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EFFECT OF FLY ASH ON THE
SULFATE RESISTANCE OF CONCRETE
CONTAINING FLY ASH

by
P. J. Tikalsky
and
R. L. Carrasquillo

Research Report Number 481-1
Durability and Performance of Concrete Containing Fly Ash
Research Project 3-5/9-87-481

Conducted for
Texas
State Department of Highways and Public Transportation
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U. S. Department of Transportation
Federal Highway Administration

by
Center for Transportation Research
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The University of Texas at Austin

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The contents of this report reflect the views of the authors who are responsible for the facts and accuracy of the data presented herein. The contents do not necessarily reflect the views or policies of the Federal Highway Administration. This report does not constitute a standard, specification or regulation.

PREFACE

This is the first in a series of reports summarizing the durability and performance of concrete containing fly ash. This report is a interim report on the sulfate resistance of concrete containing fly ash. Other reports will address the topics of scaling resistance, abrasion resistance, freeze-thaw durability, creep and shrinkage at early ages, and fly ash characterization.

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 Phil M. 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.

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 structure, pavements, structural members, and high strength applications. One area where the long term performance of concrete containing high calcium fly ash has been suspect 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 is being conducted to investigate the interrelationship between the physical, mineralogical and chemical characteristics of portland cement and fly ash and their proportions, and the sulfate resistance of concrete containing fly ash. This report summarizes the results of the first year of the study. Fourteen fly ashes and four portland cements have been studied at four cement replacement levels and two different workability levels. A wet chemistry analysis was performed to determine the bulk chemical properties of both the fly ashes and the portland cements. The mineralogy of the fly ash was determined by XRD analysis. Over 500 concrete specimens have been exposure tested in a 10 percent sodium sulfate solution and monitored for mass change and linear expansion. The study has revealed a possible correlation between the tricalcium aluminate content of the high calcium fly ash and sulfate deterioration. In addition, the results to date indicate that lignitic fly ashes result in sulfate resistant concrete. This is an interim report of an ongoing investigation to the problem of sulfate attack of concrete containing fly ash.

Key Words: fly ash, portland cement, sulfate attack, mineralogy, expansion, durability, hydration

SUMMARY

The durability of concrete is determined by its ability to endure its 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 structure, pavements, structural members, and high strength applications. One area where the long term performance of concrete containing high calcium fly ash has been suspect 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 is being conducted to investigate the interrelationship between the physical, mineralogical and chemical characteristics of portland cement and fly ash and their proportions, and the sulfate resistance of concrete containing fly ash. This report summarizes the results of the first year of the study. Fourteen fly ashes and four portland cements have been studied at four cement replacement levels and two different workability levels. A wet chemistry analysis was performed to determine the bulk chemical properties of both the fly ash and the portland cements. The mineralogy of the fly ashes was determined by XRD analysis. Over 500 concrete specimens have been exposure tested in a 10 percent sodium sulfate solution and monitored for mass change and linear expansion. The study has revealed a possible correlation between the tricalcium aluminate content of the high calcium fly ash and sulfate deterioration. In addition, the results to date indicate that lignitic fly ashes result in sulfate resistant concrete. This is an interim report of an ongoing investigation to the problem of sulfate attack of concrete containing fly ash.

IMPLEMENTATION

This report summarizes the findings of the first year of a three year study on the effects of fly ash on the sulfate resistance of concrete containing fly ash. The preliminary findings show that there is a relationship between fly ash composition and sulfate resistance.

This interim report is an overview of the complete experimental project on the sulfate resistance of concrete containing fly ash. The first year's results indicate that the use of high calcium fly ash increase the potential for sulfate attack of concrete. Some lignitic fly ashes add to the sulfate resistance of concrete. On the basis of results to date, recommendations have been made to TSDHPT officials and these recommendations have been incorporated into job concrete specifications to allow only TSDHPT Type A fly ash for the use of concrete exposed to sulfate environments. Until further research produces a means of ensuring adequate sulfate resistance of concrete containing TSDHPT type B fly ash, their use should be restricted to concrete not subjected to sulfate attack.

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CHAPTER 1

INTRODUCTION

1.1 Overview

The use of fly ash as a constituent of concrete is steadily increasing throughout Texas and the southern United States. Fly ash is being used primarily because it provides a more economical concrete mixture of equal or better quality than concrete proportioned with portland cement alone. There should be no doubt that concrete containing fly ash can be a superior product when the beneficial qualities of fly ash in concrete are understood and implemented by the designer, producer, contractor, and owner.

The materials research being conducted at the Ferguson Structural Engineering Laboratory at the University of Texas at Austin is focused on improving the quality of concrete through a better understanding of its properties, constituents and performance. The durability of concrete containing fly ash has long been a major concern of designers and the concrete construction industry. Compared to the database of research in the durability of portland cement concrete, the work done in concrete containing fly ash is still very limited. In 1986, the Center for Transportation Research, CTR, Project 364 on the "Production of Concrete Containing Fly Ash" was completed. The results provided the State of Texas and the concrete industry with guidelines for selecting materials and proportioning procedures for concrete containing fly ash.

As part of CTR Project 364 an initial investigation was conducted into the effect of fly ash in concrete on its resistance to freezing and thawing, abrasion resistance, creep, shrinkage, curing, air content, and strength. CTR Project 481 is now in the second year of a more comprehensive three year study investigating the durability and long term performance of concrete containing fly ash. Under CTR Project 481, a broad range of tests on concrete containing fly ash are being conducted including, resistance to freezing and thawing, abrasion resistance, scaling, heat generation, creep and shrinkage at early ages and sulfate resistance. In

addition, CTR Project 450 is currently in the last year of a four year program studying the effect of fly ash on alkali-silica reaction in concrete.

The durability of concrete is determined by its ability to endure its 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 concretes, such as concrete for mass structures, pavements, structural members and high strength applications. One area where the long term performance of concrete containing high calcium fly ash has been suspect is in sulfate environments. Very little information is available on the long term performance and durability of Texas State Department of Highways and Public Transportation, TSDHPT, Type B or ASTM Class C (high calcium) fly ash in sulfate rich soils and groundwater or in marine environments.

Concrete in foundations, retaining walls, piers, coastal structures, chemical tanks, channels and pavements can be severely damaged by sulfate environments. To prevent any adverse chemical reaction which would reduce the service life of the concrete, a better understanding of how sulfates affect fly ash concrete is necessary. Under the sponsorship of the Texas State Department of Highways and Public Transportation, CTR Project 481 is investigating the long term durability of concrete containing fly ash in sulfate environments.

1.2 Review of Sulfate Attack Mechanism

Soluble sulfates in concrete react with calcium hydroxide and hydrated calcium aluminates to form gypsum and calcium sulfoaluminates. The resultant compounds are more insoluble than either the calcium hydroxide or calcium aluminates and also have a greater volume. It is the increased volume that causes the degradation of concrete commonly referred to as "sulfate attack."

The precise chemical mechanism of expansion is still not clearly understood but through a series of chemical reaction, ettringite is formed in concrete subjected to sulfates. The ettringite has a solid volume of about 2.5 times that of the initial hydration products [10]. What is clearly understood is that expansions occur in concrete during the sulfate attack process and the integrity of the concrete is damaged.

1.3 Sulfate Attack in Texas

The state of Texas has two primary areas where sulfate resistant concrete is needed. Scattered throughout west Texas are many areas of sulfate rich soils that are in contact with bridge piers, building foundations, and retaining structures. Also, along the coastal region from Louisiana to Mexico, there are many piers, marine facilities and seawalls that are exposed to sulfates in the seawater of the Gulf of Mexico. Concrete placed in these regions may exhibit very poor long term performance if it is not proportioned to resist moderate to severe sulfate exposures.

Texas fly ashes are typically high calcium fly ash collected from burning subbituminous coals from Wyoming and Montana or low calcium fly ash from Texas lignite coals. When these fly ashes are used in concrete exposed to moderate sulfate environments, the long term performance and serviceability of the concrete is **uncertain**.

1.4 Purpose of Study

This study on sulfate attack on concrete containing fly ash under CTR Project 481 is being conducted to assess the effect of fly ash on concrete exposed to sulfate environments. The resulting information will be used to propose guidelines for selecting materials and proportioning concrete containing fly ash in sulfate rich environments.

1.5 Summary of Experimental Program

The experimental program consists mainly of monitoring the expansions and changes in mass of concrete specimens soaking in 10% Na_2SO_4 . In order to better understand why some specimens expand and deteriorate and other do not, a series of quantitative tests are being performed on the concrete and fly ashes used as the study progresses. These quantitative tests include the chemical and physical analysis of the fly ashes and other concrete materials, X-Ray Diffraction on the fly ash to determine the crystalline phases that are present, petrographic analysis of the concrete specimens to determine the extent of deterioration, ion permeability of concrete and periodic physical inspection of the specimens.

At the conclusion of this study, the information collected from this research will be used to develop guidelines for selecting fly ash for use in concrete exposed to sulfate environments.

CHAPTER 2

REVIEW OF SULFATE ATTACK IN CONCRETE

2.1 Definitions

The following definitions of terms have been adopted in this report:

Calcium Silicate Hydrate: Any of the various reaction products of calcium silicate and water, which provide the strongest binding force between particles.

Ettringite: A mineral, high sulfate calcium sulfoaluminate; occurring in nature or formed by sulfate attack on mortar and concrete; the product of the principal expansion-producing reaction in expansive cements.

Fly Ash: Finely divided residue resulting from the combustion of ground or powdered coal and which is transported from the furnace by flue gases.

Free Lime: Unhydrated calcium oxide which has not combined with silica, alumina or ferrite during the formation of cement or fly ash.

Gypsum: A mineral having the composition; calcium sulfate dihydrate.

Hydrogarnet: Any of a group of crystalline phases containing hydrated silicates and a combination of iron, aluminum, or magnesium.

Monosulfoaluminate: Calcium sulfoaluminate hydrate.

Portland Cement: A hydraulic cement consisting of pulverized hydraulic calcium silicates and usually containing some form of calcium sulfate.

2.2 Factors Affecting the Sulfate Resistance of Concrete

2.2.1 Types of Sulfate Attack. Sulfates are found in several forms in concrete. These sulfates can be divided into two categories, soluble sulfates and sulfates in seawater. Sulfates in either category may contribute to sulfate attack, but the

concentrations and degree of degradation between the two constitutes the main distinction.

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 compounds of hydrated portland cement to form other compounds containing sulfate. The sulfate containing compounds often have a greater volume than the original portland cement hydrates.

Seawater contains soluble sulfates as described above, however seawater also contains many other salts which are not sulfate based. For reasons which are not yet clearly understood, the presence of ions from other salts slows the formation of expansive compounds containing sulfates, thereby moderating the volumetric changes associated with the formation of ettringite.

Magnesium sulfates are a special group among the soluble sulfates. The magnesium reacts with the hydroxide in the pore water solution to form magnesium hydroxide. As the hydroxide ions are depleted the calcium silicate hydrate binder begins to degrade causing a loss in strength along with the formation of expansive sulfate compounds. Over long periods of exposure, the magnesium hydroxide will form an impermeable layer and prevent further sulfate intrusion. This protective coating may or may not form before the concrete is deemed unserviceable.

2.2.2 Sources of Sulfate Attack. A major problem in providing protection against sulfate attack is determining where problem areas lie. Over 90 percent of the concrete placed in the United States is not subjected to sulfate environments[1]. But determining the location of the less than 10 percent of concrete which is subjected to sulfate attack is difficult. Frequently, sulfates occur in high concentrations in small localized zones. The sulfates may be in soil layers or in the groundwater surrounding a structure.

Although some areas can be clearly detected as sulfate environments the localized high concentrations often lead to unsuspected damages. Concrete in foundations, slabs on grade, canals and pipelines may suffer distress from sulfate rich groundwater or soils. Harboe [1] points out that there are three

choices for the designer in areas with localized sulfate environments:

1. very extensive soil and groundwater testing,
2. construct the entire project with sulfate resistant concrete, or
3. construct the entire project with moderately sulfate resistant concrete and replace isolated sections of concrete when sulfate damage 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 groundwater several years after the completion of the project. The use of Type V cement is very expensive and may not even be available. Lastly, repairs of underground structures can be both expensive and inconvenient.

Seawater contains relatively large amounts of magnesium and calcium sulfates. However the severity of sulfate attack from seawater is diminished by the presence of other salts in solution. Seawater is not considered as a severe condition but rather as a moderate sulfate environment. Coastal and offshore structures should be designed with moderate sulfate resistant concrete.

2.2.3 Concentrations of Sulfates. The relative degree of sulfate attack on concrete depends on the sulfate ion concentration in the water or soil. Table 2.1 indicates the level of sulfate attack that should be expected under different sulfate concentrations.

The United States Bureau of Reclamation (USBR) recommends Type I cement where the sulfate concentration is negligible, Type II or equal in positive environments and Type V or equal in severe and very severe sulfate environment. The highest concentrations reported by the USBR were in the White Wood Creek Bridge in South Dakota. Concentration of 9900 ppm were reported shortly before the bridge columns were replaced because of severe sulfate damage[1].

2.2.4 Exposure of Concrete. In addition to the concentration of sulfates, the nature of the concrete environment is important in determining the severity of the concrete degradation. Table 2.2 lists four major physical exposure conditions and the degradation associated with each.

Table 2.1 Attack on Concrete by Soils and Water Containing Sulfates. [2]

Severity of Attack	Water Soluble Sulfate in Soil, percent	Sulfate in Water, ppm
Negligible	0.00 to 0.10	0 to 150
Positive	0.10 to 0.20	150 to 1500
Severe	0.20 to 2.00	1500 to 10,000
V. Severe	2.00 or More	10,000 or More

Sulfate attack will not occur in areas of low humidity and dry 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. Areas where concrete is in low relative humidity but is occasionally exposed to sulfates in solution forms a white powder on the surface. Reading [3] reports this powdered sulfate salt is in anhydrous form and is confined to a harmless surface layer. Continual sources of sulfate ions, like that in a submerged environment, provide a constant concentration of sulfates to the concrete. The sulfate expansion reactions occur over a period of time until the concrete is no longer serviceable. The Wet-Dry-Wet 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 slowly evaporated from the concrete pore structure. The crystal formation may cause surface flaking and 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 by far the most commonly observed sulfate attack environments[13]. However water line damage is sometimes present in bridge piers and marine structures. Capillary action may draw sulfates into the concrete just above the water line. As the water evaporates, the

sulfate concentration continues to increase until the crystals progressively flake off the concrete cover.

Table 2.2 Effect of Concrete Exposure on Sulfate Attack Mechanism.

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

2.2.5 Type of Portland Cement. The type of portland cement used in concrete exposed to sulfate environments is certainly one of the primary considerations in determining the resistance of concrete to sulfate attack. Since sulfate expansion is often caused by the formation of alumina hydrates, the reduction of alumina in the cement leads to a more sulfate resistant portland cement.

The American Society of Testing and Materials (ASTM) classifies portland cement into five classes. The standard chemical and physical requirements of these classes are shown in Tables 2.3 and 2.4 respectively. ASTM Type III cement is a high early strength cement while ASTM Type IV cement is a low heat of hydration cement. Neither of these portland cements adds to the sulfate resistance of concrete and therefore will not be addressed herein.

