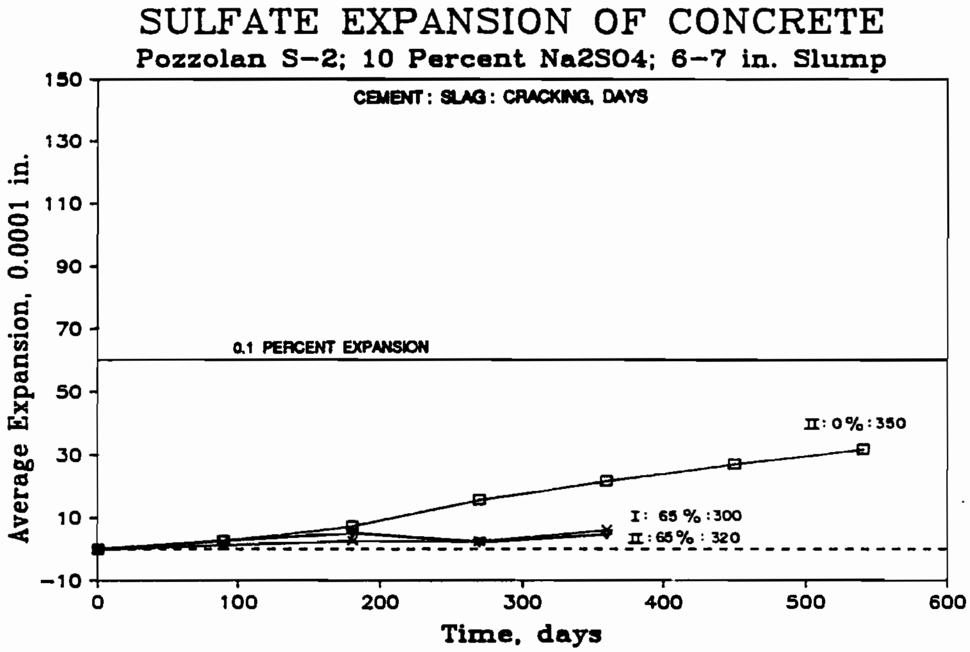


Figure 7.84 Sulfate expansion of concrete containing slag.

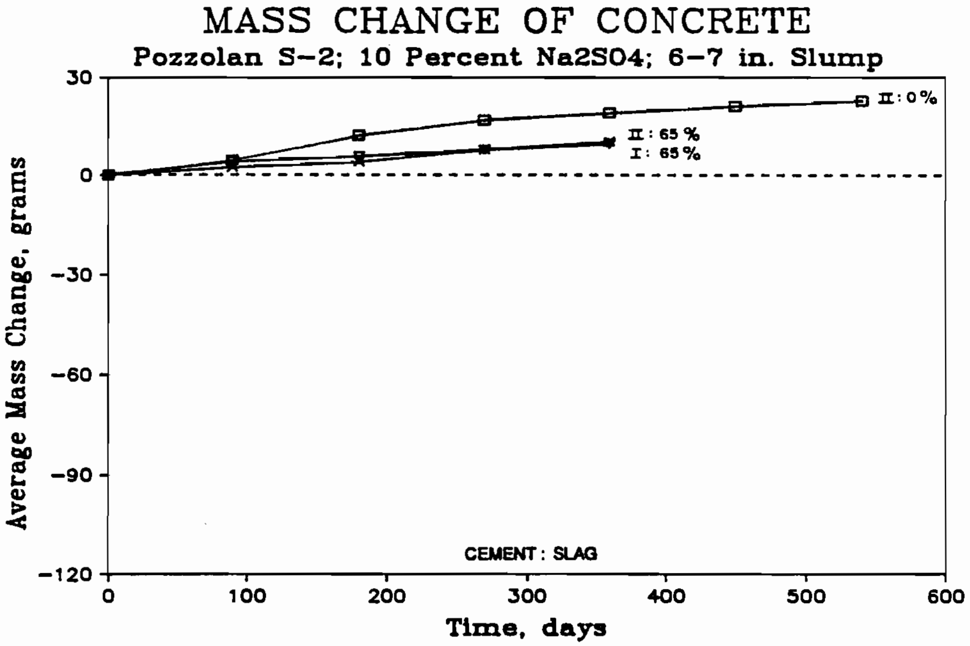


Figure 7.85 Sulfate mass loss of concrete containing slag.

CHAPTER VIII
DISCUSSION OF TEST RESULTS

8.1 General

This experimental test program was conducted to compare the sulfate resistance of concrete containing fly ash to that of Type II portland cement concrete. The test results were presented in the preceding chapter. This chapter contains the discussion of the effects of fly ash on the compressive strength and sulfate resistance of concrete. In addition, this chapter presents and discusses several methods of predicting the sulfate resistance of concrete containing fly ash.

8.2 Compressive Strength Development

The compressive strength of concrete is one of the primary considerations in concrete mixture design. The figures in Chapter 7 show that the 28 day strength of portland cement concrete can be exceeded by concrete containing fly ash, silica fume, or blast furnace slag. This is also illustrated in Figure 8.1. Although the use of low calcium fly ash typically decreased the 28 day compressive strength of concrete in this study, the addition of high calcium fly ash led to an increase in the 28 day compressive strength in over 40 concrete mixtures. In particular, concrete containing fly ashes A-10 and B-5 as a volumetric replacement for Type II cement consistently had equal or greater compressive strengths at 28 days than the Type II control, as shown in Figures 8.2 and 8.3.

The choice of portland cement used in concrete containing fly ash was also important when evaluating concrete on the basis compressive strength. The use of high calcium fly ash as a 35 percent volumetric replacement for the 0 percent C_3A cement 02 increased the 28 day compressive strength by as much as 45 percent, as shown in Figure 8.4. The use of high calcium fly ash also increased the 28 day compressive strength of Type I portland cement concrete when used as a 25 percent volumetric replacement, as shown in Figure 8.5.

The slump and cement replacement percentage also affected the 28 day compressive strength of concrete containing high calcium fly ash. Figure 8.6 shows

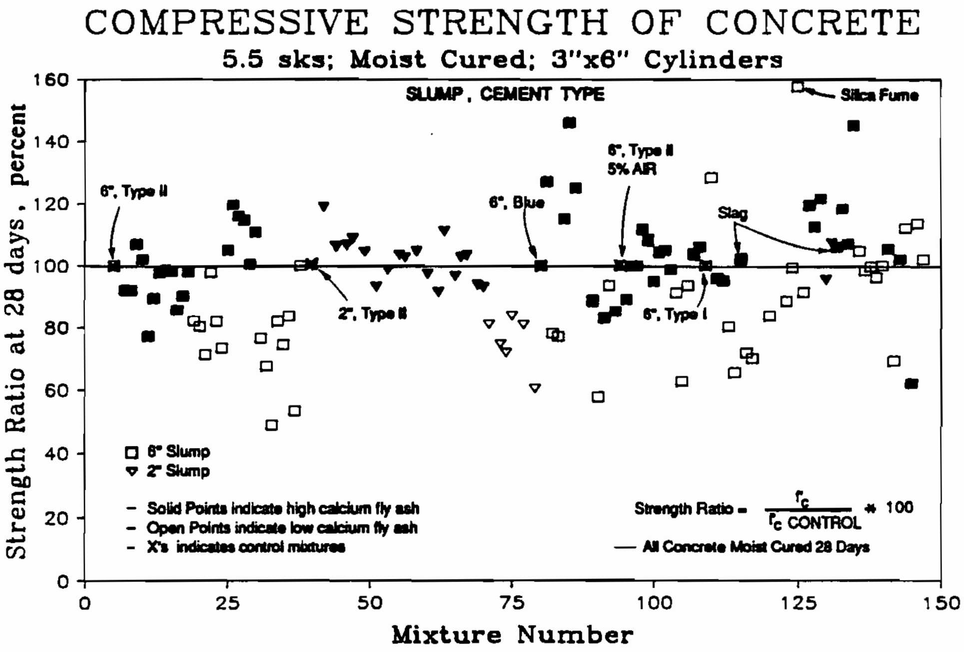


Figure 8.1 Distribution of strength ratios of concrete containing fly ash.

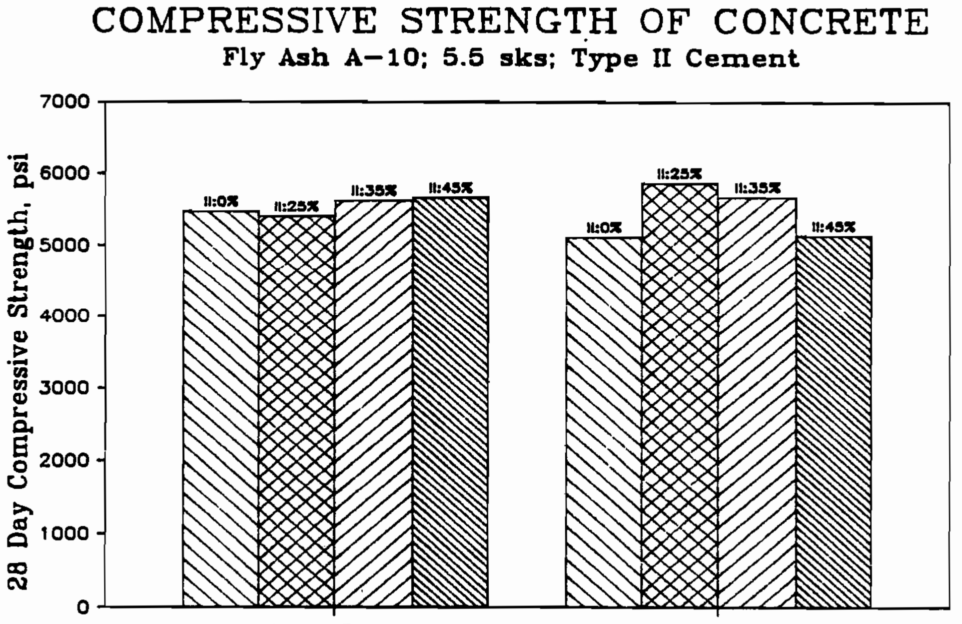


Figure 8.2 Comparison of the compressive strength of 2" and 6" slump concrete containing fly ash A-10.

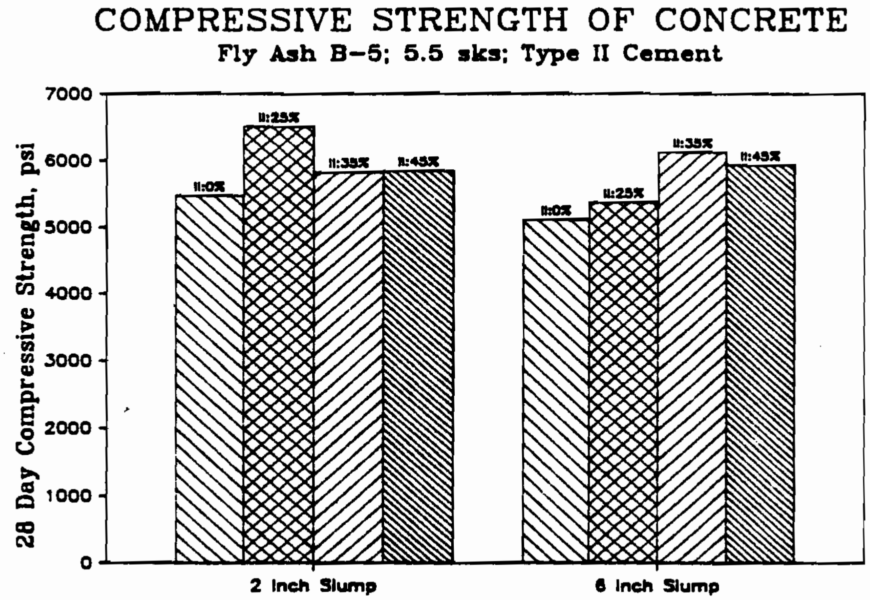


Figure 8.3 Comparison of the compresive strength of 2" and 6" slump concrete containing fly ash B-5.

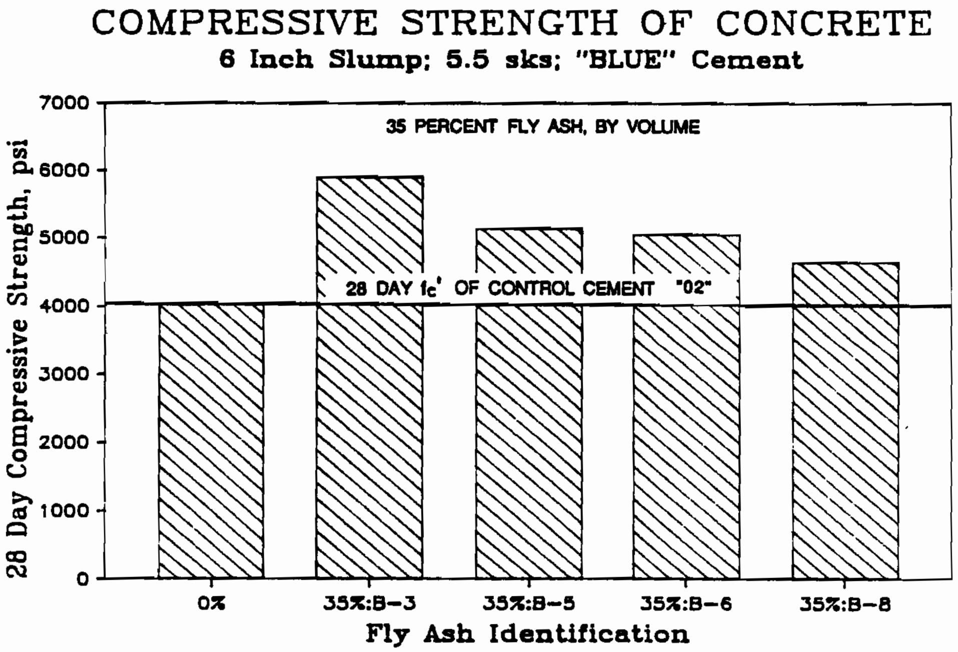


Figure 8.4 Compressive strength of concrete containing high calcium fly ash.

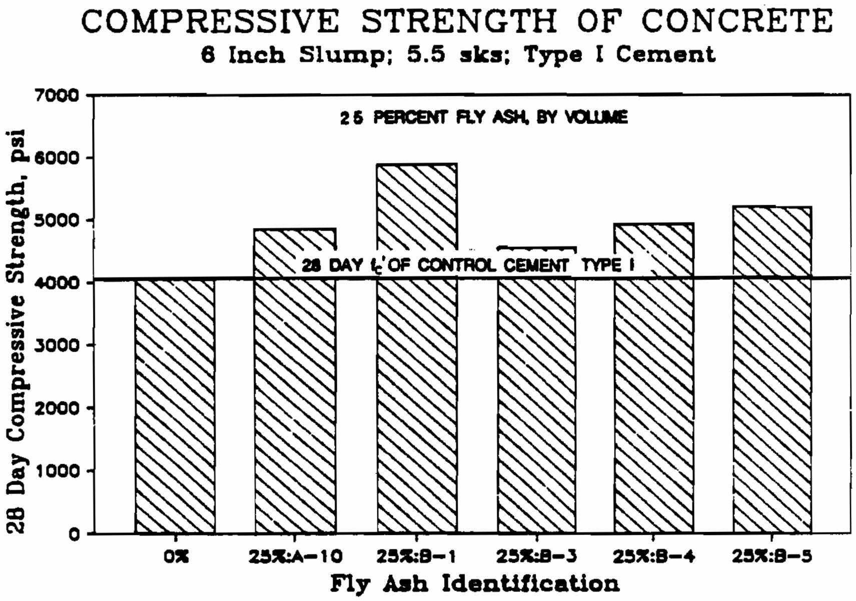


Figure 8.5 Compressive strength of Type I cement concrete containing high calcium fly ash.

a typical relationship between slump and compressive strength; a decrease in slump from 6 to 2 inches increased the 28 day compressive strength of concrete containing fly ash B-8. The compressive strength increase of the concrete containing fly ash B-8 was greater than that of the Type II control. Figure 8.6 also shows that the compressive strength of concrete containing fly ash varies with the percentage replacement of cement.

Fly ash can be used to increase the compressive strength of a normal weight concrete mixture. However trial batching is required, varying fly ash percentage and slump, to determine the compressive strength behavior of particular cement-fly ash combinations.

8.3 Effect of Fly Ash on Sulfate Resistance of Concrete

A summary of the sulfate exposure performance of each fly ash is presented in Figures 8.7 through 8.9. Figure 8.7 shows the expansion and time to cracking of

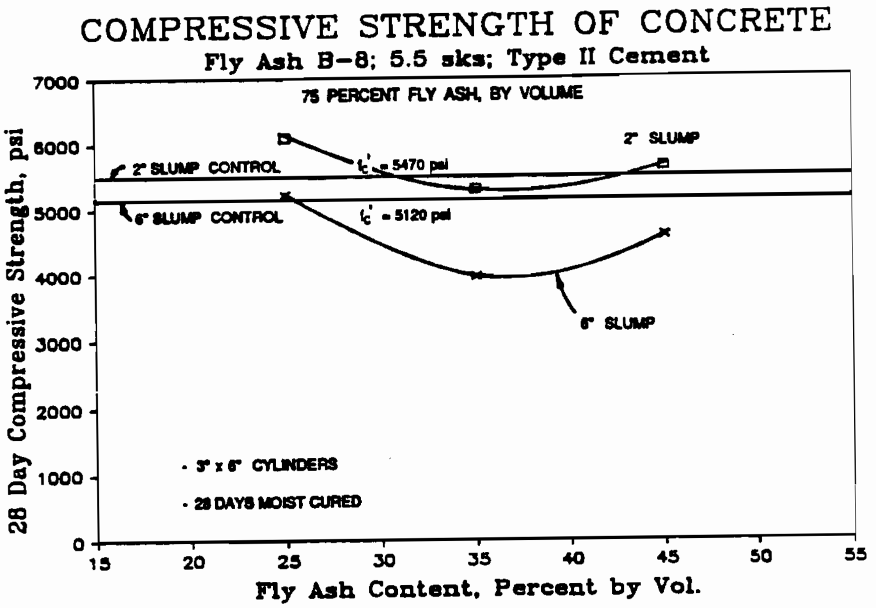


Figure 8.6 Effect of slump and fly ash content on the compressive strength of concrete.

concrete containing 25 percent fly ash as a volumetric replacement for Type II portland cement with a 6-7 inch slump, and exposed to the sulfate solution at 3500 psi. Figure 8.8 shows the expansion and time to cracking of concrete containing 35 percent fly ash as a volumetric replacement for Type II portland cement at 3500 psi. Figure 8.9 shows the expansion and time to cracking of concrete containing 45 percent fly ash as a volumetric replacement for Type II portland cement at 3500 psi. The concrete containing Texas SDHPT Type B fly ashes consistently had greater expansions and cracked at earlier ages than the control concrete with Type II portland cement. The concrete containing Texas SDHPT Type A fly ash displayed similar or less expansion than the Type II portland cement control. The concrete containing Type A fly ash exhibited first cracking at later ages than the Type II portland cement control again with the exception of fly ash A-10.

Each of the parameters of the study are addressed individually in the sections to follow. The sulfate exposure tests described herein will continue for several more years. Future developments may further refine the results presented herein.

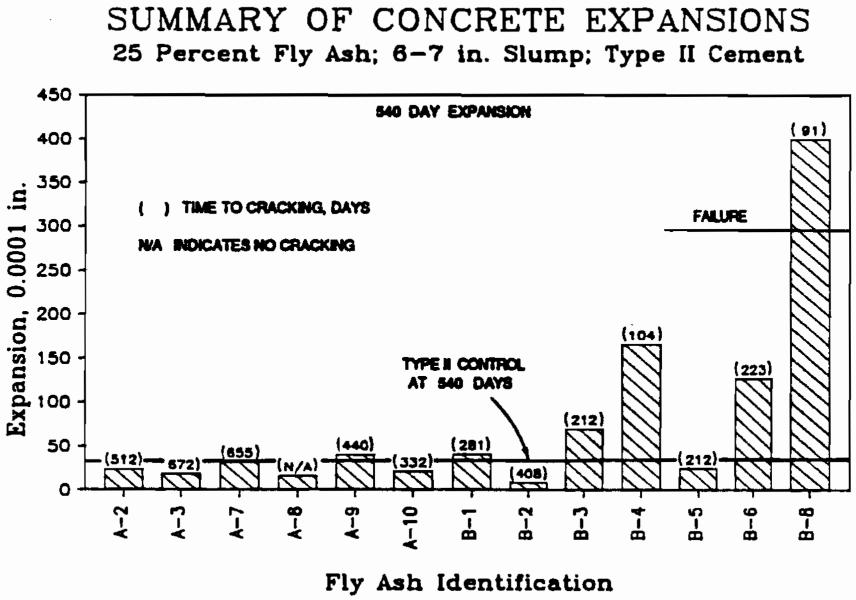


Figure 8.7 Summary of sulfate expansioin of concrete containing 25 percent fly ash.

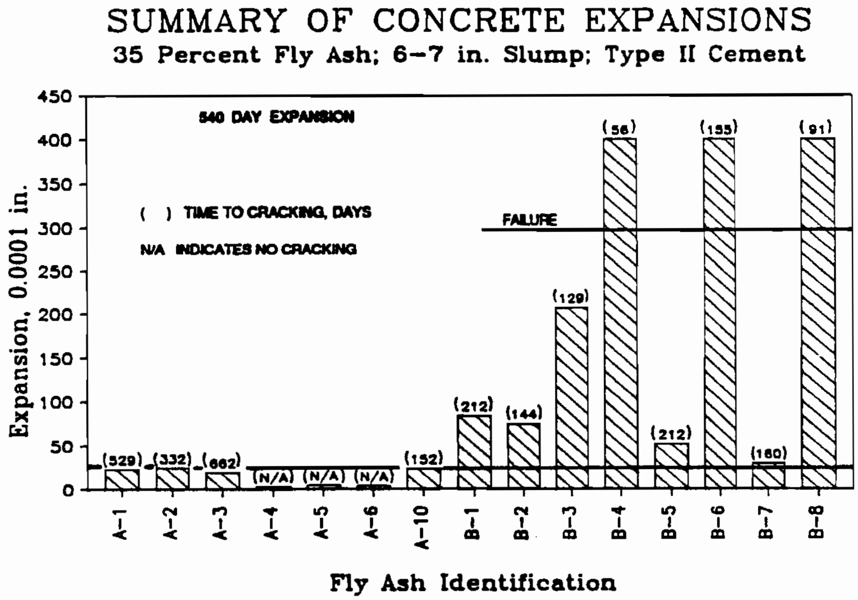


Figure 8.8 Summary of sulfate expansion of concrete containing 35 percent fly ash.

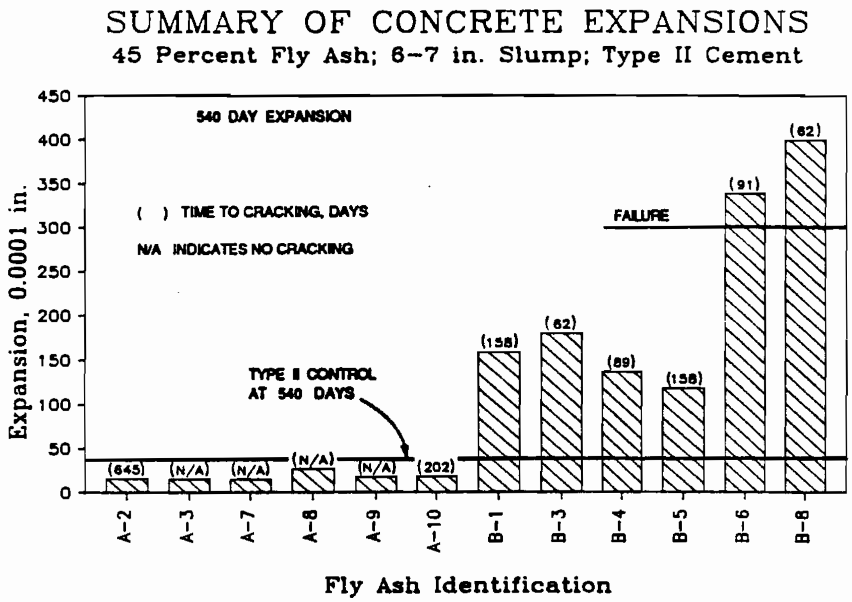


Figure 8.9 Summary of sulfate expansion of concrete containing 45 percent fly ash.

8.3.1 Effect of Fly Ash Content. Concrete containing 25, 35 and 45 percent fly ash, by volume, was cast to investigate the effect of the fly ash content on the sulfate resistance of concrete. Nine fly ashes were used in concrete at 25, 35 and 45 percent volumetric replacement and three other fly ashes were used at 25 and 45 percent volumetric replacement. A summary of the sulfate expansion of data is presented in Figures 8.10 through 8.12. The data show that concrete mixtures containing Texas SDHPT Type A fly ash have nearly the same or lower sulfate expansions than the Type II control, regardless of the amount of fly ash between 25 and 45 percent. None of these concrete mixtures exceeded 0.10 percent expansion after 540 days of exposure testing. However only the low calcium fly ashes, fly ashes A-1 through A-9, showed equal or greater resistance to cracking from sulfate attack. Type II portland cement concrete mixtures containing fly ash A-10, a high calcium fly ash, displayed cracking between 120 and 330 days of exposure testing. Concrete mixtures containing 35 or 45 percent fly ash A-10 as a replacement for Type II cement typically cracked before those mixtures containing 25 percent fly ash A-10.

Type II portland cement concrete containing Texas SDHPT Type B, high calcium, fly ash typically had 540 day expansions greater than that of the Type II

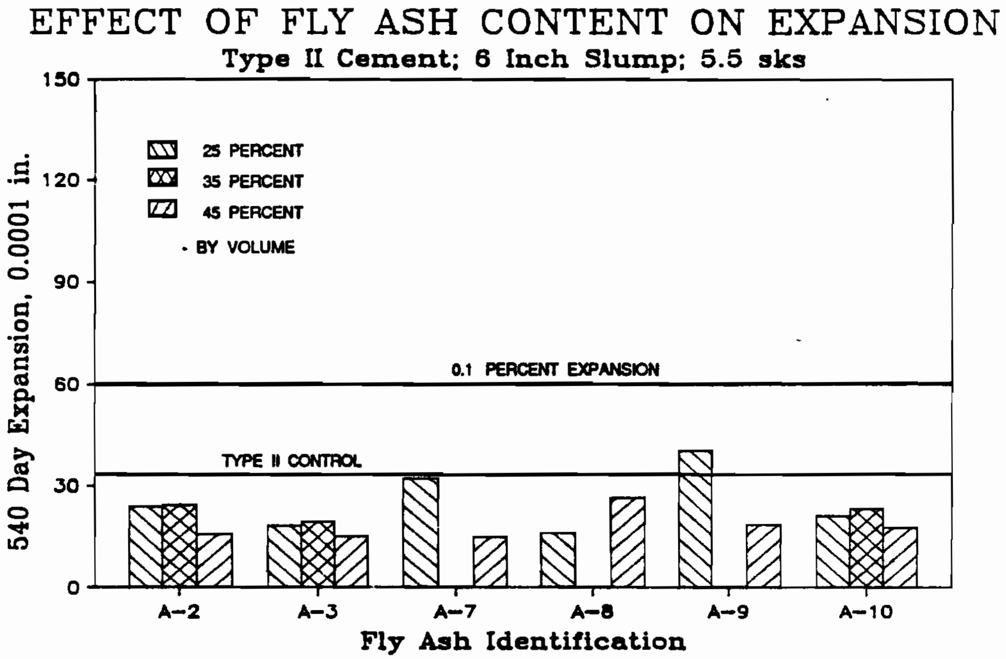


Figure 8.10 Effect of Type A fly ash content on sulfate expansion.

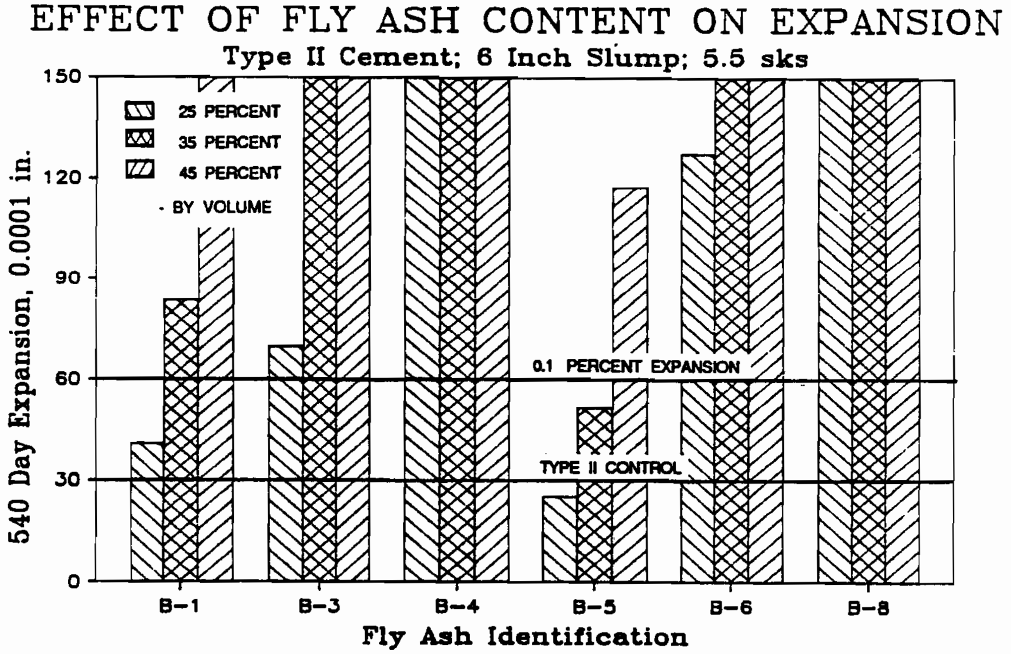


Figure 8.11 Effect of Type B fly ash content on sulfate expansion.

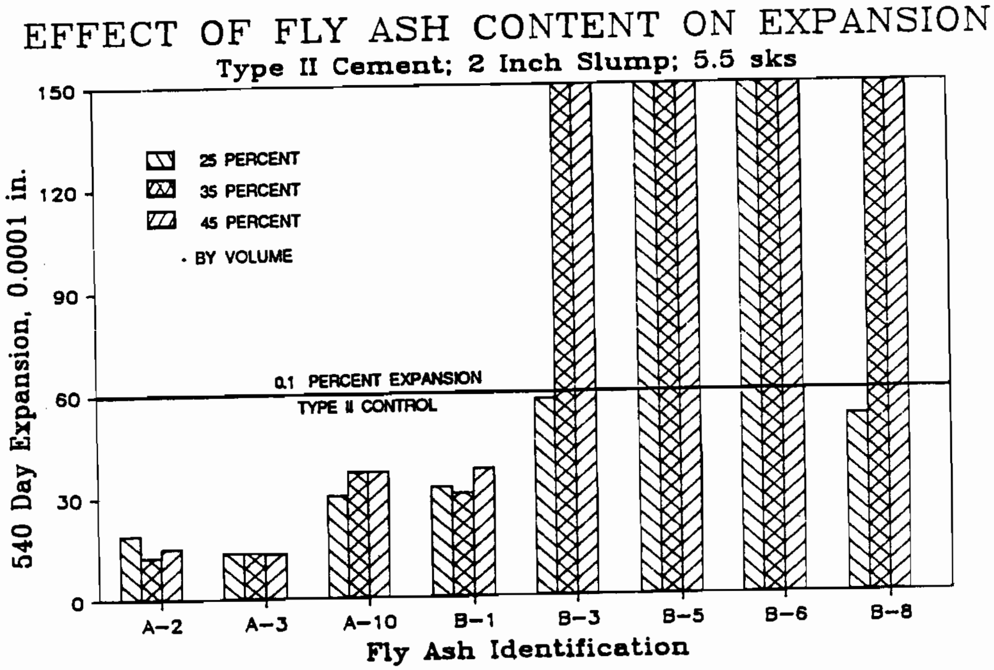


Figure 8.12 Effect of fly ash content on sulfate expansion.

control. Concrete mixtures containing 25 percent high calcium fly ash generally had lower expansion that those mixtures containing 35 or 45 percent of the same fly ash. All Type II portland cement concrete mixtures containing high calcium Type B fly ash cracked within the first 360 days of exposure testing with the exception of the 6 inch slump concrete mixture containing 25 percent fly ash B-2, which cracked at 400 days.

In summary, the use of low calcium fly ash in Type II portland cement concrete provided a level of sulfate resistance equal to or greater than the Type II control. The level of sulfate resistance was not definitively increased or decreased by changes in the content of low calcium fly ash. High calcium fly ashes reduced the sulfate resistance of Type II portland cement concrete. The reduction in the level of sulfate resistance was typically greatest at 45 percent replacement and least at 25 percent replacement.

8.3.2 Effect of Fly Ash Composition. The effect of fly ash composition must be divided into the two distinctly different material phases, the amorphous glassy phase and the structured crystalline phases. The most routine compositional analysis performed on fly ash is a bulk chemical analysis. This analysis provides information on the amount of silica, alumina, calcium oxide, iron oxide, magnesium oxide and sulfur trioxide as a percentage of the total weight of the fly ash. This type of analysis does not distinguish between crystalline silica (nonreactive quartz) and amorphous silica (pozzolanically reactive glass) or similar compositional differences in each of the bulk oxides.

It would be useful to use the bulk chemical analysis to aid in evaluating fly ash for use in sulfate exposed concrete because the analysis is nearly always available. A mineralogical and glass composition analysis is neither routine nor trivial. These analyses are nonetheless more descriptive in relation to the actual hydration processes which are taking place during the sulfate expansion mechanism. Both the bulk chemical and the phase analyses will be discussed in this section to illustrate their relevance to the sulfate resistance of concrete containing fly ash.

8.3.2.1 Chemical Effects. Several previous studies have suggested that there is a direct relationship between the bulk chemical composition of fly ash and the sulfate resistance of concrete containing fly ash[24,34]. The total silica, alumina, iron oxide, sum of metallic oxides, sulfur trioxide and calcium oxide contents have been plotted versus the 540 day expansion and the time to first cracking in Figures 8.13 to 8.24.

The silica content is plotted versus the performance of concrete exposed to sulfate in Figures 8.13 and 8.14. A direct dependence between silica content and sulfate resistance was not observed for concrete containing fly ash having a silica content between 30 and 40 percent. Concrete containing fly ashes with a total silica content greater than 40 percent were resistant to sulfate attack.

The alumina content of fly ash is plotted versus sulfate exposure performance in Figures 8.15 and 8.16. There was no direct correlation observed between the alumina content and sulfate resistance.

The iron oxide content of fly ash is plotted versus sulfate exposure performance in Figures 8.17 and 8.18. The iron oxide content was not a reliable indicator

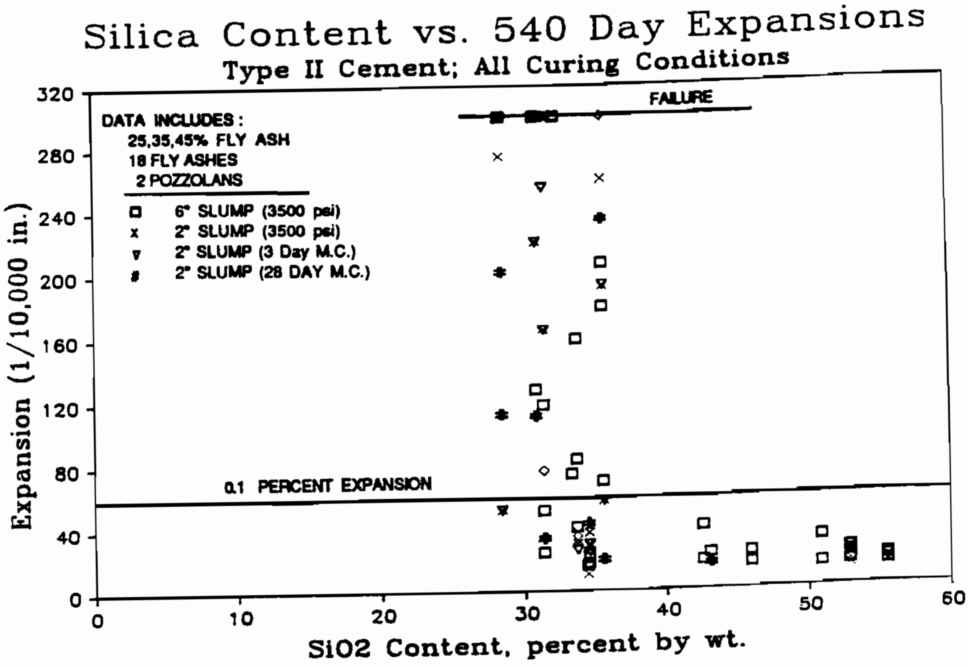


Figure 8.13 Effect of fly ash bulk SiO_2 on sulfate expansion.

of sulfate resistance. However, the 2 fly ashes with total iron oxide contents greater than 9 percent were resistant to sulfate attack.

The weighted sum of metallic oxides (SiO_2+Al_2O_3+Fe_2O_3) is plotted versus sulfate exposure performance in Figures 8.19 and 8.20. The sum of the metallic oxides was not a reliable indicator of sulfate resistance except that concrete containing fly ash with greater than 70 percent bulk sum of metallic oxides was sulfate resistant.

The presence of sulfur measured as sulfur trioxide in the fly ash is plotted versus sulfate exposure performance in Figures 8.21 and 8.22. The sulfate exposure performance of concrete was generally increased with fly ashes having low sulfur trioxide contents. This trend is especially evident in Figure 8.22 where first cracking time is used as the indicator of performance. The maximum total sulfur trioxide in the fly ashes in this study was 5.6 percent. The trend may not continue at higher sulfur trioxide contents because of the supersulfating mechanism of ettringite stabilization discussed in Chapter 2.

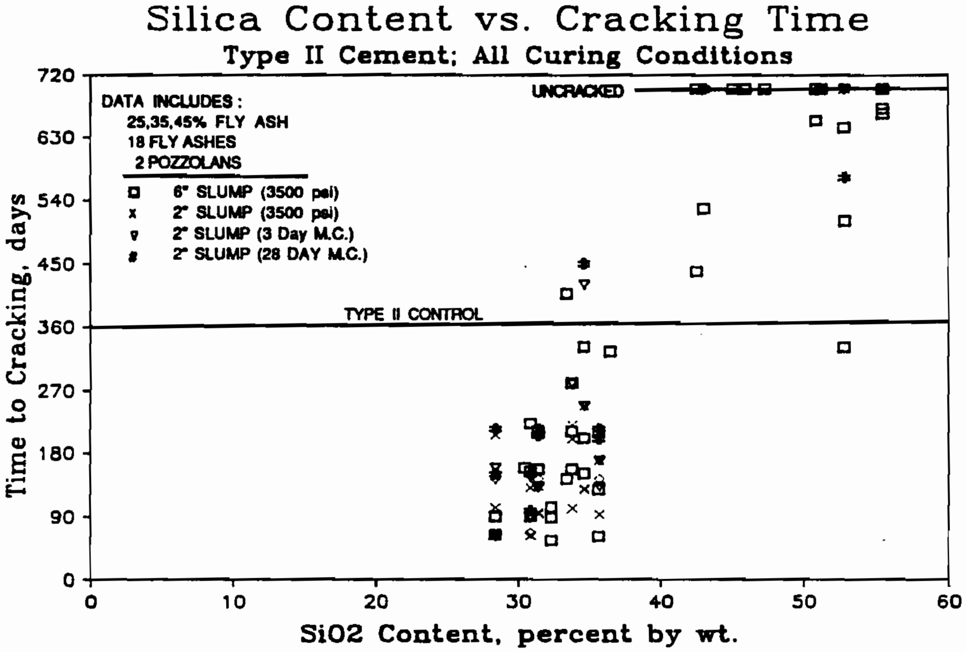


Figure 8.14 Effect of fly ash bulk SiO_2 on sulfate cracking.