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 the least expensive of the five classes of portland cement. The ASTM Standard Specification C150, places no direct limit on the amount of tricalcium aluminate, C_3A , in Type I cement. Typical C_3A contents for Type I cement

range between ten and thirteen percent. Cements with C_3A contents in this range will perform at an unacceptable level in moderate to severe sulfate environments. ASTM Type II cements are considered moderate exposure cements. The heat of hydration of Type II cements is reduced from that of a Type I cement and a maximum C_3A content of 8 percent is specified. The C_3A limitation provides the cement with considerable sulfate resistance. The ASTM Type V portland cement is the most sulfate resistant of the five classes. The Type V cement has a 5 percent C_3A content limit and has performed very well in all sulfate environments.

A sixth type of portland cement is available in some areas; the zero percent C_3A cement has demonstrated a high resistance to sulfate attack for reasons already discussed. Both the Type V and the zero percent C_3A cements are costly and are used only in the severest environments.

2.2.6 Permeability. There are four factors that have not yet been addressed but affect the sulfate resistance of concrete because these factors affect the permeability of concrete. The water to cement ratio, cementitious content, air content and the maturity of the concrete all contribute to the permeability of the concrete. Many researchers, including Reynolds [5], have found that concrete which is nearly 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 less permeable concrete. 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 benefits from increasing the cement content outweigh the potential detriment of additional expansive chemical compounds, provided that the concrete is properly proportioned, mixed, placed, consolidated and cured.

2.2.7 Pozzolans. There are several common types of pozzolans: natural pozzolans, silica fume, slag and fly ash. The later three are the by-products of industrial burning processes. Natural pozzolans are generally volcanic ashes and have been used for centuries to improve the durability of coastal structures. Silica

Table 2.3 Standard Chemical Requirements for Portland Cement
According to ASTM C150 [4].

Cement Type	I	II	III	IV	V
SiO ₂ (min %)	—	20	—	—	—
Al ₂ O ₃ (max %)	—	6.0	—	—	—
Fe ₂ O ₃ (max %)	—	6.0	—	6.5	—
MgO (max %)	6.0	6.0	6.0	6.0	6.0
SO ₃ (max %)					
C ₃ A ≤ 8%	3.0	3.0	3.5	2.3	2.3
C ₃ A > 8%	3.5	—	4.5	—	—
LOI (max %)	3.0	3.0	3.0	2.5	3.0
Insoluble Res.					
(max %)	0.75	0.75	0.75	0.75	0.75
C ₃ S (max %)	—	—	—	35	—
C ₂ S (min %)	—	—	—	40	—
C ₃ A (max %)	—	8	15	7	5
C ₄ AF + C ₂ F					
(max %)	—	—	—	—	25

See appendix A for chemical notation.

Additional Requirements are stated in ASTM C150 Table 1 and 1A.

Table 2.4 Standard Physical Requirements For Portland Cement According to ASTM C150 [4].

Cement Type	I	II	III	IV	V
<hr/>					
Air Content in Mortar (vol.)					
max %	12	12	12	12	12
min %	—	—	—	—	—
Fineness, Specific Surface (m ² /kg)					
Turbidimeter					
min	160	160	—	160	160
Air Permeability					
min	280	280	—	280	280
Compressive Strength (min. psi)					
1-Day	—	—	1800	—	—
3-Day	1800	1500	3500	—	1200
7-Day	2800	2500	—	1000	2200
28-Day	—	—	—	2500	3000
Time of Setting					
Gilmore Test					
Initial Set					
(> minutes)	60	60	60	60	60
Final Set					
(< hours)	10	10	10	10	10
Vicat Test					
Initial Set					
(> minutes)	45	45	45	45	45
Final Set					
(< hours)	8	8	8	8	8

Additional Requirements are stated in ASTM C150 Table 2 and 2A.

fume has been found to improve the sulfate resistance of concrete by increasing the silica to calcium ratio, depleting the calcium hydroxide and decreasing the permeability of hardened concrete[14]. Blast furnace slag has a high alumina composition and will not improve the sulfate resistance of concrete. The effect of fly ash will be discussed in the next section.

2.3 Chemical and Mineralogical Characteristics of Fly Ash

The subject of this study provides for an in depth look at the characteristics of fly ash. Of specific importance is how these characteristics relate to the sulfate resistance of concrete. Fly ash consists of finely divided particles which are formed at furnace temperatures of nearly 2500°F and carried out of the furnace by flue gases. The ash particles solidify into spherical particles and are collected by electrostatic or mechanical precipitators.

2.3.1 Chemical Composition. The chemical composition of most fly ashes consists largely of metallic oxides. Crystalline phases account for between 11 to 17 percent of the fly ash while glassy phases consist of between 71 to 88 percent of the fly ash composition[12,15]. The actual chemical composition of the fly ash depends on both the furnace conditions and the source of the pulverized coal. Since most modern furnaces burn the coal efficiently, the coal source is of prime importance.

There are four major types of coal: anthracite, bituminous, subbituminous and lignite. Anthracite and bituminous coals yield an ash which is typically rich in silica and low in calcium oxide. The metal oxides in these fly ashes are in excess of 70 percent of the total composition. Subbituminous coal yields fly ashes which are often rich in calcium oxide and have metal oxides between 50 to 70 percent of the total composition. Lignite coal is the least energy efficient of the coals and produces a fly ash with a broad range of chemical compositions. It has been assumed in the past that lignitic based fly ash was similar to subbituminous coal derived fly ash. This has been found to be not always correct. While lignites from the northern plains of the United States produce high calcium oxide fly ash the lignite coal in Texas and the southwest have produced low calcium fly ashes with high metal oxides much the same as the eastern bituminous coals.

Tables 2.5a and b shows the typical composition of fly ash from different sources and the ASTM and TSDHPT criteria for classifying the fly ash. The chemical composition of fly ash is similar to that of burnt clay, high in alumina and iron oxides[9]. The silica and alumina seem to have the greatest influence on the pozzolanic activity whereas the calcium oxide content contributes to the cementitious properties of the fly ash.

The sulfate resistance of concrete containing fly ash has been hypothesized by Dunstan [2] to be related to the calcium oxide content of the fly ash over 5 percent and inversely related to the iron oxide content of the fly ash. The 5 percent is used as an average for the crystalline lime content in fly ash which is believed not to participate in the sulfate attack problem. Other investigators believe the silica and alumina contents also contribute to the sulfate resistance of the concrete containing fly ash [6,7,8]. The other chemical compound which contributes to the sulfate resistance of concrete is the sulfate content of the fly ash. The sulfate is present in fly ash as anhydrite, gypsum or in glass and is measured as sulfur trioxide, SO_3 . When the SO_3 content is high, the mortar is effectively supersulfated and hardens in an expanded form[6]. The expanded form of the concrete is protected from deterioration due to sulfate expansion.

2.3.2 Physical Characteristics of Fly Ash. There are two physical properties of fly ash which need to be addressed briefly. Fineness and pozzolanic activity both contribute to the effect of fly ash on concrete. The pozzolanic activity has no direct effect on the sulfate resistance of concrete but is a measure of the materials ability to react with calcium hydroxide to form compounds which have cementing properties. The fineness of fly ash has long been recognized as an important factor in the strength gain of fly ash - portland cement concrete. Although fly ash fineness is difficult to measure consistently, finer fly ash reacts more thoroughly and reduces the permeability of the mortar matrix within the concrete.

2.3.3 Mineralogical Characteristics of Fly Ash. Fly ash is composed of nearly 15 percent crystalline material. The

Table 2.5a Typical Chemical Composition of Fly Ashes

	Kentucky Bituminous	Wyoming Subbitu- minous	Texas Lignite
SiO ₂	54	33	50
Al ₂ O ₃	26	23	20
Fe ₂ O ₃	11	5	6
Total Metal Oxides	91	61	76
CaO	1.5	27	9
MgO	1.3	5.3	4.1
SO ₃	1.1	2.5	0.6
LOI	4.1	0.3	0.4
Other	< 1.0	< 4.0	< 10

Table 2.5b Specifications for Chemical Composition of Fly Ashes.

%	ASTM CLASS C	ASTM CLASS F	TSDHPT TYPE B	TSDHPT TYPE A
SiO ₂	—	—	—	—
Al ₂ O ₃	—	—	—	—
Fe ₂ O ₃	—	—	—	—
Metal Oxides	>50	>70	>50	>65
CaO	—	—	—	—
MgO	—	—	—	—
SO ₃	<5.0	<5.0	<5.0	<5.0
LOI	<6.0	<6.0	<3.0	<3.0
Other	—	—	—	—

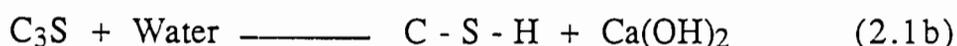
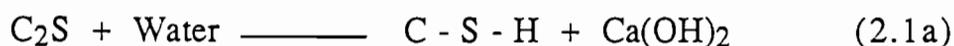
See ASTM C618 for supplemental requirement.

remaining material in fly ash is glassy in nature. The crystalline material can be readily identified by X-Ray diffraction analysis and quantified through the use of known standards. Table 2.6 lists the most common crystalline phases found in fly ash and their corresponding chemical composition[15].

The mineralogical composition of fly ash was determined by Watt and Thorne [9] and has been related to the sulfate attack mechanism by Mehta [7]. ASTM Class F fly ashes from bituminous sources commonly contain four crystalline phases: quartz, mullite, hematite and magnetite. ASTM Class C fly ashes from subbituminous sources typically contain the same four phases plus several additional crystalline materials such as: anhydrite, tricalcium aluminate (C₃A), crystalline lime, merwinite, melilite, periclase, and dicalcium silicate (C₂S). With the exception of anhydrite, lime, C₃A and C₂S, these crystalline materials are non-hydraulic.

The silica, alumina and iron oxide in the glassy spheres of the fly ash react with lime to form hydrate compounds which contribute to the long term strength of the concrete. This reaction is referred to as a pozzolaanic reaction. The C₃A crystalline phase of the fly ash may be a major mineralogical influence in the sulfate attack mechanism. Several research studies are now under way to better understand the relationship between fly ash composition and sulfate resistance and to quantify the results to predict the effect of fly ash on the sulfate resistance of concrete containing fly ash.

2.3.4 Chemistry of Cement. The chemical reactions of both portland cement and fly ash are very complex. The chemical shorthand notation used in this section is that commonly used in cement chemistry and is defined in appendix A, Table A-1. The first is the reaction that takes place in portland cement to form the binding characteristics of concrete. Equations 2.1a and b express the formation of calcium silicate hydrates from either tricalcium silicate or dicalcium silicate and water. Calcium silicate hydrates, C-S-H, are the compounds that provide the binding qualities of portland cement concrete.

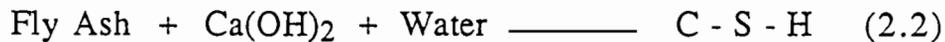


Calcium hydroxide is produced as a by-product of this reaction.

Table 2.6 Common Crystalline Phases in Fly Ash.

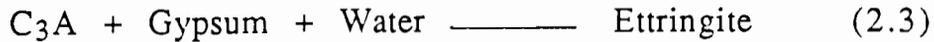
<u>Compound</u>	<u>Formula</u>	<u>Abbreviation</u>
Anhydrite:	CaSO ₄	CaSO ₄
Tricalcium Aluminate:	Ca ₃ Al ₂ O ₆	C ₃ A
Lime:	CaO	CaO
Merwinite:	Ca ₃ Mg(SiO ₄) ₂	Mer
Melilite:	Ca ₂ (Mg,Al)(Al,Si)O ₇	Mel
Periclase:	MgO	MgO
Quartz:	SiO ₂	SiO ₂
Magnetite:	(Mg,Fe)(Fe,Al) ₂ O ₄	Mag
"Ferrite Spinel"		Sp
Mullite:	Al ₆ Si ₂ O ₁₃	Mul
Dicalcium Silicate:	Ca ₂ SiO ₄	C ₂ S
Hematite:	Fe ₂ O ₃	Hem
Alkali Sulfate:	(Na,K) ₂ SO ₄	(Na,K) ₂ SO ₄
Tetracalcium Aluminate Sulfate	4CaO•3Al ₂ O ₃ •SO ₄	C ₄ A ₃ SO ₄

The calcium hydroxide in the cement matrix will react in the presence of water with the silica glassy phases of fly ash to form more calcium silicate hydrates as expressed in equation 2.2.



The reactions in equations 2.1a and b are referred to as "cementitious", whereas that in equation 2.2 is a "pozzolanic" reaction.

The second series of reactions involves tricalcium aluminate, C₃A. Portland cement contains gypsum, CaSO₄•2H₂O, which has been added to control setting in hydrating portland cement. As water is added to portland cement, the reaction expressed in equation 2.3 takes place.



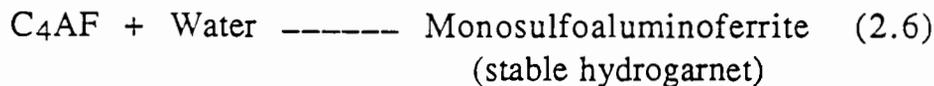
This reaction will continue until the gypsum, the source of sulfate, is depleted. The ettringite, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$, becomes an unstable compound in the diminished presence of the sulfate ions in solution and will react with the remaining C_3A to form monosulfoaluminate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot12\text{H}_2\text{O}$, a stable calcium sulfoaluminate, as shown in equation 2.4.



After the ettringite is converted back to monosulfoaluminate there may remain unreacted C_3A in the paste. The remaining C_3A will hydrate to form a calcium aluminate hydrate, C-A-H, as shown in equation 2.5.

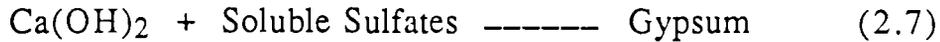


The third series of reaction is the hydration process of tetracalcium aluminoferrite, C_4AF , in portland cement. C_4AF reacts much in the same manner as C_3A , as expressed in equation 2.6, and results in the formation of a crystalline phase called a hydrogarnet, $\text{C}_6\text{AFH}_{12}$. This compound is stable regardless of whether sulfate ions are present in the solution or not.



Upon the completion of this series of reactions, the remaining C_4AF will hydrate to form calcium aluminate hydrates, C-A-H, and calcium ferrite hydrates, C-F-H. These hydrates are similar to those formed in equation 2.5.

2.3.5 Sulfate Expansion Reactions. The degradation of concrete under sulfate attack is due to the expansion of hydrated compounds in the hardened concrete. As the concrete is exposed to sulfates in solution, the available calcium hydroxide in the mortar will react with the sulfate to form gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, as shown in equation 2.7.



The gypsum will react with the monosulfoaluminates to reform ettringite as expressed in equation 2.8.



In addition, the C-A-H will react with the gypsum to form ettringite, as shown in equation 2.9.

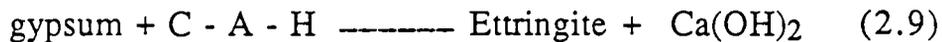


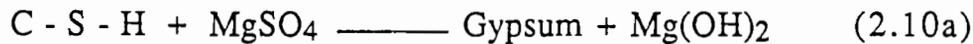
Table 2.7 lists the compound associated with sulfate expansion and their associated molecular volumes[10]. From this table it can be seen that there is a significant increase in solid volume associated with the formation of ettringite from either monosulfoaluminate or C-A-H. The total solid volume expansion during the sulfate attack mechanism has been conservatively estimated as 2.5 times [10] and may be as high as 7 times the volume of the original hydrates in hardened concrete.

Magnesium sulfate has a broader effect on concrete than other forms of soluble sulfates. In addition to causing the formation of gypsum and ettringite as expressed above, the magnesium sulfates will decompose the C-S-H binder in the cement paste, reducing the strength of the concrete.

Equation 2.10a and b express the resulting reaction. This reaction may lead to a self inhibiting condition; in that the Mg(OH)_2 forms a coating that is impermeable and may prevent further sulfate intrusion.

Table 2.7 Calcium Hydrate Compounds.

Compound	Chemical Formula	Molecular Volume (cc)
Calcium Hydroxide	$\text{Ca}(\text{OH})_2$	33.2
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	74.2
Monosulfoaluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$	313
C - A - H	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 19\text{H}_2\text{O}$	369
Ettringite	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$	715



The reaction described above proceed as soon as sulfates s are available in solution, however the expansion depends upon crystal growth which is time dependent. This accounts for the lag between sulfate exposure and measurable degradation.

2.3.6 Effects of Fly Ash Composition on Sulfate Resistance.
The chemical and mineralogical composition of fly ash has an effect on the sulfate resistance of concrete containing fly ash. Early uses of fly ash showed improved sulfate resistance with the use of fly ash and natural pozzolans. These fly ashes were ASTM Class F fly ashes with low calcium oxide contents. Many of the fly ashes produced from western coals are ASTM Class C fly ash with high calcium oxide contents. Dunstan [2] found that the use of high calcium fly ash may lead to reduced sulfate resistance of concrete. He found that fly ash in the mullite field of the equilibrium phase diagram, shown in Figure 2.1, are not reactive

with sulfates in solution and therefore do not form ettringite when exposed to sulfates. The mullite rich fly ashes are characterized by low calcium contents; bringing about the conclusion that a low calcium content in fly ash is beneficial to sulfate resistance.

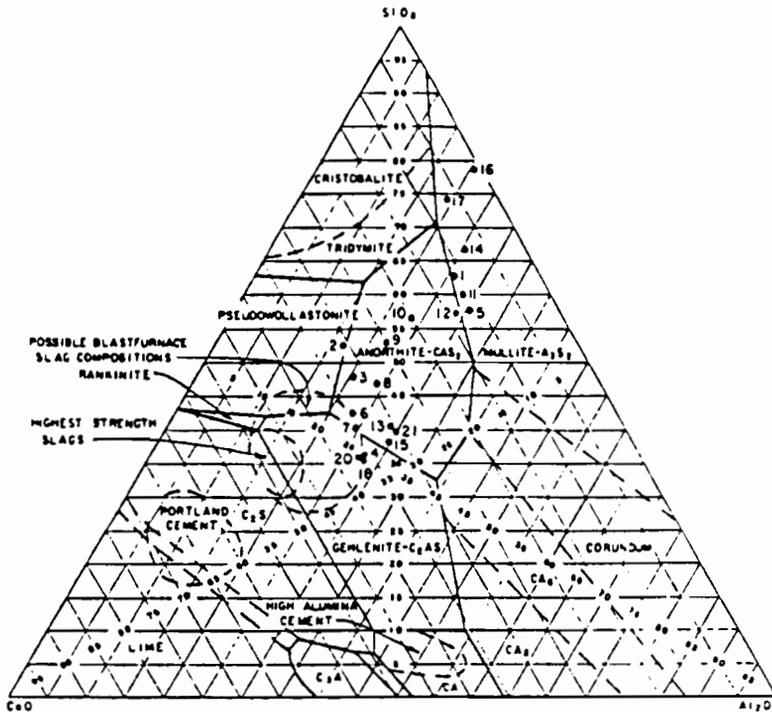


Fig. 2.1 Equilibrium Phase Diagram.

Dunstan also suggests that, based on Kalousek's work [11], iron rich ettringite crystals grow very slowly or not at all in the presence of sulfate ions in solution. From this he associates the presence of iron oxide in fly ash as beneficial to the sulfate resistance of concrete.

Calcium silicate hydrates formed through pozzolanic reactions have a lower calcium-silica ratio than those formed from the cementitious reaction of portland cement. This reduction allows magnesium, alkalis, sulfates and alumina to occupy a position in the lattice of the calcium silicate hydrate, thereby making them unavailable to expansive compounds [12].

The use of bulk chemical analysis is not sufficient to classify fly ash for use in predicting their effect on concrete subjected to sulfate exposures. Many of the crystalline phases in fly ash are unavailable to either the pozzolanic reaction or the sulfate

reactions. In some cases C_3A in fly ash may promote sulfate attack while SO_3 may act to supersulfate the mixture, making it more resistant to sulfate attack.

In addition, Lea[10] points out that low calcium pozzolans use the calcium hydroxide from the portland cement hydration, reducing the amount of calcium hydroxide available for the formation of gypsum. The complete effect of fly ash on the sulfate resistance of concretes is not fully understood at this time, however the dominant factors are being identified and analyzed.

CHAPTER 3

SULFATE RESISTANCE PREDICTION METHODS

3.1 Methods for Evaluating Fly Ash for Sulfate Attack.

There have been several methods developed in recent years to evaluate the performance of fly ash in concrete subjected to sulfate environments. None of these methods have been accurate for predicting the behavior of a broad range of portland cement and fly ash combinations. Each of the methods discussed in this section have merit in their conception but fail to encompass all the factors involved, some of which are still not clearly understood.

3.1.1 The R Value. This simple factor was proposed by Dunstan of the United States Bureau of Reclamation for use in their specifications[2]. He later proposed this factor for broader use. The R factor is based on the calcium-silicate-aluminate equilibrium phase diagram. As discussed in the previous chapter, Dunstan found the total calcium oxide and iron oxide contents to be important factors in the expansion of concrete containing fly ash in sulfate solution. His proposed factor, equation 3.1, has been the subject of controversy because it disallows almost all ASTM Class C fly ashes by emphasizing calcium oxide content and not taking into account factors such as the SO₃ content, mineralogical considerations, replacement levels of fly ash, and portland cement properties.

$$R = \frac{\text{CaO (\%)} - 5}{\text{Fe}_2\text{O}_3 (\%)} \quad (3.1)$$

A later paper by Dunstan on sulfate resistance [16] addressed the amount of fly ash used in the form of another factor called the R_v factor but this concept has not taken hold in the technical community because of lack of research evidence.

3.1.2 Oxide Durability Factor. The OD factor was proposed by Hartmann and Mangotich of the Western Institute of Technology [8]. This factor, expressed in equation 3.2, uses the chemical properties of both the portland cement and the fly ash to calculate

the resistance of concrete to sulfate attack. This factor also incorporates the level of replacement by weighting the chemical composition according to its replacement level.

$$\text{OD Factor} = \frac{\text{Total CaO (\%)} * \text{Free Lime (\%)}}{\text{SiO}_2 (\%) + \text{Al}_2\text{O}_3 (\%) + \text{Fe}_2\text{O}_3 (\%)} \quad (3.2)$$

Hartmann and Mangotich found a relationship between the free lime content of the cementitious material and the sulfate resistance of concrete containing fly ash. In addition, they included all the metallic oxides in the prediction formula, but they did not consider the importance of the crystalline phases of the fly ash.

3.1.3 MinChem R Factor. This is the newest of the rating systems and it is still under development by Manz at the University of North Dakota [6]. The theory behind this factor is credited to P. K. Mehta. This more complicated factor expressed in equation 3.3, uses both the mineralogical and chemical characteristics of a fly ash to determine its resistance to sulfate attack.

$$\text{MinChem R Factor} = f(\text{SiO}_2, \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{CaO}, \text{SO}_3, \text{Lime}, \text{Anhydrite}, \text{C}_2\text{S}, \text{C}_3\text{A}, \text{Hematite}, \text{Mullite}, \text{Spinel Ferrite}) \quad (3.3)$$

The proposed MinChem R factor has two components. The first component, the "calcium aluminate potential", is a function of the metallic oxides, total CaO content and the crystalline phases: quartz, mullite, ferrite spinel, hematite, melilite, merwinite, lime and dicalcium silicate found in fly ash. The second component of the equation, the "calcium sulfate equivalent", is a function of the anhydrite and SO₃ contents of the fly ash.

3.2 Finding the True Measure of Sulfate Resistance

The development of equations such as the R factor, the OD factor and the MinChem R factor has not yet produced a meaningful, reliable means for predicting the performance of concrete containing fly ash in sulfate environments. The small pool of available information on the performance of high calcium fly ash in concrete is the primary reason for the slow progress.

The research completed up to now has made substantial contributions in isolating several important variables that either contribute to or detract from the sulfate resistance of concrete containing fly ash. These variables include certain physical concrete properties such as permeability, strength and maturity of the concrete at the time it is exposed to the sulfate environment. Other variables that are independent of the exposure and physical condition of the concrete include the chemical, physical and mineralogical characteristics of the cementitious and pozzolanic materials.

The physical characteristics of the fly ash and cement are important to the extent that they affect the permeability of the concrete. However the effects of the chemical and mineralogical composition of these materials are not clearly understood. Yet the prediction equations are all based on these properties.

The sulfate-resistance prediction equations developed up to now do not provide an adequate assessment of the concrete. In some cases where good performance in the field is observed the equations predict failure. In other cases, poor performance results from fly ashes which are predicted to yield sulfate resistant concrete. For this reason TSDHPT Project 481 is investigating a broad spectrum of prediction criteria for the sulfate resistance of concrete containing fly ash.

The first component of the binder that is widely recognized as a detrimental factor in the sulfate resistance of fly ash concrete is calcium. Calcium hydroxide in the hardened concrete reacts with sulfates to form gypsum and start the expansive series of reactions. Free lime in fly ash is thought by some to be of some significance in the sulfate resistance equations. However, hard-burned crystalline lime is very dense and reacts very slowly with moisture whereas free lime in portland cement and fly ash is consumed in the early hydration of portland cement. The R factor does not consider free lime, but rather uses the total CaO content of the fly ash as a detriment to sulfate resistance. The OD factor considers the combined total CaO content and the free lime content over 1.0 percent of both the cement and fly ash as detrimental to the sulfate resistance. The MinChem R factor subtracts out the crystalline free lime from the total CaO content of the fly ash and considers the remainder as detrimental to the sulfate resistance of concrete containing fly ash.

Calcium hydroxide is present in most hardened concrete. It is necessary for the formation of C-S-H through the pozzolanic reactions of fly ash. The amount of free lime in fly ash, as measured by the Franke Method, is small compared to the total CaO content of the combined portland cement and fly ash. The best estimate of total available calcium may be the combined CaO of the portland cement and fly ash minus any hard-burned lime present in either.

The second component of the chemical analysis to be considered is the alumina content. The R factor does not include the Al_2O_3 content in any form, while the OD factor and the MinChem R factor use the Al_2O_3 content in conflicting terms. The OD factor considers the Al_2O_3 content as compounds contributing to sulfate resistance. Whereas the MinChem R factor eliminates stable crystalline forms of alumina in fly ash and considers the remainder of the Al_2O_3 content as detrimental. The preliminary results from Project 481 show that C_3A in fly ash is detrimental to the sulfate resistance of concrete containing fly ash. The research findings of this study agree with other studies which have found other alumina bearing minerals in fly ash such as mullite and melilite do not contribute to the sulfate attack problem.

The third oxide in fly ash to consider is iron oxide, Fe_2O_3 . The iron in portland cement is largely combined in tetracalcium aluminoferrite, C_4AF , which in the presence of water, hydrates to very stable hydrogarnets. The iron contained in fly ashes is not in the C_4AF crystalline form, but rather in a variety of compounds including hematite and magnetite (ferrite spinel). The R factor and the OD factor consider the Fe_2O_3 content as beneficial to the sulfate resistance of concrete containing fly ash. However the MinChem R factor calculates the active Fe_2O_3 content by subtracting out the stable crystalline iron compounds and considers them detrimental to the performance of concrete containing fly ash in sulfate environments.. Except for very large contents, iron oxides have shown to be beneficial to the sulfate resistance of concrete containing fly ash.

The fourth chemical compound is silica, SiO_2 . Silica is the main building block of the binder in concrete. The R factor does not consider silica as a variable participating in the sulfate resistance of fly ash concrete. Both the OD factor and the MinChem R factor consider silica in fly ash as beneficial to the

performance of concrete in sulfate environments. Reactive silica is likely to consume calcium and moisture to form a stronger, more dense binder, thereby contributing to sulfate resistance.

The last chemical compound contributing to the sulfate resistance of concrete containing fly ash is sulfates measured as sulfur trioxide, SO_3 . Sulfates react in the fresh concrete to form ettringite while the concrete is still plastic, which then digress to monosulfoaluminates as the sulfate is expended. High SO_3 contents effectively supersulfate the portland cement and fly ash paste, resulting in a sulfate resistant concrete. Neither the R factor or the OD factor account for the effect of supersulfating. The MinChem R factor considers the SO_3 content in combination with crystalline anhydrite, CaSO_4 , as beneficial agents in sulfate resistance of concrete. The effect of sulfates in the cement and the fly ash are an important factor in the resistance of concrete containing fly ash.

The solution for predicting the potential sulfate resistance of concrete from laboratory analysis of the binder compounds lies in some combination of the three factors already proposed and possibly several undiscovered components. The solution should make use of bulk chemical analysis, as the R factor proposed, the combined chemical characteristics of the portland cement and the fly ash, as the OD factor proposes, and the mineralogical composition of the fly ash, as proposed by the MinChem R factor. Project 481 will investigate the combination of these three concepts to predict the sulfate resistance of concrete containing fly ash.

CHAPTER 4

MATERIALS AND TESTING PROCEDURES

4.1 Introduction.

The materials used in this study are commercially available in Texas and are described in this chapter. The testing procedures used in this experimental program conform to the American Society of Testing and Materials, ASTM, the Texas State Department of Highways and Public Transportation, TSDHPT, or the American Association of State Highway Transportation Officials, AASHTO, standards and testing procedures as noted in this chapter.

4.2 Material Properties.

The chemical and physical properties of the materials used in this study are listed in Appendix B. The materials were obtained directly from the manufacturers at the request of the investigators and were tested by the TSDHPT Materials and Testing Division when chemical and physical characteristics were required. The materials are those typically used in the production of concrete containing fly ash in the State of Texas or elsewhere in the United States.

4.2.1 Portland Cements. Four different portland cements were used in proportioning the concrete mixtures in this study. The properties of each cement were tested according to ASTM C114, "Chemical Analysis of Hydraulic Cements" to determine the chemical characteristics of the portland cements. The test results are presented in Table B-1 of Appendix B. The Type II and V cements were produced according to ASTM C150-86, "Standard Specification for Portland Cement." The Type V and a zero percent C₃A specialty cement were also used as control cements. A second Type II cement containing zero percent C₃A was used in combination with several fly ashes.

The bulk specific gravity of the portland cements used for mix design purposes was 3.10 as recommended by TSDHPT Construction Bulletin C-11.

4.2.2 Aggregates. The coarse aggregate used to proportion concrete in this study was TSDHPT Grade 5, 5/8 inch nominal maximum size, crushed limestone from a source near Austin, Texas. The coarse aggregate had specific gravity at SSD of 2.50 and an absorption of 3.50 percent.

The fine aggregate was a Colorado River natural siliceous sand from Austin, Texas. The fine aggregate had a bulk specific gravity at SSD of 2.64 and an absorption of 1.19 percent. The sand had a fineness modulus of 2.78.