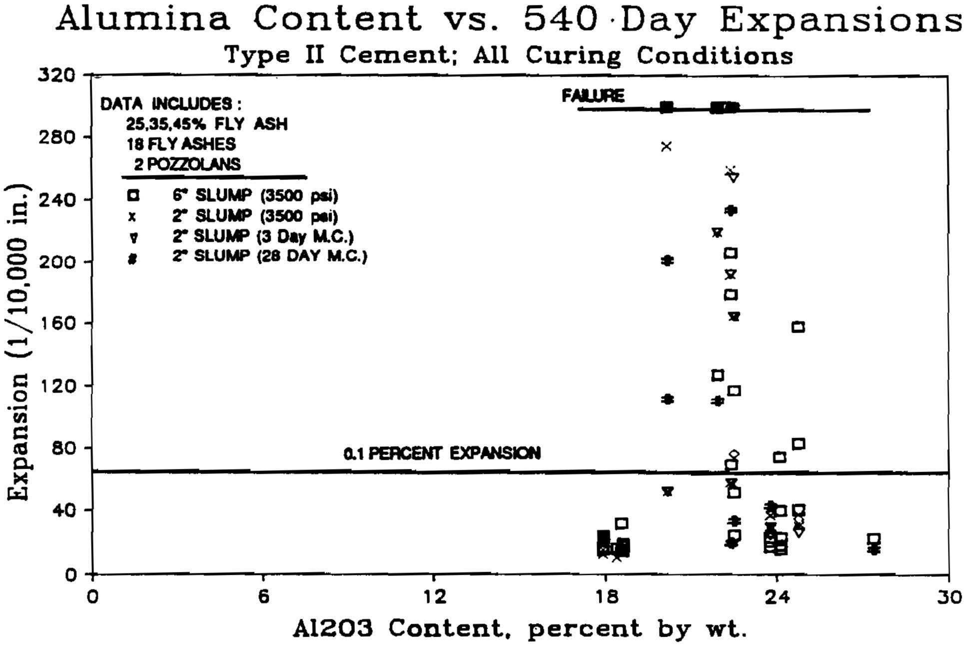


Figure 8.15 Effect of fly ash bulk Al_2O_3 on sulfate expansion.

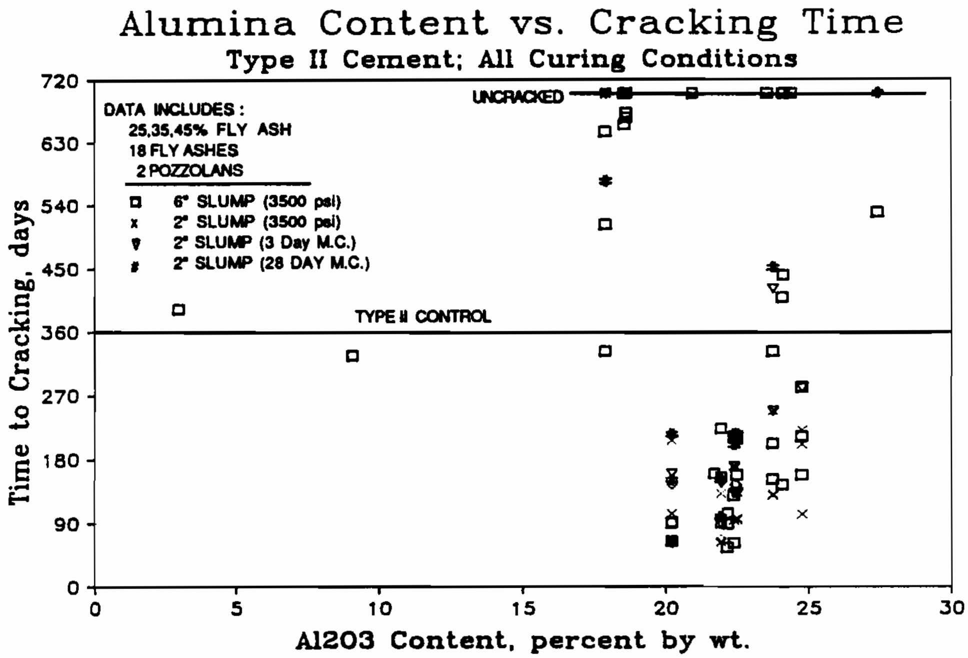


Figure 8.16 Effect of fly ash bulk Al_2O_3 on sulfate cracking.

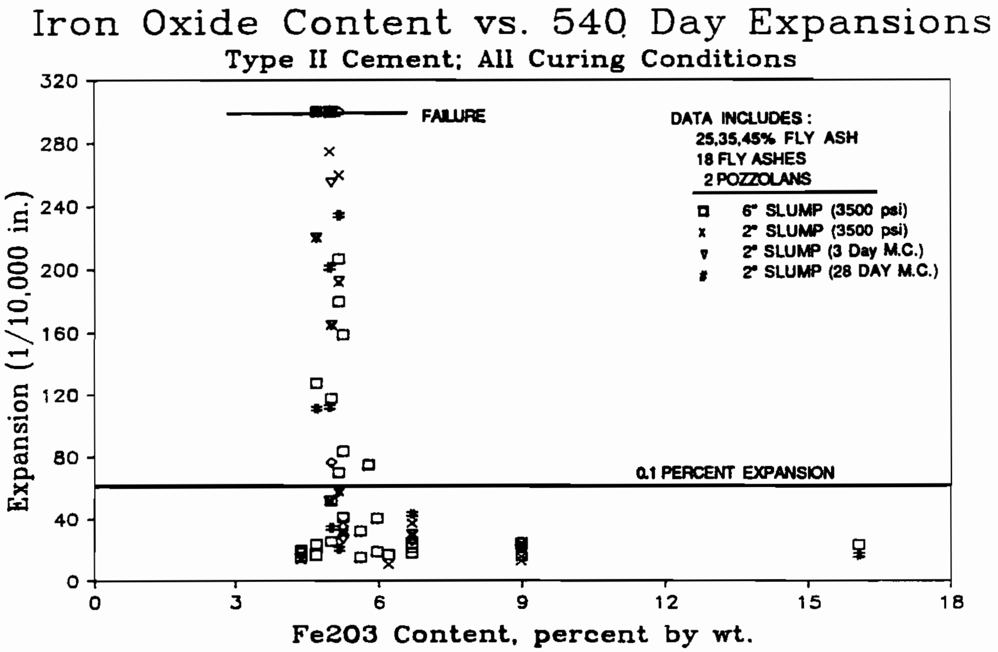


Figure 8.17 Effect of fly ash bulk Fe_2O_3 on sulfate expansion.

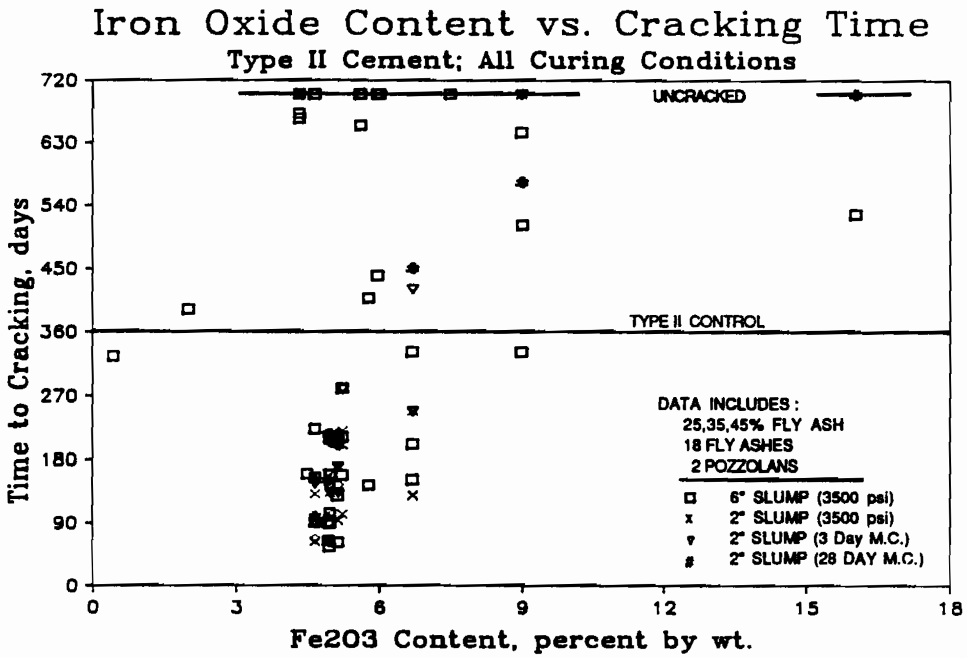


Figure 8.18 Effect of fly ash bulk Fe_2O_3 on sulfate cracking.

The calcium oxide content is plotted versus sulfate exposure performance in Figures 8.23 and 8.24. The most reliable indicator of the effect of fly ash on the sulfate resistance of concrete containing a given cement was found to be the calcium oxide content of the fly ash. For example, for all cases the sulfate resistance of concrete was improved by the replacement of part of the cement with a fly ash containing less than 10 percent calcium oxide. The sulfate resistance of concrete was decreased by the replacement of part of the cement with a fly ash containing greater than 20 percent calcium oxide. The range between 10 and 20 percent calcium oxide content will be investigated at a later time. The trend is especially evident in the time to first cracking data presented in Figure 8.24. Phases I and II of this study used 18 fly ashes, 9 with calcium oxide contents between 1 and 10 percent and 9 with calcium oxide contents greater than 20 percent. Of the concrete containing these fly ashes, the low calcium oxide group produced concrete with equal or increased sulfate resistance, while the high calcium oxide fly ash produced concrete with equal or reduced sulfate resistance when compared to the Type II control.

Of the bulk chemical compounds typically analyzed in fly ash, calcium oxide showed the greatest dependence with respect to sulfate exposure performance.

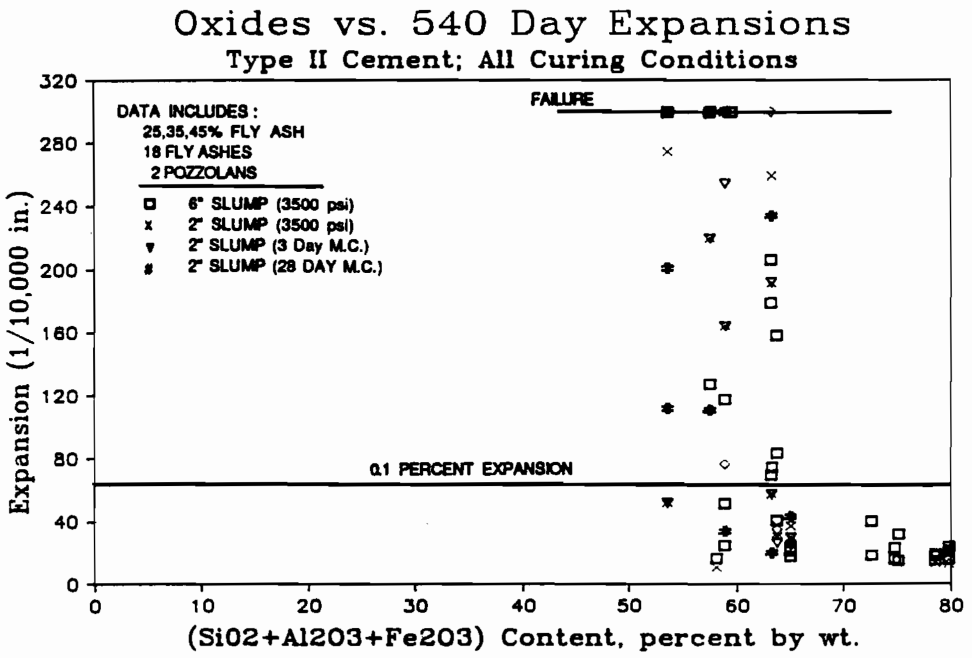


Figure 8.19 Effect of fly ash oxides on sulfate expansion.

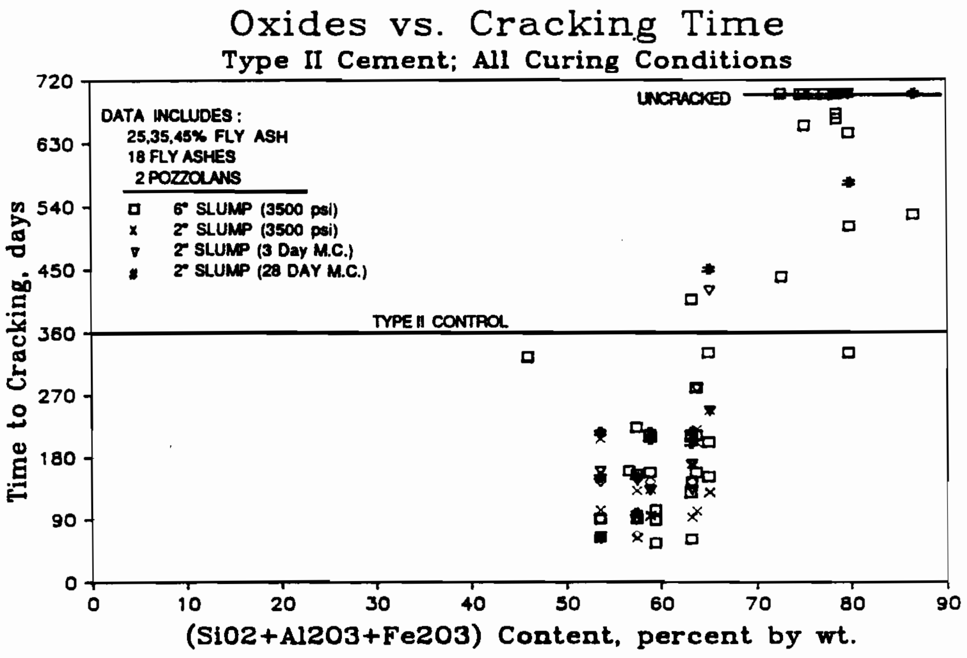


Figure 8.20 Effect of fly ash oxides on sulfate cracking.

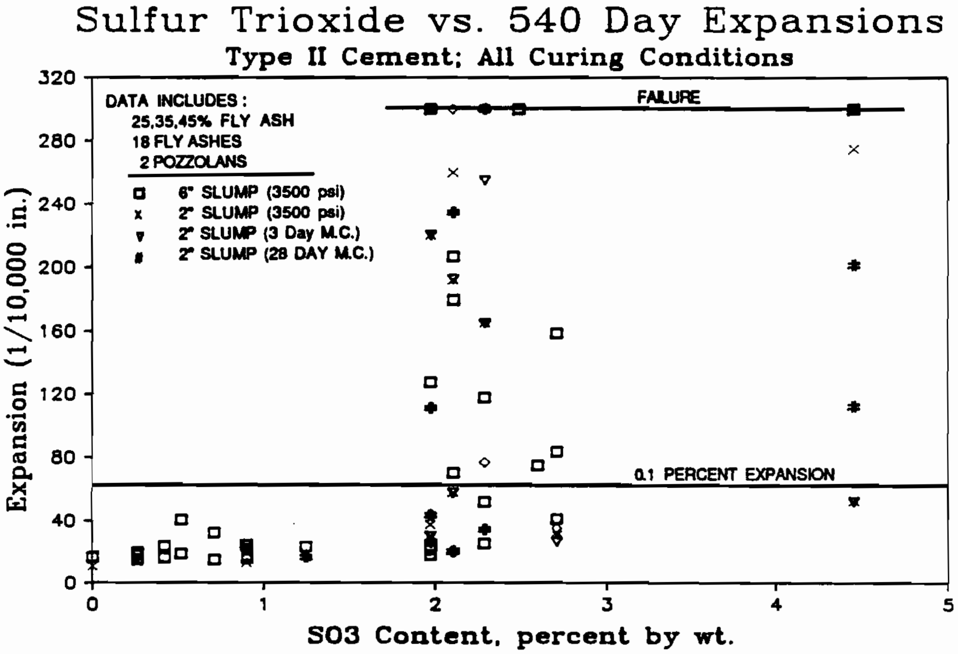


Figure 8.21 Effect of fly ash bulk SO_3 on sulfate expansion.

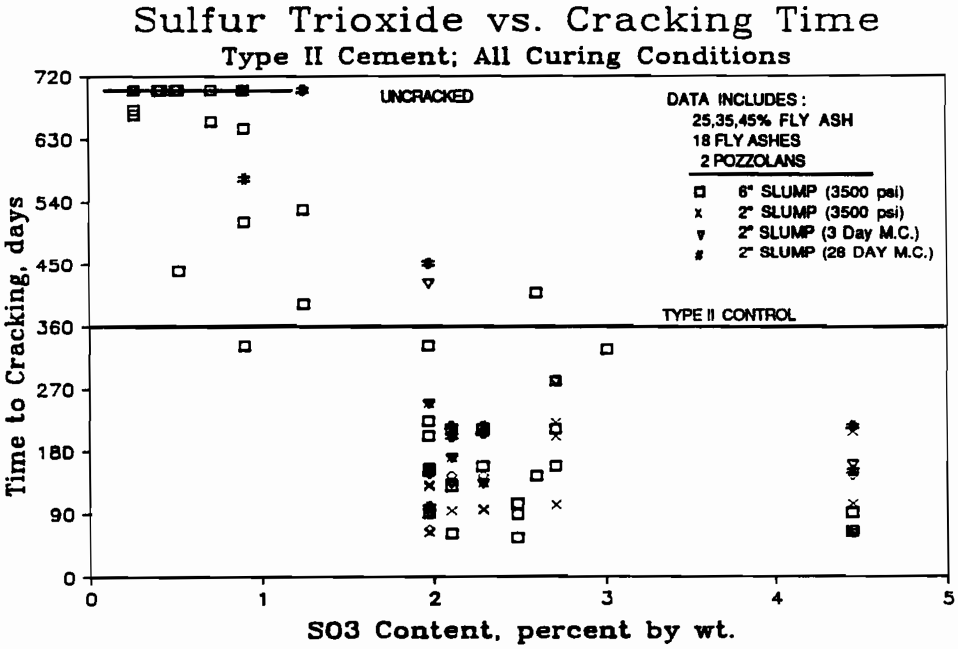


Figure 8.22 Effect of fly ash bulk SO_3 on sulfate cracking.

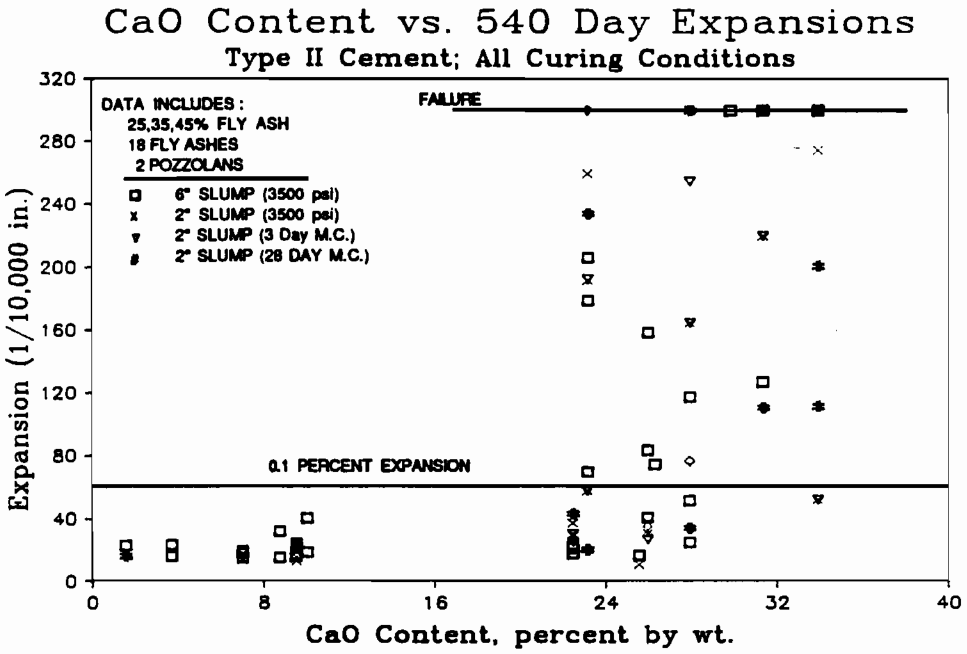


Figure 8.23 Effect of fly ash bulk CaO on sulfate expansion.

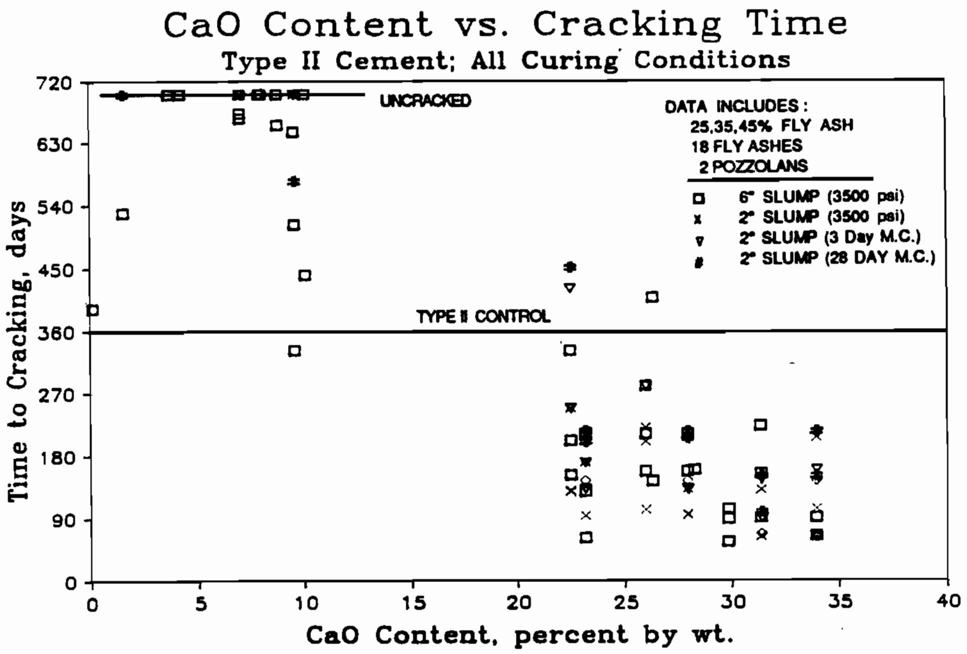


Figure 8.24 Effect of fly ash bulk CaO on sulfate cracking.

High silica contents and low sulfur trioxide contents were also important to sulfate resistant concrete, however these compounds and the sulfate resistance of concrete only showed a relationship at or near the extremes stated.

8.3.2.2 Mineralogical and Glassy Phase Effects. The phase analysis of the fly ashes was performed by qualitatively and semi-quantitatively determining the crystalline phases present in fly ash and subtracting these quantities from the total bulk chemical composition of the fly ash. The resultant of this computation was the average composition of the glassy phase of the fly ash. The crystalline phases in fly ash were typically inert minerals and phases that hydrated upon the addition of mixing water to the fresh concrete. Neither of these types of mineral phases drastically alter the sulfate attack mechanism. Some fly ashes contained up to 3 percent C_3A, this remains below the C_3A content of the cement being replaced and does not explain the severe observed reduction in durability to sulfate attack.

The effect of glass composition on the sulfate resistance of concrete is presented herein. The individual glassy oxide contents of fly ash are presented versus the sulfate exposure performance in Figures 8.25 through 8.32. Figure 8.33 presents the relationship between the ternary phase diagram and the resistance of concrete to sulfate attack.

High silica glasses hydrate pozzolanically over a long period of time to provide concrete with a refined and durable pore structure. Generally, as the silica content of the glass increases, the longer the time for the dissolution of the glass into binding compounds. The glassy silica content of the fly ashes is plotted versus 540 day expansion and time to first cracking in Figures 8.25 and 8.26. The concrete containing high silica glass fly ash had a greater resistance to sulfate attack than concrete containing moderate and low silica glass fly ash.

Alumina within glass also hydrates pozzolanically over a long period of time to provide concrete with a refined and durable pore structure. The alumina content of the fly ashes is plotted versus 540 day expansion and time to first cracking in Figures 8.27 and 8.28. The alumina content of the glassy phases of fly ash showed no direct correlation to the resistance of concrete to sulfate attack.

Small amounts of iron oxide are found in the glassy portion of fly ash. The iron oxide content of the glassy phases of fly ash are plotted versus the expansion

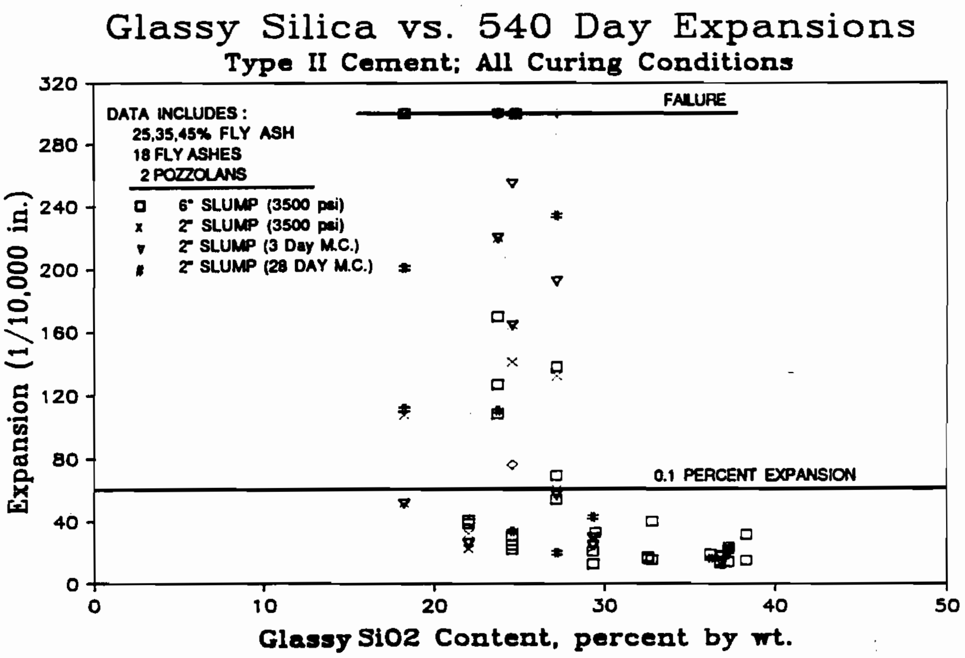


Figure 8.25 Effect of fly ash glassy SiO_2 on sulfate expansion.

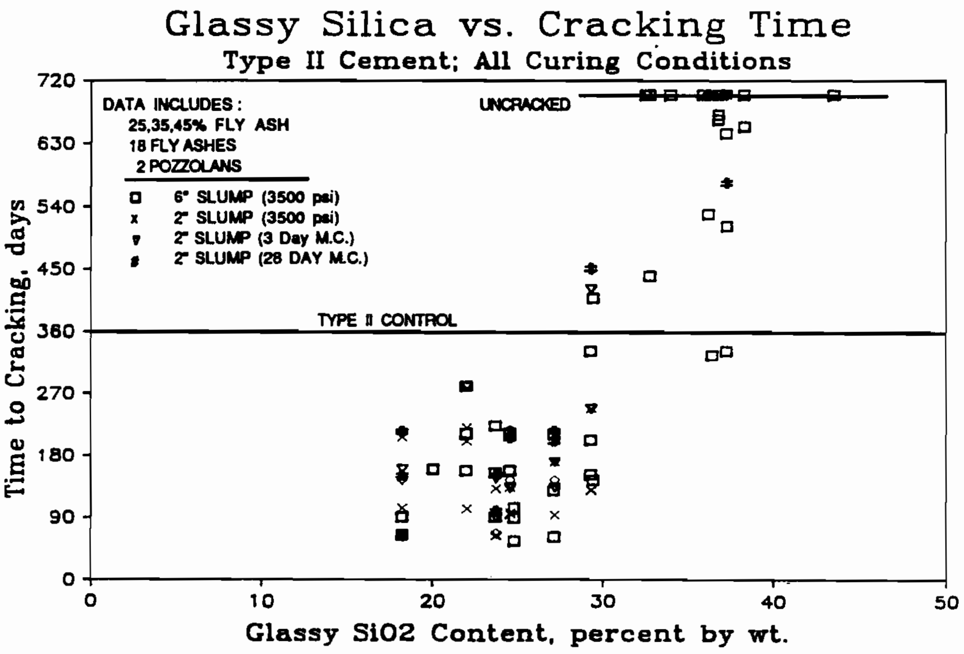


Figure 8.26 Effect of fly ash glassy SiO_2 on sulfate cracking.

and time to cracking in Figures 8.29 and 8.30. The iron oxide content of the glassy portion of fly ash was not found to be a reliable indicator of the sulfate resistance of concrete containing fly ash. However, expansions were reduced in concrete containing fly ash having more than 3 percent iron oxide, as a percentage of total glass. These fly ashes include, A-10, B-2, B-5, and most of the Texas SDHPT Type A fly ashes. A similar statement cannot be made for the time to first cracking.

The calcium oxide in the glassy portion of the fly ash is plotted versus expansion and time to first cracking in Figures 8.31 and 8.32. There was a clear relationship between the calcium oxide content and the sulfate exposure performance of concrete. The relationship was most evident in the time to cracking data presented in Figure 8.32, where fly ashes with calcium rich glasses showed signs of cracking within the first year of exposure testing.

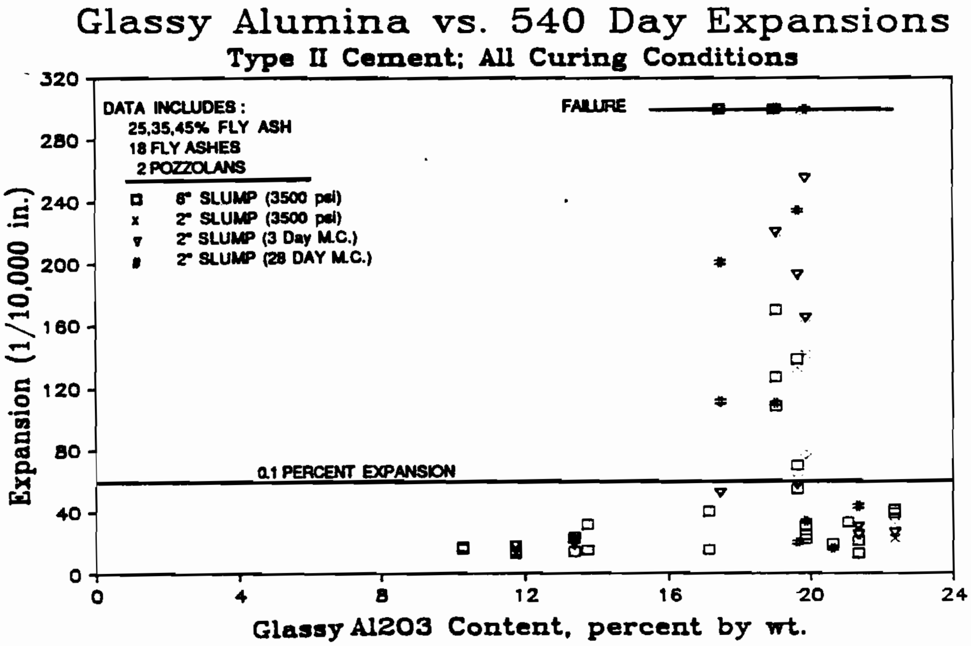


Figure 8.27 Effect of fly ash glassy Al_2O_3 on sulfate expansion.

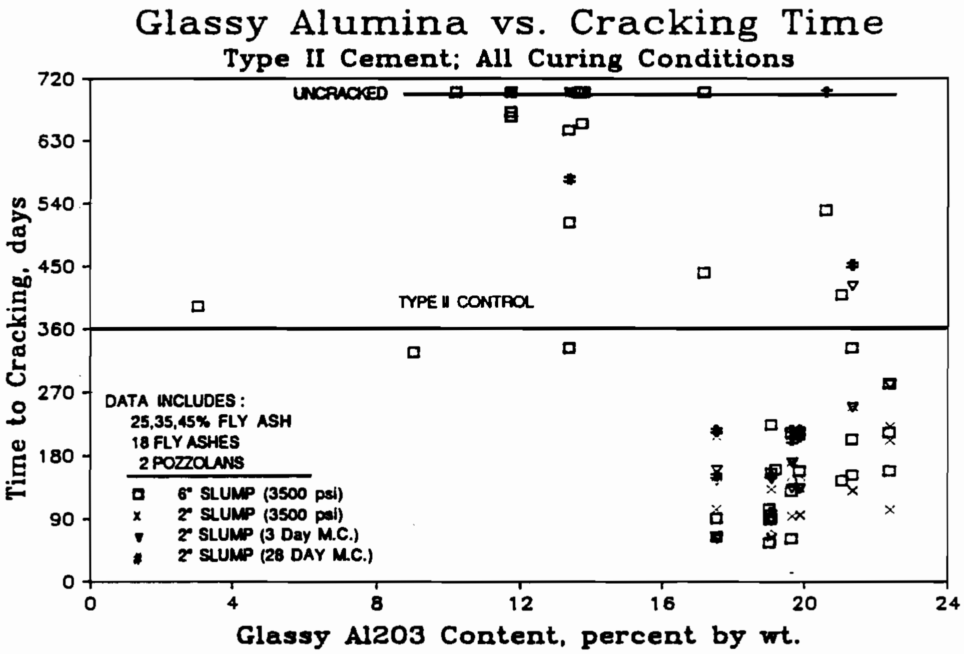


Figure 8.28 Effect of fly ash glassy Al_2O_3 on sulfate cracking.

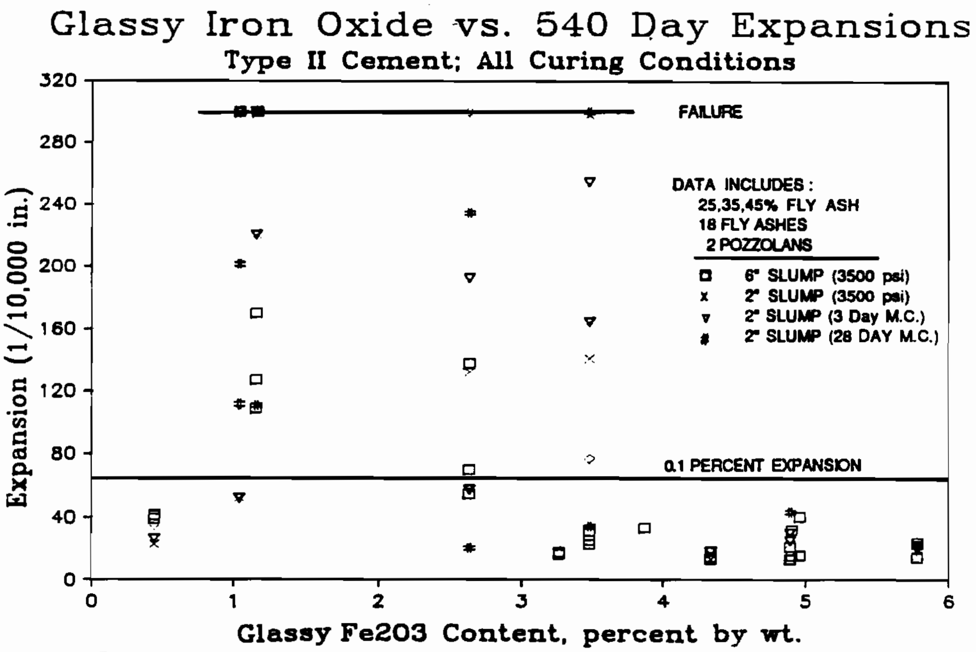
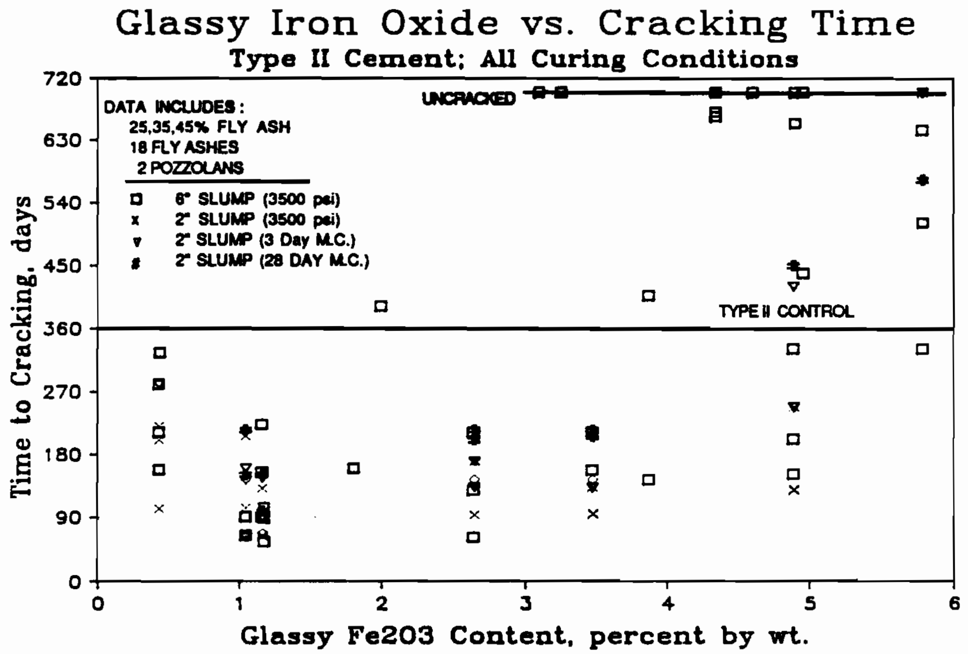


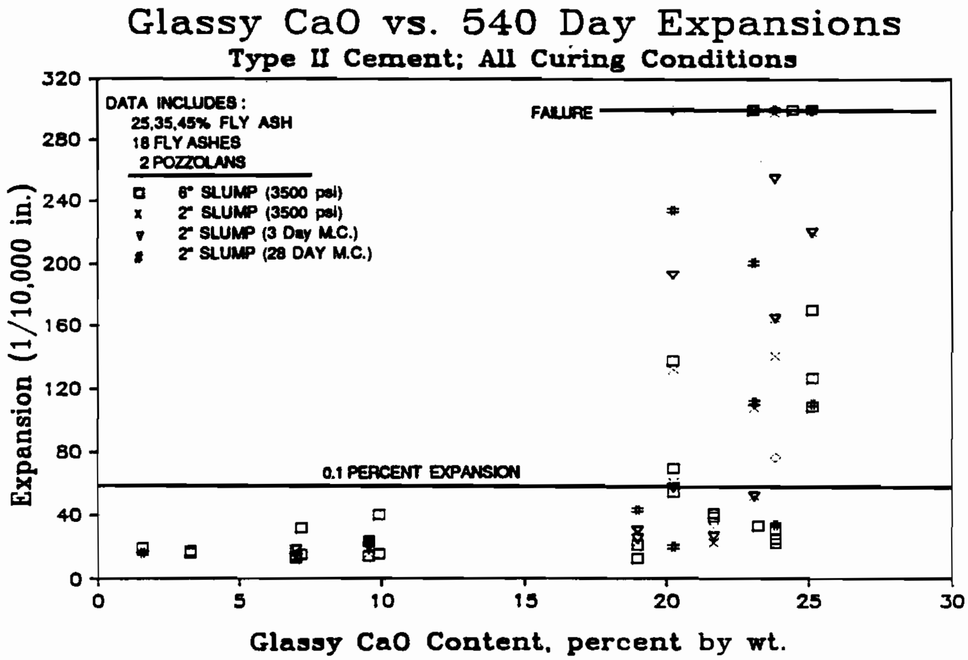
Figure 8.29 Effect of fly ash glassy Fe_2O_3 on sulfate expansion.