4.2.3 Fly Ash. Fourteen different fly ashes were used in this program. The fly ashes were produced in Georgia, Oklahoma, Louisiana, Utah, and Texas from bituminous, subbituminous and lignite coal sources. The chemical and physical characteristics of the fly ashes are given in Table B-2 of Appendix B. The crystalline phase composition of the fly ashes are listed in Table B-3. All the fly ashes met the standards of ASTM C618-85, "Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan For Use as a Mineral Admixture in Portland Cement Concrete", and with the exception of fly ash U, TSDHPT "Departmental Materials Specification: D-9-8900 Fly Ash". Fly ash U had an LOI greater than 3 percent.

4.2.4 Water and Admixtures. The water utilized throughout this experimental program was potable tap water approved by the Texas State Health Department in compliance with TSDHPT Standard Specification Item 421.2.

Two liquid admixtures were used in this study. Where entrained air is indicated the air entraining admixture was a neutralized vinsol resin conforming to ASTM C260-86. Low slump mixtures were mixed with the use of a water reducing-retarding chemical admixture meeting the requirements of ASTM C494-86. The admixtures were used in compliance with TSDHPT Specification Item 437.

4.3 Concrete Mix Proportioning.

The fundamental concrete mix proportions used in this study were designed according to the TSDHPT 1982 Standard Specification for Construction of Highways, Streets and Bridges, Item 360.

4.3.1 Mixture Designs. There were two basic mixture designs used in this research. The first series was designed to have a slump between 6 and 7 inches. This mixture design contained no admixtures and the water content was adjusted to yield the required slump. The second series of mixtures was designed to have a slump between 2 and 3 inches. This series of mixes contained 4 ounces of water reducing-retarding admixture per 100 weight of portland cement.

Both mix designs had a cement factor of 5.5 sacks per cubic yard and a coarse aggregate factor of 0.77. Fly ash was used as a volumetric replacement for portland cement at replacement levels of 0, 25, 35, and 45 percent. A list of the individual mixture designs is given in Table B-4 of Appendix B.

4.3.2 Mixing Procedure. Concrete mixing was performed under laboratory conditions in a 3 cu. ft. electric revolving drum tilting mixer according to ASTM C192-81, "Standard Method of Making and Curing Concrete Test Specimens in the Laboratory". All concrete batches exceeded 1/3 of the capacity of the mixer and the laboratory temperature was **in the range of 70 to 80° F.**

The aggregates were stored in outside covered bins until batching was ready to begin. The moisture content of the aggregates was measured prior to batching by drying in a microwave oven. The aggregates were placed in the oven for twenty five minutes or until the 300 gram sample maintained the same weight, to the .01 gram, for two consecutive five minute readings. Portland cement, fly ash and admixtures were stored at laboratory temperatures **in the range of 70 to 80° F.**

Concrete was placed into four different cylindrical forms. Standard 6 x 12 inch and 3 x 6 inch cylindrical specimens were cast in plastic disposable molds for compressive strength testing, and 4 x 8 inch cylindrical specimens were cast for permeability testing. The fourth type of specimen was a 3 x 6 inch cylinder with a 1/4 x 13/16 inch stainless steel gage stud at each end. These specimens were cast to measure expansion and changes in specimen mass due to exposure testing.

4.3.3 Curing Specimens. The concrete cylindrical specimens were placed in plastic forms and covered with air tight covers.

The specimens were kept in the sealed molds for 48 ± 1 hours at laboratory temperatures to prevent scoring of the smaller specimens from the demolding tools. Upon demolding, the specimens were placed in a lime bath at $73 \pm 2^\circ\text{F}$ until testing, according to ASTM C511-85, "Moist Cabinets, Moist Rooms and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes".

4.4 Testing Procedures.

4.4.1 Fresh Concrete Testing. The fresh concrete was tested for slump according to TSDHPT procedure TEX 415-A and ASTM C143-78, "Standard Test Method for Slump of Portland Cement Concrete". One of every five mixes containing no entrained air and all air entrained concrete were tested for air content according to ASTM C173-78, "Standard Test Method for Air Content of Freshly Mixed Concrete by the Volumetric Method".

4.4.2 Hardened Concrete Testing. Tests were performed on the hardened concrete to determine the effect of sulfates on the concrete, to monitor and verify the strength of the concrete specimens and to measure to permeability of the concrete.

4.4.2.1 Compressive Strength. Two 6 x 12 inch and two 3 x 6 inch cylindrical specimens were tested to determine the 28-day strength of the concrete from each mix. Intermediate compressive strength tests of the concrete were determined by testing 3 x 6 inch cylindrical specimens between 3 and 28 days after casting. The compressive strength tests were performed according to ASTM C39-86, "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens", with the exception that solid neoprene rubber caps inside steel retaining rings were used to cap the cylinders. The load during testing was applied at a rate of approximately 40 psi per second using a Forney 600-kip compression testing machine calibrated in accordance with ASTM E-79, "Standard Method of Load Verification of Test Machines".

4.4.2.2 Sulfate Testing. Four 3 x 6 inch concrete specimens from each mix had stainless steel gage studs embedded on either end for the purpose of monitoring length changes over time. These four specimens and one unengaged 3 x 6 inch cylindrical specimen were placed in a 10 percent sodium sulfate solution

when the concrete reached a nominal strength of 3500 psi or at 28 days after casting, whichever was reached first.

The sodium sulfate solution was monitored using an Altex Digital pH Meter, Model 3500, with an Orion combination electrode. The solution was flushed from the tanks when the pH rose above 10.50 and a fresh sodium sulfate solution was added to the tank. Water was periodically added to a constant level to replace that lost from evaporation. Covers were later placed on the tanks to prevent evaporation during longer term storage.

Specimens soaking in the sodium sulfate solution were measured for expansion, weighed and inspected for damage approximately every 30 days. Expansions were measured using a Humbolt Length Comparitor with a 6 ⁵/₈ inch gage length and a Mitutoyo Digimatic Indicator with a 0.0001 inch accuracy and minimum hold function. The instrument was calibrated between each set of specimens. If the instrument was found to be off by more than 0.0001 from the previous zero reading the measurements were repeated. After the length measurement, the specimen was weighted to the nearest 0.1 gram using a Mettler PE 3600 digital balance, visually inspected for cracking and spalling and returned to the sulfate solution.

4.4.2.3 Permeability. Specimens cast for permeability testing will be tested according to AASHTO T277-83, "Standard Method of Test for Rapid Determination of the Chloride Permeability of Concrete". This test will be reported on in a later publication.

CHAPTER 5

EXPERIMENTAL PROGRAM

5.1 Introduction.

The experimental testing program described herein is part of a broader study on the durability and performance of concrete containing fly ash. This portion of the study is concentrated on the effects of fly ash on the sulfate resistance of concrete containing fly ash. This program was conceived to view the problem of sulfate attack from several different angles, making use of past and present research performed at other laboratories to bring together a better understanding of the sulfate attack problem.

As described in the last chapter, three methods of evaluation for sulfate damage were used. The first was to measure the expansion over time of 3 x 6 in. concrete cylinders subjected to a 10 percent sodium sulfate solution. The second method was to measure mass changes in the concrete cylinders. The third method of evaluation was a visual inspection for cracking and spalling of the concrete specimens.

In addition to the sulfate attack evaluation, a material analysis was performed on the constituents of the concrete to correlate the properties of portland cement and fly ash to the sulfate resistance of concrete. This evaluation included bulk chemical and physical analysis of both the cement and fly ash and crystalline phase identification of the fly ash used in this program. Further material testing to determine the crystalline phases of the hydration products and the permeability of the concrete will be conducted in the next stage of the research.

5.2 Testing Parameters.

The testing parameters of Phase I reported herein, were chosen for the purpose of confirming the research of others and studying areas which have not been fully investigated. The mixing series shown in Figure 5.1 are those completed in the first portion of this study. As a result of the concrete casting series described, 525 3 x 6 in. concrete specimens were cast and are

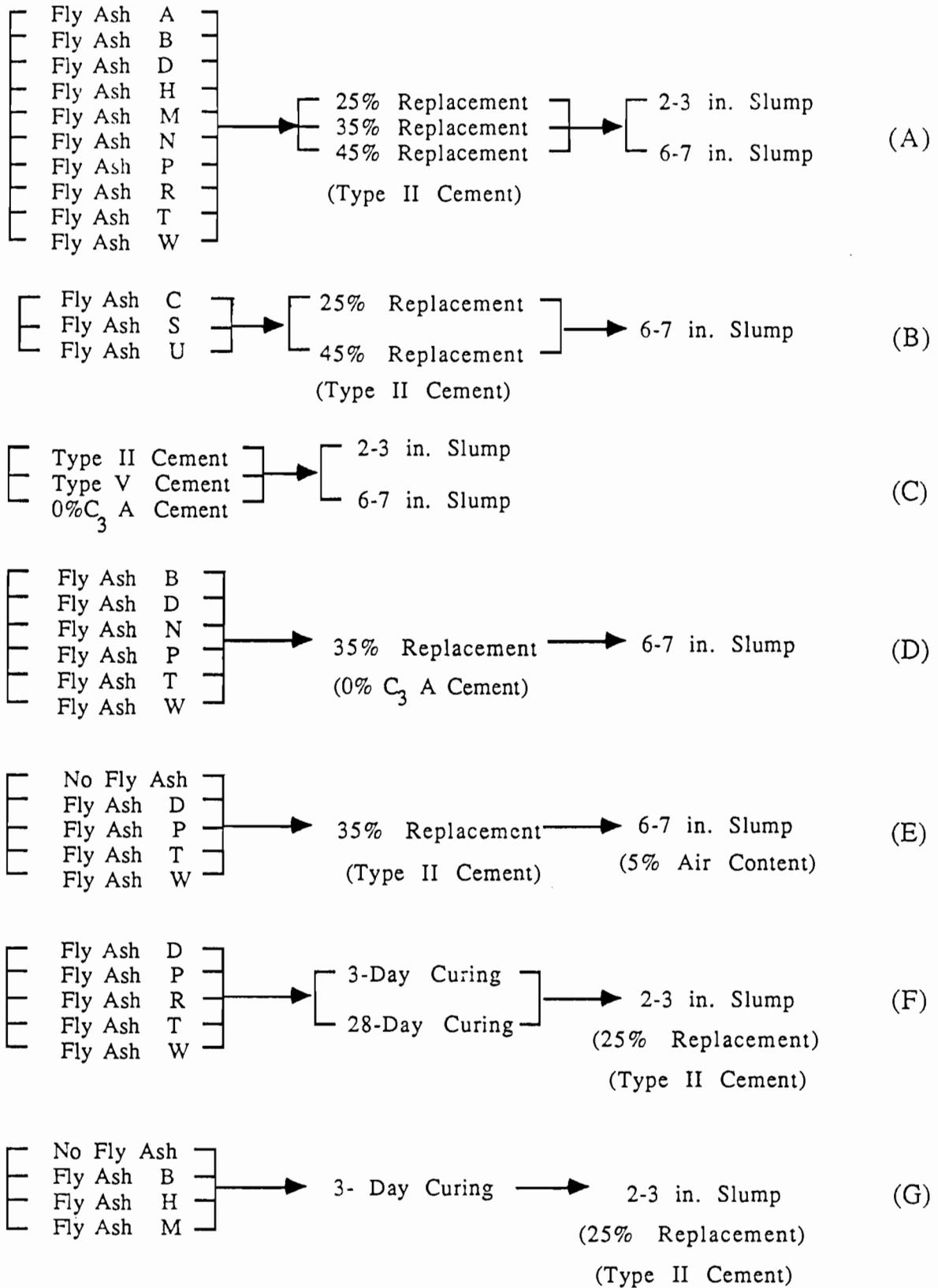


Fig. 5.1 Sulfate Attack Test Series.

currently soaking in a 10 percent sodium sulfate solution. These specimens are removed and evaluated every 30 days for deterioration and returned to the sulfate solution.

5.2.1 Fly Ashes and Cements. The thirteen fly ashes used in test series (A) and (B) of Figure 5.1 were selected to represent a wide variety of material characteristics present in fly ashes. A fourteenth fly ash, Fly Ash F, has been added to these series and was used as a 35 percent replacement, by volume. Of these fourteen fly ashes, six are, by chemical requirements alone, ASTM Class F or TSDHPT Type A (low calcium) fly ashes. Three of these fly ashes are from lignite coal sources and three are from bituminous coal sources. The eight other fly ashes are, by chemical content, ASTM Class C or TSDHPT Type B (high calcium) fly ashes and all eight are from subbituminous sources. The fly ash characteristics are given in Table B-2 in Appendix B.

Test series (A) and (B) were also designed to study the effects of the fly ash content on the sulfate resistance of concrete. A volumetric replacement scheme was chosen so as to not increase the volume of binder material in the mortar matrix. ASTM Type II cement was used both as a control mix series (C), and as the cement in the series (A) and (B) mixes. Type II portland cement is the cement most often used in areas where moderate sulfate exposure is anticipated and it is widely available in central Texas.

Test series (C) was the control cement series. A Type II and a Type V portland cement were used as cements used to resist sulfate attack in different environmental conditions. The 0% C₃A cement used is a specialty cement. The portland cement in series (D) is a Type II cement with a 0 percent C₃A content. This is not a specialty cement but rather a regional cement with a low alumina characteristic.

Six fly ashes were combined with the Type II cement with 0 percent C₃A to study the effects of alumina in fly ash. Of the six fly ashes used two were ASTM Class F and TSDHPT Type A fly ashes and 4 were ASTM Class C and TSDHPT Type B fly ashes.

5.2.2 Workability and Curing. In test series (A) and (C) two different workabilities were studied to investigate the effect of permeability and water/binder ratio on the sulfate attack mechanism. Series (B), (D) and (E) were mixed with 6-7 in. slump

to encourage the permeability of sulfate ions from solution into the mortar matrix.

The sulfate exposure was started when the concrete reached 3500 psi. A minimum strength was used because concrete at early ages is susceptible to severe damage from high concentrations of sodium sulfate. Concentrations in excess of 2 percent are not common in the field and early exposure to the 10 percent sodium sulfate solution in this study would skew the experimental results of this study.

Test series (F) and (G) were designed to investigate the effect of curing time on the sulfate resistance of concrete containing fly ash. A typical strength gain between 3 and 28 day cured specimens was 2500 psi.

5.2.3 Other Factors. Air content was studied in test series (E) to determine the effect of air content on the sulfate resistance of the concrete. The amount of admixture for each mix was adjusted to yield 5 percent air. Test series (A), (B), (C), (D), (F) and (G) all contained no entrained air. The 2-3 in. slump mixes in the test program all contained a water reducing-retarding admixture. The results of these mixes will be compared with similar mixes without a water reducer-retarder to determine the effect of the admixture on the sulfate resistance of concrete containing fly ash.

5.3 Test Results.

At the completion of the first year of CTR Project 481, the sulfate expansion facilities are in place and 85 percent of the studies long term specimens have been cast and are soaking in a 10 percent solution of sodium sulfate. The specimens in the primary study using Type II cement; with a slump between 6-7 inches, 5.5 sacks of cementitious material and a fly ash replacement level between 25 and 45 percent by volume, are over 150 days old. A parallel series with a 2-3 inch slump is also complete and soaking in the sulfate bath. Three other cements are being used to study the effect of cement type on the sulfate resistance of concrete containing fly ash and as control mixes.

Supplementary studies on the effect of 3 day moist curing, 28 day moist curing and air entrainment have also been cast and placed in the sulfate solution. Some of these specimens have not been in the sulfate environment long enough to yield meaningful

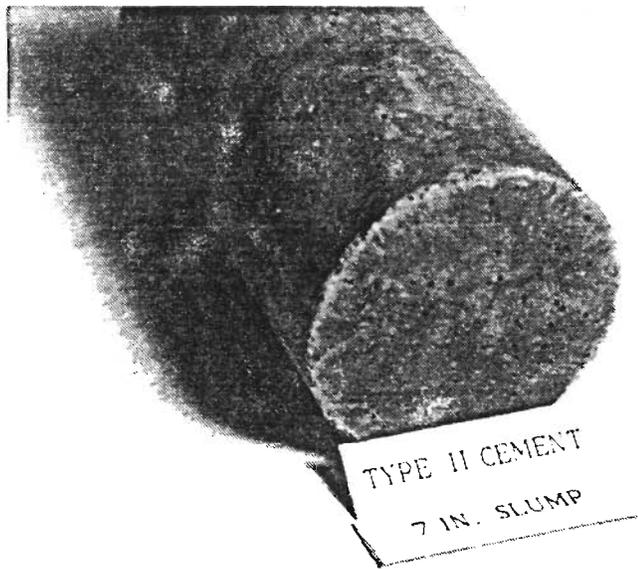


Photo 5.1 Concrete specimen containing Type II cement at 170 days.

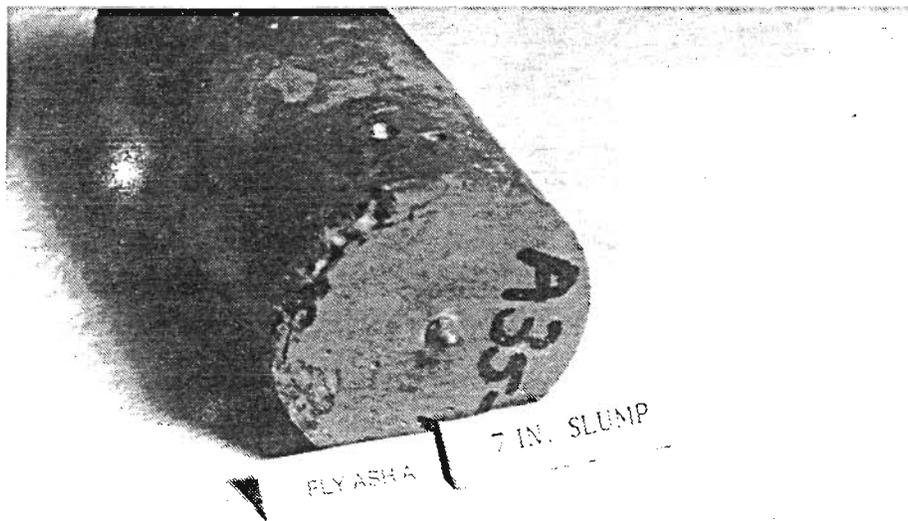


Photo 5.2 Concrete specimen containing 35% fly ash A at 56 days.



Photo 5.3 Concrete specimen containing 45% fly ash B at 137 days.



Photo 5.4 Concrete specimen containing 45% fly ash C at 137 days.



Photo 5.5 Concrete specimen containing 35% fly ash D at 165 days.



Photo 5.6 Concrete specimen containing 35% fly ash F at 56 days.



Photo 5.7 Concrete specimen containing 35% fly ash H at 169 days.



Photo 5.8 Concrete specimen containing 35% fly ash M at 151 days.



Photo 5.9 Concrete specimen containing 35% fly ash N at 42 days.



Photo 5.10 Concrete specimen containing 35% fly ash P at 165 days.

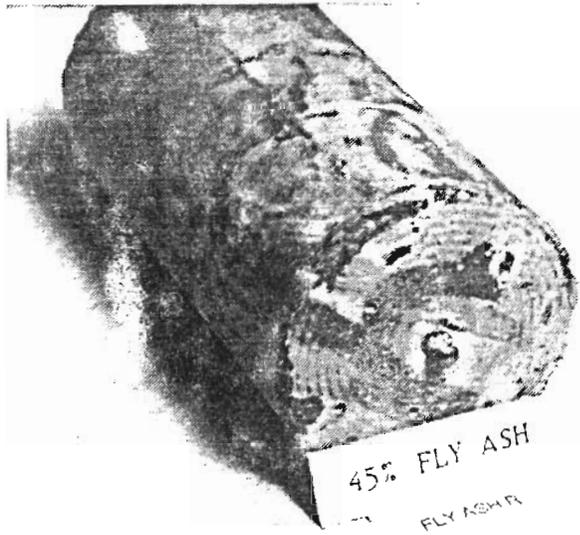


Photo 5.11 Concrete specimen containing 45% fly ash R at 151 days.

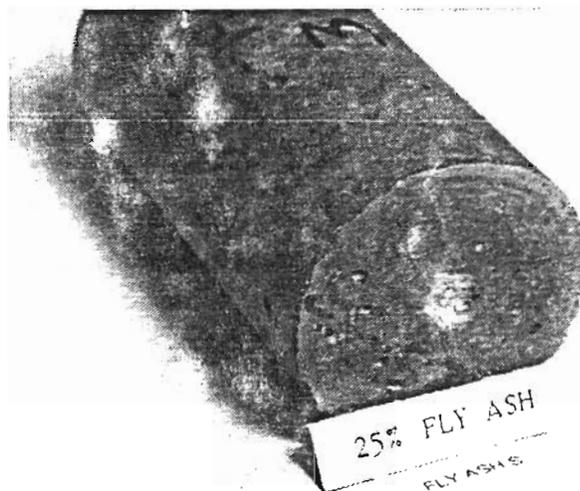


Photo 5.12 Concrete specimen containing 25% fly ash S at 119 days.

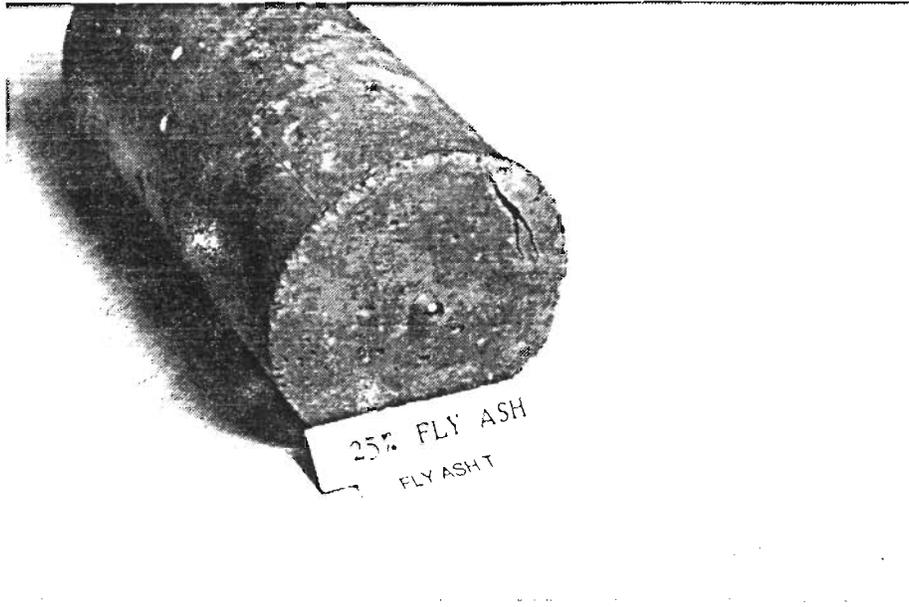


Photo 5.13 Concrete specimen containing 25% fly ash T at 175 days.

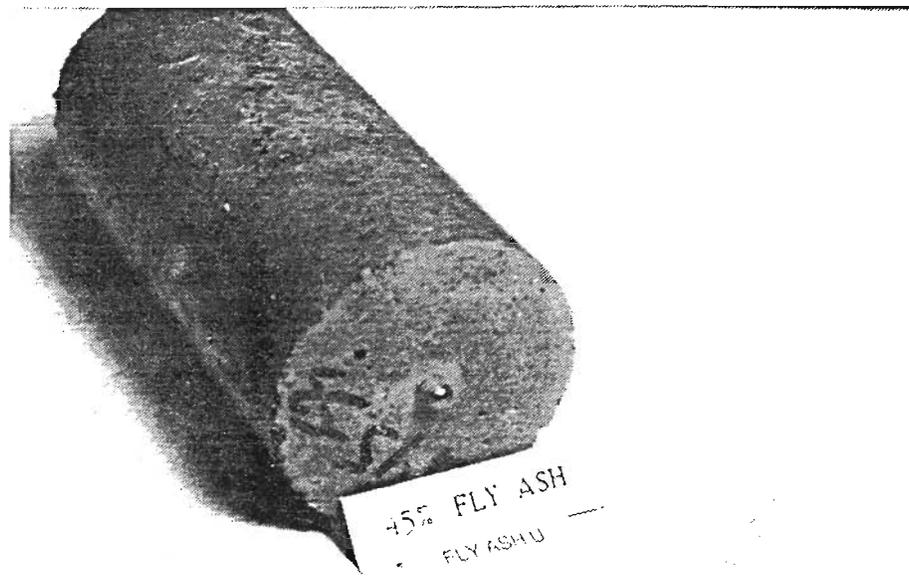


Photo 5.14 Concrete specimen containing 45% fly ash U at 120 days.

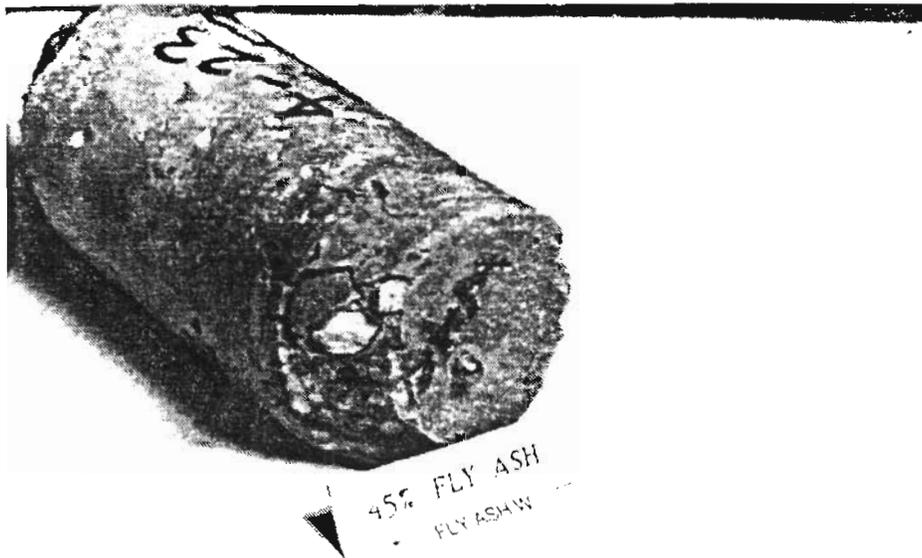


Photo 5.15 Concrete specimen containing 35% fly ash W at 165 days.

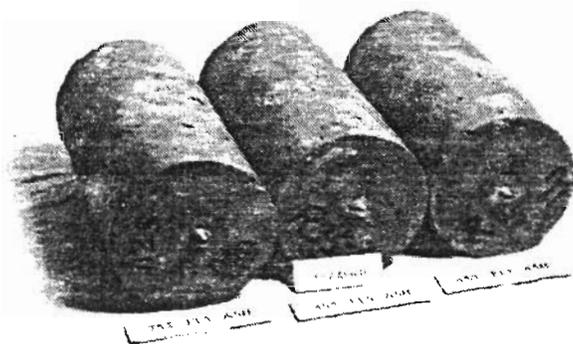


Photo 5.16 Comparison of concrete specimens containing fly ash R with 25, 35 and 45 percent replacement by volume.

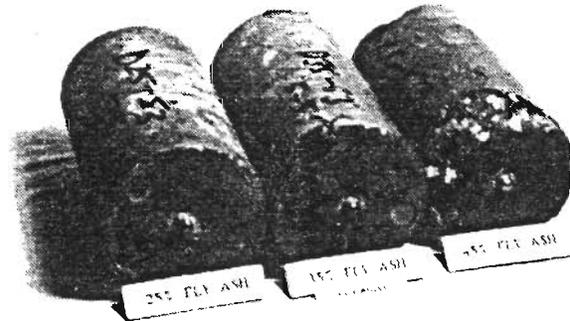


Photo 5.17 Comparison of concrete specimens containing fly ash D with 25, 35 and 45 percent replacement by volume.

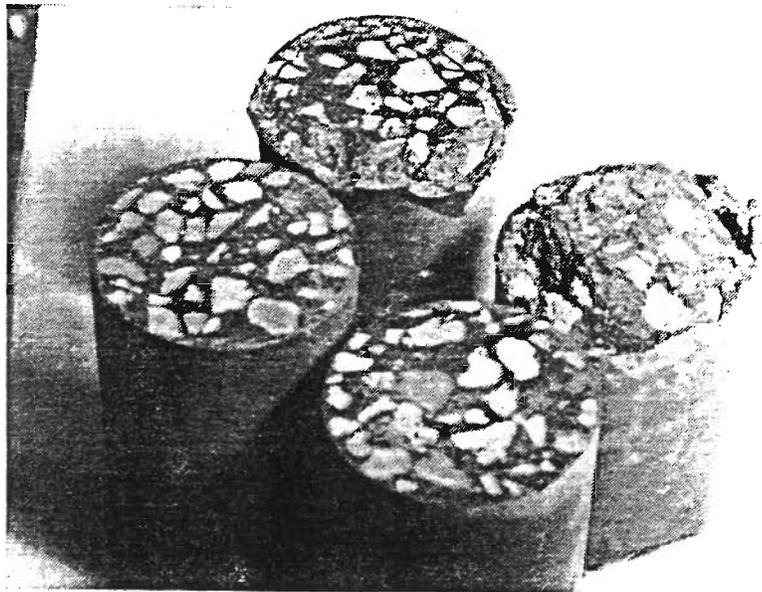


Photo 5.18 Four phases of sulfate attack on concrete.

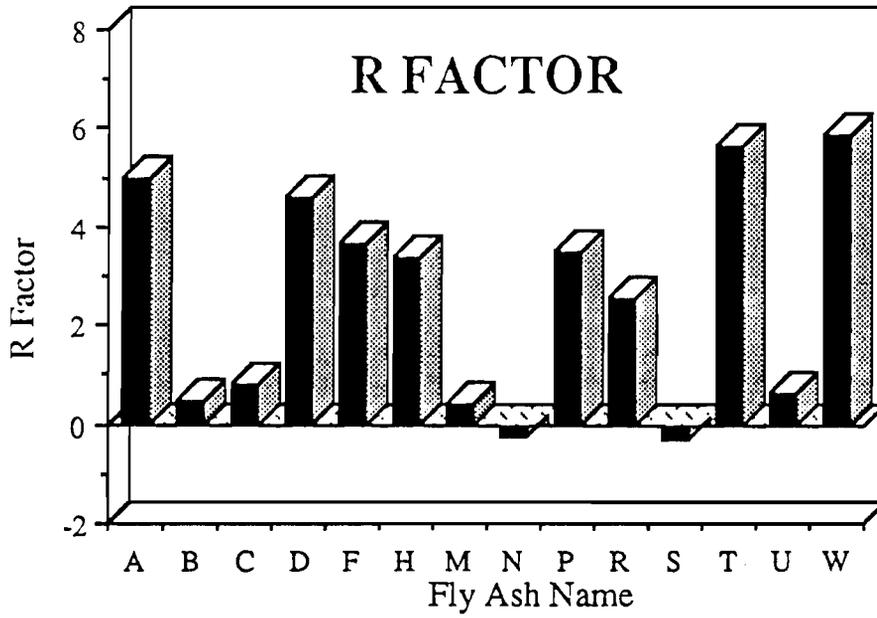


Fig. 5.2 R factors of Study 481 Fly Ashes.