Glassy Iron Oxide vs. Cracking Time

Type II Cement; All Curing Conditions

Figure 8.30 Effect of fly ash glassy Fe_2O_3 on sulfate cracking.



Glassy CaO vs. 540 Day Expansions

Type II Cement; All Curing Conditions

Figure 8.31 Effect of fly ash glassy CaO on sulfate expansion.

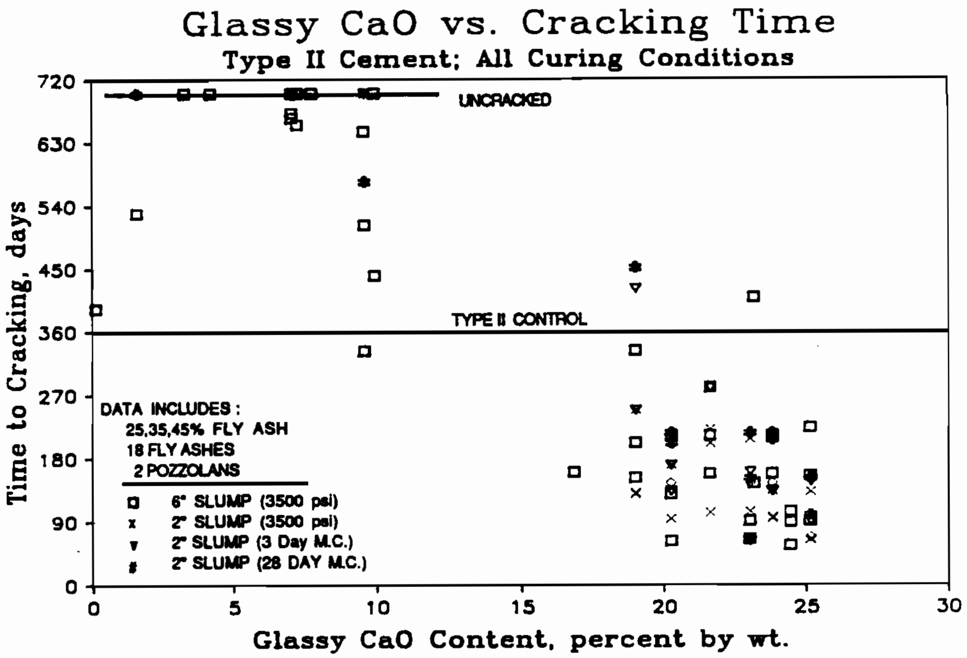


Figure 8.32 Effect of fly ash glassy CaO on sulfate cracking.

The ternary phase diagram of SiO_2-Al_2O_3-CaO is an effective means of simplifying the composition of the glass in fly ash. This diagram expresses the glassy phase composition of the fly ash as an equivalent glass containing only the three major compounds typically found in fly ash glassy phases. The increase in calcium content can be expressed as a percentage of an equivalent ternary glass, as is shown in Figure 8.33. This figure shows a distinct correlation between the glassy calcium oxide content of the equivalent ternary glass and time to first cracking.

In summary, the sulfate resistance of concrete was affected by the phase composition of the fly ash. Fly ashes containing calcium rich glassy phases decreased the sulfate resistance of concrete. In addition, modest amounts of iron oxide in the glassy phases of fly ash reduced the rate of sulfate expansion, but did not prevent cracking or provide sulfate resistance greater than the Type II control.

8.3.3 Effect of Moist Curing Time. Moist curing benefits concrete at early ages in two ways. The first way is to allow the concrete to gain strength and stiffness at a rate faster than that of air curing. The second way concrete benefits from moist curing is that the pore structure of the paste becomes better defined

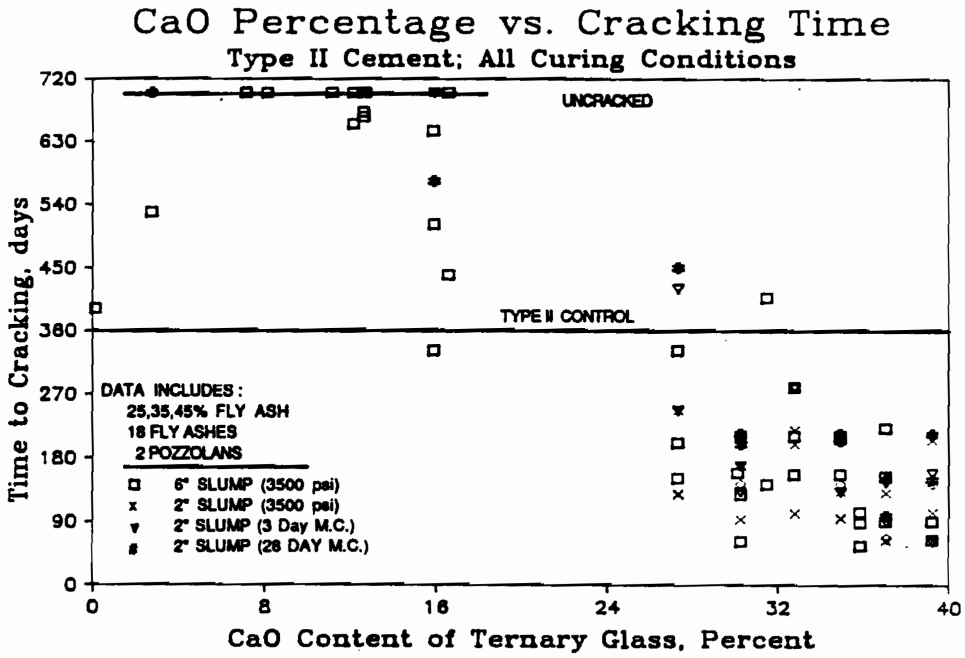


Figure 8.33 Effect of the equivalent ternary CaO of fly ash on sulfate cracking.

with longer moist curing times. Moist curing time was investigated in this research study to better understand the relationship between these two effects and the sulfate resistance of concrete containing fly ash.

Concrete mixtures containing fly ash were submerged in the sulfate solution at ages for up to 28 days. The results are shown in Figures 8.34 through 8.44. No relationship between moist curing time and sulfate resistance was found. One half of the concrete mixtures moist cured for up to 28 days had greater expansions than identical concrete moist cured only 3 days before sulfate exposure. The other half of the concrete mixtures moist cured for up to 28 days had equal or less sulfate expansion than concrete moist cured 3 days before sulfate exposure.

The concrete moist cured 3 days before sulfate exposure typically had compressive strengths at or below 3500 psi. The low strength concrete also has a lower stiffness and therefore may accommodate expansions due to gypsum and ettringite formation through inelastic deformation of the paste. However, as shown in Chapter 6, concrete moist cured only 3 days is highly permeable to sulfate ions. The high permeability of the concrete may lead to the saturation of the concrete

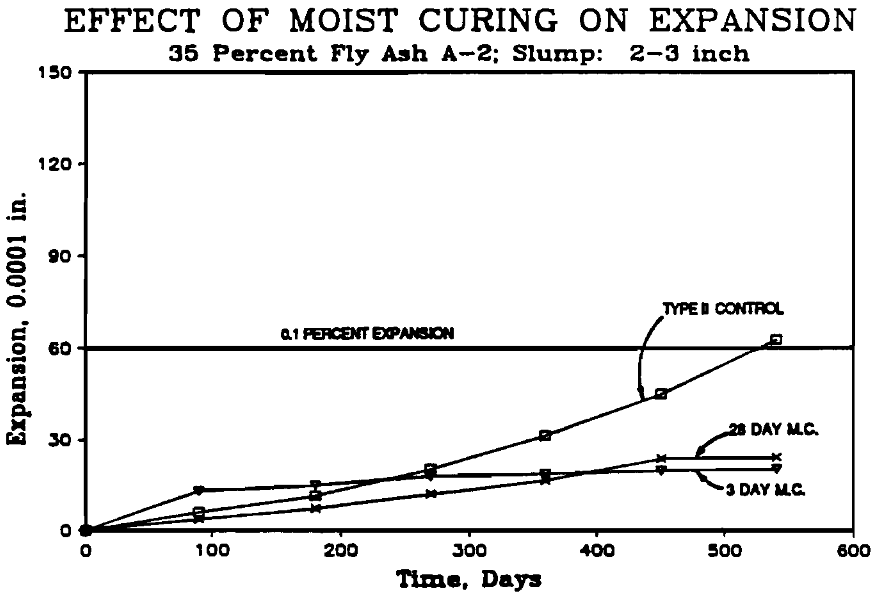


Figure 8.34 Effect of moist curing on sulfate expansion of concrete containing fly ash A-2.

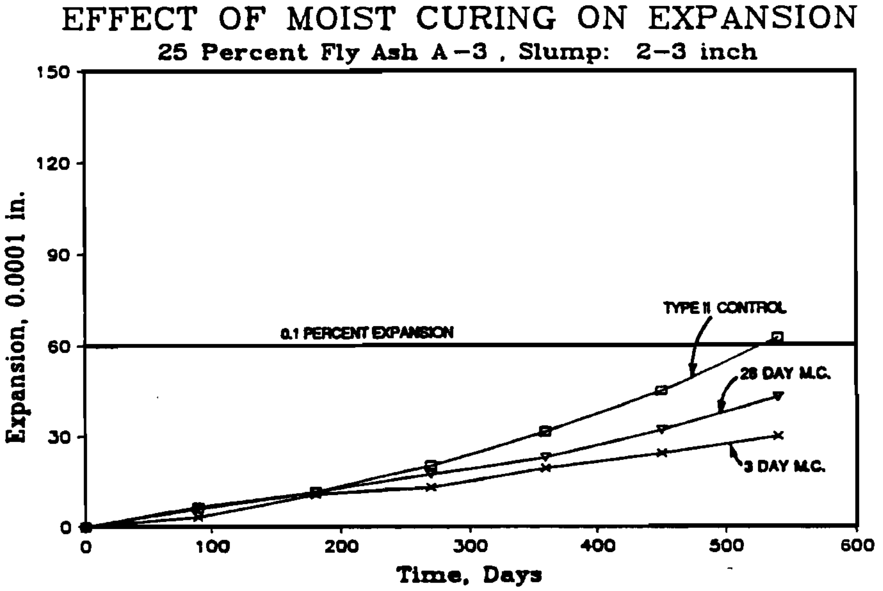


Figure 8.35 Effect of moist curing on sulfate expansion of concrete containing fly ash A-3.

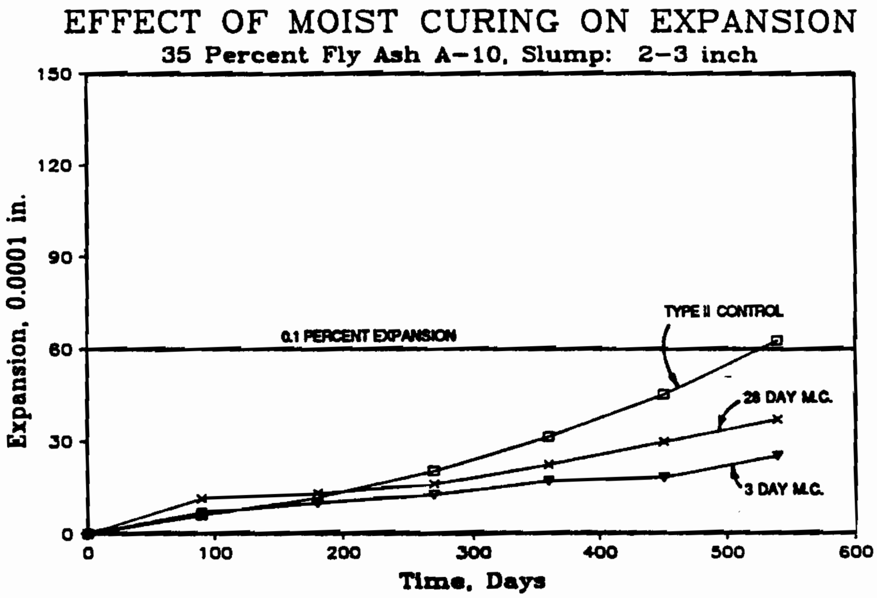


Figure 8.36 Effect of moist curing on sulfate expansion of concrete containing fly ash A-10.

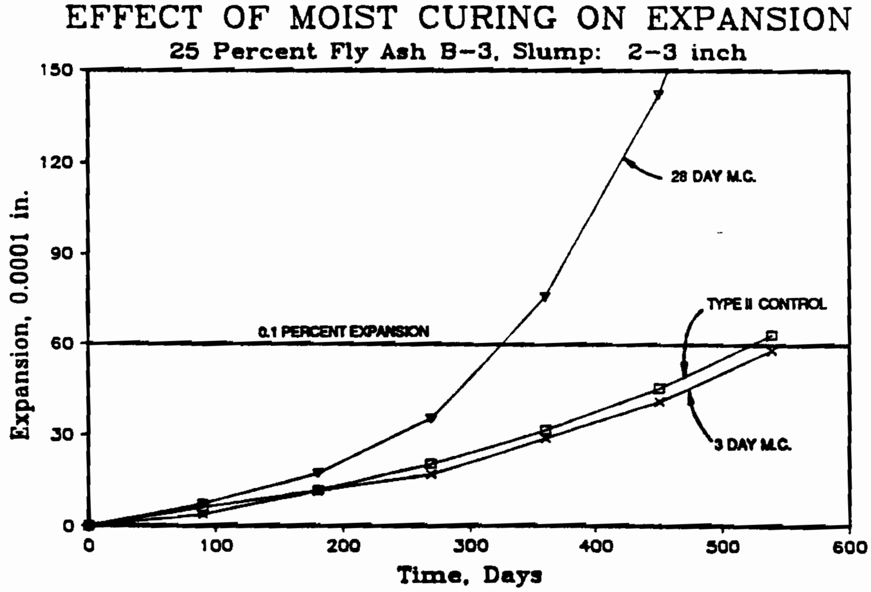


Figure 8.37 Effect of moist curing on sulfate expansion of concrete containing fly ash B-3.

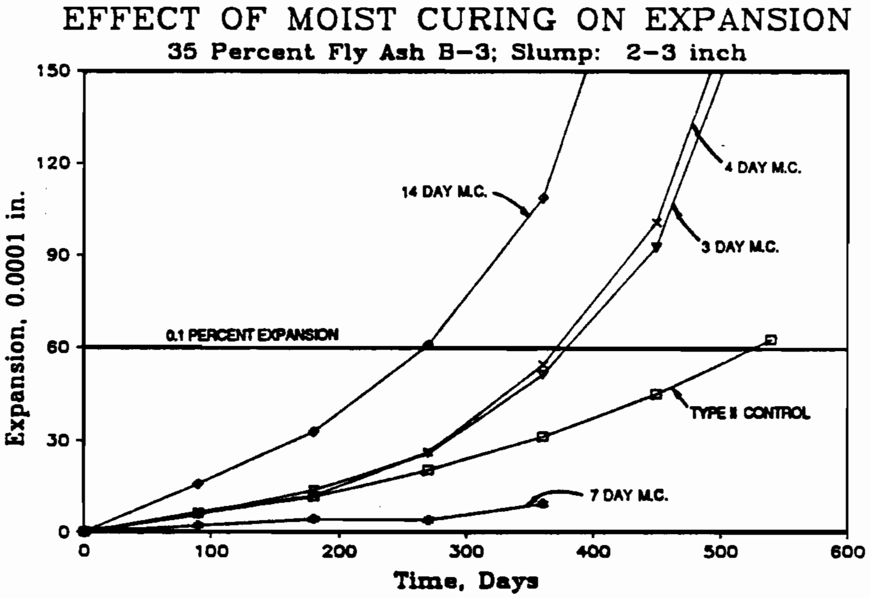


Figure 8.38 Effect of moist curing on sulfate expansion of concrete containing fly ash B-3.

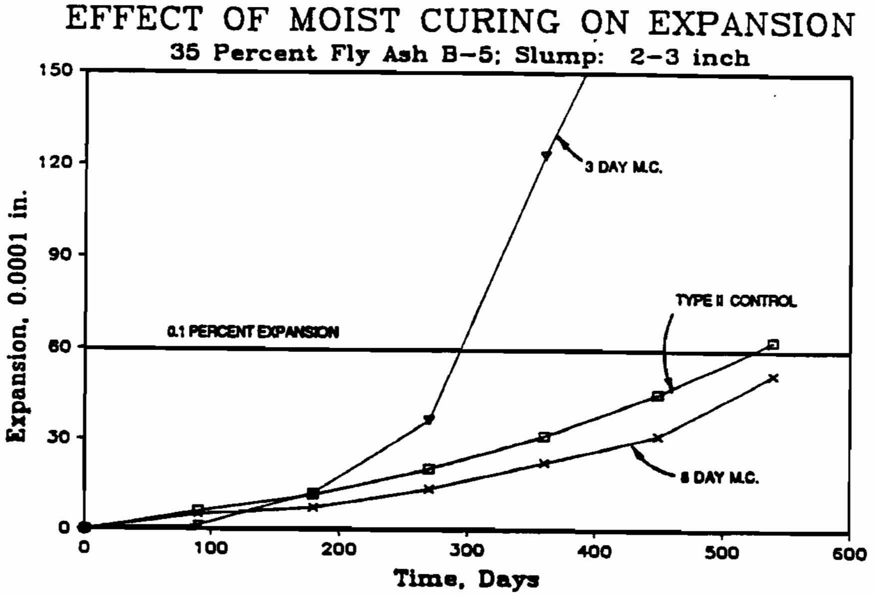


Figure 8.39 Effect of moist curing on sulfate expansion of concrete containing fly ash B-5.

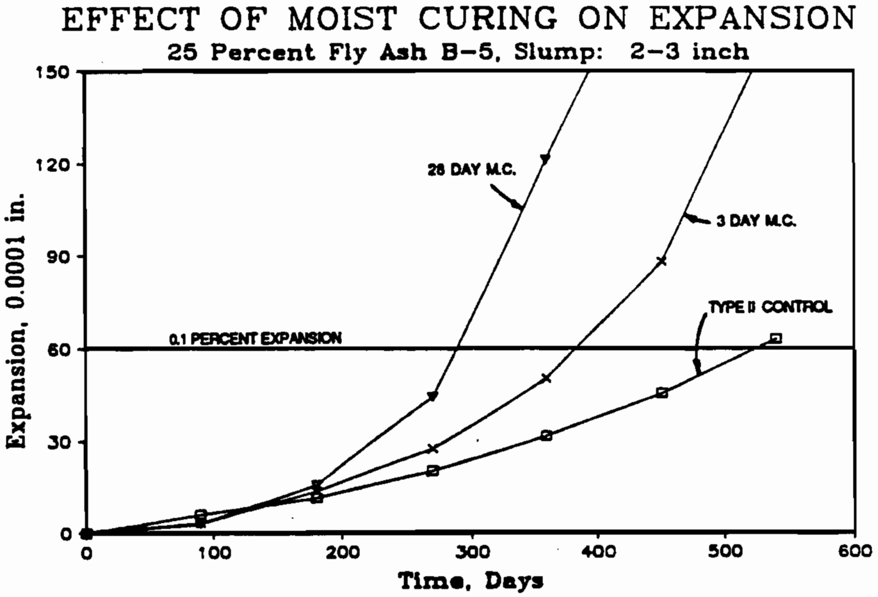


Figure 8.40 Effect of moist curing on sulfate expansion of concrete containing fly ash B-5.

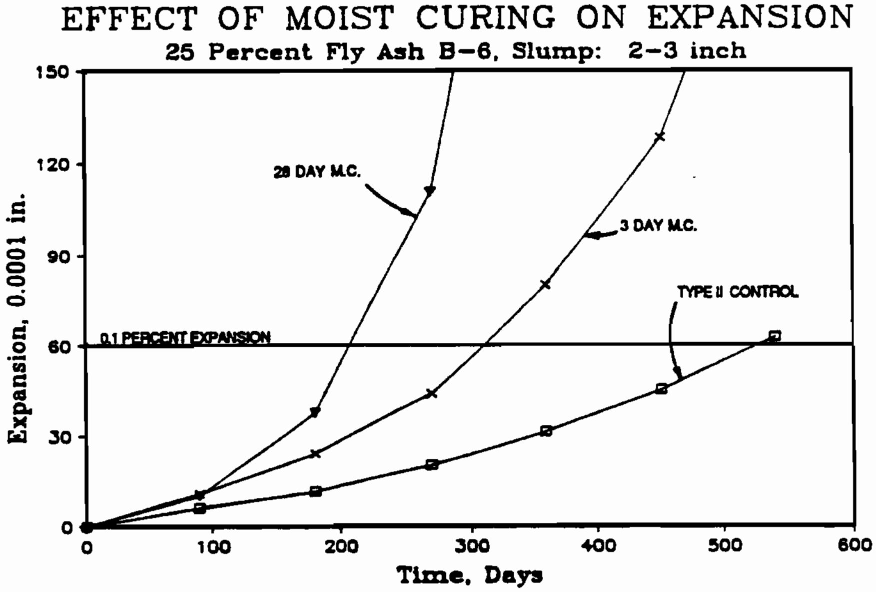


Figure 8.41 Effect of moist curing on sulfate expansion of concrete containing fly ash B-6.

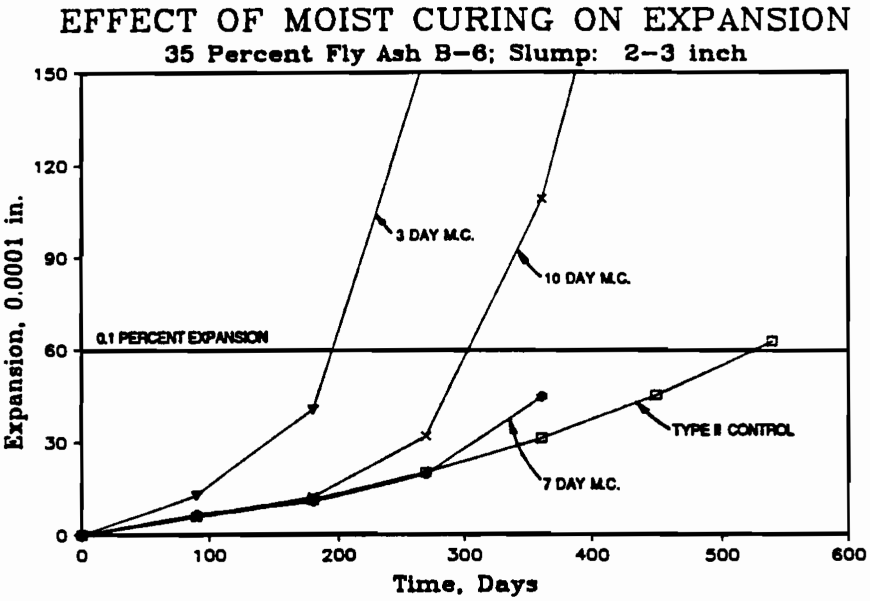


Figure 8.42 Effect of moist curing on sulfate expansion of concrete containing fly ash B-6.

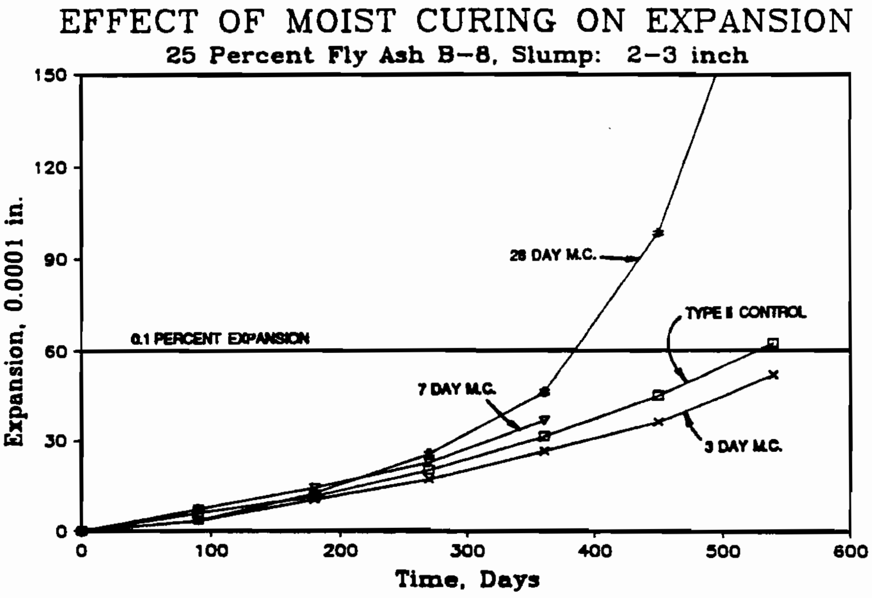


Figure 8.43 Effect of moist curing on sulfate expansion of concrete containing fly ash B-8.

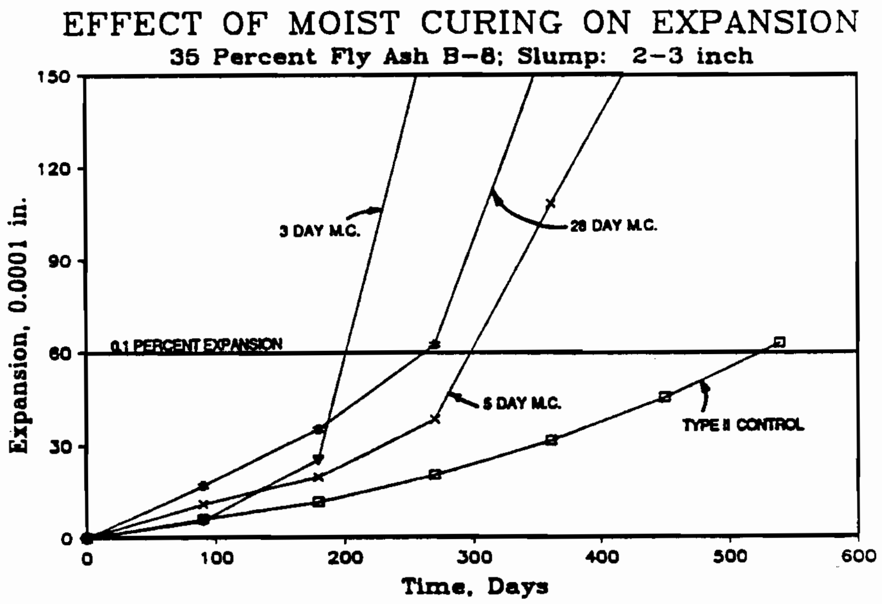


Figure 8.44 Effect of moist curing on sulfate expansion of concrete containing fly ash B-8.

with sulfate ions. Where the low stiffness may provide a short term benefit to the concrete, the sulfate saturation may provide a source for continual sulfate attack on a long-term basis. The combination of these two effects in concrete at ages between 3 and 28 days, made the time to exposure a minor consideration between these ages. *8.3.4 Effect of Air Content.* An entrained air system within the mortar of concrete decreases the capillary flow of fluid through concrete and improves many aspects of concrete durability[99]. Figure 8.45 summarizes the results of the exposure testing of air entrained concrete mixtures. In each case, air entrained concrete had approximately the same sulfate expansion as the concrete without entrained air. Air entrainment did not increase the sulfate resistance of concrete containing fly ash.

8.3.5 Effect of Slump. The slump requirement of concrete is a measure of the desired flow characteristics of fresh concrete mixture. The effect of slump on the sulfate resistance of concrete was investigated in this study using 2 inch and 6 inch slump concrete containing fly ash. The results are summarized in Figures 8.46 through 8.48. A reduction in slump reduces the water content and permeability of concrete, however there was no definitive effect of slump on sulfate resistance found in this study. Concrete which was not sulfate resistant with 6-7 inch slump was not

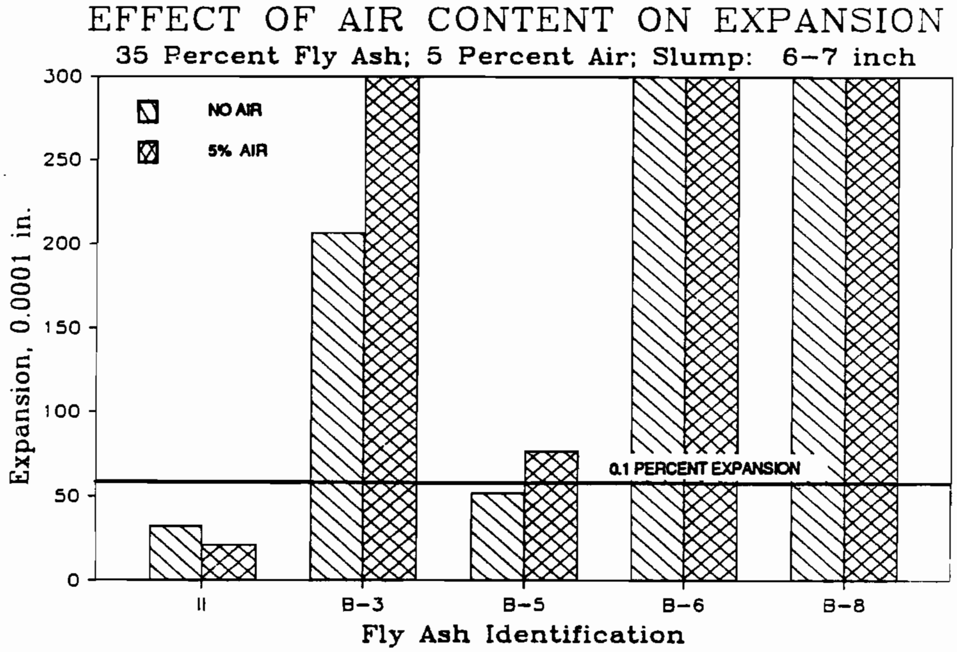


Figure 8.45 Effect of entrained air on the sulfate resistance of concrete.

made sulfate resistant through the reduction of slump, nor was a reduction of sulfate resistance noted with an increase in slump in concretes which were sulfate resistant at a 2-3 inch slump.

8.3.6 Effect of Cement Type. The primary contributing compound to sulfate attack in concrete is the C_3A in the portland cement. In this study, Type II with 6 percent C_3A, 02 cement with 0 percent C_3A, and Type I cement with 9.9 percent C_3A were used partially replaced by an equal volume of fly ash at level of 25 and 35 percent to investigate the effect of fly ash on the sulfate resistance of different type cements.

Figures 8.49 and 8.50 summarize the results of these tests. Concrete containing fly ash as a volumetric replacement for 0 percent C_3A portland cement consistently had lower sulfate expansions than concrete containing the same fly ash and 6 percent C_3A Type II portland cement. However 0 percent C_3A cement concrete containing fly ashes B-6 and B-8 showed 540 day expansions greater than that of the 6 percent C_3A Type II portland cement control. All the concrete mixtures containing 0 percent C_3A cement and high calcium fly ash cracked within the first

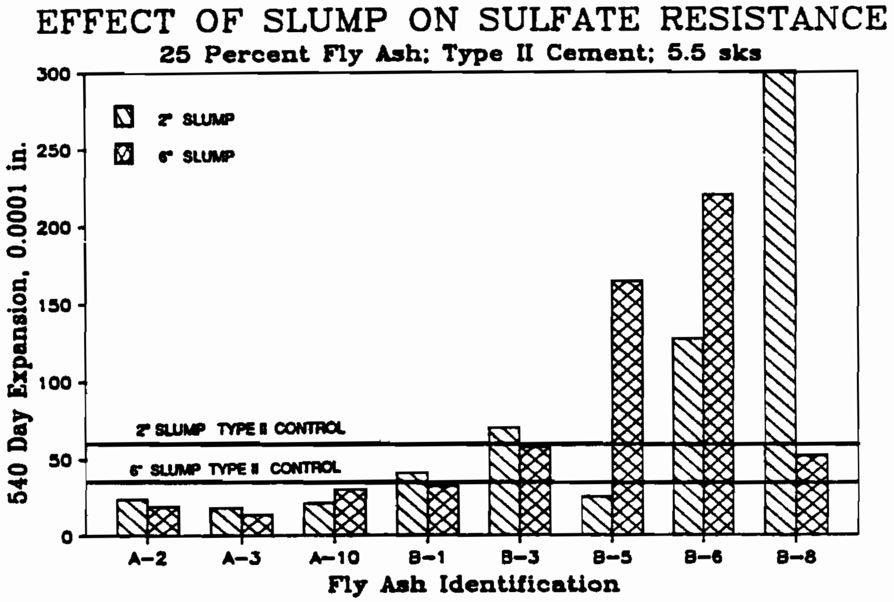


Figure 8.46 Effect of slump on the sulfate resistance of concrete containing 25 percent fly ash.

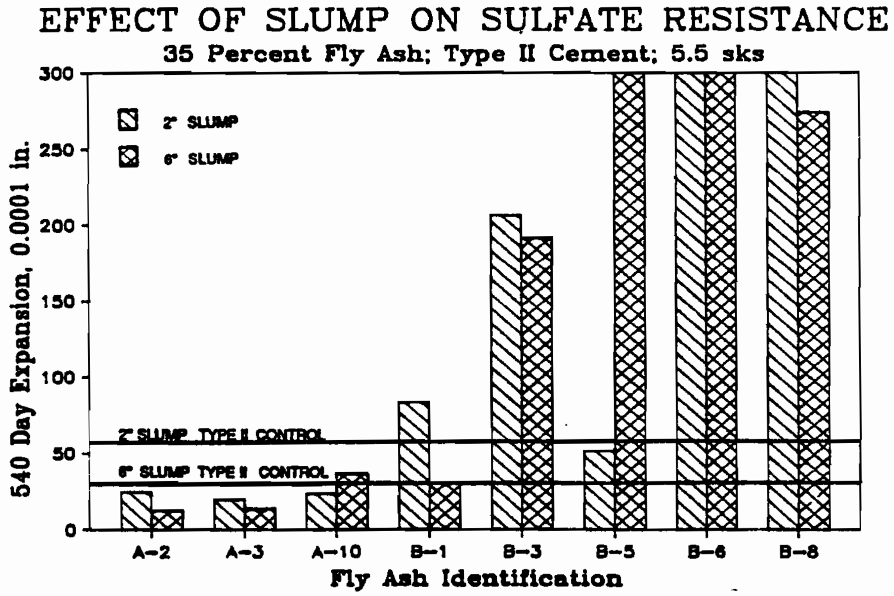


Figure 8.47 Effect of slump on the sulfate resistance of concrete containing 35 percent fly ash.

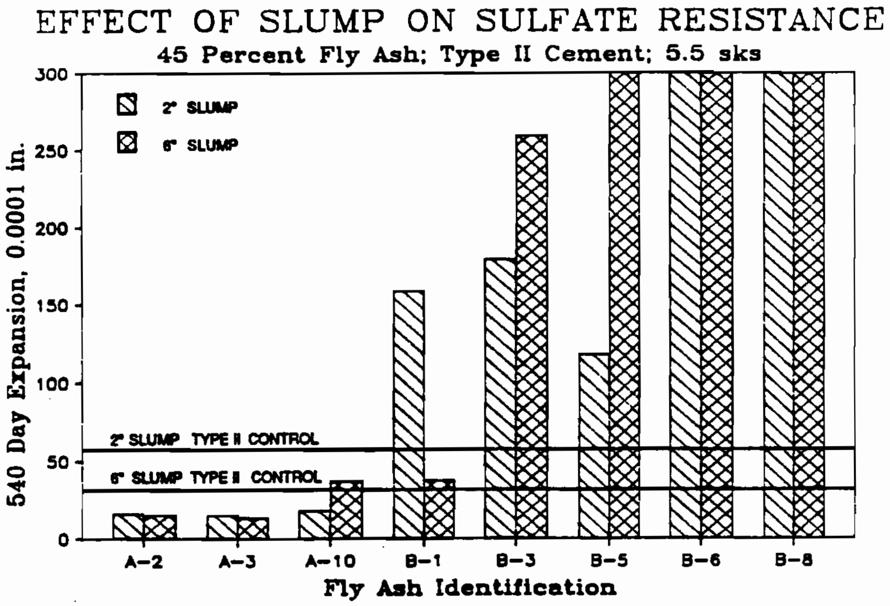


Figure 8.48 Effect of slump on the sulfate resistance of concrete containing 45 percent fly ash.

year of sulfate exposure. (Fly ash B-3 was also used as a 35 percent replacement for Type V portland cement with 3.6 percent C_3A. The expansion of this concrete was approximately the same as the Type V control, but had cracked after just 110 days of sulfate exposure.)

Figure 8.50 is presented as 360 day exposure data because some of these mixtures were cast at later dates than others. Concrete containing fly ash as a volumetric replacement for 9.9 percent C_3A Type I portland cement consistently had equal or lower 360 day sulfate expansions than concrete containing fly ash and 6 percent C_3A portland cement. The concrete mixtures containing 9.9 percent C_3A cement and high calcium fly ash cracked within the first year of sulfate exposure.

This series of mixtures illustrates that even high sulfate resistant cement such as 0 percent C_3A cement may become susceptible to sulfate attack if a high calcium fly ash, such as B-6 or B-8, is used as a replacement for part of the portland cement. Additionally, the preliminary data on fly ash-Type I cement combinations show the potential for blended Type IP cements to exhibit sulfate resistance equal to that of Type II cement.