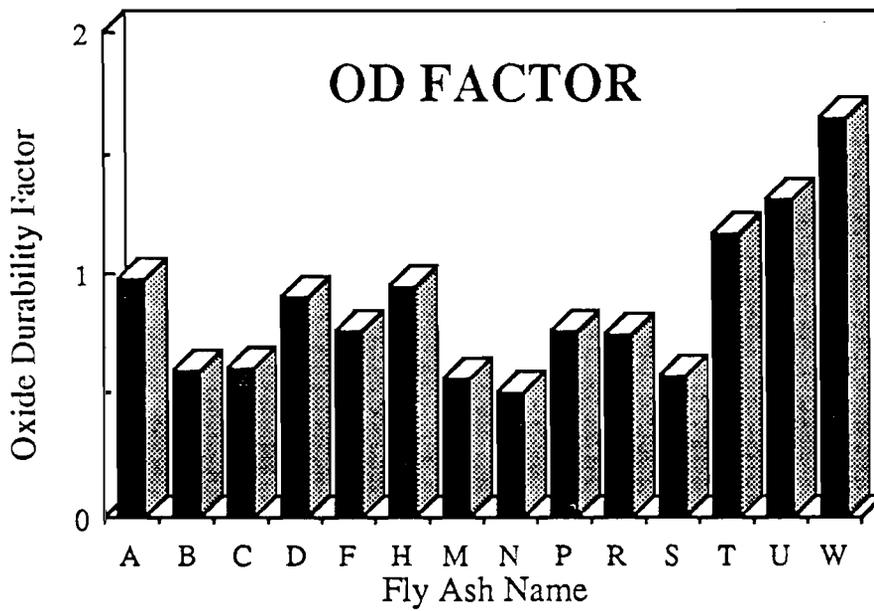
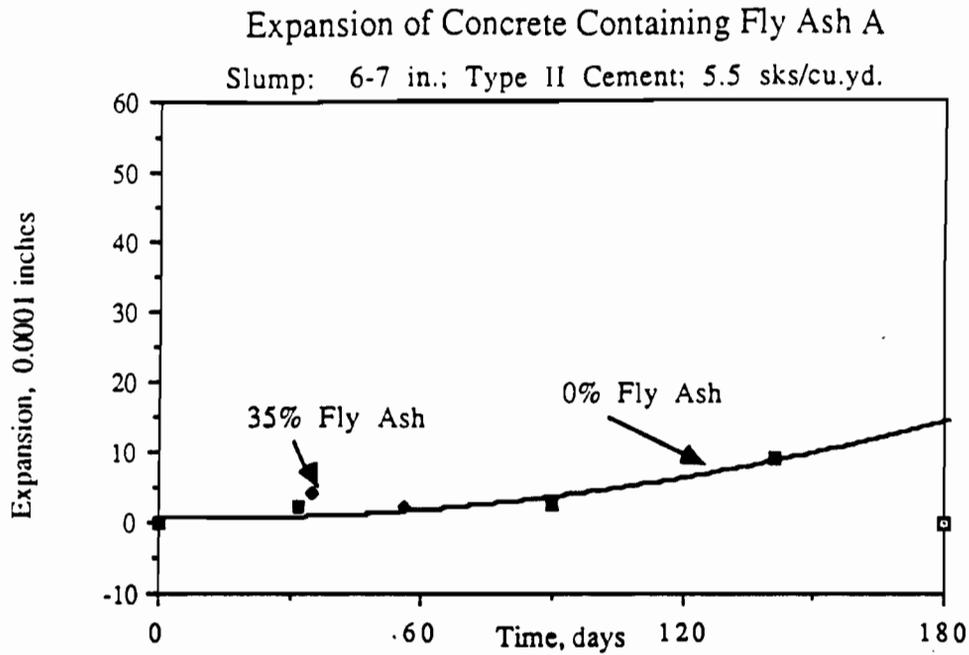


Fig. 5.3 Oxide Durability Factors of 481 Fly Ashes.

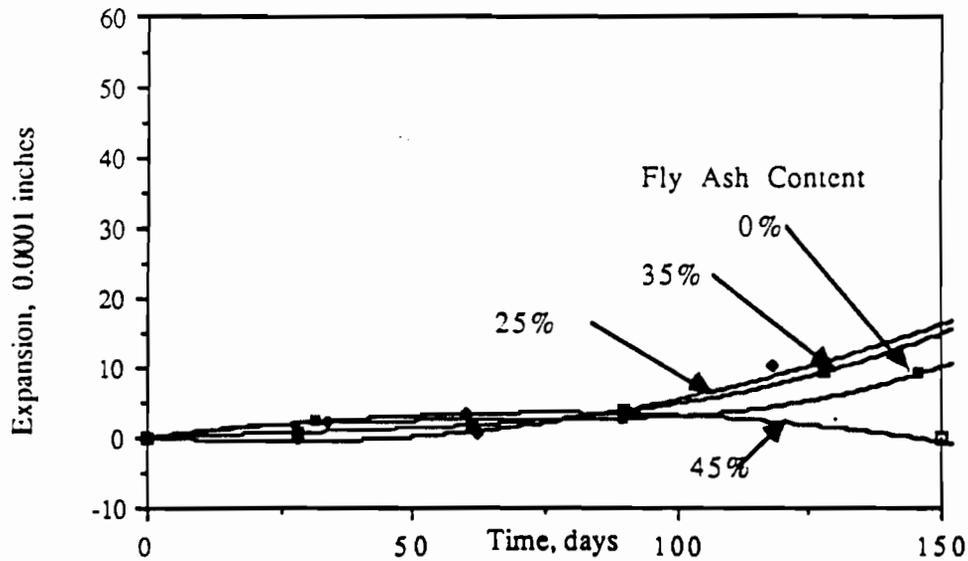


Fly Ash A		TSDHPT Type B Fly Ash	
Subbituminous Coal			
R factor: 5.00			
Chemical Composition		Mineralogical Composition	
CaO %	29.86	CaSO ₄ %	X
SiO ₂ %	32.23	C ₃ A %	X
Al ₂ O ₃ %	22.18	Hem %	X
Fe ₂ O ₃ %	4.97	CaO %	X
SO ₃ %	2.48	Mag %	
MgO %	5.63	Mel %	X
LOI %	0.03	Mul %	
		MgO %	X
		SiO ₂ %	X
		Sp %	X

Fig. 5.4 The effect of fly ash A on sulfate resistance.

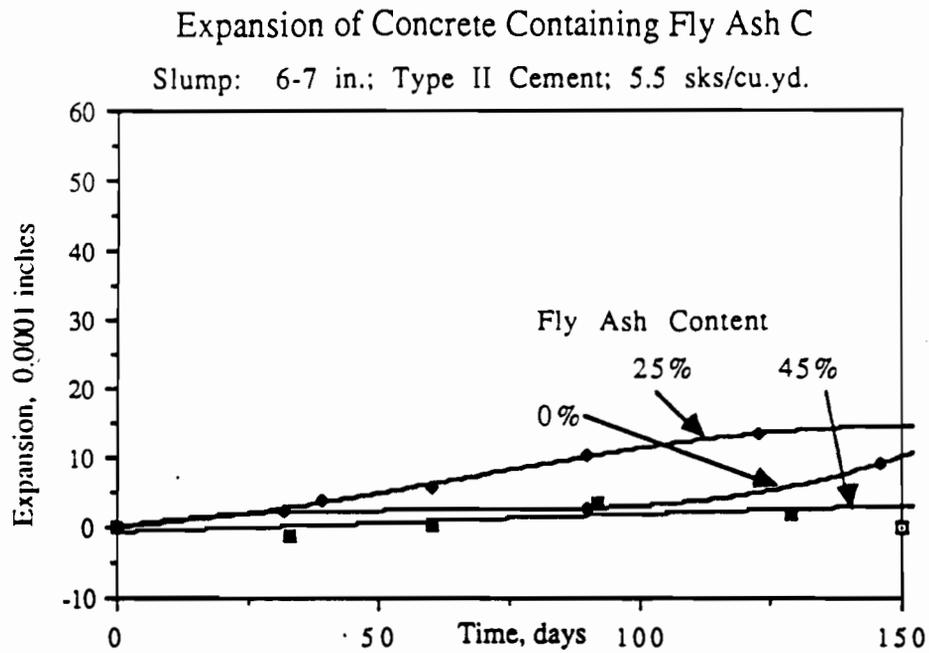
Expansion of Concrete Containing Fly Ash B

Slump: 6-7 in.; Type II Cement; 5.5 sks/cu.yd.



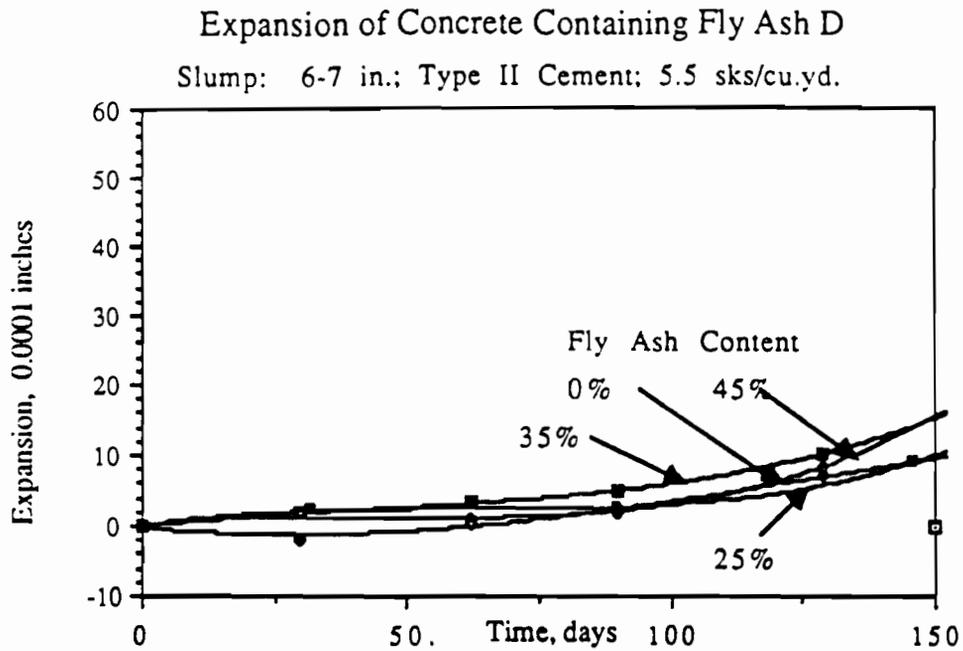
Fly Ash B		TSDHPT Type A Fly Ash	
Texas Lignite Coal			
R factor: 0.51			
Chemical Composition		Mineralogical Composition	
CaO %	9.55	CaSO ₄ %	
SiO ₂ %	52.90	C ₃ A %	
Al ₂ O ₃ %	17.89	Hem %	X
Fe ₂ O ₃ %	8.98	CaO %	
SO ₃ %	0.90	Mag %	X
MgO %	1.66	Mel %	
LOI %	0.19	Mul %	X
		MgO %	X
		SiO ₂ %	X
		Sp %	

Fig. 5.5 The effect of fly ash B on sulfate resistance.



Fly Ash C		TSDHPT Type A Fly Ash	
Texas Lignite Coal			
R factor: 0.85			
Chemical Composition		Mineralogical Composition	
CaO %	10.09	CaSO ₄ %	
SiO ₂ %	42.48	C ₃ A %	
Al ₂ O ₃ %	24.12	Hem %	X
Fe ₂ O ₃ %	5.96	CaO %	X
SO ₃ %	0.52	Mag %	X
MgO %	1.58	Mel %	X
LOI %	0.93	Mul %	
		MgO %	X
		SiO ₂ %	X
		Sp %	X

Fig. 5.6 The effect of fly ash C on sulfate resistance.

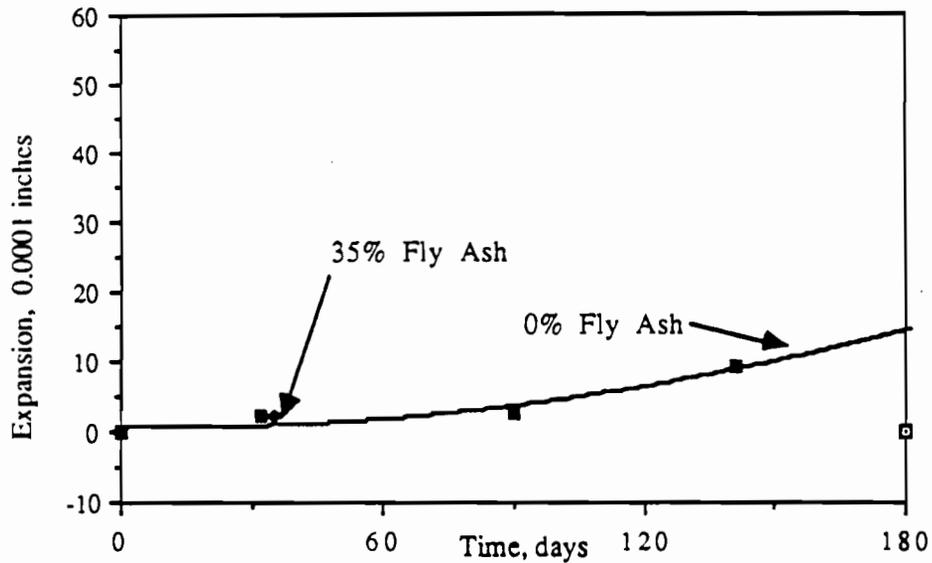


Fly Ash D		TSDHPT Type B Fly Ash	
Subbituminous Coal			
R factor: 4.61			
Chemical Composition		Mineralogical Composition	
CaO %	27.95	CaSO ₄ %	X
SiO ₂ %	31.34	C ₃ A %	X
Al ₂ O ₃ %	22.51	Hem %	X
Fe ₂ O ₃ %	4.98	CaO %	X
SO ₃ %	1.97	Mag %	
MgO %	4.34	Mel %	X
LOI %	0.45	Mul %	X
		MgO %	X
		SiO ₂ %	X
		Sp %	X

Fig. 5.7 The effect of fly ash D on sulfate resistance.