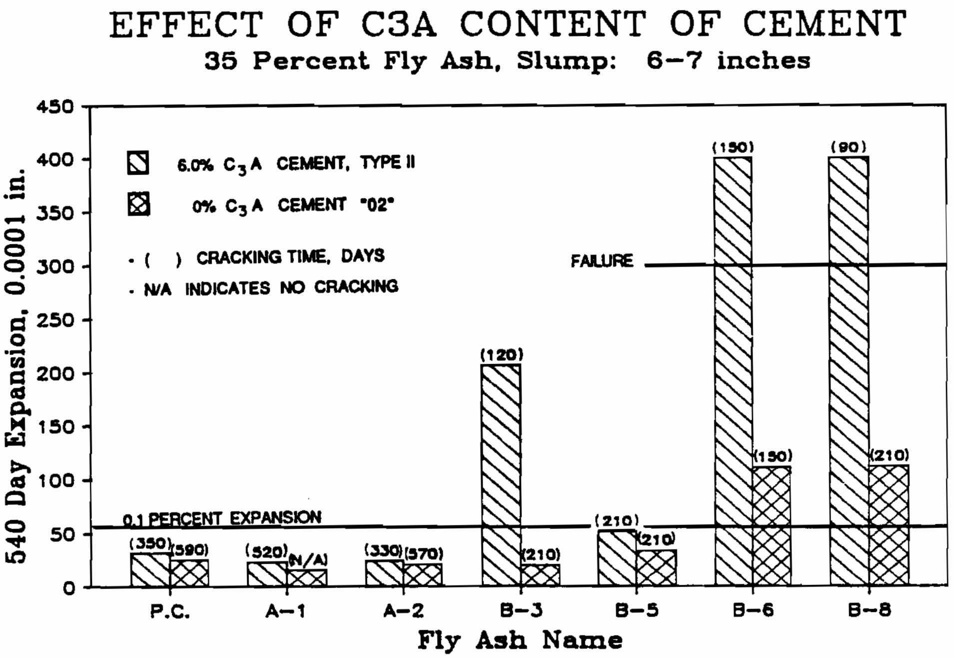


Figure 8.49 Effect of fly ash on the sulfate resistance of sulfate resistant cements.

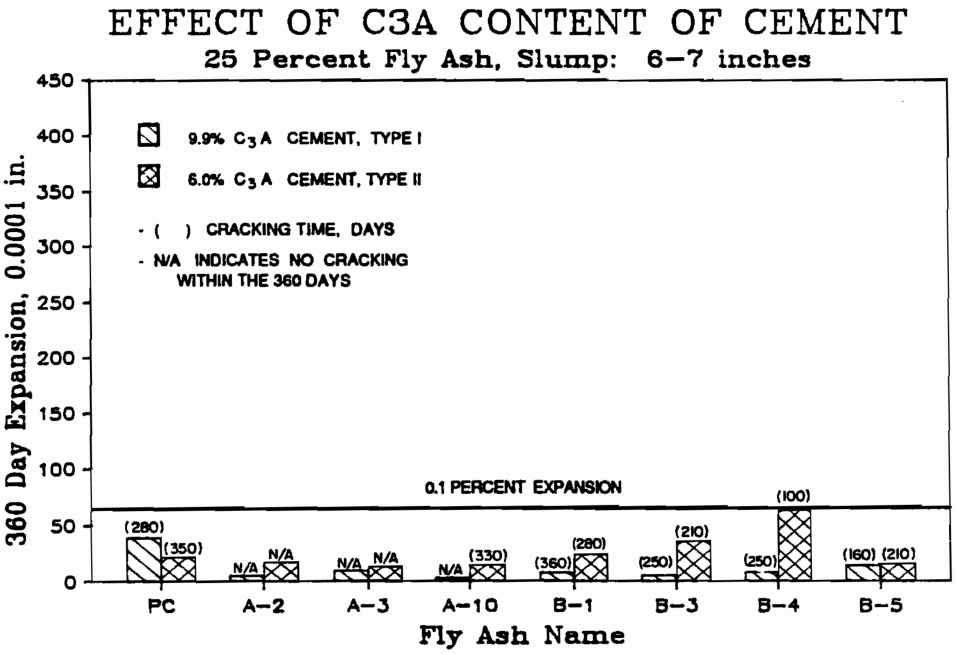


Figure 8.50 Effect of fly ash on the sulfate resistance of two different cements.

8.3.7 Effect of Admixtures. Two admixtures were used in this study: a water reducer-retarder and a waterproofing admixture. Concrete with the water reducer-retarder performed in the same manner as concrete with the same slump and no admixtures. The waterproofing admixture provided no additional resistance to sulfate attack when used in portland cement concrete or concrete containing fly ash B-3. The results of the mixtures containing the water reducing-retarding admixture and the waterproofing admixture are shown in Figure 8.51 and 8.52.

8.3.8 Effect of Seawater. Artificial seawater was used as mixing water in two concrete mixtures to observe the effect of salt water on the sulfate resistance of concrete containing high calcium fly ash. The results are presented in Figure 8.53. The concrete containing seawater showed a delayed expansion as compared to the concrete without seawater, but both sets of specimens containing seawater cracked within 200 days of sulfate exposure. The use of seawater as mixing water did not prevent the onset of sulfate attack.

8.4 Sulfate Resistance Evaluation

The overall sulfate resistance of concrete was evaluated through the use of a performance scale which combines the test results of both expansion testing and time to first cracking[58]. The change in mass was not used in determining the sulfate performance rating (SPR), because it did not provide a consistent correlation with sulfate damage. Some concrete mixtures expanded to near failure with very large cracks, yet did not spall. Other specimens spalled near the edges of the concrete, yet did not expand to failure. The SPR system is described in Table 8.1. The Sulfate Performance Rating scale of 1-5 represents the relative deterioration of concrete specimens tested according the sulfate exposure test USBR 4908 Method B. An SPR value of 1.0 represents concrete with the highest sulfate resistance using cementitious and pozzolanic materials.

The Sulfate Performance Rating (SPR) is expressed as the average of the expansive and cracking performance indices. For example, if a set of concrete specimens had an average expansion of 0.072 percent after 360 days of exposure testing and a time to first cracking of 310 days, the SPR would be computed as follows:

$$\text{Performance Index (expansion)} = 3$$

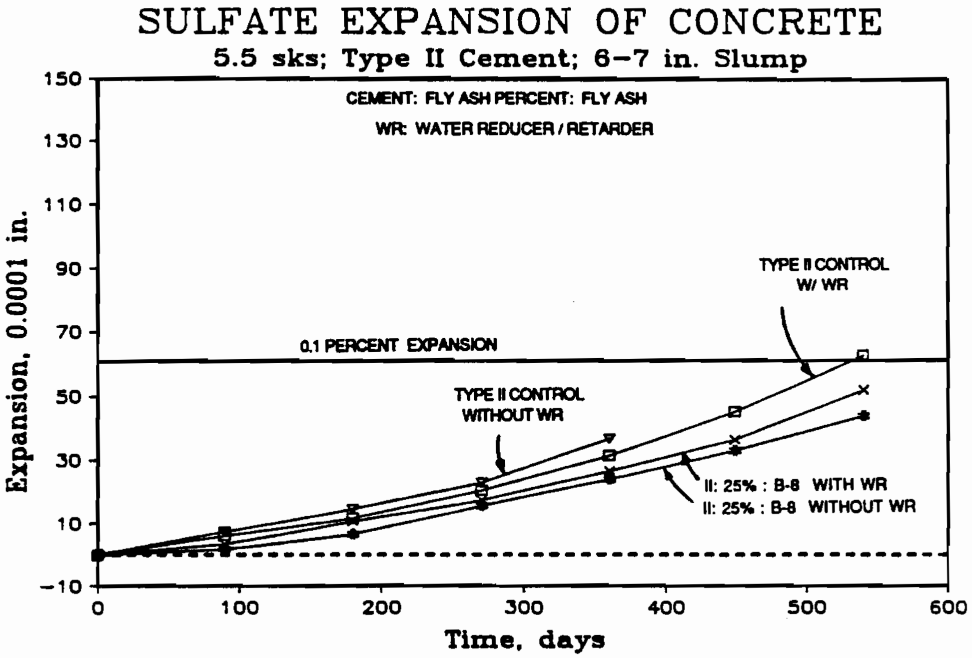


Figure 8.51 Effect of water reducer on sulfate expansion.

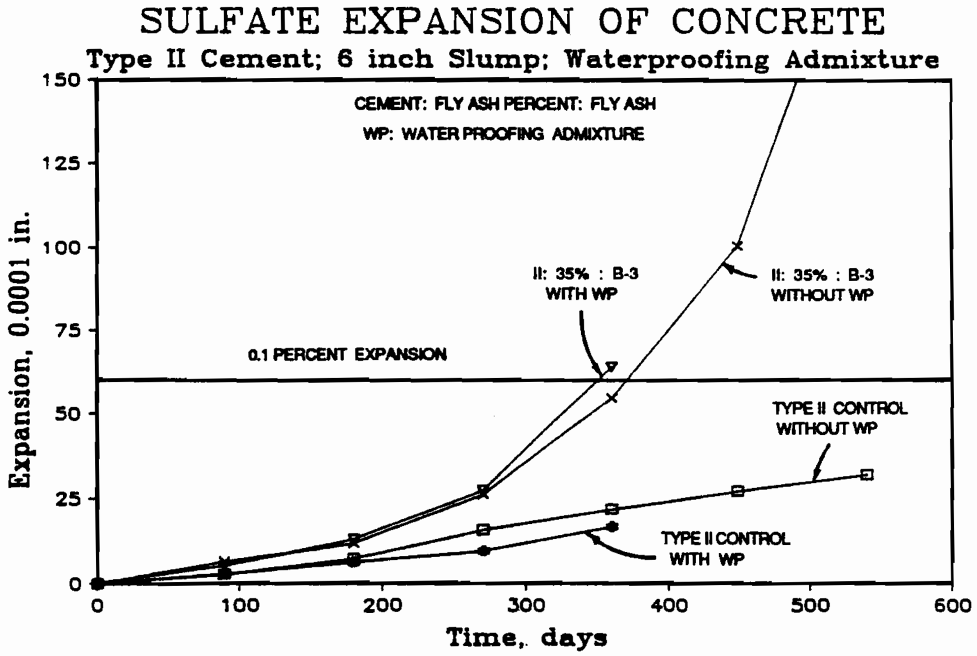


Figure 8.52 Effect of water-proofing admixture on the sulfate expansion of concrete.

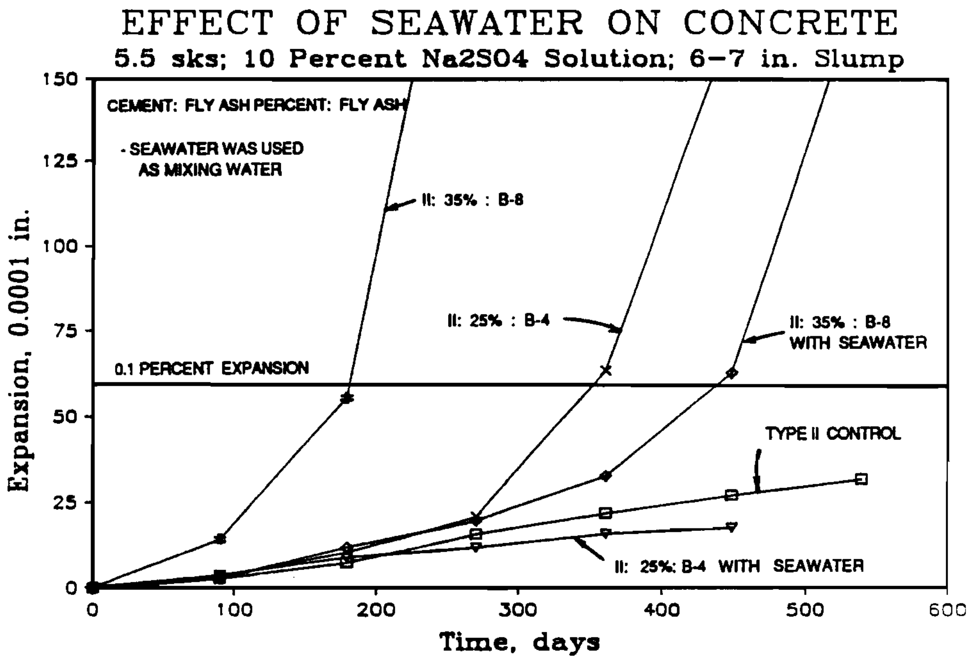


Figure 8.53 Effect of seawater mixing water on sulfate expansion.

Table 8.1 Sulfate Performance Rating* System

Performance Index	360 Day Expansion percent	First Visual** Cracking, days
1	< 0.030	> 500
2	0.031-0.050	300-499
3	0.051-0.080	200-299
4	0.081-0.100	100-199
5	> 0.100	0-99

$$* \ \text{SPR} = \frac{\text{Performance (Expansion)} + \text{Performance (Cracking)}}{2}$$

** 20 mm crack observed in half of the test specimens

Performance Index (cracking) = 2

$$SPR = \frac{3+2}{2} = 2.5$$

Concrete with Type II portland cement had a SPR value of 2.0, while concrete with Type V and 0 percent C_3A portland cements had SPR values of 1.5, and concrete containing Type I portland cement had a SPR of 3.0. Table 8.2 lists the average SPR values for all concrete mixtures containing Type II cement and each of the fly ashes and pozzolans S-1 and S-2 used in this study. For example, fly ash A-7 was used in the two concrete mixtures II:25%:A-7 and II:45%:A-7. The SPR values of these two mixtures were 1.5 and 1.0, respectively. The average SPR value for fly ash A-7 is 1.25, rounded up to 1.3 in Table 8.2.

Table 8.2 Average Sulfate Performance Rating of Concrete Containing Fly Ash.

FLY ASH	AVERAGE SPR
A-1	1.5
A-2	1.2
A-3	1.1
A-4	1.5
A-5	1.5
A-6	1.5
A-7	1.3
A-8	1.0
A-9	1.5
A-10	2.3
B-1	2.8
B-2	2.5
B-3	4.1
B-4	4.8
B-5	3.7
B-6	4.6
B-7	3.0
B-8	4.3
S-1	1.5
S-2	1.5

The SPR is a scale which is independent of the type of cement or fly ash used in the concrete mixture. This evaluation scale measures the relative performance of a concrete mixture subjected to the 10 percent Na_2SO_4 exposure test described, irrespective of mixture proportions and curing conditions prior to the exposure testing. The SPR values for all the concrete mixtures are presented in Table E-4 of Appendix E. The SPR will be used in the succeeding section to evaluate various concrete sulfate resistance prediction methods.

8.5 Sulfate Resistance Prediction Methods.

Several methods have been developed to predict the sulfate resistance of concrete containing fly ash. Dunstan proposed the R factor in 1976[25], and Manz and McCarthy proposed the Calcium Aluminate Potential and the Calculated Sulfate Equivalence in 1987[50]. Both based on a knowledge of hydration reactions and the material composition of fly ash. The Oxide Durability Factor proposed by Mangotich has not been developed further because it incorporated the cement and fly ash composition into a single material factor[34]. Portland cement and fly ash are chemically similar, however their crystalline phase composition and hydration rates are vastly dissimilar. For this reason, a lumped factor would require an intense study of hydration products over time between particular fly ash and portland cement combinations.

The R Factor, Calcium Aluminate Potential, Calculated Sulfate Equivalence, and an alternate method were investigated using the SPR to evaluate the most effective means of predicting the potential sulfate resistance of concrete containing fly ash. The results are presented in this section.

8.5.1 R Factor. The R Factor is a simple factor proposed by Dunstan and adopted by the United States Bureau of Reclamation for use in their specifications. This factor is based on the bulk chemical ternary SiO_2-Al_2O_3-CaO equilibrium phase diagram. The development of this equation was discussed in Chapter 3. The factor is stated in Equation 8.1.

$$R = \frac{CaO(\%) - 5\%}{Fe_2O_3(\%)} \tag{8.1}$$

Table 8.3 Sulfate Resistance of Concrete Containing Fly Ash.

R Limit	Sulfate Resistance
< 0.75	Greatly Improved
0.75 to 1.5	Moderately Improved
1.5 to 3.0	No Significant Change
> 3.0	Reduced Resistance

R=(CaO-5)/Fe_2O_3

Dunstan did not strictly differentiate between crystalline and amorphous phases, but rather used the bulk chemical composition and an estimated correction for reactive lime in this factor. This makes the R Factor an empirical factor based on an observed relationship between concrete performance in a sulfate environment and the bulk chemical composition of fly ash. Furthermore this factor was based on a fly ash content of 25 percent replacement of portland cement. The R factor of each of the concrete mixtures in this study is presented in Figure 8.54. There is a clear division between the levels of performance at different ranges of the R Factor value. Fly ashes with R Factors less than 1 performed better than the Type II cement alone (SPR=2), and fly ashes with an R Factors greater than 3.5 performed worse than the Type II control concrete. Since no fly ashes with R Factors between 1.0 and 2.8 were used in Phases I and II of this study, the intermediate behavior remains unresolved.

Weighting the R Factor by a ratio of the percentage fly ash to the 25 percent used in the development of the equation, as in Equation 8.2, the Modified R Factor is plotted versus the sulfate performance rating (SPR) of the mixtures containing Type II portland cement and fly ash in Figure 8.55.

$$R = \frac{(CaO(\%) - 5\%) * (\%F.A./25\%)}{Fe_2O_3(\%)} \tag{8.2}$$

The Modified R factor shows a correlation with the SPR of the concrete tested in this study. However this factor indicates a reduction in the sulfate resistance with an increase in fly ash content. This trend was only observed in the

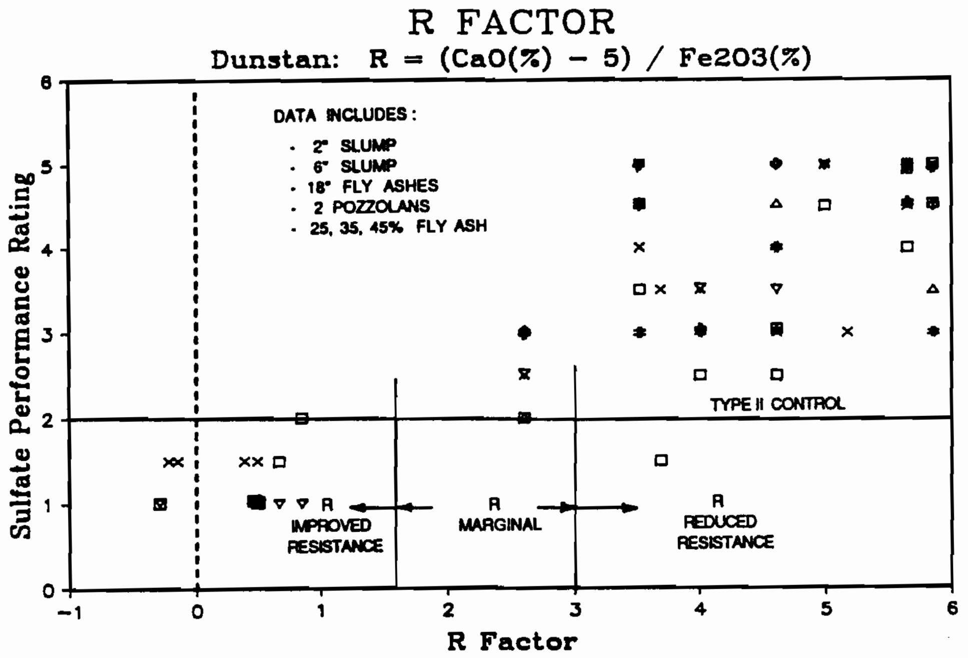


Figure 8.54 Sulfate resistance of fly ashes with the R factor method.

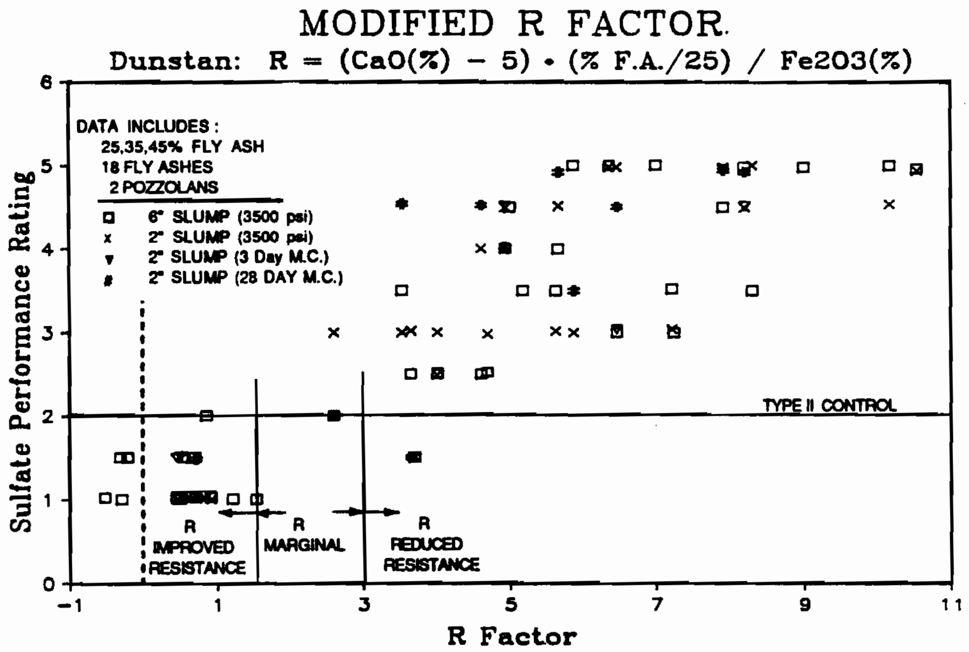


Figure 8.55 Weighted R factor versus sulfate performance.

high calcium fly ashes. The low calcium fly ashes typically displayed an improved sulfate resistance when higher fly ash contents were used. Furthermore, the R factor maintains some negative numbers which would indicate improved resistance with increased fly ash contents. The Modified R Factor could be improved by reducing the 5 percent calcium oxide correction to a level closer to the average calcium oxide crystalline composition of low calcium fly ash. The R Factor shows the same correlation to sulfate resistance as was observed with the total calcium oxide content, as is illustrated in Figure 8.56. The Modified R factor is an adequate conservative estimate of the sulfate performance of the concrete in this study, but could be simplified by using only the calcium oxide content.

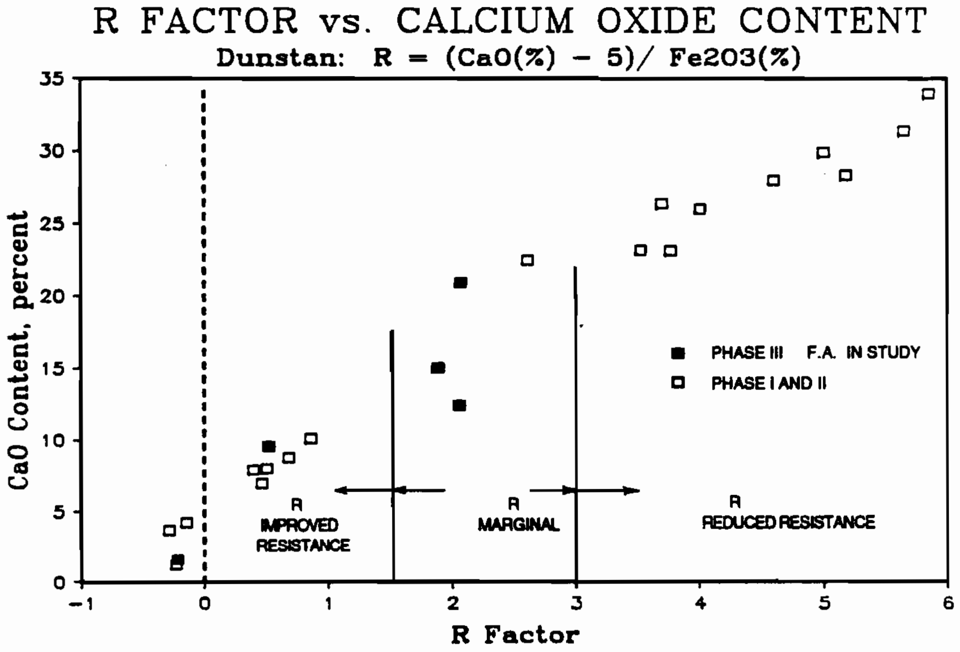


Figure 8.56 The influence of CaO content on the R factor.

8.5.2 Calcium Aluminate Potential. The Calcium Aluminate Potential is a prediction method presently under development by Manz and McCarthy[50]. This factor subtracts the portion of inert crystalline material and highly reactive crystalline materials in fly ash from the bulk chemical composition to arrive at a potentially reactive portion of the fly ash. The Calcium Aluminate Potential (CAP) is stated in Equation 8.3.

$$CAP = \frac{C' + A' + F'}{S'} \tag{8.3}$$

C′(%) = Bulk CaO - Reactive Crystalline CaO(lime, anhydrite, C_2S) - Inert Crystalline CaO(melilite, merwinite)

A′(%) = Bulk Al_2O_3 - Inert Al_2O_3(mullite)

F′(%) = Bulk Fe_2O_3 - Inert Crystalline Fe_2O_3(hematite, spinel)

S′(%) = Bulk SiO_2 - Inert Crystalline SiO_2(quartz, mullite)

The CAP is plotted versus the Sulfate Performance Rating of the concrete mixtures in this study in Figure 8.57. Weighing the CAP as the Modified R Factor was weighed, the results are shown in Figure 8.58. Concrete containing fly ash with a CAP values greater than 1.5 was not typically sulfate resistant, and concrete containing fly ash with a CAP less than 1.0 was sulfate resistant. None of the 18 fly ashes in Phase I or II had a CAP between 1.0 and 1.5.

The CAP prediction method is based on the reactive nature of the calcium aluminates in the fly ash; however it treats the effects of reactive calcium, aluminum, and iron oxides as equally detrimental to the sulfate resistance of concrete. Contrary to the R Factor, the CAP factor considers reactive iron oxide as a detriment to the sulfate resistance of concrete. For the relative complex material analysis required for this method, the CAP is not yet a refined method of prediction for concrete sulfate resistance; however, fly ash with a CAP less than 1.0 can reasonably be assumed to enhance the sulfate resistance of concrete.

8.5.3 Calculated Sulfate Equivalence. The Calculated Sulfate Equivalence is another theoretic prediction method presented by Manz and McCarthy, based on the glassy phase composition of fly ash. This method uses the idea of supersulfating the concrete with sulfates to stabilize the ettringite compound at early ages. The problem with this train of thought is that supersulfating concrete comes from reaching the supersaturation point of calcium sulfate in the pore water solution, and is not a gradual benefit to the concrete.

If the concrete is supersulfated the ettringite will stabilize, if the concrete is not supersaturated with calcium sulfate the ettringite will revert to the stable form of monosulfoaluminate.

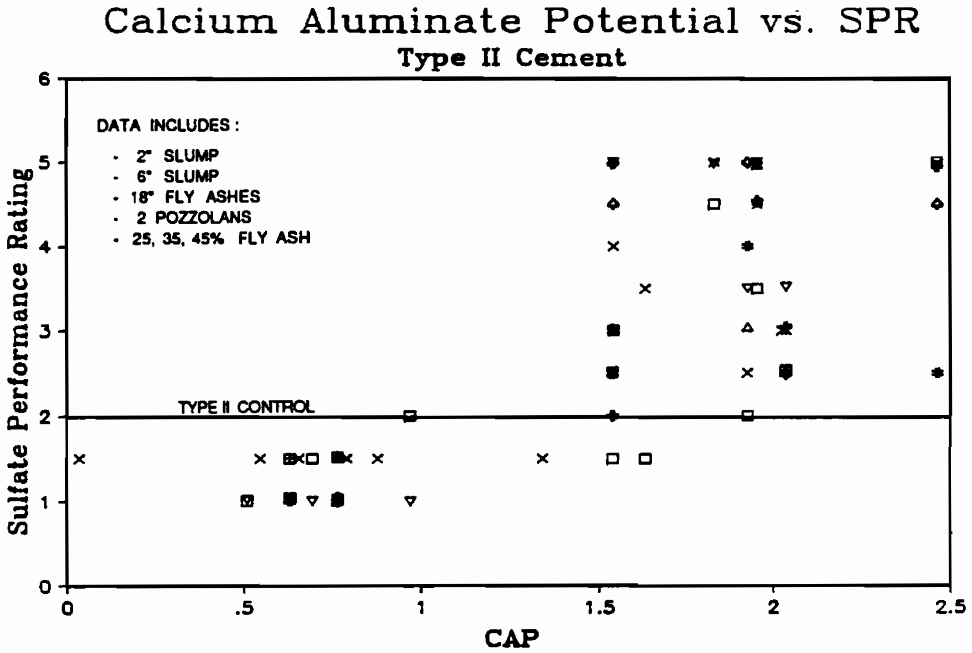


Figure 8.57 Calcium aluminate potential of concrete containing fly ash.

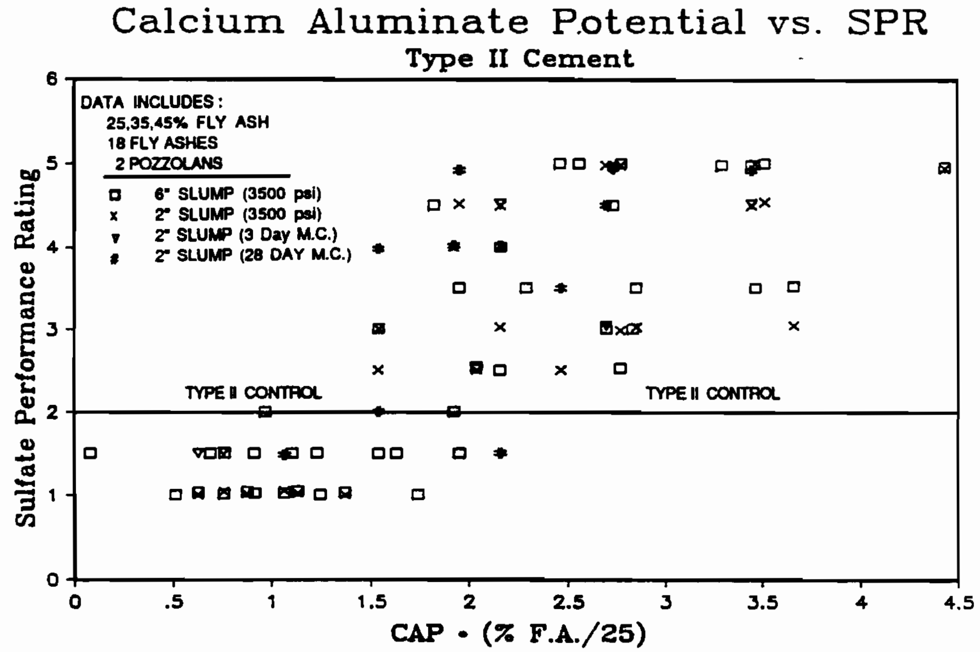


Figure 8.58 Weighted calcium aluminate potential of concrete containing fly ash.

As is shown in Figure 8.59 and 8.60, the C$\overline{S}$E and the weighted C$\overline{S}$E show no clear correlation to the Sulfate Performance Rating of the concrete in this study, except that low C$\overline{S}$E are sulfate resistant and high C$\overline{S}$E are susceptible to sulfate attack. The proposed scale by Manz suggests the opposite relationship indicating that a high C$\overline{S}$E represents a sulfate resistant concrete, as shown in Figure 8.61. The Calculate Sulfate Equivalence is not an effective means of predicting the sulfate resistance of concrete.

8.5.4 Alternate Method. An alternate method of predicting the sulfate resistance of concrete containing fly ash is presented for further development herein, using the phase analysis concept from McCarthy and Manz, the empirical observations of Dunstan and Kalousek, and the material characterization and sulfate study performed as part of this research program. There are three major criteria for this model. The first criterion for a prediction model to evaluate the potential sulfate resistance of concrete containing fly ash with a conservative bias, i.e. it does not predict the adequate performance of concrete which has the potential to later suffer distress from the sulfate attack mechanism. Secondly, there should be no need for a weighting factor. The fly ashes in this study either showed the potential to equal or increase the sulfate resistance of Type II cement, or equal or decrease the sulfate resistance of Type II cement. This was true independent of slump, normal curing conditions, air content, and fly ash content. The fly ash should be determined either suitable or unsuitable, and the mixture proportions and percent replacement determined by the concrete producer. The third criterion for a prediction model is that it is based on the actual hydration reactions present in concrete containing fly ash, and is consistently substantiated by both theoretic and empirical data.

The fly ashes that make concrete most susceptible to sulfate attack are the fly ashes that contain calcium rich glasses. These calcium rich gehlenite or anorthite field glasses are more soluble than the calcium deficient mullite field glasses. The greater solubility of the calcium rich glasses releases calcium aluminates into the paste mixture at a much greater rate than the mullite glasses[79]. As shown in the ternary diagram of SiO_2-Al_2O_3-CaO shown in Figure 8.62, the greater the amount of calcium in the glassy phases of the fly ash the closer the fly ash approaches the C_3A composition. This figure also shows the average SPR values of the fly ashes used in this study plotted at the fly ashes' ternary glass phase composition. The

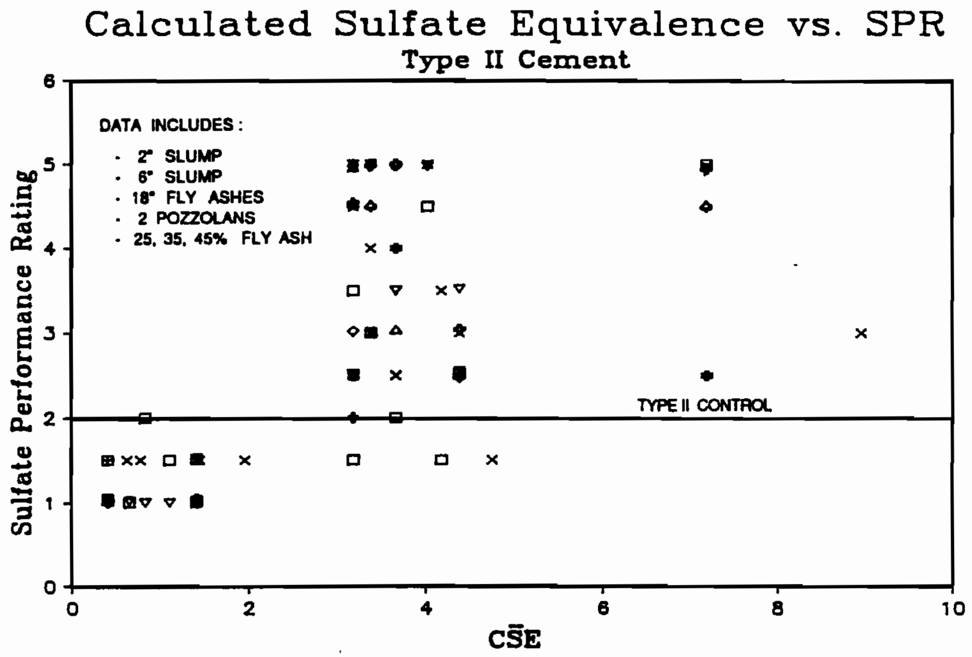


Figure 8.59 Calculate sulfate equivalence of concrete containing fly ash.

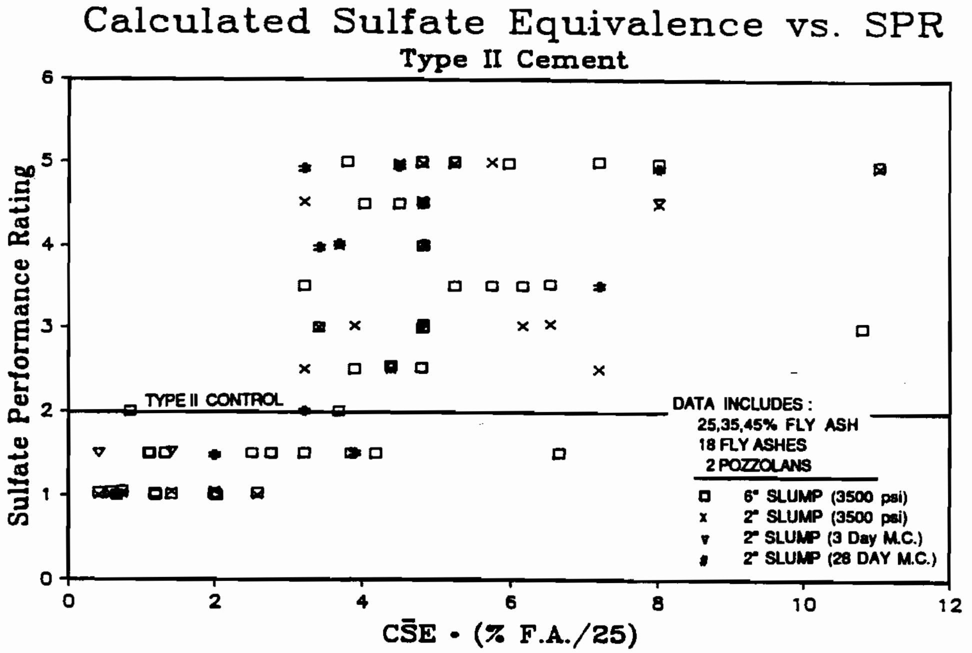


Figure 8.60 Weighted calculated sulfate equivalence of concrete containing fly ash.

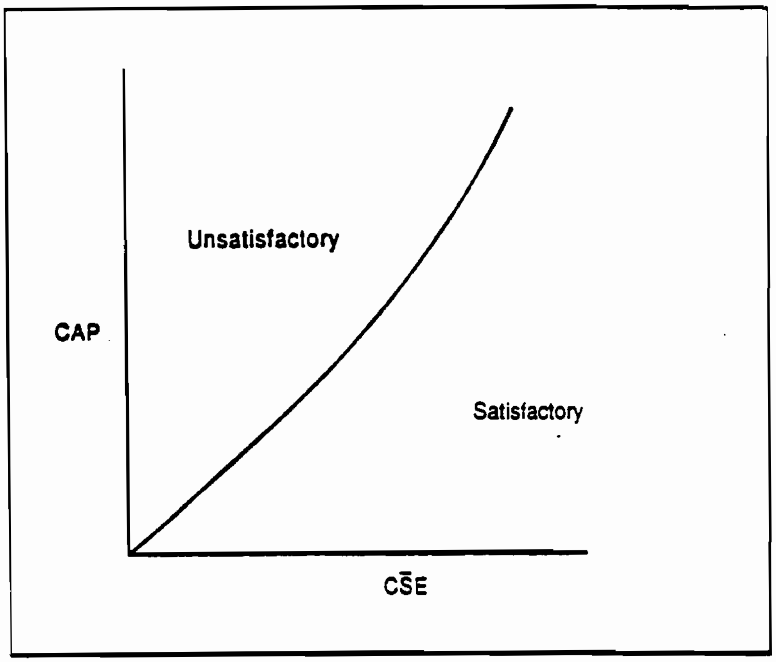
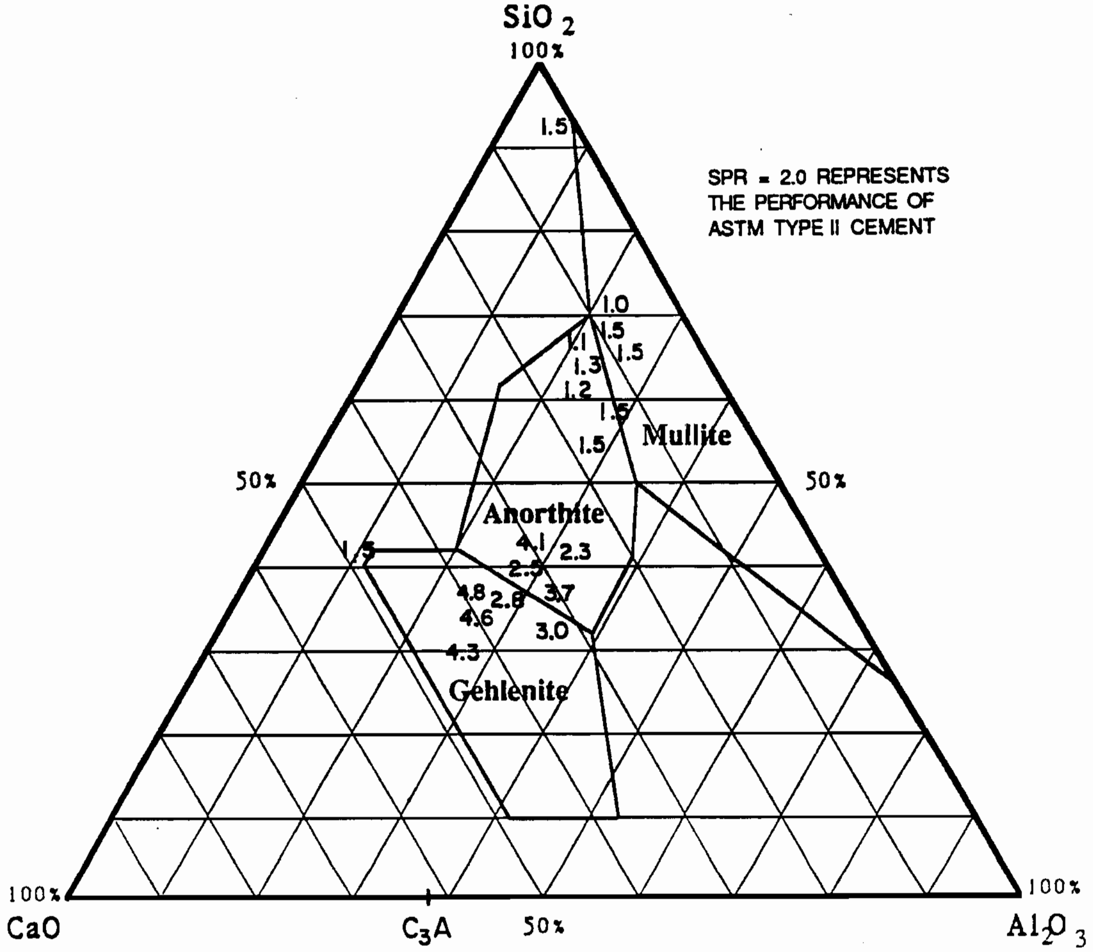


Figure 8.61 Proposed relationship between the CAP and C$\bar{S}$E factors.

fly ashes with a mullite field ternary glass had SPR values less than that of the Type II control (SPR=2.0). Likewise the fly ashes with gehlenite field ternary glass compositions had SPR values greater than the Type II control.

Fly ash is not comprised of a single glassy amorphous phase of uniform composition, but rather a band of glass compositions with their average composition shown on the ternary diagram as a single point. Stevenson has shown that low calcium fly ashes have a range of glass compositions from sillmanite to mullite, and high calcium fly ashes from mullite to pure C_3A. This is shown in Figure 8.63, where each point represents the ternary bulk composition of a discrete particle of fly ash as determined by SEM microprobe analysis. Fly ashes with the greater portions of their composition near the C_3A point on the ternary diagram are most susceptible to contributing to the sulfate attack mechanism in concrete.

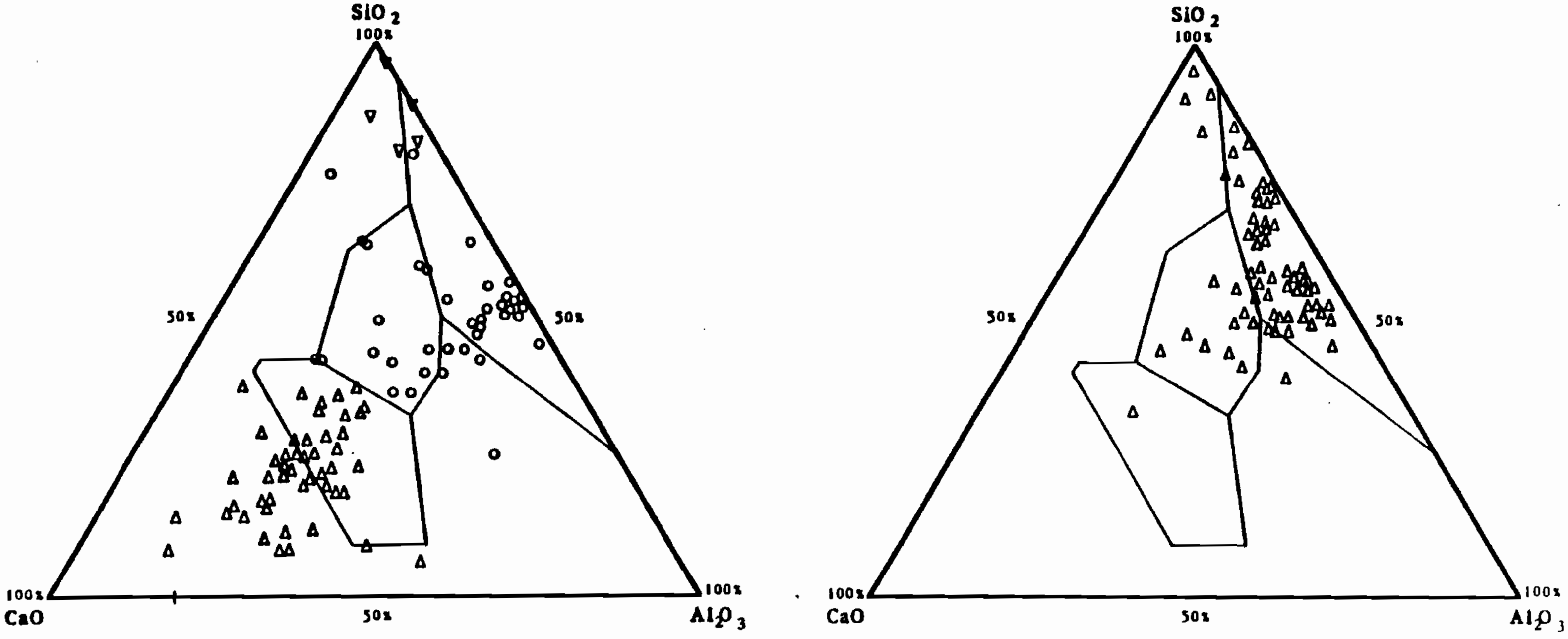
In addition to the compounds represented on the ternary diagram, there are two other components of the glassy phases to consider, alkalies and iron oxide. Each of these are typically found in quantities less than 5 percent of the total composition of the glass. The presence of alkalies has the potential to make the glass



SPR = 2.0 REPRESENTS THE PERFORMANCE OF ASTM TYPE II CEMENT

CaO • Al2O3 • SiO2 ternary oxide system diagram of glass portion of fly ashes.

Figure 8.62 Sulfate performance of fly ashes with respect to the equivalent ternary glass composition.



$CaO \cdot Al_2O_3 \cdot SiO_2$ ternary oxide system diagram of high calcium subbituminous fly ash

$CaO \cdot Al_2O_3 \cdot SiO_2$ ternary oxide system diagram of low calcium Texas lignite fly ash

Figure 8.63 Typical ternary compositions of high and low calcium fly ash[94].

more soluble and therefore more readily reactive. Iron oxide in the glass has the potential to act as a stabilizing effect in the sulfate mechanism, much like that of C_4AF reacts in a much less detrimental manner than C_3A in portland cement.

The calcium aluminates in the glassy portion of fly ash are released at a rate that is slower than the rate of hydration of portland cement or the reactive crystalline phases within fly ash, but at a faster rate than the pozzolanic hydration of aluminosilicate (mullite field) glassy phases. The probable sulfate attack mechanism in high calcium fly ash is that calcium aluminates are released from the glassy phases between the time of casting and the first several months after the concrete is hardened and in service. In a sulfate deficient environment, the calcium aluminates become calcium aluminate hydrate or monosulfoaluminate contributing to the long term strength gain of the concrete. In the event the concrete is subjected to sulfate exposure, the calcium aluminate hydrate and monosulfoaluminate react to become ettringite. The expansion associated with the ettringite formation cannot be accommodated by elastic concrete strain, and thereby cracks the concrete causing the distress known as sulfate attack.

In the low calcium fly ashes, the aluminosilicate glassy phases react with water and calcium hydroxide in the concrete to form an intertwined refined matrix of calcium silicate hydrate and calcium aluminate hydrate. This hydrated matrix is resistant to both the intrusion of sulfate ions and the formation of ettringite because of the refined nature of the paste structure and the reduced presence of calcium hydroxide.

To accurately determine the exact composition of the glassy phases in the fly ash is not economically possible. A comprehensive SEM analysis or TEM analysis would be required to reasonably determine the composition of each glassy phase. However, the research conducted by Stevenson and McCarthy on fly ash characterization confirms certain phase composition distributions. Using XRD and bulk chemical analysis, an estimate of the average glass composition can be made and used to predict the sulfate resistance of concrete containing the fly ash by determining the potential for the fly ash to release calcium aluminate into the concrete. The single, most dominant, parameter in this study and in those of Dunstan and Manz and McCarthy was the calcium content of the fly ash. Correlating the calcium content of the glass as a percentage of the four major oxide in the glass, SiO_2,

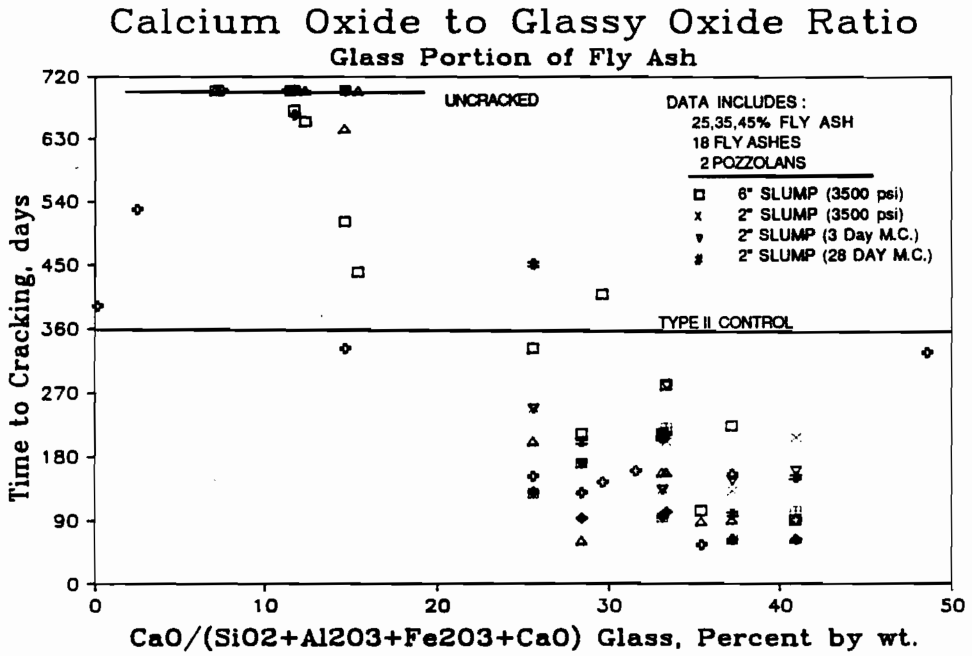


Figure 8.64 Calcium content of 4 phase glassy phases versus time to cracking.

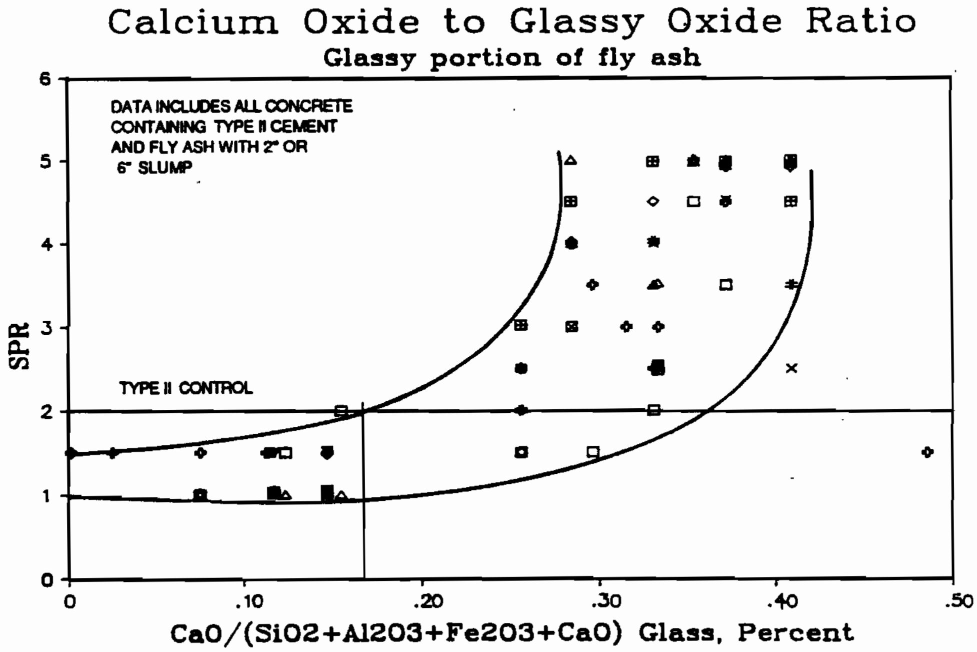


Figure 8.65 Sulfate performance of concrete with respect to the CaO content of equivalent 4 phase glass.

Al_2O_3, Fe_2O_3 and CaO, Figures 8.64 and 8.65 show a distinct relationship between the calcium oxide content of the glass and the sulfate resistance of the concrete. Fly ashes which hold the potential to lessen the concrete's sulfate resistance are those which have more than 25 percent calcium content in the glassy phases. In the ashes studied this corresponded to fly ashes with an average glass composition of gehlenite and anorthite glass. Fly ashes with less than 17 percent calcium content in the glassy phases show excellent sulfate resistance.

The further development of the alternate method of predicting the sulfate resistance of concrete containing fly ash will continue through the remaining phases of the research program. The addition of fly ashes A-11, A-12, A-13, A-14, B-9, and B-10 and the continued monitoring of the specimens from Phases I and II will refine the relationship between the chemical and mineralogical composition of fly ash and the sulfate resistance of concrete containing fly ash.

CHAPTER IX
THE POTENTIAL OF SULFATE RESISTANT CONCRETE CONTAINING FLY ASH

9.1 General

As has been shown throughout this document, a specific class of fly ashes can be used in concrete exposed to sulfate environments. These fly ashes will typically improve the sulfate resistance of the concrete over that of concrete containing portland cement without fly ash.

The fly ashes which have the potential to improve the sulfate resistance of concrete are those containing low calcium glassy phases. These fly ashes are characterized by having a total calcium content less than 15 percent and are typically derived from low calcium coals. These coals include: bituminous sources from Utah and the eastern U.S., lignite sources from Texas, and subbituminous sources from Colorado. Fly ashes resulting from each of these coal sources have proven to provide a level of sulfate resistance in concrete equal to or greater than concrete containing moderate sulfate resistant cement.

An indiscriminate or purely economic choice of a fly ash for use in concrete exposed to sulfates may lead to the use of a fly ash with a high calcium glassy phase. The use of this class of fly ash may lead to the premature deterioration of concrete exposed to sulfates. With the use of each of the 8 high calcium fly ashes tested in this study, the sulfate resistance of concrete was decreased from that level provided by moderate sulfate resistant portland cement. This poses a serious problem for the fly ash and concrete industries.

The purpose of this chapter is to discuss potential alternatives which may provide concrete containing high calcium fly ash with greater sulfate resistance. Several theoretic alterations to the hydration process will be suggested, as well as the potential for using a physical barrier to prevent sulfate intrusion.

9.2 Marginal Fly Ashes

The marginal fly ashes are those which provide no additional or a decreased sulfate resistance of concrete. These are typically the fly ashes with greater than 20 percent total calcium oxide. High calcium fly ashes can provide concrete with excellent strength characteristics, as well as an improvement in the fresh concrete properties. The problem of sulfate resistance of concrete containing marginal fly ashes may be understood more clearly or solved by investigating several additives which will alter the hydration process of the concrete. These alternatives will be investigated in the laboratory in the future phases of this research program.

9.2.1 Gypsum Compensation. Often in the study of sulfate attack, the effect of gypsum on the hydration process is overlooked. In ordinary portland cement, gypsum acts to regulate setting time through its property of low solubility. Gypsum dissolves into the mixing water to form a saturated solution of about 0.2 Molar $CaSO_4$. As the C_3A consumes the calcium sulfate from solution to form ettringite, more gypsum is dissolved to maintain the saturated solution. By controlling the rate of hydration of the C_3A, the gypsum controls the setting time of the portland cement. When nearly all the gypsum is consumed, the ettringite begins to revert to monosulfoaluminate. The conversion of ettringite to monosulfoaluminate continues until the monosulfate phase is the only phase present in the concrete. The presence of monosulfoaluminate is what makes concrete susceptible to sulfate attack. As was explained in Chapter 2, when the concrete is exposed to a sulfate environment, the monosulfoaluminate converts back to ettringite creating internal expansions.

If excess gypsum exists in the portland cement, the C_3A in the portland cement will react to completion forming stable ettringite as the primary calcium aluminosulfate. This is what is known as a supersulfated portland cement. This portland cement is sulfate resistant because the concrete hardens around the expanded calcium sulfoaluminate, ettringite, providing adequate space in the matrix of hydration products.

Type II cement, moderate sulfate resistant cement, contains a sufficiently low content of C_3A so as to be minimally affected by the conversion of monosulfoaluminate to ettringite in the hardened concrete. A Type I cement, on the other hand, with a high C_3A content contains proportionally high contents of monosulfoaluminate. When concrete containing Type I cement is exposed to a sulfate environment, the concrete deteriorates rapidly.

The replacement of portland cement with a pozzolan dilutes the total quantity of C_3A in the concrete mixture, thereby reducing the monosulfoaluminate content of the hardened concrete. Even if the pozzolan, fly ash, contains small quantities of crystalline C_3A, the dilution effect is still substantial.

There are two cryptic factors which have been overlooked in this discourse. First, the reduction of portland cement has also reduced the gypsum content of the total binding material. If C_3A, $C_4A_3\overline{S}$, or anhydrite, $CaSO_4$, is present in the fly ash, the setting time will no longer be the well timed clock controlled by the cement chemist. This effect is seldom severe and the setting time can be easily predicted by monitoring trial batches. The second factor, one which may greatly affect the sulfate resistance of concrete, is the effect of noncrystalline calcium aluminate. Calcium aluminates are released with the dissolution of the glassy phases of fly ash. In laboratory test performed by Peterson and Rochelle at the University of Texas at Austin, the dissolution of high calcium fly ashes was shown to be much greater than that of low calcium fly ashes. Along with this difference in dissolution rates, Peterson and Rochelle documented a high alumina conversion in high calcium fly ashes as compared to low calcium fly ashes, as shown in Figure 9.1 [79]. This work was performed in a saturated lime and high alkali environment, much like that in a hydrating portland cement.

Although there is not enough information available on this precise reaction, it can be hypothesized that the rapid dissolution of high calcium fly ash glassy phases adds calcium aluminates to the concrete which form monosulfoaluminate, much like that from the crystalline C_3A in portland cement and fly ash. Slow dissolution of aluminosilicate glasses may cause the formation of calcium silicate (aluminate) hydrate preferentially over monosulfoaluminate because of the calcium deficient environment in the long term pozzolanic environment.

One potential method to reduce the sulfate attack on concrete containing fly ashes with high calcium glassy phases is to provide sufficient quantities of gypsum to stabilize the ettringite from the reaction of crystalline C_3A in the portland

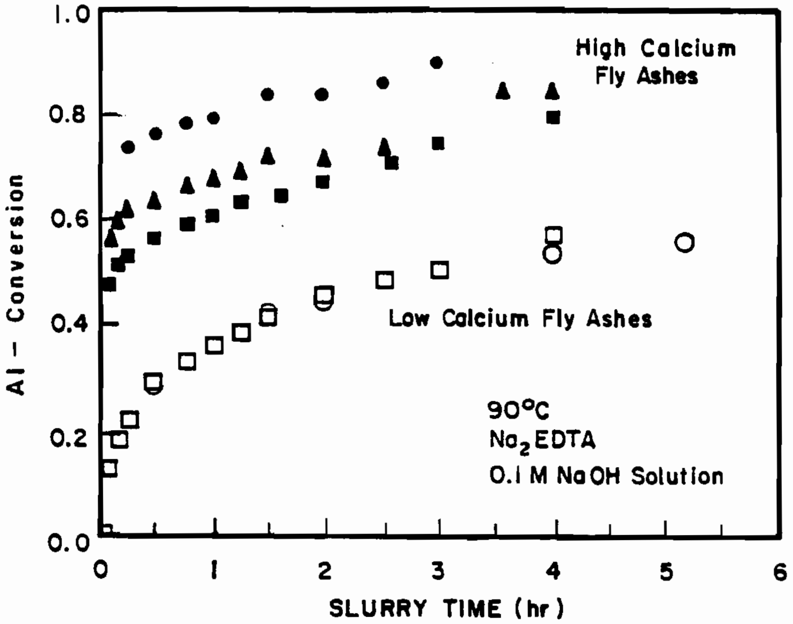


Figure 9.1 Alumina conversion in fly ash in high alkali solution[79].

cement and in the fly ash and the noncrystalline calcium aluminate released while the concrete is at early ages. Calcium aluminates released after the concrete has substantial stiffness will still form ettringite in a sulfate environment, but may be on the order of the conversion observed with Type II cement.

The amount of sulfate required to stabilize ettringite from the C_3A can be determined from the stoichiometry of the chemical equation expressed in Equation 9.1.

$$Ca_3Al_3O_6 + 3CaSO_4 \bullet 2H_2O + 26H_2O \longrightarrow 3CaOyAl_2O_3 \bullet 3CaSO_4 \bullet 32H_2O \tag{9.1}$$

C_3A gypsum water (Ettringite)

The crystalline C_3A from the portland cement and fly ash can be obtained from chemical and mineralogical analysis of the materials. The noncrystalline calcium aluminate in fly ash can only be estimated. From SEM analysis of some high calcium fly ashes, its inferred that the reactive crystalline and noncrystalline calcium aluminates are mainly those phases in the gehlenite field extending to the pure C_3A composition in the SiO_2-Al_2O_3-CaO ternary diagram. Figure 8.53 showed that in high calcium fly ashes the reactive calcium aluminates are about 1/3 of the total chemical aluminates. This number can be used as upper bound to lump the calcium aluminates which may be released during the initial hydration processes, both crystalline and noncrystalline.

As an example, if a Type II cement with 6 percent C_3A is replaced with 25 percent high calcium fly ash by weight with an 21 percent Al_2O_3, then the equivalent C_3A of the cement- fly ash combination may be conservatively estimated by Equation 9.2.

$$0.75\,(6.0) \quad + \quad 0.25\,(21.0/3)\,(2.65) \quad = \quad 9.1 \qquad (9.2)$$

The constant 2.65 is the weight ratio of C_3A to Al_2O_3. This equation is only relevant to high calcium fly ashes with the assumed ternary composition distribution. This should include most of the fly ashes from the Wyoming subbituminous coal sources, the typical fly ash for which the distribution represents. The chemical alumina content has been used as the parameter because the entire range of ternary compounds found in fly ash have nearly the same alumina content. Some compounds may be rich in calcium and others rich in silica, but most of the compounds contain moderate amounts of alumina. However it is the calcium rich glasses which appears to make the alumina available to the early hydration reactions.

From the equivalent C_3A computed in equation 9.2 the cement-fly ash combination can be blended with a stoichiometric quantity of gypsum to stabilize ettringite, as is computed in Equation 9.3.

$$\begin{array}{ccccccc} C_3A & + & 3(Gypsum) & + & 26(Water) & \longrightarrow & Ettringite \\ \text{270g} & & \text{3(172g)} & & \text{26(18g)} & & \text{1254g} \end{array} \qquad (9.3)$$

From this equation, the amount of gypsum required to saturate the cement-fly ash combination is 1.9 times (3(172g)/270g) the weight of the equivalent C_3A, minus the SO_3 present in the clinker and fly ash. A gram of SO_3 has the mass equivalent of 2.15 grams of gypsum i.e., 2.15 grams of gypsum equals 1 gram of SO_3. To supersaturate the blended cement a slightly greater quantity of gypsum would be needed.

9.2.2 Sulfate Additives. A sulfate additive to the mixing water has the potential to provide the required sulfate ions to stabilize ettringite in the fresh concrete and ultimately in the hardened concrete. Mehta showed that if ettringite is the prominent alumina phase after 14 days the concrete has a higher potential to be sulfate resistant than if monosulfoaluminate or calcium alumina hydrate are the stable phases[64].

There are several sulfates that could be suitable for this application. Ammonium sulfate, calcium sulfate, magnesium sulfate and sodium sulfate are all relatively inexpensive soluble sulfate salts. Ammonium sulfate generates ammonium gas when it is reacted in a portland cement and water mixture. Calcium sulfate, anhydrite, has a low solubility in water, 0.1 Molar solution, making it difficult to use as an additive to the mixing water. The addition of powdered anhydrite would react much like that of gypsum, which was covered in the previous section. While magnesium sulfate has a higher solubility, it causes a precipitate, brucite, that could increase the rate of the sulfate attack mechanism at early ages. Although this same precipitate may later form an impermeable layer over the hydration products at later ages to slow the sulfate mechanism, it may induce cracking and thereby encourage other forms of corrosion in concrete. The addition of sodium sulfate has the potential to be most suited for use in concrete containing fly ash as an additive to the mixing water. It is highly soluble in water however, it may also add the consideration of high alkalies, which will be discussed in a succeeding section.

9.2.3 Alkali Additives. Glasses within fly ash dissolve at an increased rate when placed in a high alkali solution. An alkali additive to the mixing water may cause the rapid dissolution of the glassy phases of the fly ash, releasing reactive alumina into the fresh concrete allowing ettringite to form while the concrete has greater plasticity. This process may prevent the aluminates from reacting later during the sulfate exposure, and therefore providing increased sulfate resistance. The addition of the alkali sodium sulfate has the additional effect of adding sulfate to the solution which may stabilize the ettringite when used in sufficient quantities.

9.2.4 Silica Fume Blending. The addition of silica fume to concrete provides the concrete with a more refined pore structure which is less susceptible to sulfate intrusion. The addition of 5 to 10 percent silica fume to the fly ash has the potential to deplete the paste of excess calcium hydroxide and decrease the permeability of the concrete. Both actions have the potential to increase the sulfate resistance of concrete.

9.2.5 Intergrinding. Intergrinding fly ash with portland cement has a positive effect on concrete strength and durability[72,99]. Interground fly ash-cement has been shown to be more reactive and superior to cements that contain fly ash as an admixture. The intergrinding of cement and fly ash in the mill disperses the fly ash evenly throughout the blended cement and breaks the larger fly ash particles to increase the surface area of the fly ash fraction. Intergrinding also permits the addition of ground gypsum to the blended cement to compensate for the C_3A and other reactive aluminates in the fly ash.

The effect of intergrinding may increase the reactivity of the fly ash to a level where the calcium aluminates are released at early ages. Whether enough calcium aluminates can be reacted before the concrete hardens is unknown. Producing interground Type IIP cements using high calcium fly ash will allow this effect to be documented.

9.2.6 Impermeable Barriers. Impermeable barriers within or on the surface of the concrete will prevent sulfate intrusion into the concrete. In Chapter 6 the effect of blast furnace slag and silica fume on the ion permeability was documented and discussed. If the sulfate ions are prevented from entering the concrete, the sulfate attack mechanism will not be initiated.

There are also several "waterproofing" admixtures that may provide concrete with a barrier to sulfate intrusion. The "waterproofing" admixture used in Phase II of this study did not form a sufficient barrier to arrest the sulfate attack mechanism. The addition of magnesium salts may provide an internal barrier to sulfate attack. Magnesium salts will coat the hydration products with brucite over a period of time, but may also degrade the calcium silicate hydrate crystalline structure.

External coatings are not considered the most viable solutions because they can typically be abraded away. However external coatings which are absorbed into the surface layer of the concrete may have the potential to reduce sulfate intrusion. Each of these barriers will be investigated in Phase III and IV of the continuing research program.

CHAPTER X
SUMMARY AND CONCLUSIONS

10.1 Summary

The use of fly ash in concrete is becoming the standard rather than the exception throughout Texas in highway and structural applications. The economic and technical advantages of using concrete containing fly ashhave been well documented, but there remain material considerations which limit specific applications of concrete containing fly ash. One of these applications is in concrete exposed to sulfate environments.

This dissertation addresses the effect of fly ash on the sulfate resistance of concrete, the material characterization of fly ash, and the permeability of concrete containing fly ash. The results of the study presented herein establish interim guidelines for the selection of fly ash for use in concrete exposed to sulfates. A specific class of fly ash can be used to improve the sulfate resistance of concrete, while a separate class of fly ash will decrease the sulfate resistance of concrete. In addition, this study shows that concrete containing fly ash is less permeable to chloride ion intrusion than concrete without fly ash. This study investigated eighteen fly ashes and five different portland cements. The fly ash was used as a volumetric replacement for portland cement in the quantities of 25, 35 and 45 percent. Curing time, air content, and slump were also varied to investigate their effect on the sulfate resistance of concrete containing fly ash. Each of the fly ashes differed in chemical and mineralogical composition. A material phase analysis was performed on the fly ash to determine the crystalline and noncrystalline phases present. The sulfate resistance of concrete containing fly ash was found to be related to the composition of the noncrystalline glassy phases of the fly ash. Concrete containing low calcium fly ash was found to have a sulfate resistance greater than that of concrete containing only portland cement. Concrete containing high calcium fly ash was found to decrease the sulfate resistance of concrete.

Although a reduction in the water content, the addition of entrained air, and extended moist curing of concrete are known to improve the overall durability of concrete, test results from this study showed the chemical and mineralogical composition of fly ash to be the most relevant factor governing the effect of fly ash on the sulfate resistance of concrete. Extended moist curing, the addition of entrained air or a reduction in the water content did not improve the sulfate resistace of concrete containing high calcium fly ash to the level of sulfate resistance of similar concrete without fly ash.

10.2 Conclusions

This work was conducted to provide engineers with a better understanding of the effect of fly ash on the performance of concrete exposed to a sulfate environment. Although fly ash can be used to improve the quality and performance of concrete, the work presented herein documents several effects which must be considered by engineers before allowing the use of fly ash for use in concrete exposed to a sulfate environment. The most important conclusions from this study are as follows:

1) Fly ashes conforming to the Texas SDHPT Type A or ASTM Class F standard specification and which contain low calcium oxide contents improve the sulfate resistance of concrete when used as a 25 to 45 percent replacement for Type I, II and 0 percent C_3A portland cement.

2) Fly ashes conforming to the Texas SDHPT Type B or ASTM Class C standard specification and which contain high calcium contents decrease the sulfate resistance of concrete when used as a 25 to 45 percent replacement for Type I, II, V and 0 percent C_3A portland cement.

3) The chemical and mineralogical composition of fly ash strongly influences the sulfate resistance of concrete. The calcium oxide content of the fly ash is the best indicator of the effect of fly ash on the sulfate resistance of concrete.

4) Extended moist curing is not a reliable means for producing sulfate resistant concrete containing fly ash.

5) The addition of entrained air is not a reliable means for producing sulfate resistant concrete containing fly ash.

6) Minor changes in the water content of concrete do not significantly affect the sulfate resistance of concrete containing fly ash.

7) The effects of a particular fly ash on the sulfate resistance of concrete are amplified by increasing the amount of fly ash between 25 and 45 percent, as a volumetric replacement for portland cement.

8) Conventional concrete exposed to low concentrations of sulfates may become susceptible to sulfate attack because of the addition of high calcium fly ash.

9) A new standard should be added to the exsisting fly ash specification which specifies sulfate exposure testing of fly ashes with greater than 10 percent calcium oxide if the fly ash is to be used in concrete exposed to sulfates.

10) Fly ash reduces the permeability of concrete to chloride ions. Low calcium fly ashes provide a greater reduction in chloride ion permeability than high calcium fly ashes.

11) At early ages, silica fume and blast furnace slag substantially reduce the permeability of concrete to chloride ions as compared to similar concrete with or without fly ash.

12) At later ages, low calcium fly ash, silica fume and blast furnace slag are effective means of producing low permeable concrete.

10.3 Recommendations for Engineers

Several recommendations can be made to improve the quality of concrete exposed to sulfate environments. These recommendations are as follows:

1) Wherever a specific type portland cement is specified for the express purpose of providing sulfate resistant concrete, fly ashes conforming to Texas SDHPT Type A or ASTM Class F standards with a total calcium oxide content less than 10 percent can be used as a partial portland cement replacement to increase the sulfate resistance of the concrete.

2) Fly ashes containing greater than 10 percent calcium oxide and conforming to the Texas SDHPT D-9-8900 or ASTM C618-87 standard specifications

should not be used in concrete exposed to sulfate environments unless sulfate exposure testing has verified the performance of the concrete using the proposed materials for the particular job.

3) Pozzolans should be specified in concrete where low permeability is required.

10.4 Recommendations for Future Research

Recommendations for future research can be made from a review of this study. Those recommendations are as follows:

1) Investigate the use of sulfate additives for concrete containing high calcium fly ash to determine the potential for the production of supersulfated blended cements.

2) Investigate the use of alkali additives for concrete containing high calcium fly ash to determine the potential for the production of sulfate resistant blended cements.

3) Conduct basic research on the dissolution rate of fly ash glassy phases in concrete.

4) Investigate the effect of impermeable barriers on the sulfate resistance of concrete containing high calcium fly ash.

5) Investigate the sulfate resistance of interground blended cements containing high calciumfly ash.

6) Conduct a parallel field study on the sulfate resistance of concrete using similar mixture proportions and materials as were used in the research reported herein.

7) Expand the present study to include fly ash containing between 12 and 20 percent total calcium oxide.