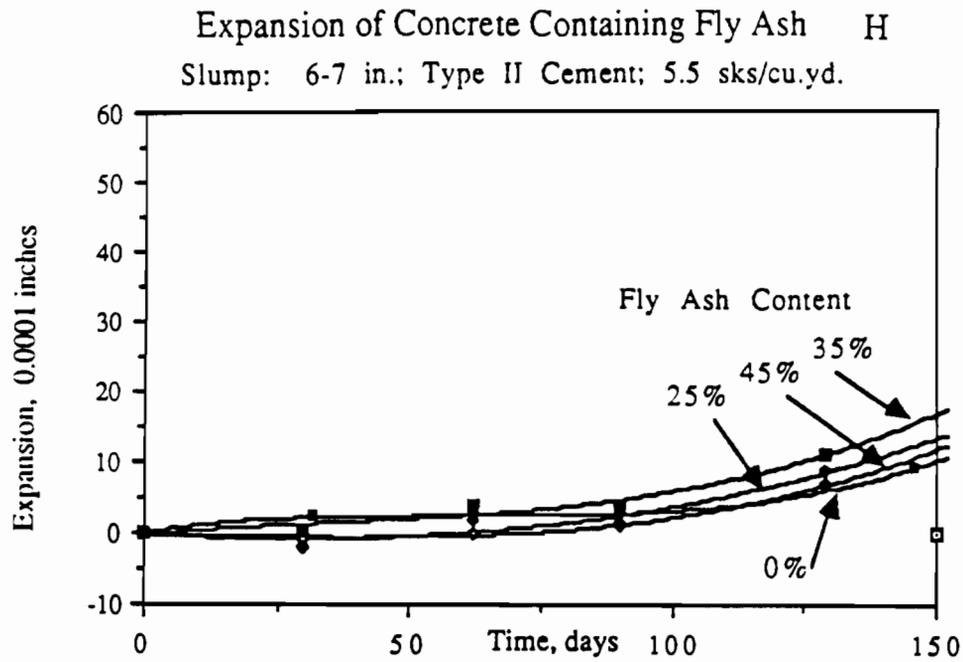
Expansion of Concrete Containing Fly Ash F

Slump: 6-7 in.; Type II Cement; 5.5 sks/cu.yd.



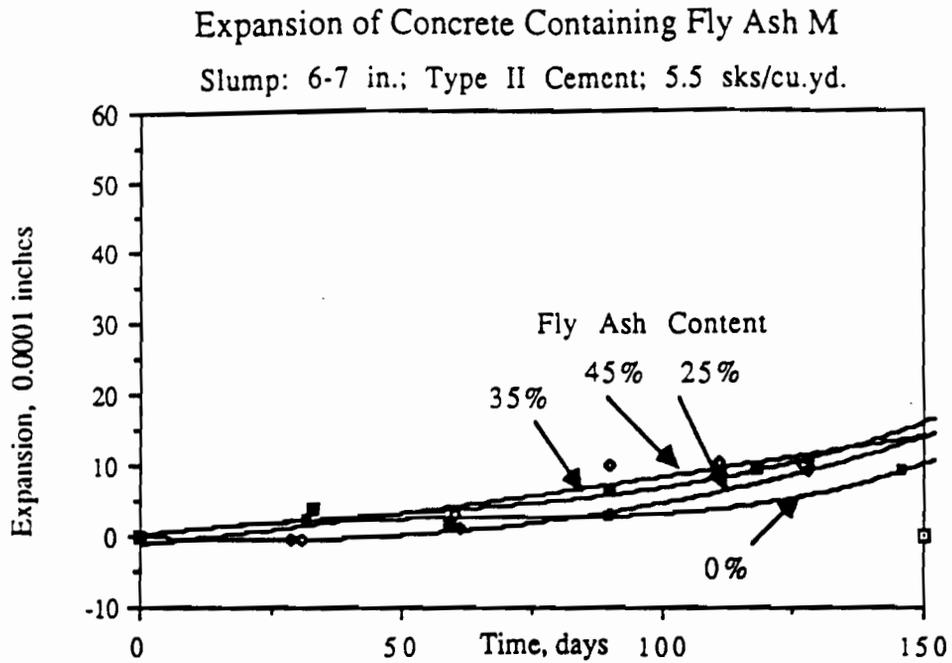
Fly Ash F		TSDHPT Type B Fly Ash	
Subbituminous Coal			
R factor: 3.70			
Chemical Composition		Mineralogical Composition	
CaO %	26.34	CaSO ₄ %	X
SiO ₂ %	33.31	C ₃ A %	X
Al ₂ O ₃ %	24.10	Hem %	X
Fe ₂ O ₃ %	5.77	CaO %	X
SO ₃ %	0.00	Mag %	X
MgO %	4.24	Mel %	X
LOI %	0.46	Mul %	X
		MgO %	X
		SiO ₂ %	X
		Sp %	X

Fig. 5.8 The effect of fly ash F on sulfate resistance.



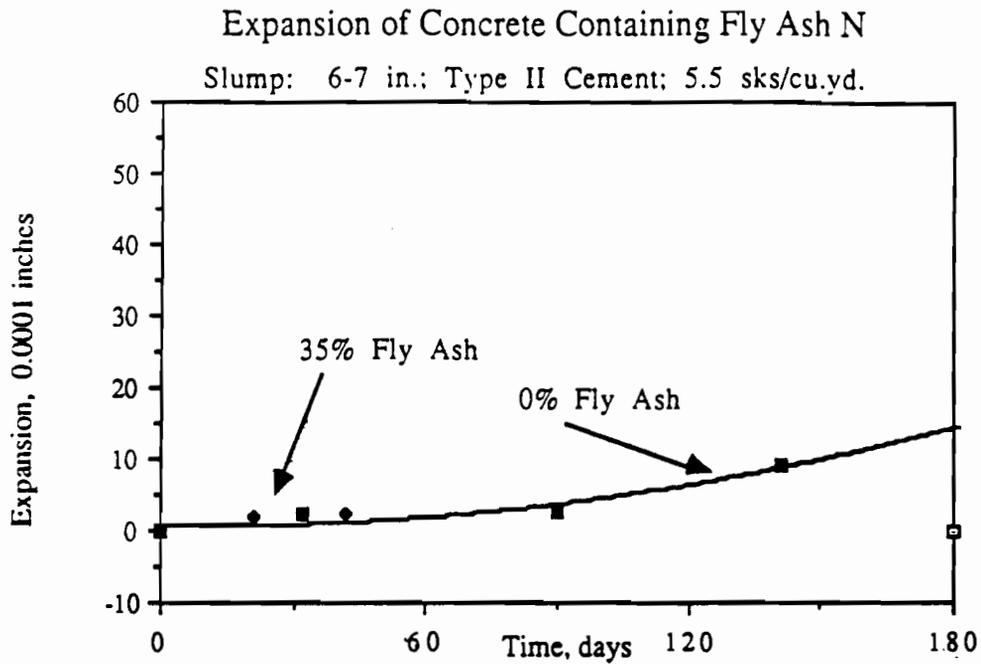
Fly Ash H Subbituminous Coal R factor: 3.41		TSDHPT Type B Fly Ash	
Chemical Composition		Mineralogical Composition	
CaO %	22.84	CaSO ₄ %	X
SiO ₂ %	33.70	C ₃ A %	X
Al ₂ O ₃ %	24.77	Hem %	X
Fe ₂ O ₃ %	5.23	CaO %	X
SO ₃ %	0.00	Mag %	X
MgO %	5.71	Mel %	X
LOI %	0.06	Mul %	X
		MgO %	X
		SiO ₂ %	X
		Sp %	X

Fig. 5.9 The effect of fly ash H on sulfate resistance.



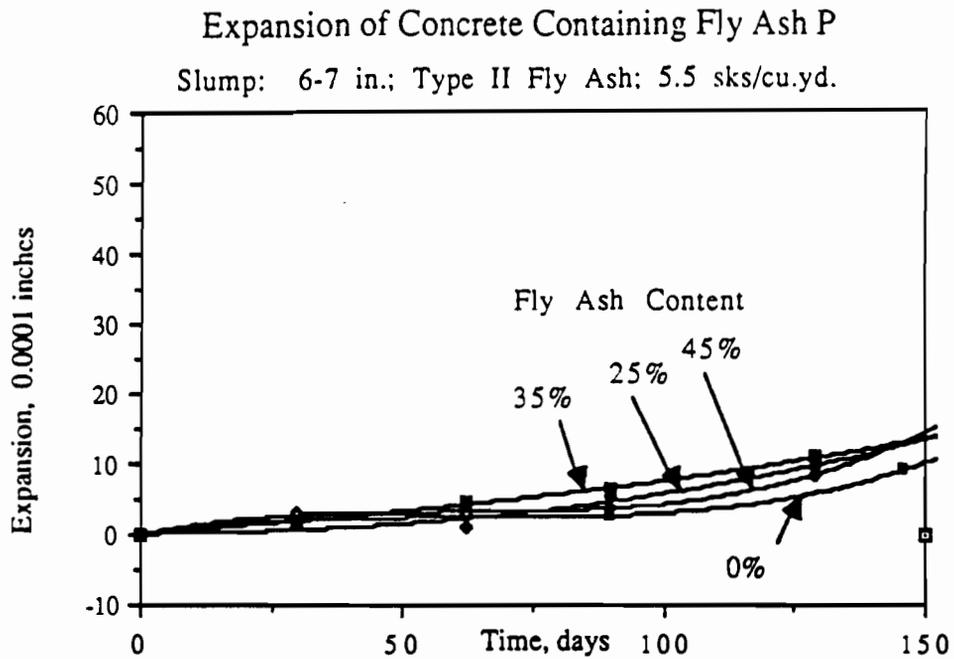
Fly Ash M		TSDHPT Type A Fly Ash	
Texas Lignite Coal			
R factor: 0.45			
Chemical Composition		Mineralogical Composition	
CaO %	6.97	CaSO ₄ %	
SiO ₂ %	55.54	C ₃ A %	
Al ₂ O ₃ %	18.61	Hem %	X
Fe ₂ O ₃ %	4.33	CaO %	
SO ₃ %	0.26	Mag %	X
MgO %	0.81	Mel %	X
LOI %	0.04	Mul %	X
		MgO %	X
		SiO ₂ %	X
		Sp %	

Fig. 5.10 The effect of fly ash M on sulfate resistance.



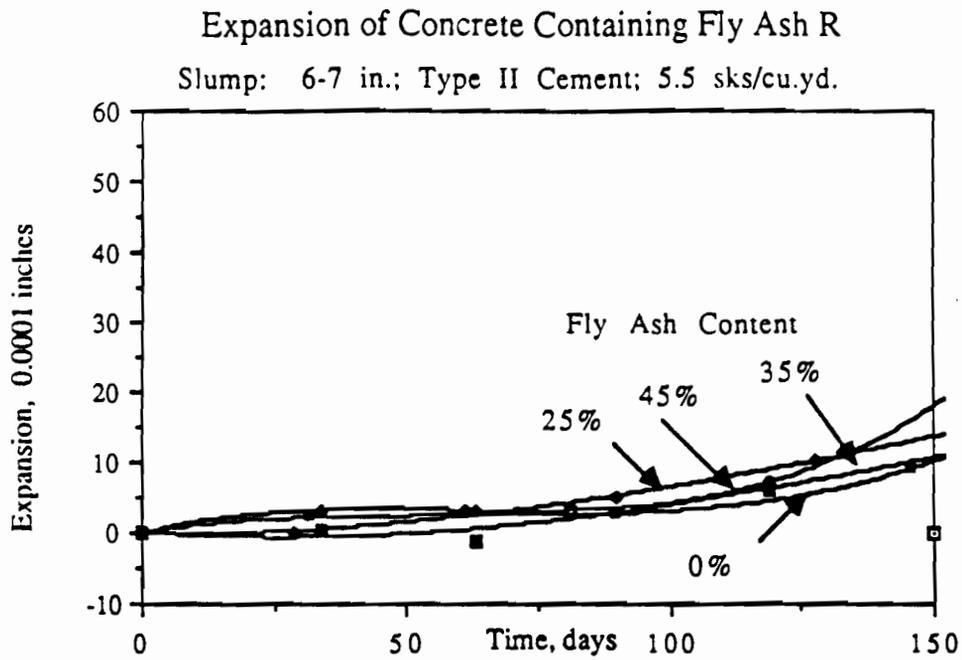
Fly Ash N		TSDHPT Type A Fly Ash	
Bituminous Coal			
R factor: -0.21			
Chemical Composition		Mineralogical Composition	
CaO %	1.57	CaSO ₄ %	
SiO ₂ %	43.04	C ₃ A %	
Al ₂ O ₃ %	27.44	Hem %	X
Fe ₂ O ₃ %	16.06	CaO %	X
SO ₃ %	1.24	Mag %	X
MgO %	0.00	Mel %	
LOI %	0.90	Mul %	X
		MgO %	X
		SiO ₂ %	X
		Sp %	X

Fig. 5.11 The effect of fly ash N on sulfate resistance.



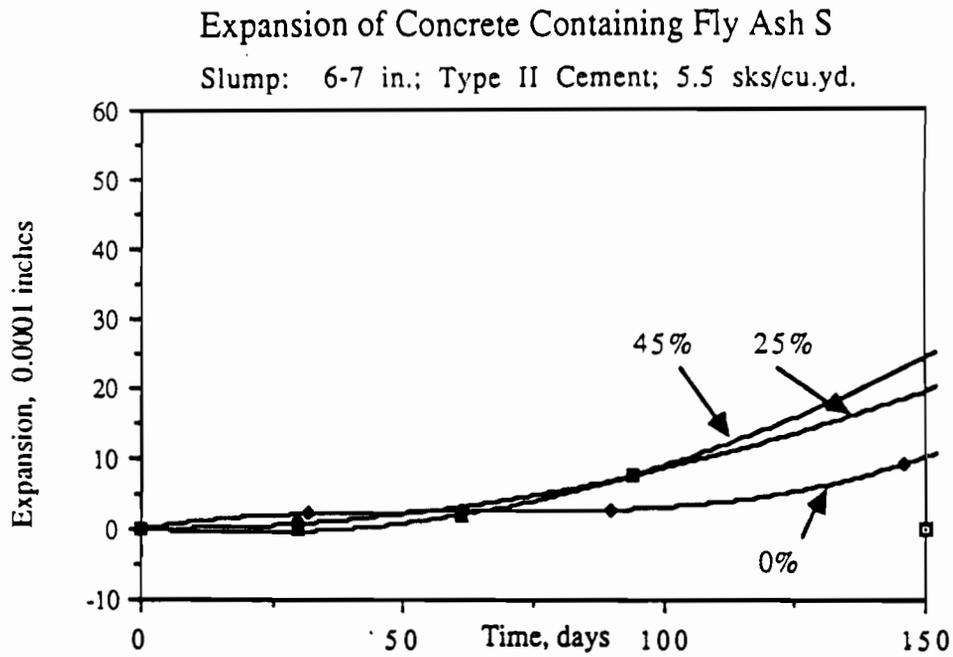
Fly Ash P		TSDHPT Type B Fly Ash	
Subbituminous Coal			
R factor: 3.53			
Chemical Composition		Mineralogical Composition	
CaO %	23.13	CaSO ₄ %	X
SiO ₂ %	35.59	C ₃ A %	X
Al ₂ O ₃ %	22.41	Hem %	X
Fe ₂ O ₃ %	5.14	CaO %	X
SO ₃ %	2.10	Mag %	X
MgO %	4.25	Mel %	X
LOI %	0.52	Mul %	X
		MgO %	X
		SiO ₂ %	X
		Sp %	X

Fig. 5.12 The effect of fly ash P on sulfate resistance.