APPENDIX A

TABLE A-1 CEMENT CHEMISTRY SHORTHAND NOTATION

SHORTHAND NOTATION	CHEMICAL FORMULA	COMMON NAME
A	Al_2O_3	Aluminum Oxide
C	CaO	Calcium Oxide
F	Fe_2O_3	Ferric Oxide
H	H_2O	Water
M	MgO	Magnesium Oxide
S	SiO_2	Silicon Dioxide
$\overline{S}$	SO_3	Sulfur Trioxide

APPENDIX B

Table B-1 Mix Proportions

CUBIC YARD PROPORTIONS (SSD WEIGHTS)											
Mix No.	Cem.	FA	FA pct.	F'_c psi	Slump in.	Cem. lbs.	FA lbs.	Rock lbs.	Sand lbs.	Water lbs.	W/C+P
1	II		0	5880	2	565	0	1613	1499	246	.43
2	II		0	5960	6	580	0	1657	1387	267	.45
3	II		0	6380	2	558	0	1581	1534	248	.44
4	II		0	6000	6	568	0	1607	1357	301	.53
5	II		0	5120	6	516	0	1565	1519	274	.53
6	II		0	5390	2	508	0	1543	1586	259	.51
7	II	B-6	25	4720	6	390	114	1579	1532	262	.51
8	II	B-6	35	4710	6	335	159	1565	1519	274	.55
9	II	B-6	45	5480	6	284	205	1570	1524	269	.55
10	II	B-8	25	5220	6	387	116	1565	1519	274	.54
11	II	B-8	35	3950	6	337	163	1575	1528	266	.53
12	II	B-8	45	4580	6	286	211	1575	1534	263	.52
13	II	B-1	25	5010	6	389	111	1576	1529	264	.52
14	II	B-1	35	5050	6	341	156	1591	1543	252	.50
15	II	B-1	45	5030	6	298	200	1582	1535	256	.51
16	II	B-3	25	4380	6	388	107	1572	1525	268	.54
17	II	B-3	35	4620	6	337	151	1574	1527	266	.54
18	II	B-3	45	5020	6	287	195	1584	1537	257	.53
19	II	A-2	25	4200	6	391	102	1583	1536	258	.52
20	II	A-2	35	4110	6	347	146	1619	1516	247	.50
21	II	A-2	45	3660	6	283	181	1565	1519	274	.58
22	II	A-3	25	5010	6	391	97	1584	1537	258	.52
23	II	A-3	35	4200	6	342	137	1595	1548	248	.51
24	II	A-3	45	3760	6	288	176	1590	1543	252	.54
25	II	B-5	25	5380	6	389	112	1573	1526	267	.53
26	II	B-5	35	6130	6	338	158	1577	1530	264	.53
27	II	B-5	45	5940	6	289	205	1594	1546	249	.50
28	II	A-10	25	5870	6	394	109	1596	1549	247	.49
29	II	A-10	35	5140	6	335	149	1558	1519	277	.57
30	II	A-10	45	5680	6	285	193	1563	1525	272	.56
31	InCor		0	3920	6	507	0	1530	1492	301	.59
32	II	A-8	25	3470	6	380	89	1537	1491	299	.63
33	II	A-8	45	2510	6	289	166	1595	1548	248	.54
34	II	A-9	25	4200	6	387	94	1565	1519	274	.56
35	II	A-9	45	3810	6	283	170	1565	1519	274	.60
36	II	A-7	25	4280	6	389	93	1574	1527	266	.55
37	II	A-7	45	2740	6	285	168	1577	1530	264	.58
38	V		0	4410	6	522	0	1583	1536	258	.49
39	II		0	5550	2	519	0	1506	1662	242	.46
40	II		0	5470	2	505	0	1533	1590	263	.52

Table B-1 Mix Proportions

CUBIC YARD PROPORTIONS (SSD WEIGHTS)											
Mix No.	Cem.	FA	FA pct.	F'_c psi	Slump in.	Cem. lbs.	FA lbs.	Rock lbs.	Sand lbs.	Water lbs.	W/C+P
41	II		0	5470	2	505	0	1533	1590	263	.52
42	II	B-5	25	6510	2	383	111	1550	1607	248	.50
43	II	B-5	25	6510	2	383	111	1550	1607	248	.50
44	II	B-5	35	5830	2	335	157	1565	1623	235	.47
45	II	B-5	35	5820	2	335	157	1565	1623	235	.47
46	II	B-5	45	5850	2	278	198	1537	1594	260	.54
47	II	B-3	25	5960	2	388	107	1571	1627	230	.46
48	II	B-3	25	5960	2	388	107	1571	1627	230	.46
49	II	B-3	35	5720	2	337	151	1576	1632	225	.46
50	II	B-3	35	5760	2	337	151	1576	1632	225	.46
51	II	B-3	45	5110	2	283	193	1565	1621	235	.49
52	II	B-3	45	5460	2	283	193	1565	1621	235	.49
53	II	A-10	25	5410	2	387	106	1565	1621	235	.47
54	II	A-10	25	6130	2	387	106	1565	1621	235	.47
55	II	A-10	45	5670	2	283	192	1565	1621	235	.49
56	II	A-10	35	5630	2	335	149	1565	1621	235	.48
57	II	A-10	35	5770	2	335	149	1565	1621	235	.48
58	II	B-6	25	5740	2	387	113	1565	1621	235	.47
59	II	B-6	25	6260	2	387	113	1565	1621	235	.47
60	II	B-6	35	5330	2	331	157	1545	1601	253	.51
61	II	B-6	35	5630	2	331	157	1545	1601	253	.51
62	II	B-6	45	5010	2	279	201	1544	1600	254	.52
63	II	B-8	25	6090	2	388	116	1571	1637	227	.44
64	II	B-8	25	5910	2	388	116	1571	1637	227	.44
65	II	B-8	35	5290	2	336	163	1571	1637	227	.45
66	II	B-8	45	5630	2	284	209	1571	1637	227	.45
67	II	B-1	25	5670	2	385	109	1559	1625	237	.47
68	II	B-1	25	5810	2	385	109	1559	1625	237	.47
69	II	B-1	35	5140	2	334	118	1560	1625	250	.55
70	II	B-1	45	5090	2	284	199	1571	1637	227	.46
71	II	A-3	25	4430	2	391	97	1588	1644	215	.44
72	II	A-3	25	5470	2	391	97	1588	1644	215	.44
73	II	A-3	35	4090	2	339	136	1584	1641	218	.45
74	II	A-3	45	3940	2	288	176	1589	1647	213	.45
75	II	A-2	25	4580	2	389	101	1573	1630	228	.46
76	II	A-2	25	5100	2	389	101	1573	1630	228	.46
77	II	A-2	35	4420	2	339	143	1579	1636	222	.46
78	II	A-2	35	4880	2	339	143	1579	1636	222	.46
79	II	A-2	45	3310	2	283	182	1565	1621	235	.50
80	Blue		0	4040	6	516	0	1565	1518	274	.53

Table B-1 Mix Proportions

CUBIC YARD PROPORTIONS (SSD WEIGHTS)											
Mix No.	Cem.	FA	FA pct.	F'_c psi	Slump in.	Cem. lbs.	FA lbs.	Rock lbs.	Sand lbs.	Water lbs.	W/C+P
81	Blue	B-5	35	5130	6	335	157	1565	1518	274	.55
82	Blue	A-2	35	3160	6	337	142	1573	1526	267	.55
83	Blue	A-1	35	3120	6	335	141	1565	1518	274	.57
84	Blue	B-8	35	4650	6	335	162	1565	1518	274	.55
85	Blue	B-3	35	5900	6	336	150	1570	1523	270	.55
86	Blue	B-6	35	5050	6	339	160	1582	1535	259	.52
87	V		0	4700	2	511	0	1550	1605	249	.48
88	InCor		0	4900	2	516	0	1565	1621	235	.45
89	II	B-4	35	4560	6	337	158	1573	1526	267	.54
90	II	A-1	35	2960	6	336	141	1567	1521	272	.57
91	II	B-2	35	4260	6	338	152	1577	1530	263	.53
92	II		0	3780	6	483	0	1465	1422	252	.52
93	II	B-5	35	3450	6	335	157	1563	1517	242	.49
94	II	B-6	35	4030	6	334	158	1558	1512	250	.50
95	II	B-5	35	4570	6	335	157	1565	1519	274	.55
96	II		0	4030	6	5064	0	1537	1434	245	.48
97	II		0	4040	6	513	0	1557	1453	261	.50
98	II	B-3	35	4520	6	346	155	1614	1506	271	.54
99	II	B-8	35	4380	6	339	164	1583	1477	247	.49
100	II	B-8	35	4860	6	345	167	1611	1503	257	.50
101	II	B-4	25	5270	6	387	112	1565	1518	274	.54
102	II	B-4	25	5260	6	387	112	1565	1518	274	.54
103	II	B-8	35	5070	6	335	162	1565	1518	274	.55
104	II	B-8	35	4730	6	335	162	1565	1518	274	.55
105	I	A-3	35	3560	6	341	137	1592	1544	251	.52
106	I	A-10	35	3800	6	338	151	1578	1531	263	.53
107	I	B-3	35	4220	6	338	151	1581	1534	260	.53
108	I	B-4	35	4310	6	341	160	1593	1545	250	.49
109	I		0	4050	6	518	0	1573	1526	267	.51
110	I	A-2	35	3710	6	390	113	1578	1531	262	.52
111	II	B-8	35	4920	6	341	165	1593	1546	249	.49
112	II	B-2	25	4880	6	392	109	1588	1541	254	.50
113	II	B-7	35	4120	6	335	152	1565	1518	274	.56
114	II	A-5	35	3360	6	336	118	1571	1524	269	.59
115	II	B-4	45	4250	6	287	204	1586	1539	256	.52
116	II	A-6	35	3690	6	341	131	1593	1546	249	.52
117	II	A-4	35	3600	6	341	136	1595	1547	229	.51
118	II	B-8	25		6	375	112	1520	1474	314	.64
119	II	B-8	25	5220	2	375	112	1518	1560	282	.57
120	II	B-3	35	4300	6	333	149	1553	1520	279	.58

Table B-1 Mix Proportions

CUBIC YARD PROPORTIONS (SSD WEIGHTS)											
No.	Cem.	FA	FA pct.	F'_c psi	Slump in.	Cem. lbs.	FA lbs.	Rock lbs.	Sand lbs.	Water lbs.	W/C+P
121	II	B-3	35		6	325	145	1519	1473	314	.66
122	II		0	5090	2	494	0	1499	1541	299	.60
123	II		0	4540	6	500	0	1519	1486	310	.61
124	II		0		6	512	0	1554	1507	284	.55
125	I	S-1	+9	6390	6	516	46	1565	1411	297	.52
126	I	A-2	25	3710	6	385	100	1557	1499	285	.58
127	I	A-10	25	4850	6	390	107	1578	1519	268	.53
128	I	B-3	25	3900	6	382	105	1546	1488	295	.60
129	I	B-4	25	4930	6	387	112	1565	1507	279	.55
130	II	B-3	35	5230	2	332	149	1551	1565	263	.54
131	II	B-6	35	5880	2	335	159	1565	1579	251	.50
132	II	S-2	65	5430	6	181	317	1573	1514	272	.54
133	I	S-2	65	4500	6	174	305	1515	1459	322	.67
134	V	B-3	35	4700	6	329	147	1536	1491	299	.62
135	I	B-1	25	5700	6	383	109	1552	1494	290	.58
136	I	A-6	25	4100	6	382	91	1545	1487	296	.62
137	I	A-5	25	3850	6	380	82	1539	1490	301	.65
138	I	A-4	25	3950	6	382	94	1545	1487	296	.62
139	I	A-3	25	3800	6	387	96	1565	1507	279	.57
140	II		0	4310	6	517	0	1568	1521	275	.53
141	II	B-4	35	4540	6	336	157	1568	1521	275	.53
142	II	A-4	35	2990	6	336	134	1568	1521	275	.53
143	I		0	4550	6	517	0	1568	1521	275	.53
144	I	B-4	35	4700	6	336	157	1568	1521	275	.53
145	I	A-4	35	4490	6	336	134	1568	1521	275	.53
146	I	B-4	25	3390	6	387	112	1568	1521	275	.53
147	I	A-4	25	4350	6	387	95	1568	1521	275	.53
148	II		0		6	517	0	1568	1521	275	.53
149	II	B-4	35		6	336	157	1568	1521	275	.53
150	II	A-4	35		6	336	134	1568	1521	275	.53
151	II	S-2	65		6	180	316	1538	1521	275	.53
152	II	S-1	+9		6	517	39	1568	1482	279	.53

Table B-2 Concrete Exposure Properties

Mix No.	Cem.	FA	FA pct.	Fc at exposure	Age at exposure	Slump in.	W/C+P
1	II		0	3500	4	2	.43
2	II		0	3600	4	6	.45
3	II		0	3500	4	2	.44
4	II		0	3500	4	6	.53
5	II		0	3500	6	6	.53
6	II		0	3740	8	2	.51
7	II	B-6	25	3500	6	6	.51
8	II	B-6	35	4290	10	6	.55
9	II	B-6	45	3900	10	6	.55
10	II	B-8	25	3850	10	6	.54
11	II	B-8	35	3580	10	6	.53
12	II	B-8	45	3600	10	6	.52
13	II	B-1	25	3640	9	6	.52
14	II	B-1	35	3840	9	6	.50
15	II	B-1	45	3500	11	6	.51
16	II	B-3	25	3500	11	6	.54
17	II	B-3	35	3500	17	6	.54
18	II	B-3	45	3900	11	6	.53
19	II	A-2	25	3620	19	6	.52
20	II	A-2	35	3500	12	6	.50
21	II	A-2	45	3500	26	6	.58
22	II	A-3	25	3710	7	6	.52
23	II	A-3	35	3620	19	6	.51
24	II	A-3	45	3500	23	6	.54
25	II	B-5	25	3900	6	6	.53
26	II	B-5	35	4180	6	6	.53
27	II	B-5	45	3700	6	6	.50
28	II	A-10	25	4050	6	6	.49
29	II	A-10	35	3500	7	6	.57
30	II	A-10	45	3690	7	6	.56
31	01		0	3500	14	6	.59
32	II	A-8	25	3470	28	6	.63
33	II	A-8	45	2510	28	6	.54
34	II	A-9	25	4000	14	6	.56
35	II	A-9	45	3650	21	6	.60
36	II	A-7	25	3870	14	6	.55
37	II	A-7	45	2740	28	6	.58
38	V		0	3730	8	6	.49
39	II		0	4710	8	2	.46
40	II		0	3500	4	2	.51

Table B-2 Concrete Exposure Properties

Mix No.	Cem.	FA	FA pct.	Fc at exposure	Age at exposure	Slump in.	W/C+P
41	II		0	3240	3	2	.51
42	II	B-5	25	6510	28	2	.50
43	II	B-5	25	3900	3	2	.50
44	II	B-5	35	4550	8	2	.47
45	II	B-5	35	3030	3	2	.47
46	II	B-5	45	4310	8	2	.54
47	II	B-3	25	5950	28	2	.46
48	II	B-3	25	3800	3	2	.46
49	II	B-3	35	3570	4	2	.46
50	II	B-3	35	3200	3	2	.46
51	II	B-3	45	4100	13	2	.49
52	II	B-3	45	2800	3	2	.49
53	II	A-10	25	6130	28	2	.47
54	II	A-10	25	3500	3	2	.47
55	II	A-10	45	3500	5	2	.49
56	II	A-10	35	4610	10	2	.48
57	II	A-10	35	3000	3	2	.48
58	II	B-6	25	6260	28	2	.47
59	II	B-6	25	3770	3	2	.47
60	II	B-6	35	4230	10	2	.51
61	II	B-6	35	3120	3	2	.51
62	II	B-6	45	3870	10	2	.52
63	II	B-8	25	5910	29	2	.44
64	II	B-8	25	3600	3	2	.44
65	II	B-8	35	3600	5	2	.45
66	II	B-8	45	4190	9	2	.45
67	II	B-1	25	3650	5	2	.47
68	II	B-1	25	3200	3	2	.47
69	II	B-1	35	3830	9	2	.55
70	II	B-1	45	3490	9	2	.46
71	II	A-3	25	4000	14	2	.44
72	II	A-3	25	2640	3	2	.44
73	II	A-3	35	3500	14	2	.45
74	II	A-3	45	3500	19	2	.45
75	II	A-2	25	3734	14	2	.46
76	II	A-2	25	2330	3	2	.46
77	II	A-2	35	3500	16	2	.46
78	II	A-2	35	2060	3	2	.46
79	II	A-2	45	3500	37	2	.50
80	02		0	3450	9	6	.53

Table B-2 Concrete Exposure Properties

Mix No.	Cem.	FA	FA pct.	Fc at exposure	Age at exposure	Slump in.	W/C+P
81	02	B-5	35	3930	9	6	.55
82	02	A-2	35	3160	28	6	.55
83	02	A-1	35	3120	28	6	.57
84	02	B-8	35	3700	9	6	.55
85	02	B-3	35	4470	9	6	.55
86	02	B-6	35	3820	9	6	.52
87	V		0	3900	6	2	.48
88	01		0	4190	6	2	.45
89	II	B-4	35	3900	20	6	.54
90	II	A-1	35	2960	28	6	.57
91	II	B-2	35	3700	20	6	.53
92	II		0	3400	20	6	.52
93	II	B-5	35	3300	20	6	.49
94	II	B-6	35	3500	20	6	.50
95	II	B-5	35	2200	3	6	.55
96	II		0	3680	16	6	.48
97	II		0	3760	14	6	.50
98	II	B-3	35	3690	14	6	.54
99	II	B-8	35	3640	14	6	.49
100	II	B-8	35	2450	3	6	.50
101	II	B-4	25	5360	28	6	.54
102	II	B-4	25	5380	28	6	.54
103	II	B-8	35	4680	28	6	.55
104	II	B-8	35	5060	28	6	.55
105	I	A-3	35	3560	28	6	.52
106	I	A-10	35	3200	16	6	.53
107	I	B-3	35	3500	15	6	.53
108	I	B-4	35	3500	15	6	.49
109	I		0	3640	12	6	.51
110	I	A-2	35	3500	9	6	.52
111	II	B-8	35	3440	5	6	.49
112	II	B-2	25	3400	5	6	.50
113	II	B-7	35	3500	8	6	.56
114	II	A-5	35	3360	28	6	.59
115	II	B-4	45	3600	9	6	.52
116	II	A-6	35	3690	28	6	.52
117	II	A-4	35	3600	28	6	.51
118	II	B-8	25	n/a	n/a	6	.64
119	II	B-8	25	3450	7	2	.57
120	II	B-3	35	3790	15	6	.58

Table B-2 Concrete Exposure Properties

Mix No.	Cem.	FA	FA pct.	Fc at exposure	Age at exposure	Slump in.	W/C+P
121	II	B-3	35	n/a		6	.66
122	II		0			2	.60
123	II		0	4290	15	6	.61
124	II		0	n/a	n/a	6	.55
125	I	S-1	+9	4300	6	6	.57
126	I	A-2	25	3710	6	6	.58
127	I	A-10	25	3650	6	6	.53
128	I	B-3	25	3450	6	6	.60
129	I	B-4	25	3500	6	6	.55
130	II	B-3	35	3690	2	2	.54
131	II	B-6	35	3810	2	2	.50
132	II	S-2	65	4310	6	6	.54
133	I	S-2	65	3670	6	6	.67
134	V	B-3	35	3650	6	6	.62
135	I	B-1	25	3540	6	6	.58
136	I	A-6	25	3500	6	6	.62
137	I	A-5	25	3500	6	6	.65
138	I	A-4	25	3400	6	6	.62
139	I	A-3	25	3400	6	6	.57
140	II		0	3460	7	6	.53
141	II	B-4	35	3120	7	6	.53
142	II	A-4	35	1910	7	6	.53
143	I		0	n/a	n/a	6	.53
144	I	B-4	35	n/a	n/a	6	.53
145	I	A-4	35	n/a	n/a	6	.53
146	I	B-4	25	n/a	n/a	6	.53
147	I	A-4	25	n/a	n/a	6	.53
148	II		0	4990	100	6	.57
149	II	B-4	35	5080	100	6	.53
150	II	A-4	35	3760	100	6	.58
151	II	S-2	65	n/a	n/a	6	.53
152	II	S-1	+9	n/a	n/a	6	.62

APPENDIX C

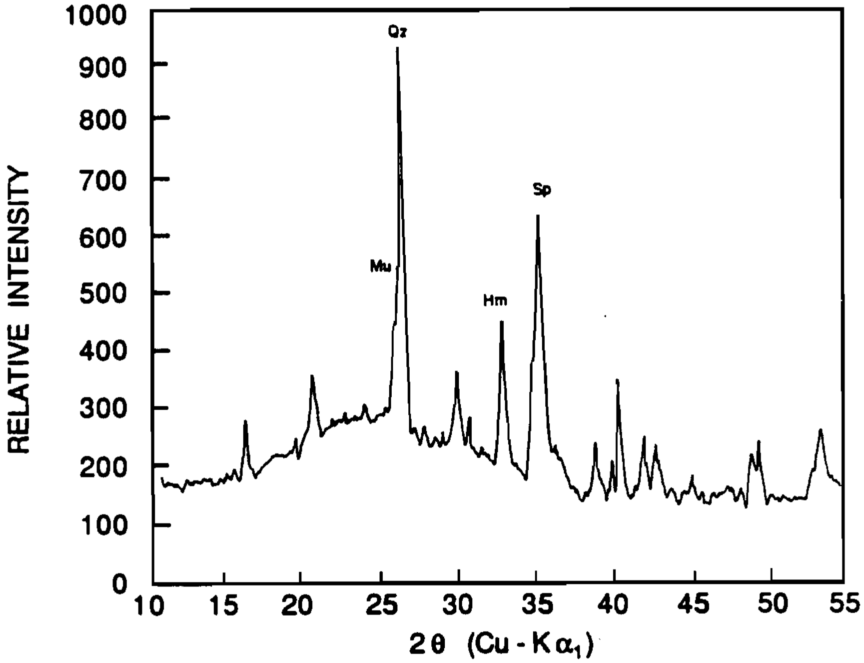


Figure C.1 X-ray diffractogram of fly ash A-1.

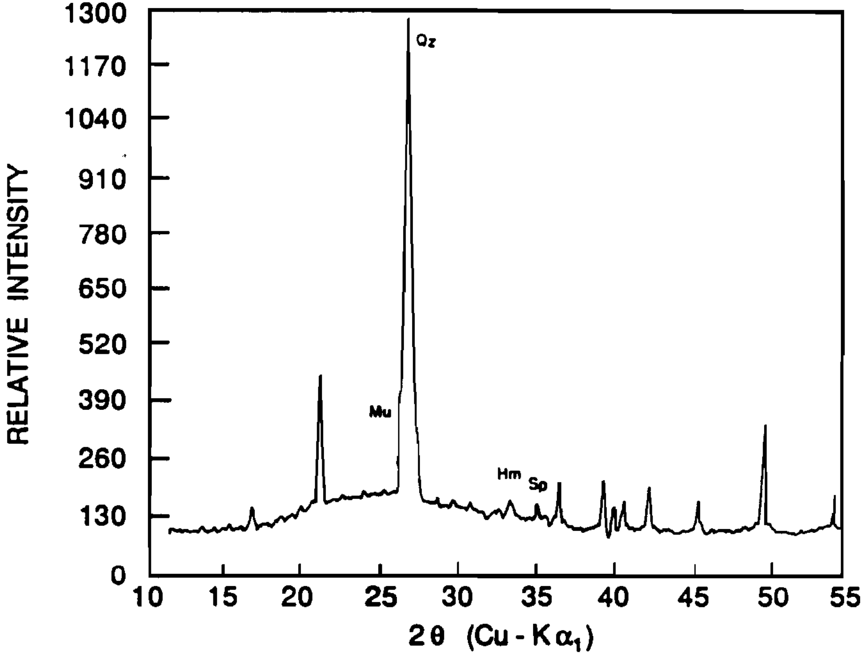


Figure C.2 X-ray diffractogram of fly ash A-2.

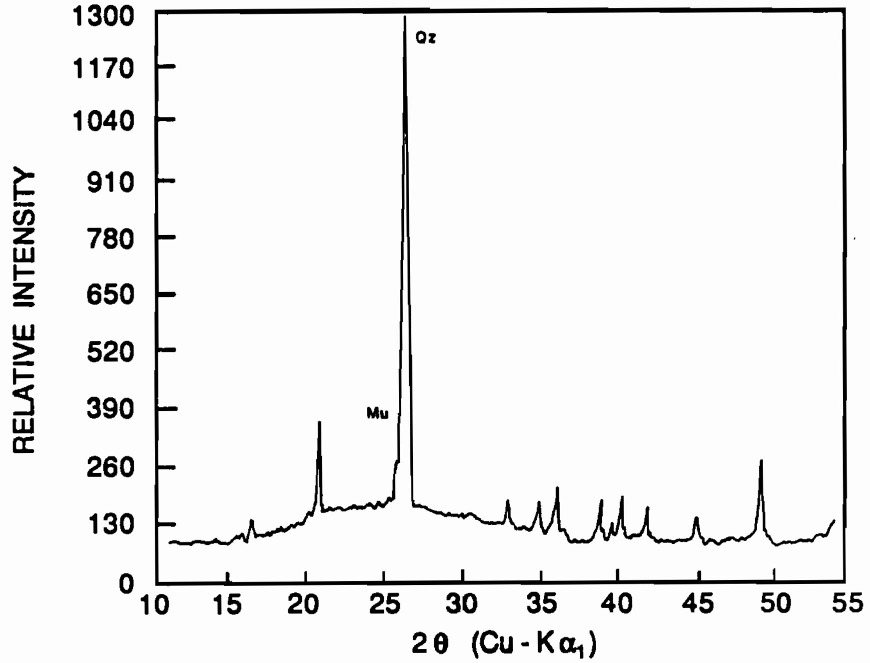


Figure C.3 X-ray diffractogram of fly ash A-3.

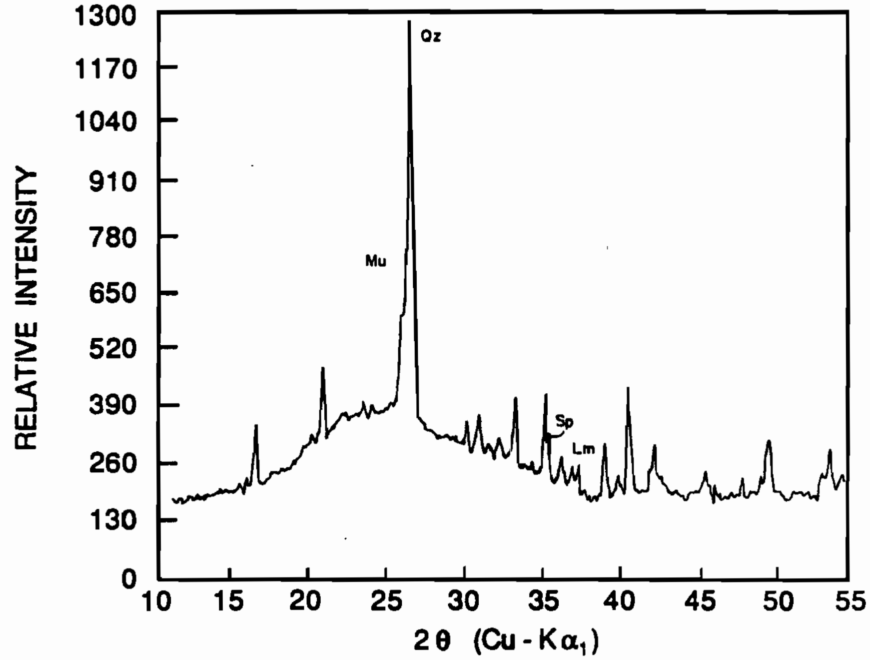


Figure C.4 X-ray diffractogram of fly ash A-4.

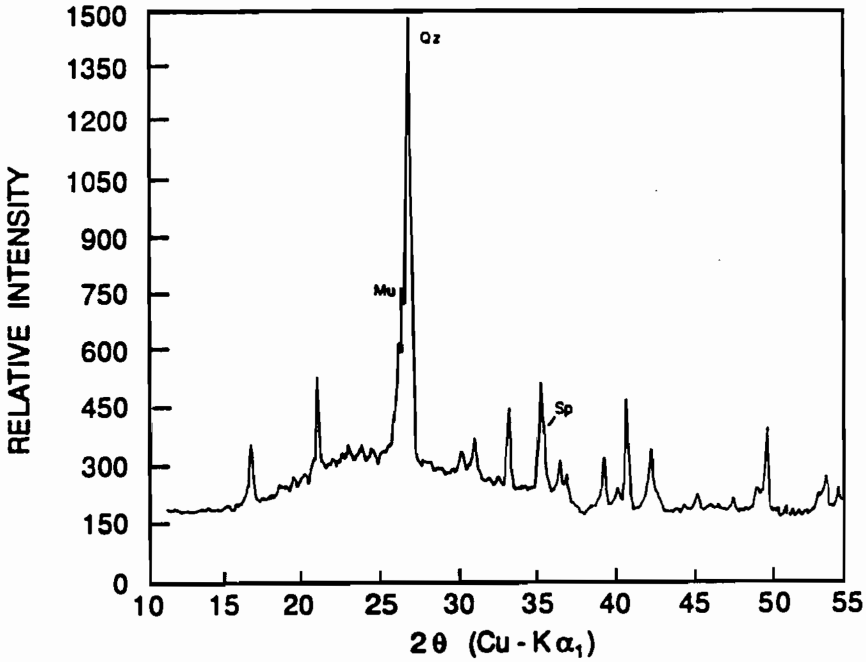


Figure C.5 X-ray diffractogram of fly ash A-5.

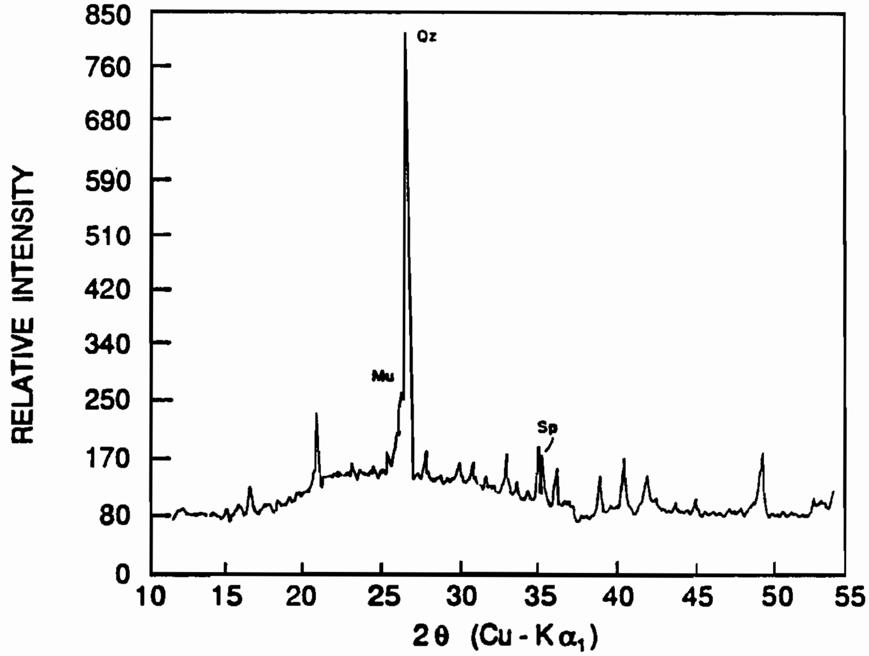


Figure C.6 X-ray diffractogram of fly ash A-6.

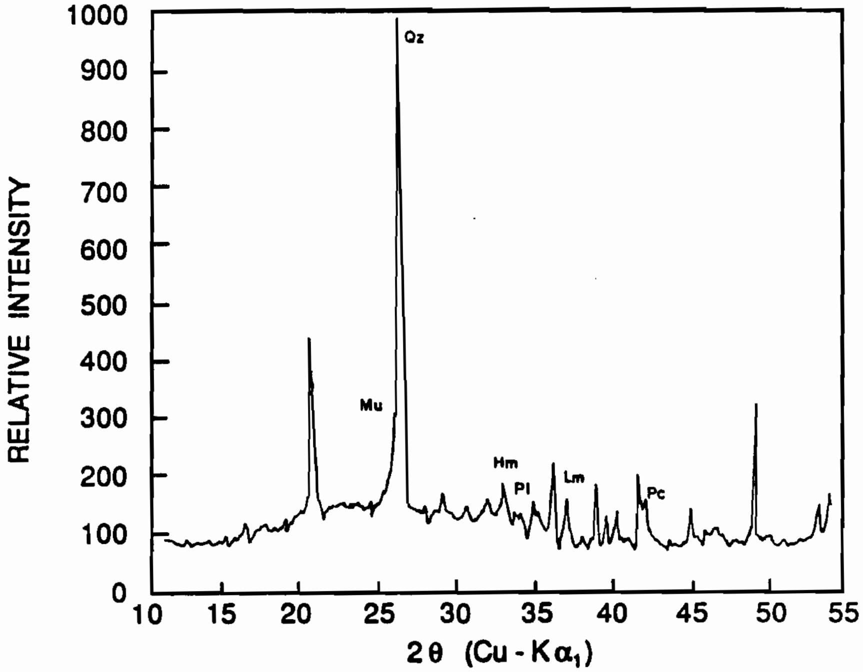


Figure C.7 X-ray diffractogram of fly ash A-7.

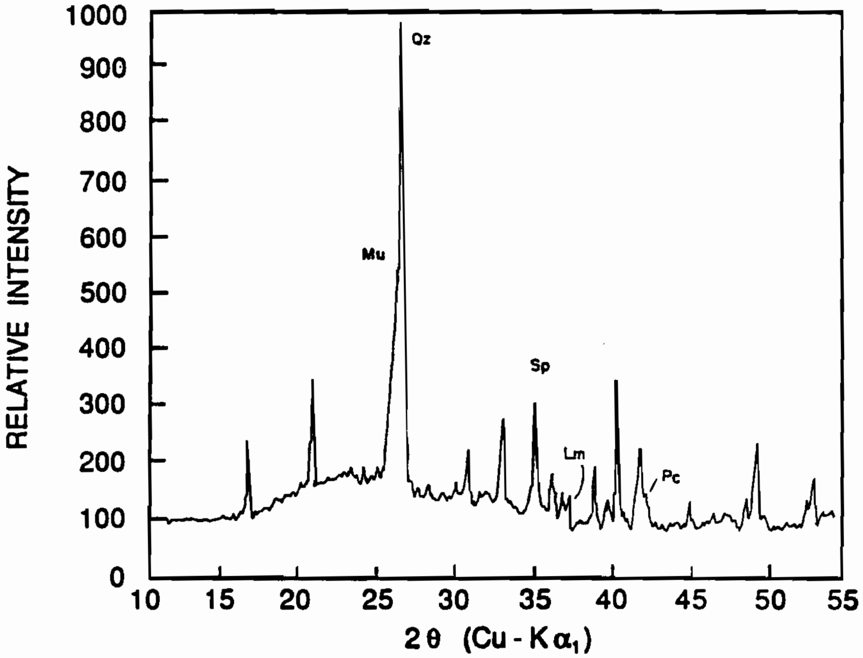


Figure C.8 X-ray diffractogram of fly ash A-8.

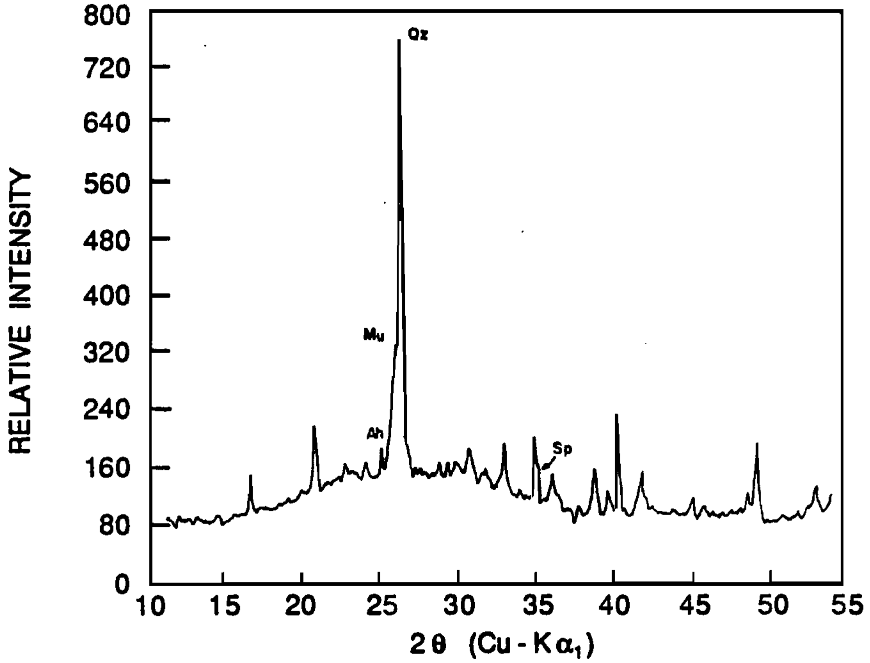


Figure C.9 X-ray diffractogram of fly ash A-9.

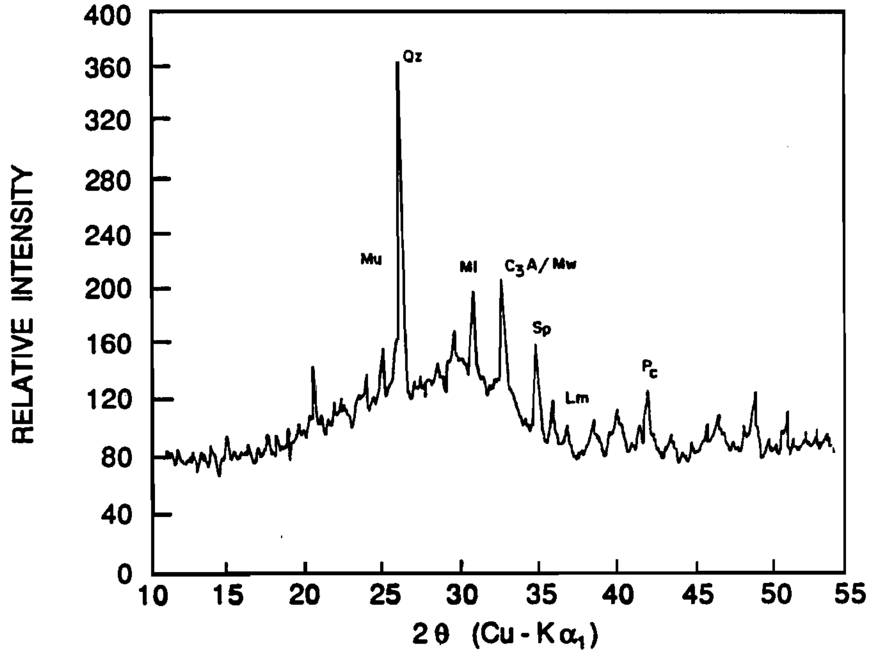


Figure C.10 X-ray diffractogram of fly ash A-10.

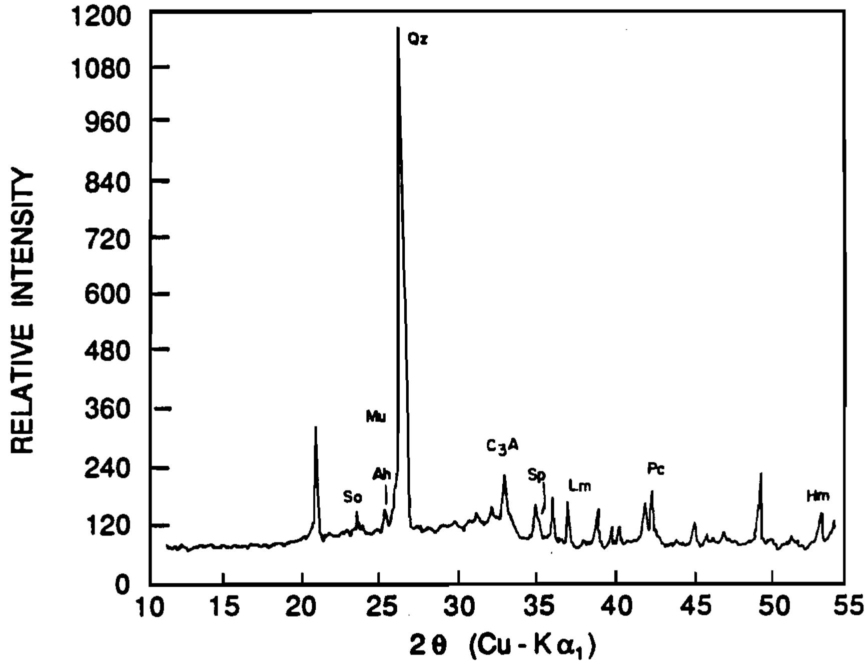


Figure C.11 X-ray diffractogram of fly ash B-1.

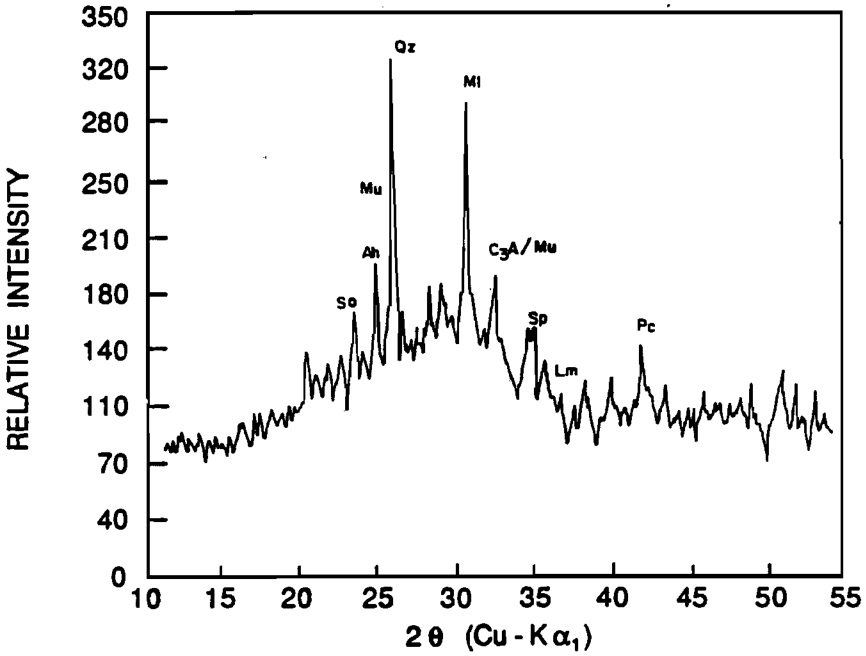


Figure C.12 X-ray diffractogram of fly ash B-2.

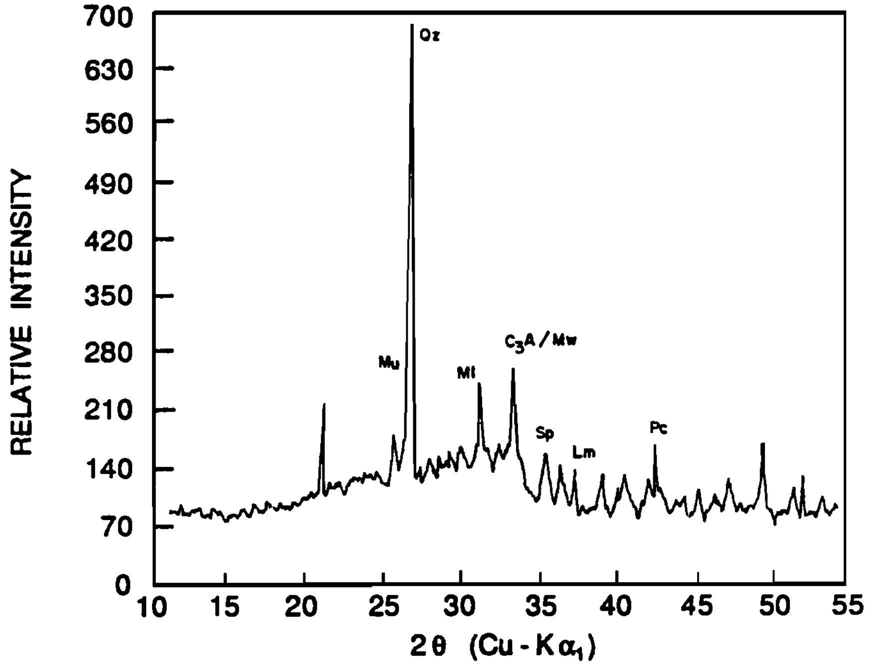


Figure C.13 X-ray diffractogram of fly ash B-3.

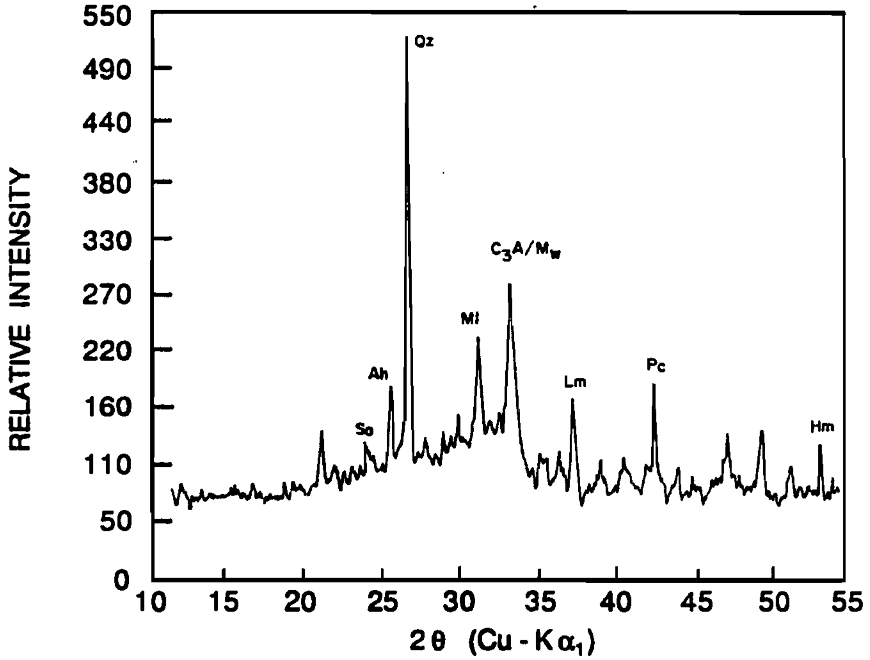


Figure C.14 X-ray diffractogram of fly ash B-4.

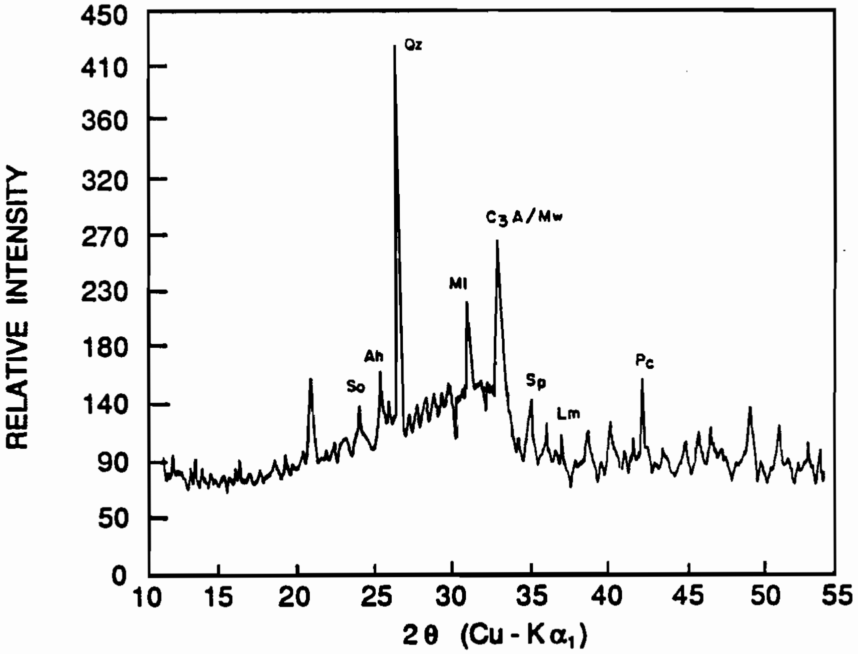


Figure C.15 X-ray diffractogram of fly ash B-5.

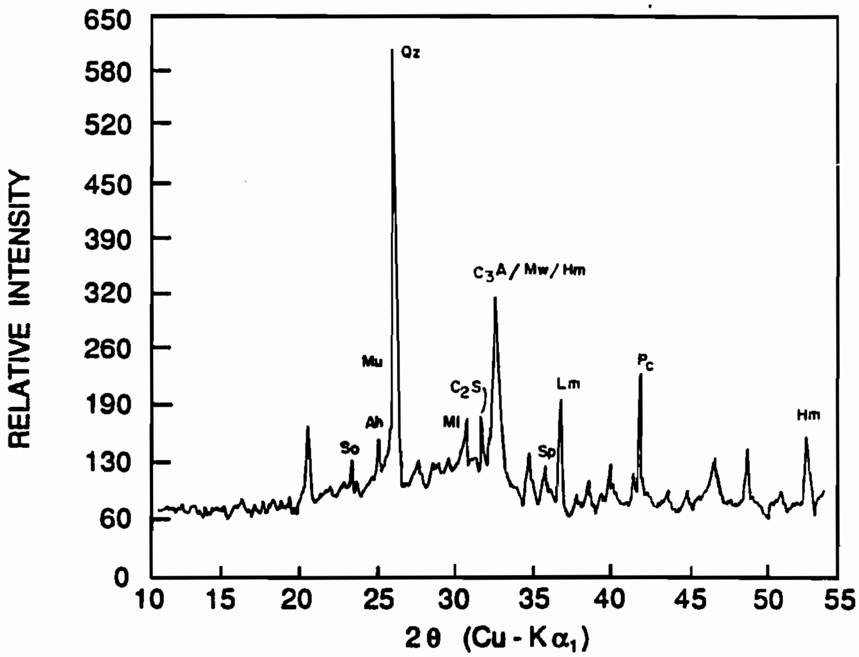


Figure C.16 X-ray diffractogram of fly ash B-6.

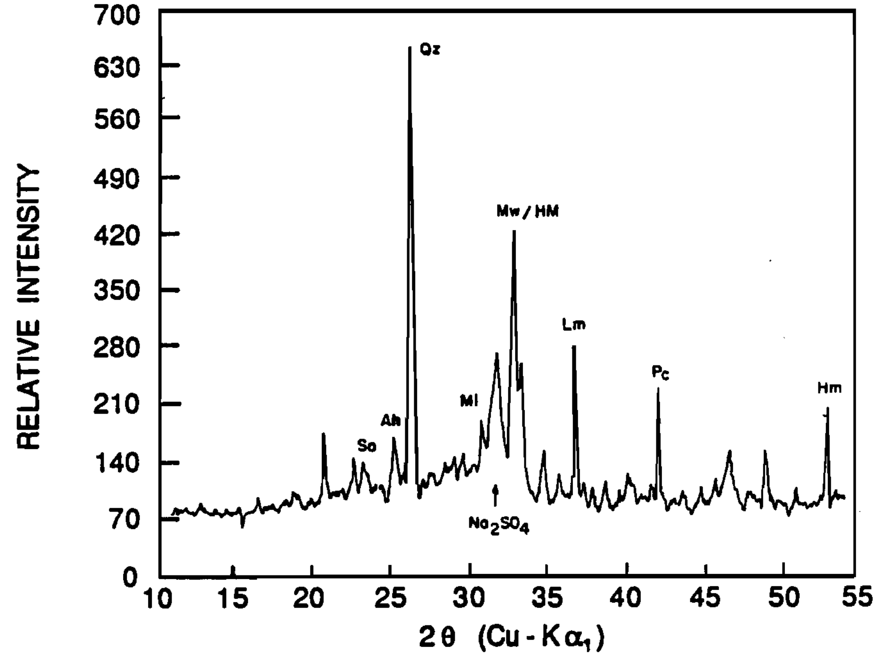


Figure C.17 X-ray diffractogram of fly ash B-7.

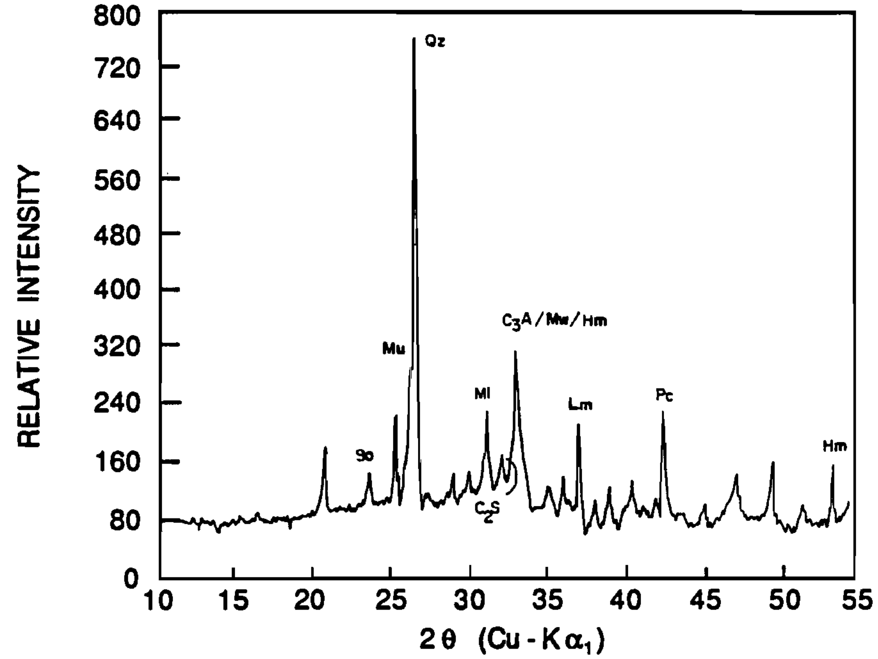


Figure C.18 X-ray diffractogram of fly ash B-8.

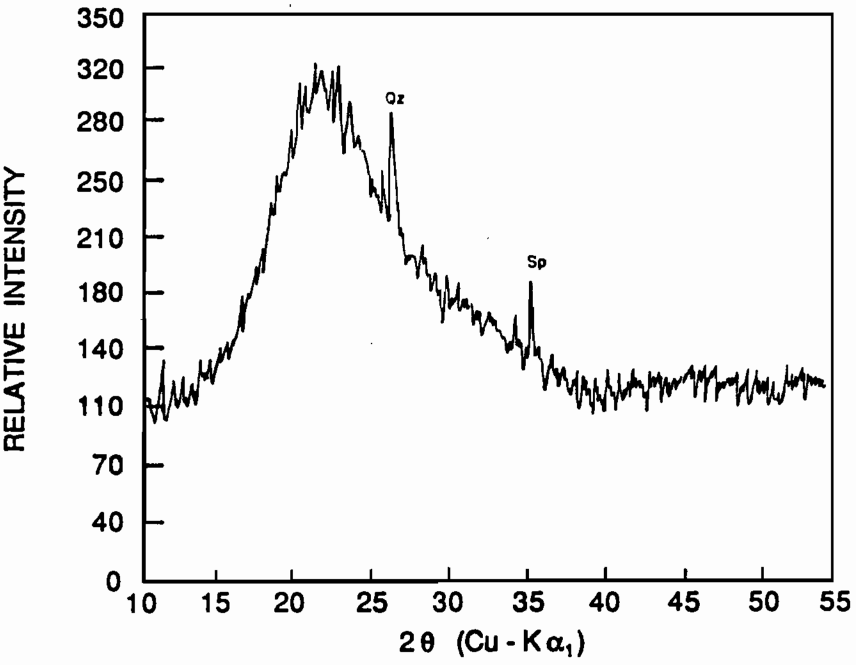


Figure C.19 X-ray diffractogram of fly ash S-1.

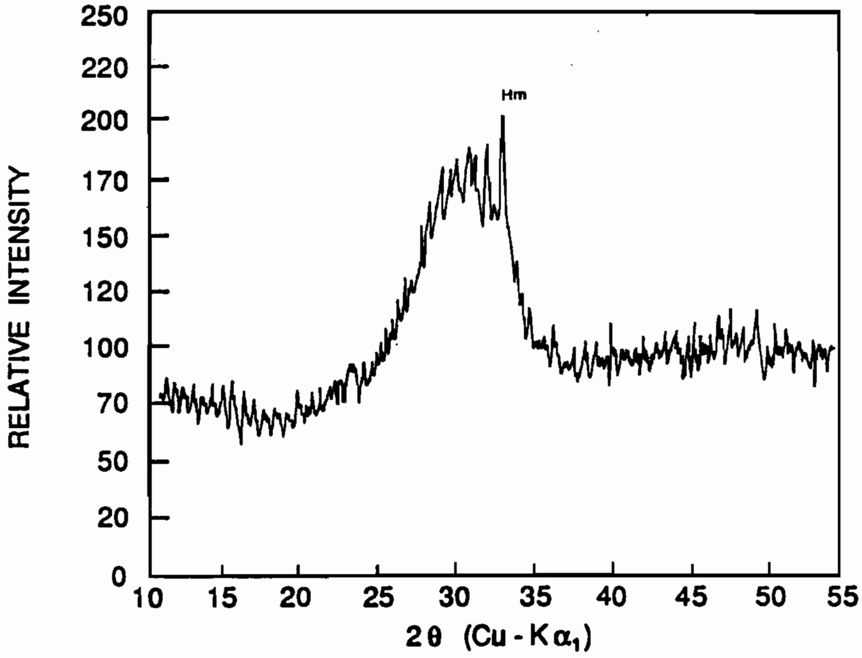


Figure C.20 X-ray diffractogram of fly ash S-2.

APPENDIX D

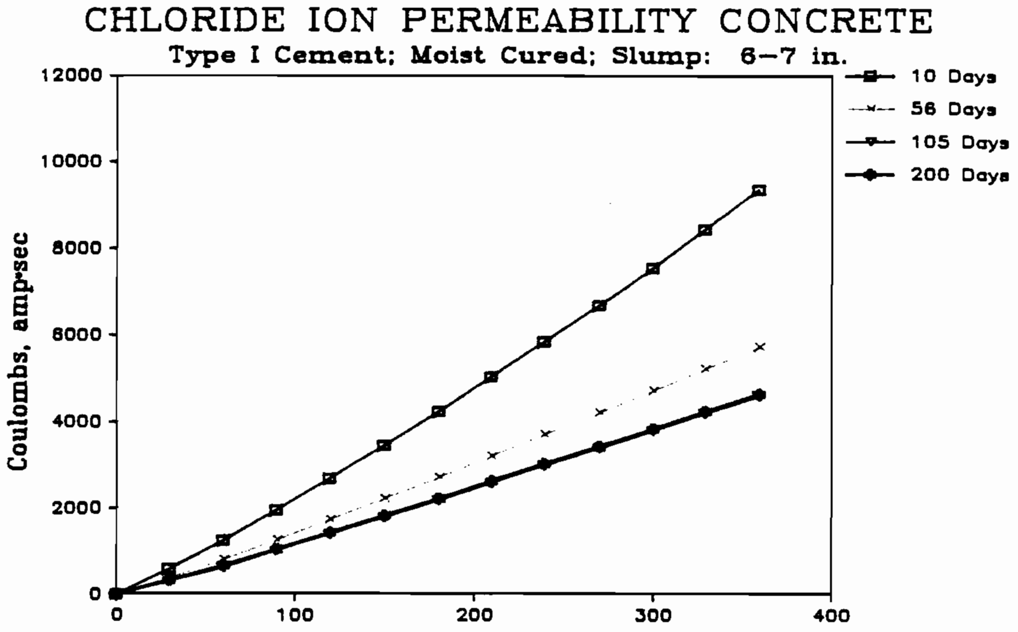


Figure D.1 Permeability of Type I cement concrete.

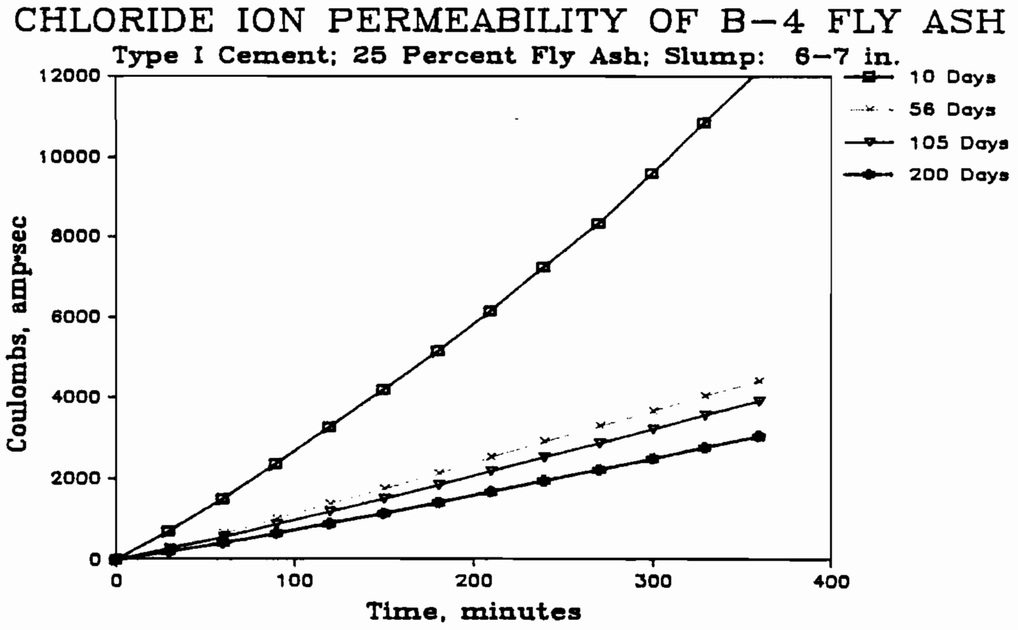


Figure D.2 Permeability of concrete containing fly ash B-4.

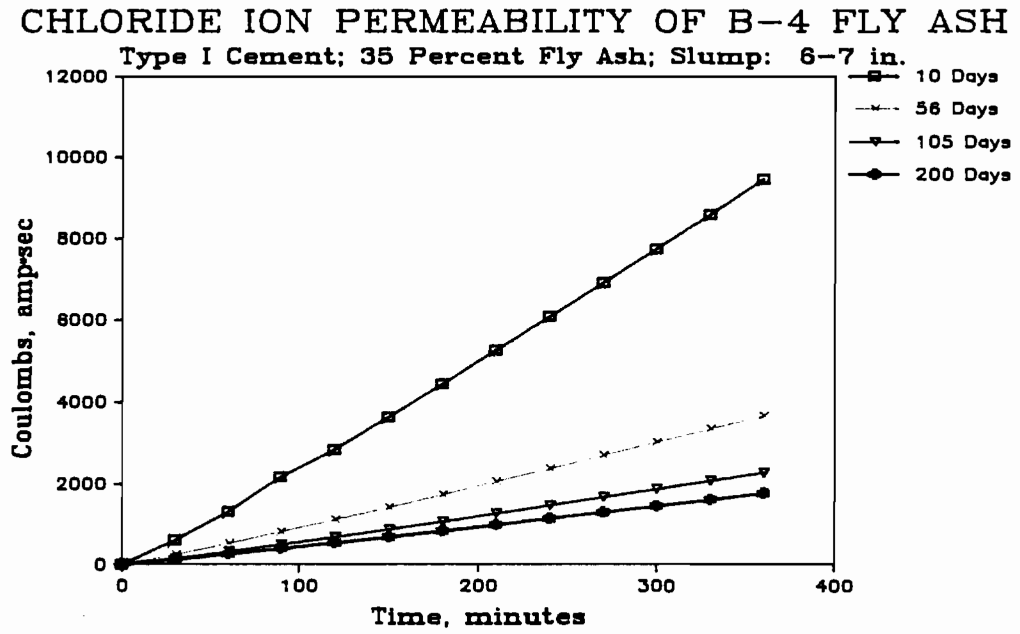


Figure D.3 Permeability of concrete containing fly ash B-4.

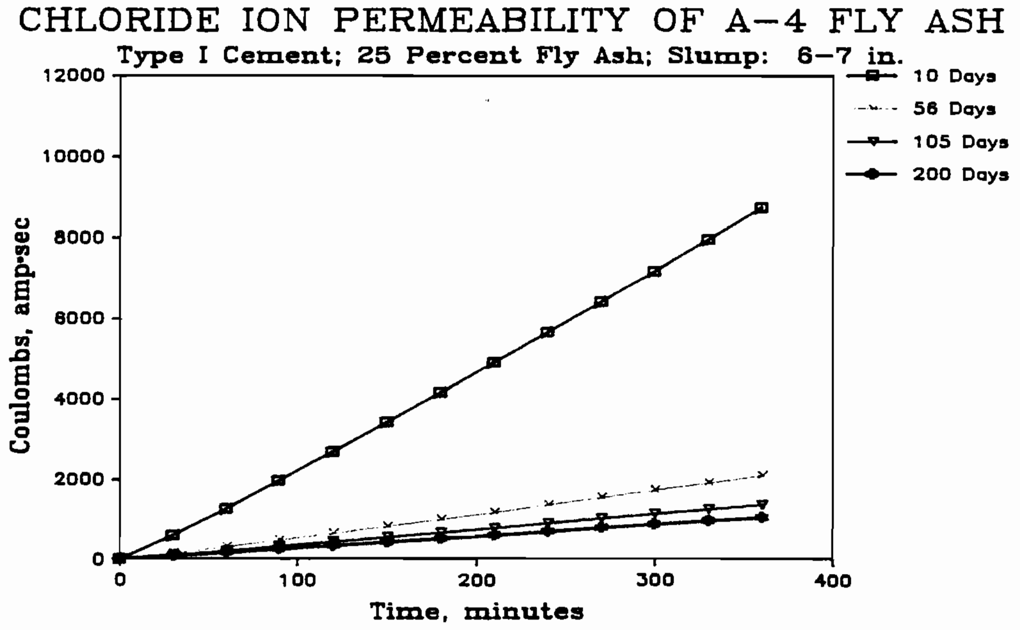


Figure D.4 Permeability of concrete containing fly ash A-4.

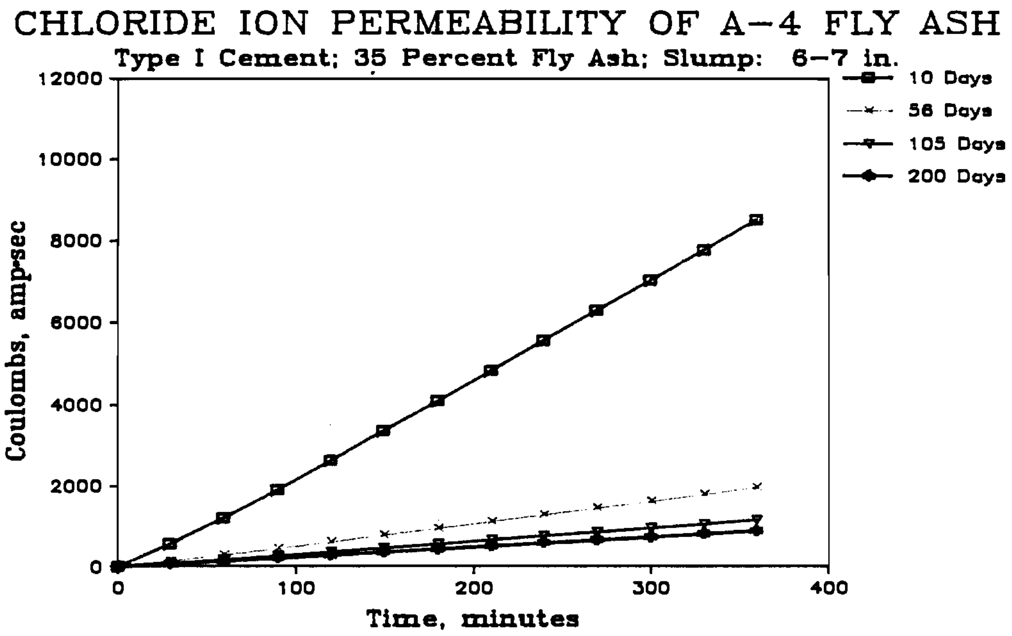


Figure D.5 Permeability of concrete containing fly ash A-4.

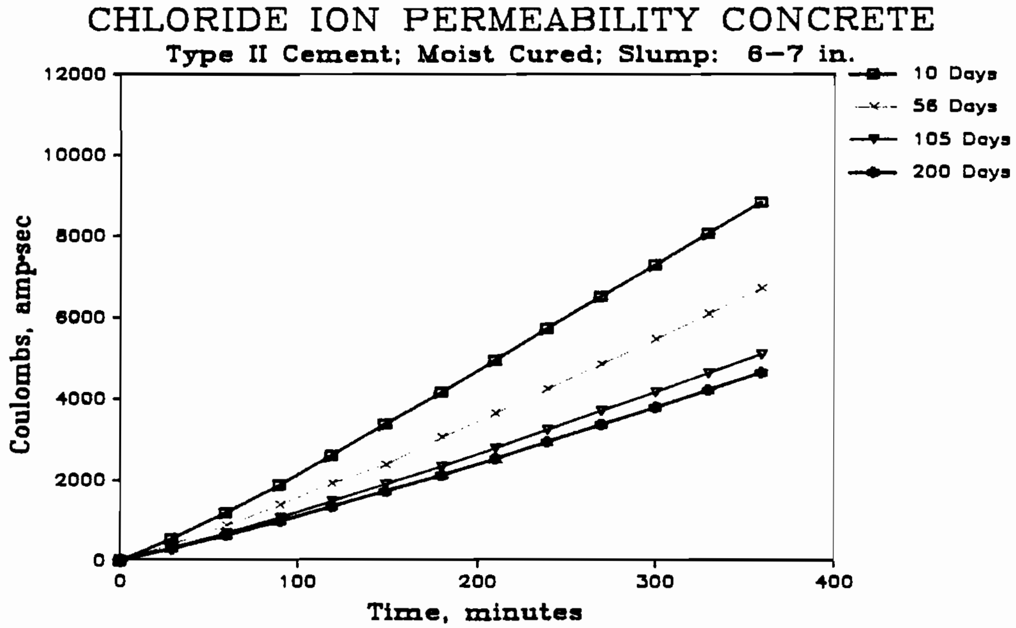


Figure D.6 Permeability of Type II cement concrete.

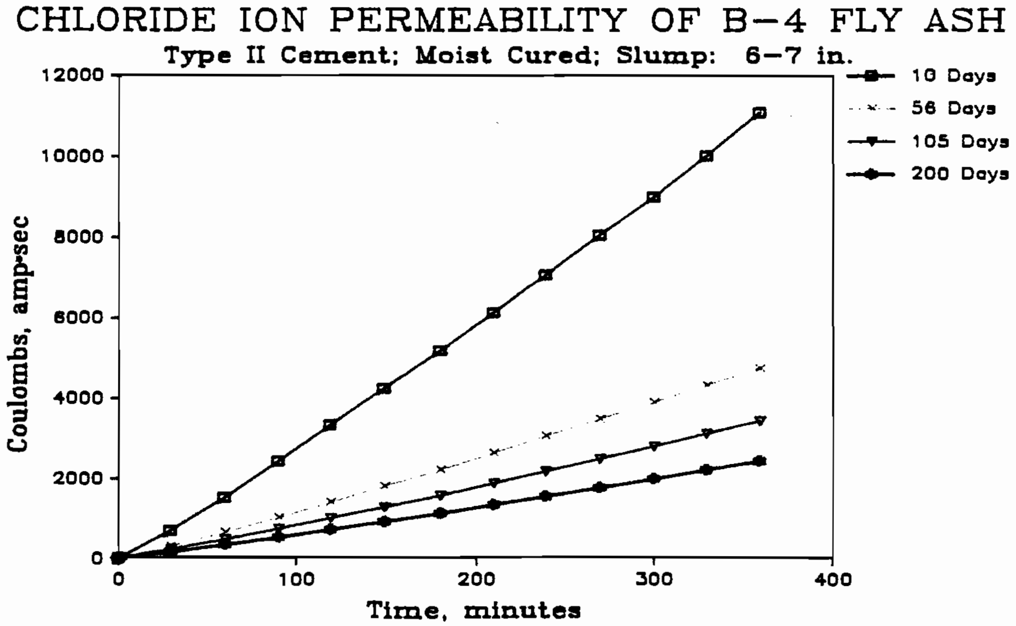


Figure D.7 Permeability of concrete containing fly ash B-4.

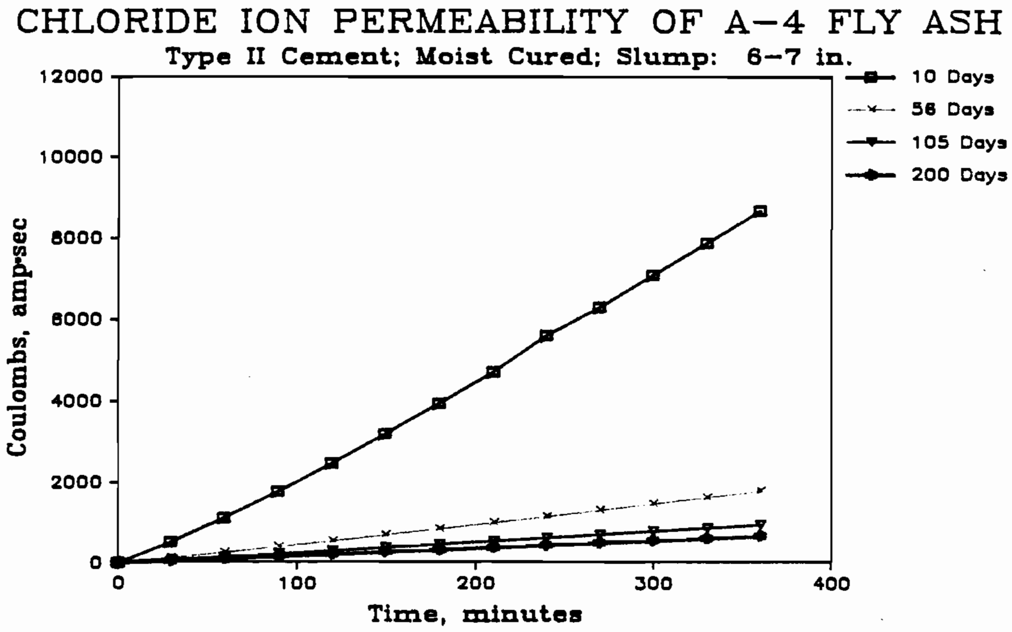


Figure D.8 Permeability of concrete containing fly ash A-4.

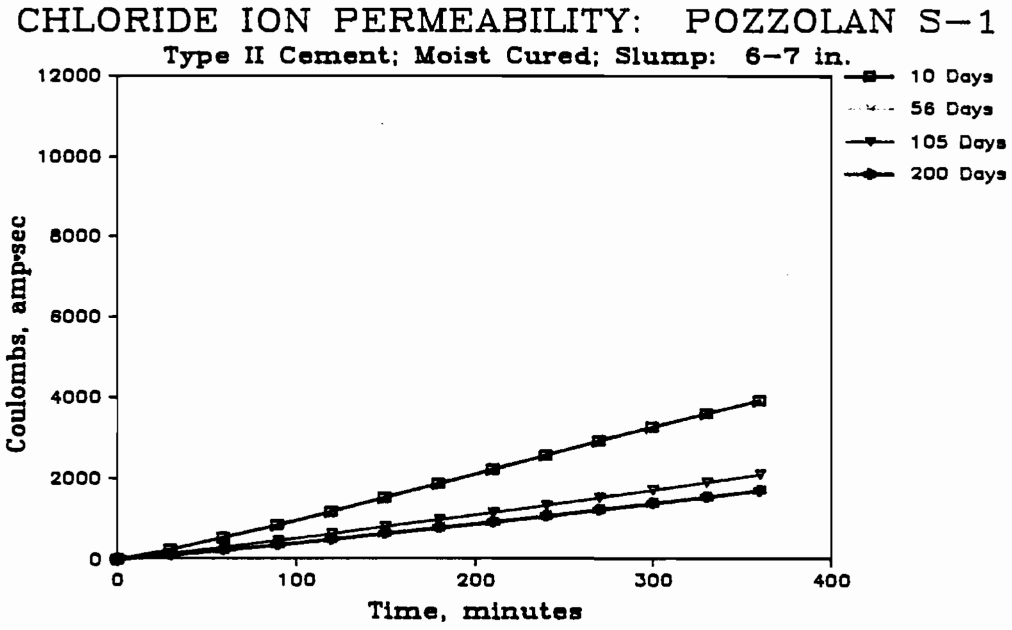


Figure D.9 Permeability of concrete containing pozzolan S-1.

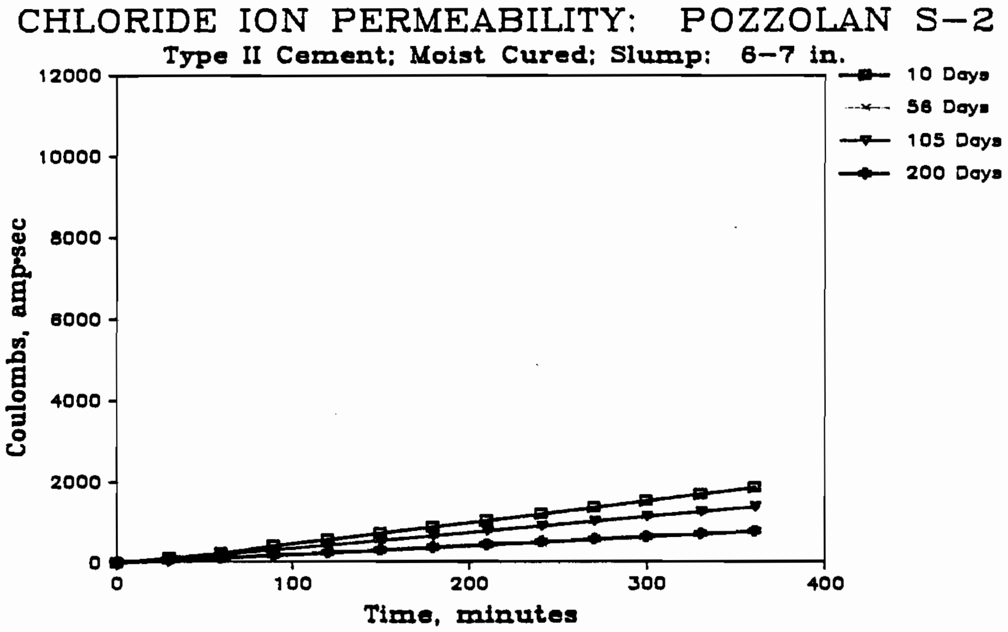


Figure D.10 Permeability of concrete containing pozzolan S-2.

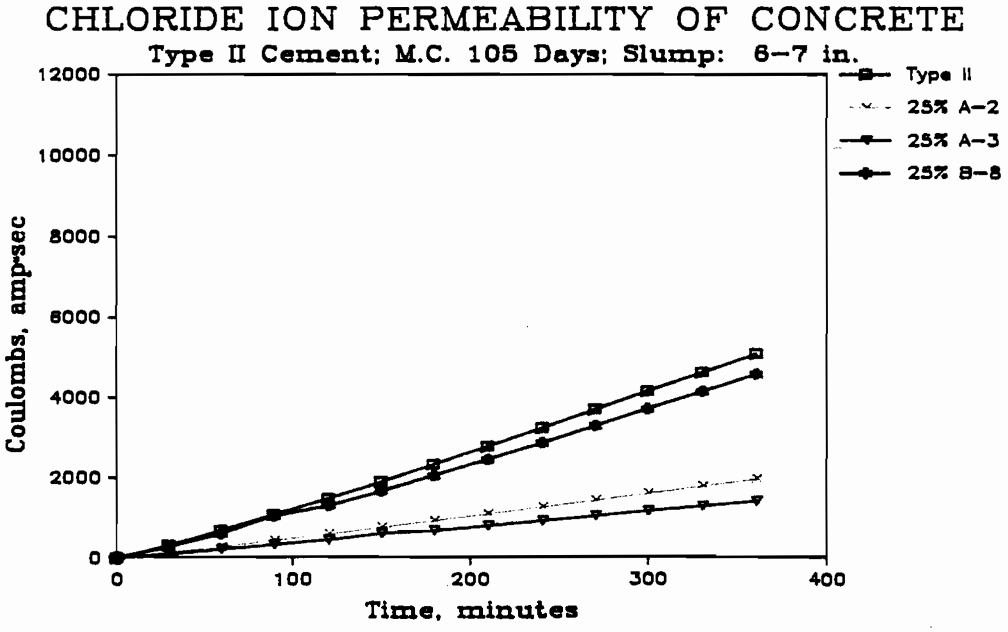


Figure D.11 Permeability of Type II cement concrete.

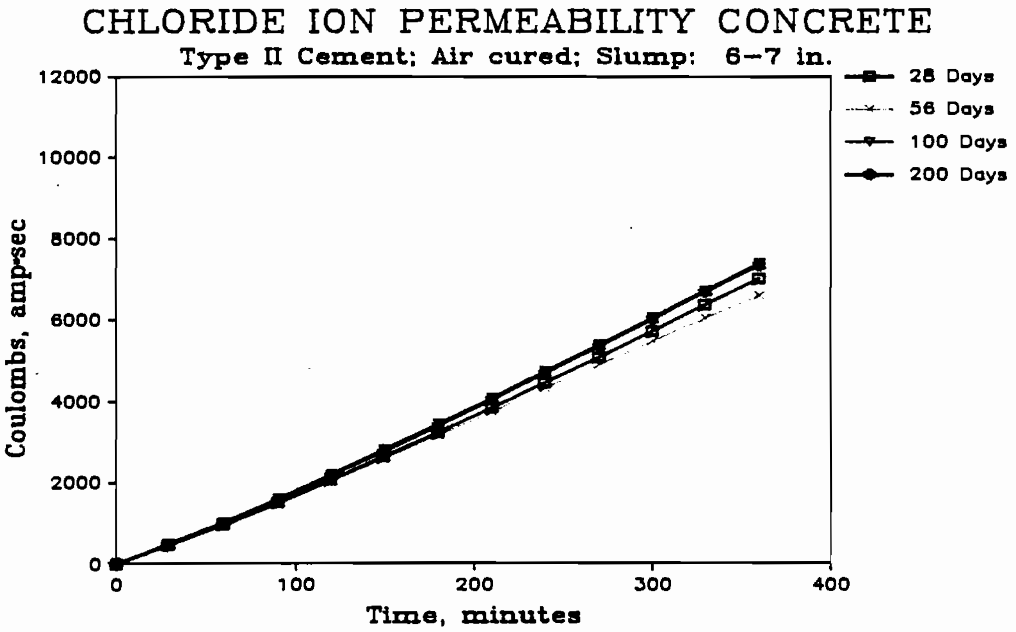


Figure D.12 Permeability of Type II cement concrete.

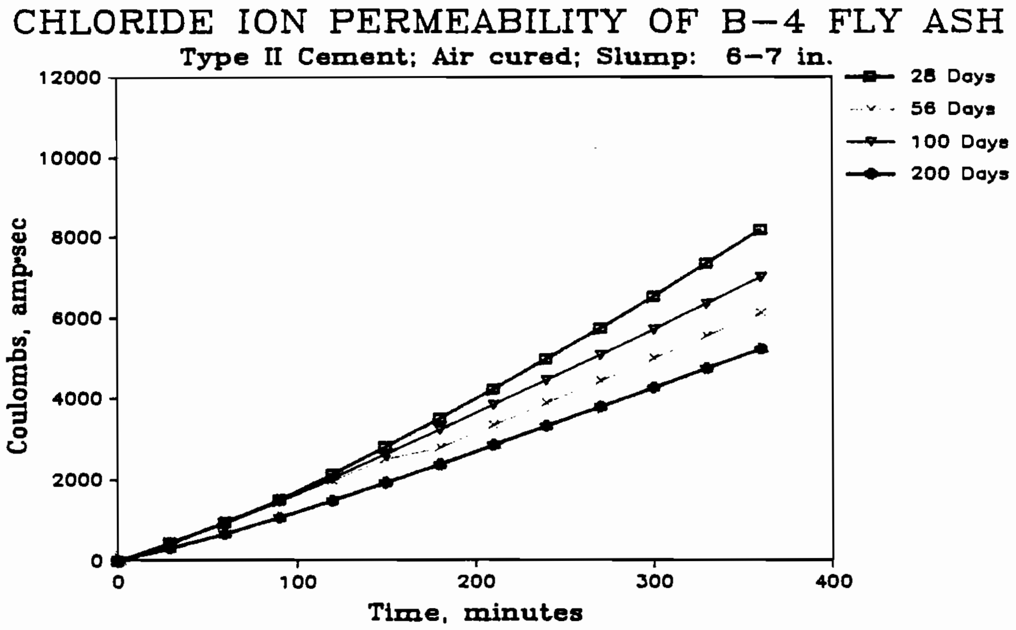


Figure D.13 Permeability of concrete containing fly ash B-4.

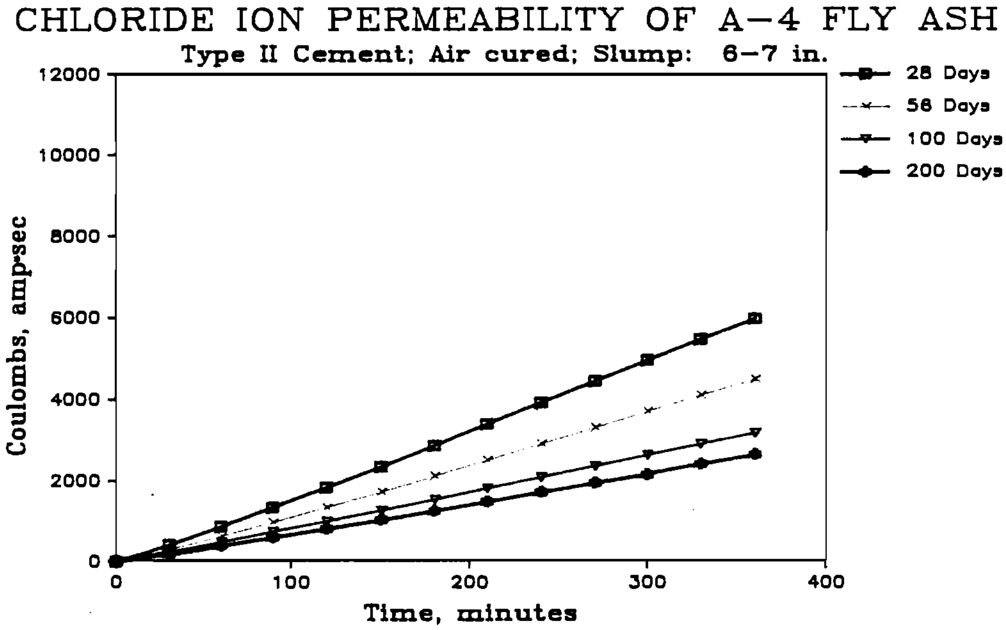


Figure D.14 Permeability of concrete containing fly ash A-4.

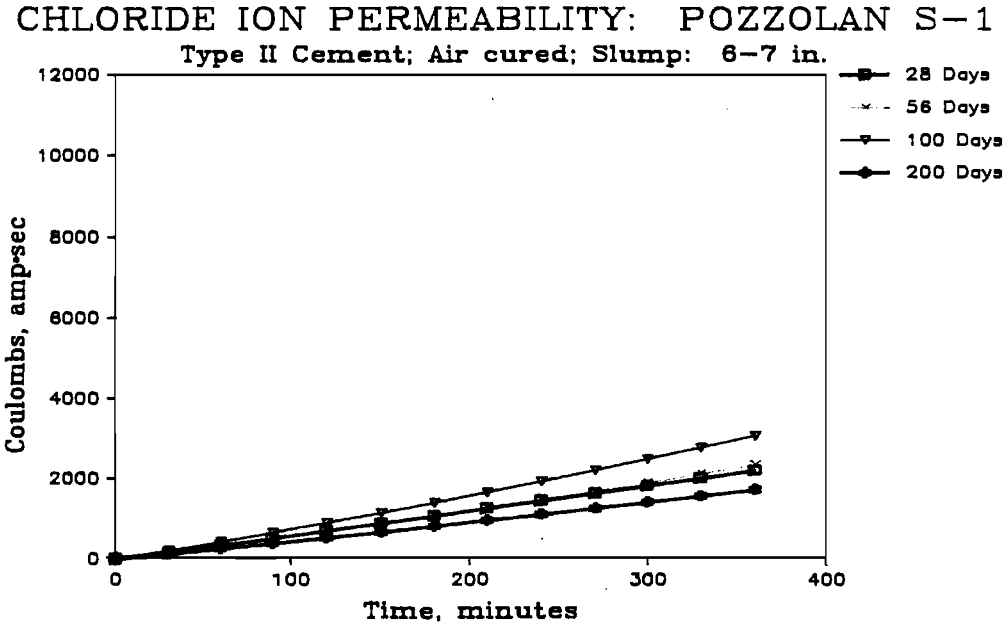


Figure D.15 Permeability of concrete containing pozzolan S-1.

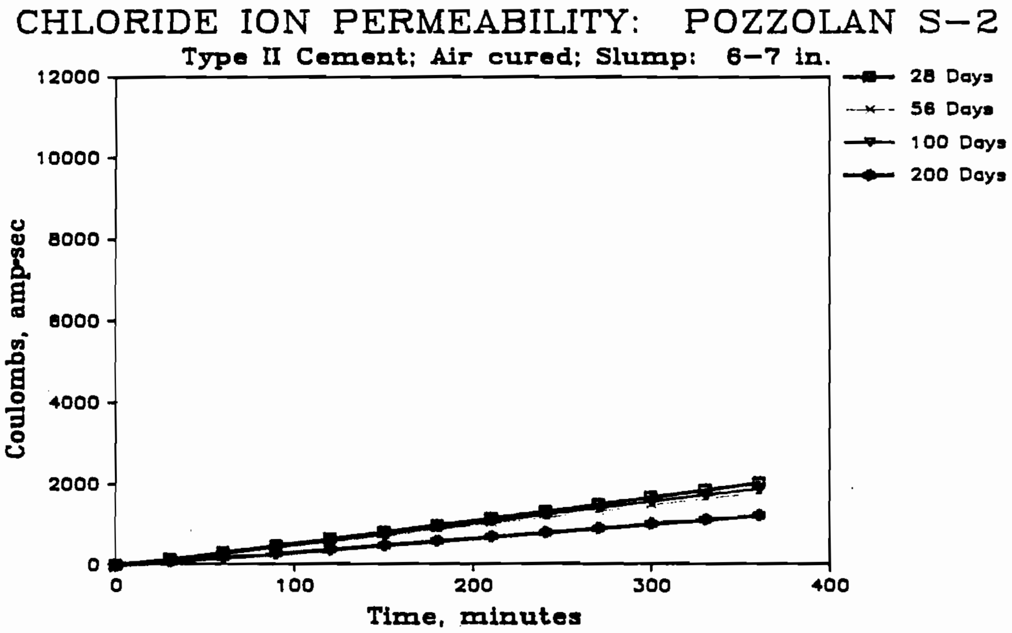


Figure D.16 Permeability of concrete containing pozzolan S-2.

APPENDIX E

Table E-1 SULFATE EXPANSION OF CONCRETE

Mix Name	0	90	180	270	360	450	540	630
01::0:2	0	7.38	12.51	17.45	28.41	34.02	43.59	*
V::0:2	0	4.68	10.85	14.27	25.24	31.34	42.62	*
II::0:2	0	6.09	11.58	20.29	31.34	45.18	62.69	82.24
II::0:6	0	2.75	7.35	15.75	21.76	27.12	31.92	*
I::0:6	0	7.19	12.66	19.50	39.21	*	*	*
02::0:6	0	5.62	9.69	13.36	17.20	22.35	25.48	*
V::0:6	0	3.93	11.02	16.98	21.69	24.96	26.85	32.73
01::0:6	0	6.25	13.46	20.00	30.01	39.06	42.81	51.46
II:A-1:35:6	0	4.70	10.61	12.75	19.43	24.21	23.17	*
02:A-1:35:6	0	5.97	10.39	13.65	16.36	17.12	15.93	*
II:A-2:25:6	0	3.50	9.49	10.75	17.15	21.07	23.92	*
II:A-2:35:6	0	3.75	7.30	12.24	16.62	23.78	24.36	*
II:A-2:45:6	0	3.50	9.19	9.83	14.21	16.22	15.83	*
II:A-2:25:6	0	1.37	1.45	0.91	5.05	*	*	*
02:A-2:35:6	0	8.30	12.89	15.61	18.40	19.88	21.21	*
II:A-2:25:2	0	1.86	6.56	11.93	13.89	15.00	19.06	*
II:A-2:35:2	0	2.29	6.09	8.23	10.5	11.72	12.55	*
II:A-2:45:2	0	7.17	11.11	12.27	15.54	16.27	15.15	*
II:A-2:25:2-3d	0	12.10	15.06	16.64	18.56	19.45	22.45	*
II:A-2:35:2-3d	0	13.22	15.08	18.03	18.79	20.04	20.5	*
II:A-3:25:6	0	3.25	6.55	9.71	13.24	17.02	18.29	17.93
II:A-3:35:6	0	6.50	9.45	9.45	14.25	18.25	19.5	*
II:A-3:45:6	0	10.00	9.60	10.33	13.10	15.07	15.14	14.62
I:A-3:25:6	0	4.47	9.20	9.25	9.50	*	*	*
I:A-3:35:6	0	1.55	3.00	2.06	4.41	*	*	*
II:A-3:25:2	0	3.52	7.34	11.7	13.81	13.59	13.71	*
II:A-3:35:2	0	2.72	7.41	9.48	12.64	13.34	13.75	*
II:A-3:45:2	0	5.95	7.46	9.44	12.92	13.02	13.38	*
II:A-3:25:2-3d	0	13.07	15.14	16.50	19.33	20.12	18.20	*
I:A-4:25:6	0	1.76	3.46	2.13	6.00	*	*	*
II:A-4:35:6	0	2.71	4.22	1.24	3.57	*	*	*
I:A-5:25:6	0	-.01	2.31	1.54	6.25	*	*	*
II:A-5:35:6	0	3.34	4.40	3.12	4.95	*	*	*
I:A-6:25:6	0	3.80	7.70	9.93	12.33	*	*	*
II:A-6:35:6	0	2.22	3.38	2.63	4.18	*	*	*
II:A-7:25:6	0	6.00	10.06	14.83	21.28	27.52	32.05	40.73
II:A-7:45:6	0	4.80	8.86	12.01	15.36	16.60	14.98	*
II:A-8:25:6	0	7.14	9.75	11.25	16.01	16.55	16.21	20
II:A-8:45:6	0	7.02	8.59	12.25	17.70	21.61	26.47	26.00
II:A-9:25:6	0	10.50	14.88	18.41	26.90	33.22	40.43	52.93
II:A-9:45:6	0	3.31	9.36	11.26	15.63	17.21	18.62	23.97

Table E-1 SULFATE EXPANSION OF CONCRETE

Mix Name	0	90	180	270	360	450	540	630
II:A-10:25:6	0	5	7.57	10.42	14.62	16.93	21.18	25.36
II:A-10:35:6	0	3.01	4.23	7.71	12.98	18.31	23.32	27.46
II:A-10:45:6	0	3.25	6.63	7.76	13.23	14.80	17.86	20.06
I:A-10:25:6	0	2.5	3.95	3.20	2.92	*	*	*
I:A-10:35:6	0	2.29	6.41	15.39	30.36	*	*	*
II:A-10:25:2	0	3.18	10.81	13.08	19.35	24.50	30.13	38.5
II:A-10:35:2	0	11.32	12.95	16.07	22.24	29.61	37.05	*
II:A-10:45:2	0	13.66	15.64	19.66	23.31	29.68	37.01	*
II:A-10:35:2-3d	0	7	9.88	12.72	17	18.08	25.11	*
II:A-10:25:2-28d	0	6.59	11.60	17.42	22.91	32.13	43.20	*
II:B-1:25:6	0	1.5	8.03	15.41	24.21	32.63	40.91	57.24
II:B-1:35:6	0	4	10.4	22.30	38.99	56.13	83.58	138.57
II:B-1:45:6	0	1	6.36	20.49	41.34	68.13	158.51	278.76
I:B-1:25:6	0	3.10	3.75	4.56	7.61	*	*	*
II:B-1:25:2	0	8.77	13.46	15.59	20.36	25.41	32.27	*
II:B-1:35:2	0	9.13	13.75	17.82	22.57	24.96	30.39	*
II:B-1:45:2	0	9.17	12.13	17.5	22.33	27.14	37.46	*
II:B-1:25:2-3d	0	3.53	8.90	14.64	18.43	21.87	26.47	*
II:B-2:25:6	0	3.24	5.19	5.55	8.68	*	*	*
II:B-2:35:6	0	5.42	10.81	18.15	33.38	50.77	74.69	*
II:B-3:25:6	0	5.5	10.54	21.01	36.44	53.78	69.8	96.75
II:B-3:35:6	0	6.5	11.90	26.16	54.60	100.49	206.5	386.39
II:B-3:45:6	0	4	11.93	35.90	138.49	162.06	179.30	204.76
I:B-3:25:6	0	2.56	3.15	3.36	5.29	*	*	*
I:B-3:35:6	0	4.45	8.95	20.4	101.3	*	*	*
II:B-3:35:6Air	0	15.81	32.90	60.91	108.48	217.92	370.16	*
02:B-3:35:6	0	4.94	7.55	12.43	15.43	16.57	20.25	*
V:B-3:35:6	0	5.45	11.79	16.4	26.50	*	*	*
II:B-3:35:6WP	0	5.34	13.125	27.42	63.88	*	*	*
II::0:6WP	0	2.9	6.31	*	*	*	*	*
II:B-3:25:2	0	3.72	11.66	16.87	28.66	40.82	57.65	82.87
II:B-3:35:2	0	4.09	12.58	26.37	61.00	142.39	191.78	291.32
II:B-3:45:2	0	12.65	24.99	61.25	132.63	200.61	259.45	*
II:B-3:35:2-3d	0	5.65	13.77	25.75	51.42	92.64	192.74	255.70
II:B-3:45:2-3d	0	14.47	13.53	29.25	56.32	129.07	154.03	172.67
II:B-3:25:2-28d	0	7.20	17.17	35.36	75.5	142.17	234.36	*
II:B-3:35:2-2	0	2.11	4.25	3.85	9.28	*	*	*
II:B-4:25:6	0	3.31	10.40	20.84	63.42	166	*	*
II:B-4:35:6	0	11.58	60.45	264.54	400	400	400	400
II:B-4:45:6	0	6.30	13.52	36.7	136.10	*	*	*
I:B-4:25:6	0	3.68	7.06	6.12	8.23	*	*	*
I:B-4:35:6	0	6.40	59.72	285.4	400	400	400	400
II:B-4:25:6SEA	0	3.81	8.95	11.85	15.82	17.68	*	*

Table E-1 SULFATE EXPANSION OF CONCRETE

Mix Name	0	90	180	270	360	450	540	630
II:B-5:25:6	0	1.75	3.93	9.27	15.91	20.60	25.09	33.30
II:B-5:35:6	0	5	7.34	13.69	22.51	31.47	51.59	106.93
II:B-5:45:6	0	2.75	5.37	15.10	31.2	53.79	117.53	197.85
I:B-5:25:6	0	6.03	8.42	9.51	14.35	*	*	*
II:B-5:35:6Air	0	4.37	8.56	15.01	24.07	40.92	76.45	*
02:B-5:35:6	0	7.83	10.25	15.93	21.16	27.68	33.93	*
II:B-5:35:6-3d	0	9.86	15.53	19.46	31.72	44.7	53.7	*
II:B-5:25:2	0	3.25	13.75	27.375	50	87.87	164.65	392.46
II:B-5:35:2	0	6.83	62.48	230.33	391.57	400	400	*
II:B-5:45:2	0	10.45	41.20	119.58	141	265.00	374.65	400
II:B-5:35:2-3d	0	1.32	12.24	36.51	123.09	199.26	254.79	359.09
II:B-5:25:2-28d	0	3.07	15.78	44.18	121.11	195.37	356.13	*
II:B-6:25:6	0	.5	10.55	26.26	49.81	82.81	127.41	210.12
II:B-6:35:6	0	6.15	12.50	31.96	109.01	243.12	400	400
II:B-6:45:6	0	9.34	25.10	112.46	170.25	263.12	338.51	*
II:B-6:35:6Air	0	11.64	102.21	288.94	321.25	377.59	400	400
02:B-6:35:6	0	14.37	28.20	42.43	61.88	83.04	110.77	*
II:B-6:25:2	0	10.70	24.12	44.05	79.72	128.16	220.15	*
II:B-6:35:2	0	21.72	222.14	400	400	400	400	400
II:B-6:45:2	0	49.26	400	400	400	400	400	400
II:B-6:35:2-3d	0	13	40.66	155.05	328.59	400	400	400
II:B-6:25:2-28d	0	10	37.68	110.58	304.34	400	400	400
II:B-6:35:2-2	0	6.81	11	19.70	44.84	*	*	*
II:B-7:35:6	0	3.04	7.79	15.28	29.31	*	*	*
II:B-8:25:6	0	10.18	35.15	186.11	349.03	400	400	400
II:B-8:35:6	0	14.24	55.49	246.75	376.00	400	400	400
II:B-8:45:6	0	7.75	262.81	400	400	400	400	400
II:B-8:35:6	0	5.53	25.35	171.21	362.91	400	400	400
II:B-8:35:6	0	8.66	17.07	25.95	42.10	*	*	*
II:B-8:35:6Air	0	11.58	35.68	89.78	334.55	383.67	400	400
02:B-8:35:6	0	10.83	19.56	32.81	54.17	78.31	111.93	*
II:B-8:35:6-3d	0	16.89	35.13	62.2	164.43	224.6	400	400
II:B-8:35:6SEA	0	2.72	11.89	19.66	32.72	62.86	180	*
II:B-8:25:2	0	3.43	10.56	17.22	26.50	36.38	52.06	*
II:B-8:35:2	0	10.97	19.69	38.31	108.16	172.90	274.47	*
II:B-8:45:2	0	11.12	23.85	58.94	253.5	400	400	400
II:B-8:25:2-28d	0	3.51	12.71	25.61	46.34	98.68	201.35	*
II:B-8:25:2-2	0	7.33	14.47	22.83	36.75	*	*	*
I:S-1:+9:6	0	1.5	2.25	2.08	2.88	*	*	*
I:S-2:65:6	0	1.33	2.74	2.5	6.25	*	*	*
II:S-2:65:6	0	2.80	5.18	2.18	4.82	*	*	*

Table E-2 MASS CHANGES OF CONCRETE

Mix Name	0	90	180	270	360	450	540	630
01::0:2	0	11.99	18.84	22.43	26.42	28.30	30.13	*
V::0:2	0	7.35	14.28	17.97	22.09	24.20	25.40	*
II::0:2	0	8.93	14.56	18.54	21.9	26.59	29.30	29.00
II::0:6	0	4.52	12.18	16.84	19.08	21.17	22.83	*
I::0:6	0	8.78	13.25	16.34	20.21	*	*	*
02::0:6	0	7.03	9.67	9.35	12.60	13.82	15.27	*
V::0:6	0	9.28	13.62	16.69	19.03	21.71	22.49	22.40
01::0:6	0	8.02	13.61	18.10	20.69	24.94	25.55	26.39
II:A-1:35:6	0	4.94	8.77	12.2	14.45	13.00	16.57	*
02:A-1:35:6	0	6.41	8.10	8.81	10.92	10.23	10.48	*
II:A-2:25:6	0	4.05	8.10	10.95	13.49	17.38	17.35	*
II:A-2:35:6	0	2.84	6.87	9.13	11.64	14.81	14.96	*
II:A-2:45:6	0	4.66	7.62	7.10	7.92	9.69	9.37	*
I:A-2:25:6	0	-7.5	-7.25	-5.93	-4.43	*	*	*
02:A-2:35:6	0	5.93	7.75	8.62	10.51	9.59	9.27	*
II:A-2:25:2	0	7.82	11.69	13.88	16.49	17.67	18.31	*
II:A-2:35:2	0	6.12	9.63	11.6	13.44	15.05	15.48	*
II:A-2:45:2	0	5.40	7.64	7.88	9.60	8.94	10.38	*
II:A-2:25:2-3d	0	5.64	9.06	10.93	12.08	13.75	13.29	*
II:A-2:35:2-3d	0	4.96	8.25	9.89	11.04	12.85	12.85	*
II:A-3:25:6	0	3.12	8.42	10.62	12.41	14.84	14.63	14.93
II:A-3:35:6	0	5.69	6.79	8.40	10.37	13.53	12.70	*
II:A-3:45:6	0	3.17	5.45	6.93	8.01	10.46	9.42	9.84
I:A-3:25:6	0	4.46	7.78	10.12	11.78	*	*	*
I:A-3:35:6	0	4.61	7.76	7.61	8.25	*	*	*
II:A-3:25:2	0	7.42	11.70	13.59	16.48	17.77	18.41	*
II:A-3:35:2	0	6.80	9.77	11.51	12.70	14.00	14.32	*
II:A-3:45:2	0	6.30	9.14	10.68	12.83	13.49	13.45	*
II:A-3:25:2-3D	0	5.59	9.42	11.29	12.72	14.51	14.35	*
I:A-4:25:6	0	.74	.81	3.66	6.33	*	*	*
II:A-4:35:6	0	-2.76	-2.99	-2.65	-1.56	*	*	*
I:A-5:25:6	0	1.06	1.61	5.35	7.25	*	*	*
II:A-5:35:6	0	-1.76	-2.35	-1.98	-1.09	*	*	*
I:A-6:25:6	0	5.20	8.68	11.23	13.43	*	*	*
II:A-6:35:6	0	-0.54	-2.38	-1.88	-0.78	*	*	*
II:A-7:25:6	0	5.52	11.24	14.30	16.64	20.38	20.94	22.08
II:A-7:45:6	0	5.71	7.24	8.65	8.49	10.02	9.74	*
II:A-8:25:6	0	5.68	7.61	8.58	6.52	11.48	11.48	11.52
II:A-8:45:6	0	6.37	8.98	10.45	11.84	13.76	13.98	14.54
II:A-9:25:6	0	6.35	11.50	14.24	16.55	20.59	21.58	23.31
II:A-9:45:6	0	7.35	9.42	11	12.25	14.87	14.89	15.27

Table E-2 MASS CHANGES OF CONCRETE

Mix Name	0	90	180	270	360	450	540	630
II:A-10:25:6	0	5.08	10.23	13.13	15.39	18.54	18.70	19.20
II:A-10:35:6	0	7.52	10.78	9.45	10.89	13.81	12.83	13.44
II:A-10:45:6	0	5.24	8.38	9.44	10.51	13.36	12.01	12.05
I:A-10:25:6	0	1.43	3.00	4.43	6.62	*	*	*
I:A-10:35:6	0	6.04	-16.87	-22.4	-40.92	*	*	*
II:A-10:25:2	0	8.20	13.93	16.71	18.77	22.32	23.06	22.9
II:A-10:35:2	0	9.77	14.85	16.91	18.29	21.73	22.00	*
II:A-10:45:2	0	9.01	12.51	11.20	6.42	4.48	2.74	*
II:A-10:35:2-3d	0	8.72	13.16	16.47	19.05	21.86	22.16	*
II:A-10:25:2-28d	0	9.20	15.60	18.46	22.09	24.41	25.57	*
II:B-1:25:6	0	5.35	11.90	15.76	17.87	21.59	23.13	25.89
II:B-1:35:6	0	5.75	12.17	6.89	-3.4	-6.99	-20.85	-48.77
II:B-1:45:6	0	-1.3	-20.6	-39.98	-54.34	-50.97	-61.31	-213.07
I:B-1:25:6	0	-0.23	1.41	4.29	7.03	*	*	*
II:B-1:25:2	0	9.11	15.22	18.50	21.34	23.70	23.78	*
II:B-1:35:2	0	8.93	13.73	15.98	16.54	14.94	16.48	*
II:B-1:45:2	0	3.70	-10.35	-20.71	-35.83	-48.99	-53.59	*
II:B-1:25:2-3d	0	9.77	14.73	18.47	21.22	22.89	20.76	*
II:B-2:25:6	0	7.94	13.19	15.15	16.29	*	*	*
II:B-2:35:6	0	8.14	12.41	17.18	22.19	23.44	29.46	*
II:B-3:25:6	0	4.50	11.20	15.40	19.87	25.04	28.51	32.63
II:B-3:35:6	0	5.25	-20.72	-65.55	-89.22	-101.25	-127.7	-200.35
II:B-3:45:6	0	-3.32	-44.4	-77.47	-143.73	-203.98	-204.72	-207.96
I:B-3:25:6	0	.86	2.12	4.11	7.33	*	*	*
I:B-3:35:6	0	6.42	-9.43	-16.02	-86.47	*	*	*
II:B-3:35:6Air	0	5.74	-0.02	-1.12	-31.65	-108.92	-361.26	*
02:B-3:35:6	0	9.67	14.64	18.15	22.05	23.97	25.23	*
V:B-3:35:6	0	7.49	11.52	10.86	12.05	*	*	*
II:B-3:35:6WP	0	11.24	10.56	-9.4	-32.5	*	*	*
II::0:6WP	0	1.94	14.22	20.13	25.64	*	*	*
II:B-3:25:2	0	8.19	12.71	15.83	20.48	25.73	28.64	31.76
II:B-3:35:2	0	8.46	14.31	10.26	-19.3	-54.89	-133.26	-170.76
II:B-3:45:2	0	-2.32	-30.67	-70.98	-116.82	-177.57	-195.41	*
II:B-3:35:2-3d	0	9.27	13.53	-13.43	-33.26	-57.43	-64.71	-221.48
II:B-3:45:2-3d	0	5.00	-19.56	-81.04	-109.65	-152.65	-187.29	-188.54
II:B-3:25:2-28d	0	9.84	18.18	25.10	33.04	39.59	-22.39	*
II:B-3:35:2	0	8.78	12.55	13.28	15.15	*	*	*
II:B-4:25:6	0	3.71	10.24	17.24	11.00	-83.76	*	*
II:B-4:35:6	0	-13.27	-76.06	-127.63	-400	-400	-400	*
II:B-4:45:6	0	7.95	-20.04	-62.55	-133.8	*	*	*
I:B-4:25:6	0	2.42	4.42	1.16	-20.77	*	*	*
I:B-4:35:6	0	5.90	-51.1	-262.3	-400	-400	-400	*
II:B-4:25:6SEA	0	2.54	6.02	11.41	11.01	14.98	*	*

Table E-2 MASS CHANGES OF CONCRETE

Mix Name	0	90	180	270	360	450	540	630
II:B-5:25:6	0	7.03	10.23	3.98	2.93	-2.01	-5.32	-15.64
II:B-5:35:6	0	3.14	5.48	2.17	-2.26	-9.34	-35.42	-41.46
II:B-5:45:6	0	-4.98	-40.56	-66.75	-98.87	-125.85	-156.26	-206.6
I:B-5:25:6	0	9.36	15.81	12.75	-12.59	*	*	*
II:B-5:35:6Air	0	5.69	14.67	18.83	25.03	18.87	12.17	*
02:B-5:35:6	0	9.78	15.19	18.23	22.23	24.51	26.69	*
II:B-5:35:6-3d	0	7.33	11.77	14.63	19.31	16.66	-25.87	*
II:B-5:25:2	0	10.49	17.32	21.09	18.38	23.65	0.78	-369.86
II:B-5:35:2	0	8.22	-58.94	-139.77	-264.78	-400	-400	*
II:B-5:45:2	0	-20.49	-69.64	-160.69	-171.98	-283.4	-353.46	-400
II:B-5:35:2-3d	0	11.41	4.72	-27.01	-39.03	-162.16	-267.65	-327.51
II:B-5:25:2-28d	0	9.34	19.08	2.63	-32.89	-69.3	-378.21	*
II:B-6:25:6	0	4.60	12.39	17.43	22.34	28.64	34.38	-0.83
II:B-6:35:6	0	3.32	-49.64	-87.59	-156.35	-248.73	-400	-400
II:B-6:45:6	0	1.87	-19.3	-40.91	-119.74	-183.36	-348.4	*
II:B-6:35:6Air	0	-0.74	-53.28	-176.78	-322.97	-374.62	-400	-400
02:B-6:35:6	0	13.24	20.16	24.61	29.94	32.33	34.18	*
II:B-6:25:2	0	12.91	21.54	23.88	23.64	29.60	11.85	*
II:B-6:35:2	0	-10.31	-400	-400	-400	-400	-400	-400
II:B-6:45:2	0	-78.56	-400	-400	-400	-400	-400	-400
II:B-6:35:2-3d	0	10.78	-45.37	-96.34	-197.35	-372.26	-400	-400
II:B-6:25:2-28d	0	13.91	26.51	22.34	-50.9	-400	-400	-400
II:B-6:35:2	0	12.58	16.43	3.87	44.84	*	*	*
II:B-7:35:6	0	9.09	16.53	21.62	16.46	*	*	*
II:B-8:25:6	0	-13.76	-39.13	-116.44	-254.23	-324.92	-400	-400
II:B-8:35:6	0	6.44	-17.46	-126.54	-232.49	-400	-400	-400
II:B-8:45:6	0	-32.18	-263.59	-400	-400	-400	-400	-400
II:B-8:35:6	0	-10.56	-63.53	-150.76	-326.57	-400	-400	-400
II:B-8:35:6	0	12.55	16.55	20.01	-1.45	*	*	*
II:B-8:35:6Air	0	15.03	9.29	-46.94	-112.29	-368.49	-400	-400
02:B-8:35:6	0	11.39	17.96	22.46	27.04	29.49	32.37	*
II:B-8:35:6-3d	0	10.65	17.09	14.62	-2.05	-117.1	-400	-400
II:B-8:35:6SEA	0	1.96	1.83	-12.65	-35.33	-65.48	-65	*
II:B-8:25:2	0	10.48	17.49	21.83	24.09	17.14	13.00	*
II:B-8:35:2	0	9.07	2.78	-12.26	-72.75	-129.95	-182.56	*
II:B-8:45:2	0	-32.55	-82.1	-123.83	-267.29	-400	-400	-400
II:B-8:25:2-28d	0	24.89	34.17	40.25	44.34	16.65	-73.41	*
II:B-8:25:2	0	11.47	19.06	23.74	28.18	*	*	*
I:S-1:+9:6	0	4.91	10.90	12.85	14.57	*	*	*
I:S-2:65:6	0	2.37	4.06	7.81	10.25	*	*	*
II:S-2:65:6	0	4.12	5.81	7.86	9.65	*	*	*

Table E-3 FIRST CRACKING OF CONCRETE

Mix Name	Days
01::0:-3	598
V::0:-3	493
II::0:46	366
II::0:53	353
I::0:-54	280
02::0:-7	598
01::0:-53	*
V::0:-53	634
II:A-1:35:6	529
02:A-1:35:6	*
II:A-2:25:6	512
II:A-2:35:6	332
II:A-2:45:6	645
I:A-2:25:6	*
02:A-2:35:6	574
II:A-2:25:2	*
II:A-2:35:2	*
II:A-2:45:2	*
II:A-2:25:2-3d	*
II:A-2:35:2-3d	*
II:A-3:25:6	672
II:A-3:35:6	662
II:A-3:45:6	*
I:A-3:25:6	*
I:A-3:35:6	*
II:A-3:25:2	*
II:A-3:35:2	*
II:A-3:45:2	*
II:A-3:25:2-3d	*
I:A-4:25:6	*
II:A-4:35:6	*
I:A-5:25:6	*
II:A-5:35:6	*
I:A-6:25:6	*
II:A-6:35:6	*
II:A-7:25:6	655
II:A-7:45:6	*
II:A-8:25:6	*
II:A-8:45:6	*
II:A-9:25:6	440
II:A-9:45:6	*

Table E-3 FIRST CRACKING OF CONCRETE

Mix Name	Days
II:A-10:25:6	332
II:A-10:35:6	152
II:A-10:45:6	202
I:A-10:25:2	*
I:A-10:35:2	160
II:A-10:25:2	248
II:A-10:35:2	128
II:A-10:45:2	130
II:A-10:35:2-3d	421
II:A-10:25:2-28d	451
II:B-1:25:6	281
II:B-1:35:6	212
II:B-1:45:2	158
I:B-1:25:2	367
II:B-1:25:2	200
II:B-1:35:2	220
II:B-1:45:2	102
II:B-1:25:2-3d	280
II:B-2:25:6	408
II:B-2:35:6	144
II:B-3:25:6	212
II:B-3:35:6	129
II:B-3:45:6	62
I:B-3:25:6	252
I:B-3:35:6	91
II:B-3:35:6Air	144
02:B-3:35:6	215
V:B-3:35:6	111
II:B-3:35:6WP	75
II::0:6WP	*
II:B-3:25:2	170
II:B-3:35:2	170
II:B-3:45:2	93
II:B-3:35:2-3d	133
II:B-3:45:2-3d	96
II:B-3:25:2-28d	201
II:B-3:35:2	146
II:B-4:25:6	104
II:B-4:35:6	56
II:B-4:45:6	89
I:B-4:25:6	252
I:B-4:35:6	91
II:B-4:25:6SEA	195

Table E-3 FIRST CRACKING OF CONCRETE

Mix Name	Days
II:B-5:25:6	212
II:B-5:35:6	212
II:B-5:45:6	158
I:B-5:25:6	160
II:B-5:35:6Air	144
02:B-5:35:6	215
II:B-5:35:6-3d	206
II:B-5:25:2	133
II:B-5:35:2	94
II:B-5:45:2	96
II:B-5:35:2-3d	133
II:B-5:25:2-28d	206
II:B-6:25:6	223
II:B-6:35:6	155
II:B-6:45:6	91
II:B-6:35:6Air	67
02:B-6:35:6	151
II:B-6:25:2	131
II:B-6:35:2	63
II:B-6:45:2	63
II:B-6:35:2-3d	90
II:B-6:25:2-28d	99
II:B-6:35:2	146
II:B-7:35:6	160
II:B-8:25:6	91
II:B-8:35:6	91
II:B-8:45:6	62
II:B-8:35:6	104
II:B-8:35:6	91
II:B-8:35:6Air	144
02:B-8:35:6	215
II:B-8:35:6-3d	62
II:B-8:35:6SEA	104
II:B-8:25:2	206
II:B-8:35:2	103
II:B-8:45:2	63
II:B-8:25:2-28d	151
II:B-8:25:2	160
I:S-1:+9:6	392
I:S-2:65:6	306
II:S-2:65:6	326

Table E-4 Sulfate Performance Rating

Mixture Number	Cracking Index	Expansion Index	Sulfate Performance Rating
1	2	2	2
2	3	2	2.5
3	2	1	1.5
4	2	2	2
5	3	1	2
6	2	1	1.5
7	1	1	1
8	3	3	3
9	2	2	2
10	2	2	2
11	2	2	2
12	2	2	2
13	2	2	2
14	2	2	2
15	3	1	2
16	1	1	1
17	1	1	1
18	1	1	1
19	1	1	1
20	2	1	1.5
21	2	1	1.5
22	1	1	1
23	2	1	1.5
24	1	1	1
25	1	1	1
26	1	1	1
27	2	1	1.5
28	1	2	1.5
29	1	1	1
30	1	1	1
31	1	1	1
32	2	1	1.5
33	1	1	1
34	1	1	1
35	1	1	1
36	1	1	1
37	1	1	1
38	1	1	1
39	1	1	1
40	1	1	1

Table E-4 Sulfate Performance Rating (continued)

Mixture Number	Cracking Performance	Expansion Performance	Sulfate Performance Rating
41	1	1	1
42	1	1	1
43	1	1	1
44	1	1	1
45	1	1	1
46	2	1	1.5
47	1	1	1
48	1	1	1
49	1	1	1
50	2	2	2
51	1	1	1
52	2	3	2.5
53	2	2	2
54	1	2	1.5
55	1	1	1
56	2	4	3
57	1	2	1.5
58	1	4	2.5
59	3	4	3.5
60	2	4	3
61	1	3	2
62	2	3	2.5
63	2	3	2.5
64	2	3	2.5
65	1	2	1.5
66	2	3	2.5
67	3	3	3
68	2	4	3
69	3	4	3.5
70	1	2	1.5
71	3	4	3.5
72	1	3	2
73	2	4	3
74	5	3	4
75	3	3	3
76	1	3	2
77	5	5	5
78	5	4	4.5
79	1	4	2.5
80	4	4	4

Table E-4 Sulfate Performance Rating (continued)

Mixture Number	Cracking Performance	Expansion Performance	Sulfate Performance Rating
81	4	4	4
82	5	4	4.5
83	5	5	5
84	2	4	3
85	5	5	5
86	4	5	4.5
87	5	5	5
88	1	4	2.5
89	5	4	4.5
90	1	3	2
91	5	5	5
92	5	5	5
93	5	5	5
94	2	3	2.5
95	4	4	4
96	5	3	4
97	1	3	2
98	1	4	2.5
99	5	5	5
100	5	4	4.5
101	2	3	2.5
102	3	4	3.5
103	2	4	3
104	5	5	5
105	3	4	3.5
106	5	4	4.5
107	5	4	4.5
108	5	5	5
109	4	3	3.5
110	5	5	5
111	3	4	3.5
112	5	5	5
113	5	4	4.5
114	5	5	5
115	5	4	4.5
116	5	5	5
117	2	4	3
118	4	3	3.5
119	3	4	3.5
120	2	3	2.5

Table E-4 Sulfate Performance Rating (continued)

Mixture Number	Cracking Performance	Expansion Performance	Sulfate Performance Rating
121	3	4	3.5
122	3	4	3.5
123	5	5	5
124	5	4	4.5
125	5	5	5
126	5	4	4.5
127	3	5	4
128	5	5	5
129	5	4	4.5
130	5	5	5
131	5	5	5
132	1	2	1.5
133	1	2	1.5
134	1	2	1.5

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