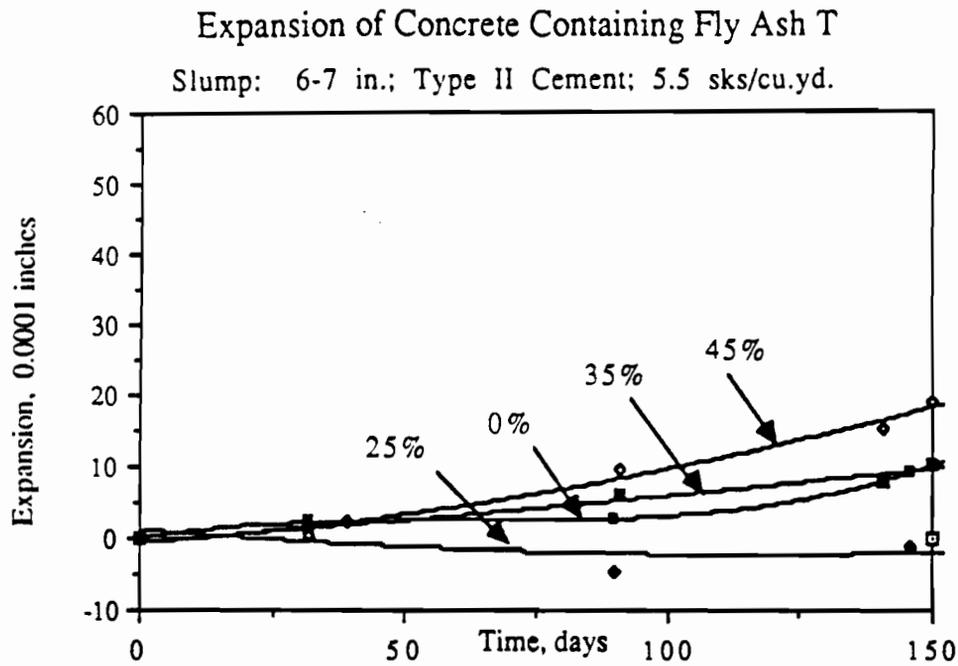
Fly Ash R		TSDHPT Type B Fly Ash	
Subbituminous Coal			
R factor: 2.60			
Chemical Composition		Mineralogical Composition	
CaO %	22.44	CaSO ₄ %	X
SiO ₂ %	34.53	C ₃ A %	X
Al ₂ O ₃ %	23.77	Hem %	X
Fe ₂ O ₃ %	6.69	CaO %	
SO ₃ %	1.97	Mag %	X
MgO %	3.88	Mel %	X
LOI %	0.28	Mul %	
		MgO %	X
		SiO ₂ %	X
		Sp %	

Fig. 5.13 The effect of fly ash R on sulfate resistance.



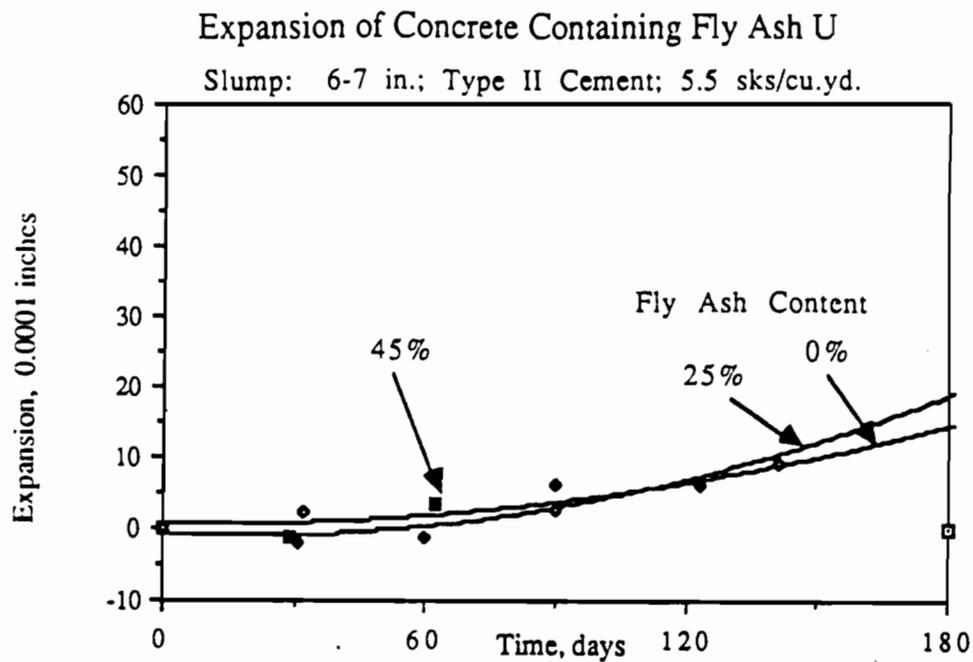
Fly Ash S		TSDHPT Type A Fly Ash	
Bituminous Coal			
R factor: -0.28			
Chemical Composition		Mineralogical Composition	
CaO %	3.68	CaSO ₄ %	X
SiO ₂ %	45.87	C ₃ A %	
Al ₂ O ₃ %	24.15	Hem %	X
Fe ₂ O ₃ %	4.66	CaO %	X
SO ₃ %	0.42	Mag %	X
MgO %	0.00	Mel %	X
LOI %	1.62	Mul %	X
		MgO %	X
		SiO ₂ %	X
		Sp %	X

Fig. 5.14 The effect of fly ash S on sulfate resistance.



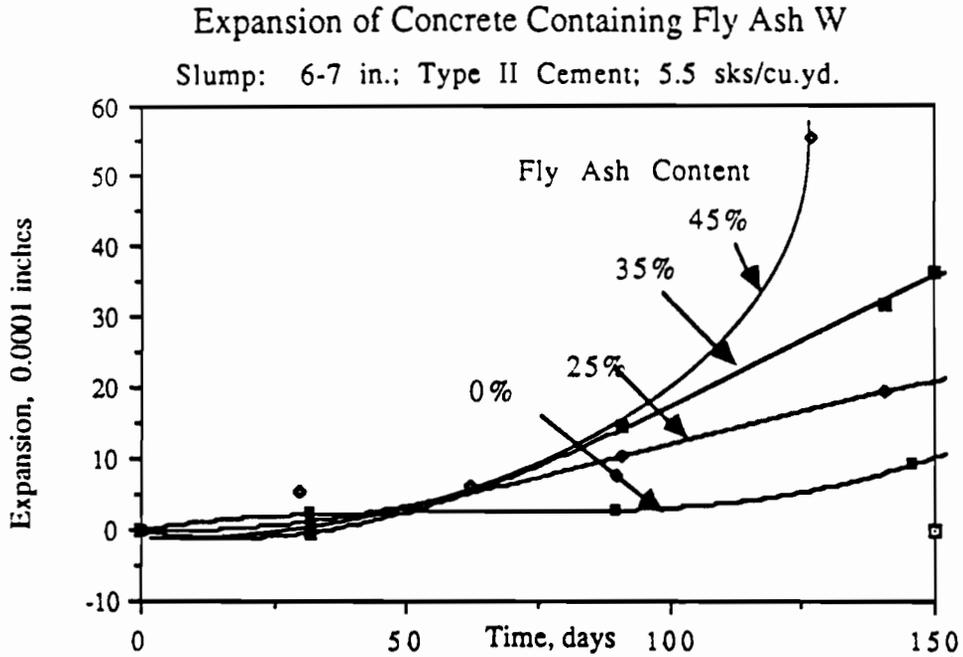
Fly Ash T		TSDHPT Type B Fly Ash	
Subbituminous Coal			
R factor: 5.65			
Chemical Composition		Mineralogical Composition	
CaO %	31.34	CaSO ₄ %	X
SiO ₂ %	30.80	C ₃ A %	X
Al ₂ O ₃ %	21.94	Hem %	X
Fe ₂ O ₃ %	4.66	CaO %	X
SO ₃ %	2.28	Mag %	X
MgO %	6.14	Mel %	X
LOI %	0.17	Mul %	
		MgO %	X
		SiO ₂ %	X
		Sp %	X

Fig. 5.15 The effect of fly ash T on sulfate resistance.



Fly Ash U		TSDHPT Type A Fly Ash	
Bituminous Coal			
R factor: 0.67			
Chemical Composition		Mineralogical Composition	
CaO %	8.76	CaSO ₄ %	
SiO ₂ %	50.89	C ₃ A %	X
Al ₂ O ₃ %	18.55	Hem %	X
Fe ₂ O ₃ %	5.60	CaO %	X
SO ₃ %	0.71	Mag %	X
MgO %	0.47	Mel %	
LOI %	3.90	Mul %	X
		MgO %	X
		SiO ₂ %	X
		Sp %	X

Fig. 5.16 The effect of fly ash U on sulfate resistance.



Fly Ash W		TSDHPT Type B Fly Ash	
Subbituminous Coal			
R factor: 5.86			
Chemical Composition		Mineralogical Composition	
CaO %	33.93	CaSO ₄ %	X
SiO ₂ %	28.38	C ₃ A %	X
Al ₂ O ₃ %	20.19	Hem %	X
Fe ₂ O ₃ %	4.94	CaO %	X
SO ₃ %	2.28	Mag %	
MgO %	8.41	Mel %	X
LOI %	0.25	Mul %	
		MgO %	X
		SiO ₂ %	X
		Sp %	X

Fig. 5.17 The effect of fly ash W on sulfate resistance.

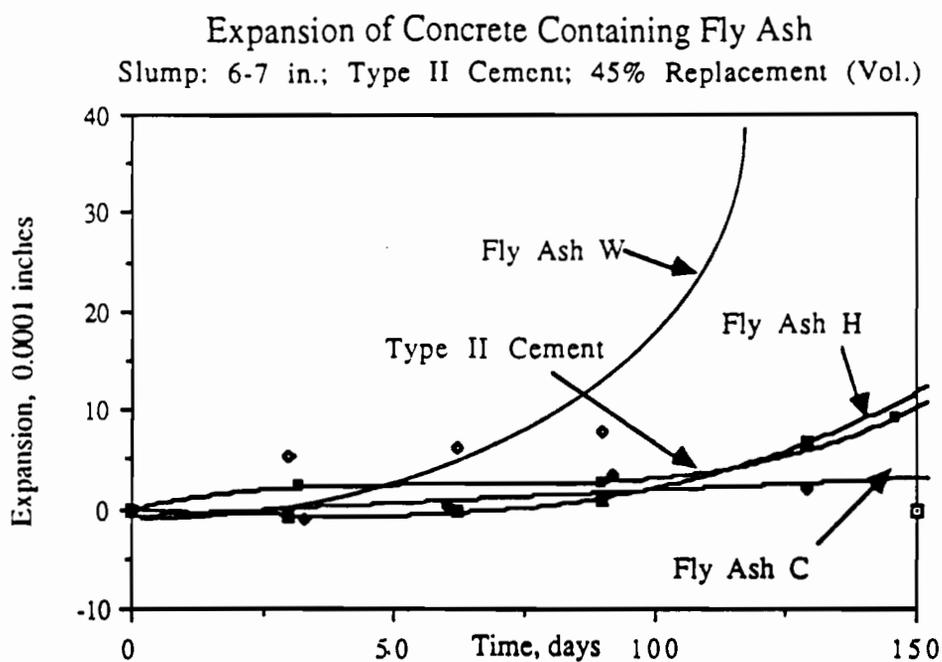


Fig. 5.18 Expansion of three different fly ashes.

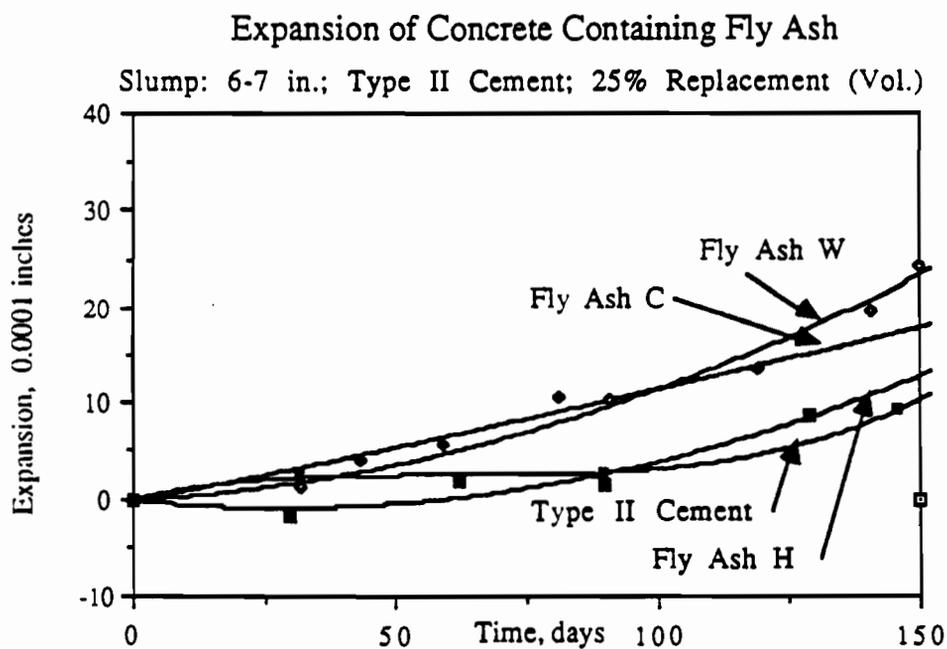


Table 5.19 Expansion of three different fly ashes.

Expansion of Concrete Containing Fly Ash T

Slump: 2-3 in.; Type II Cement; 5.5 sks/cu.yd.

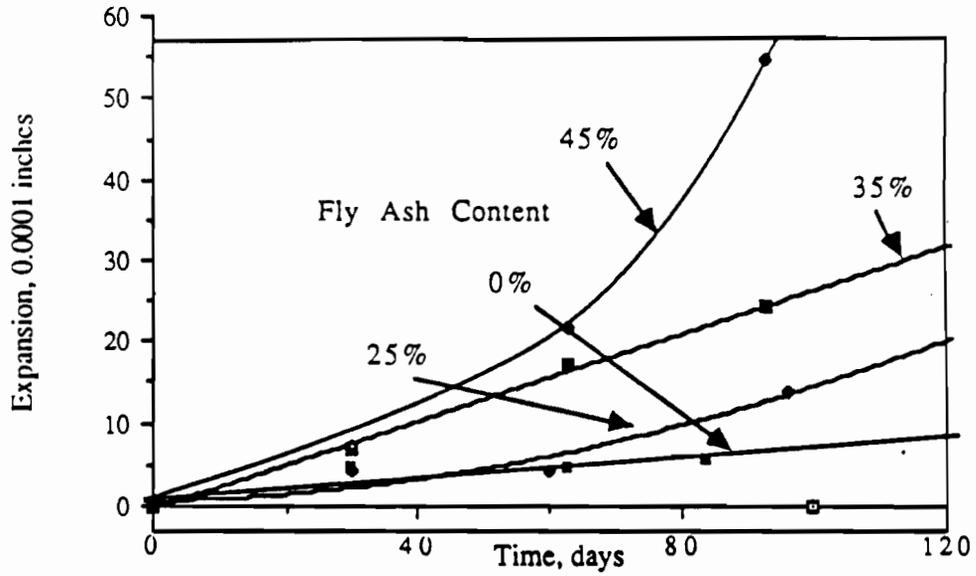


Fig. 5.20 Expansion of Concrete Concrete Containing Fly Ash T.

Expansion of Concrete Containing Fly Ash R

Slump: 2-3 in.; Type II Cement; 5.5 sks/cu.yd.

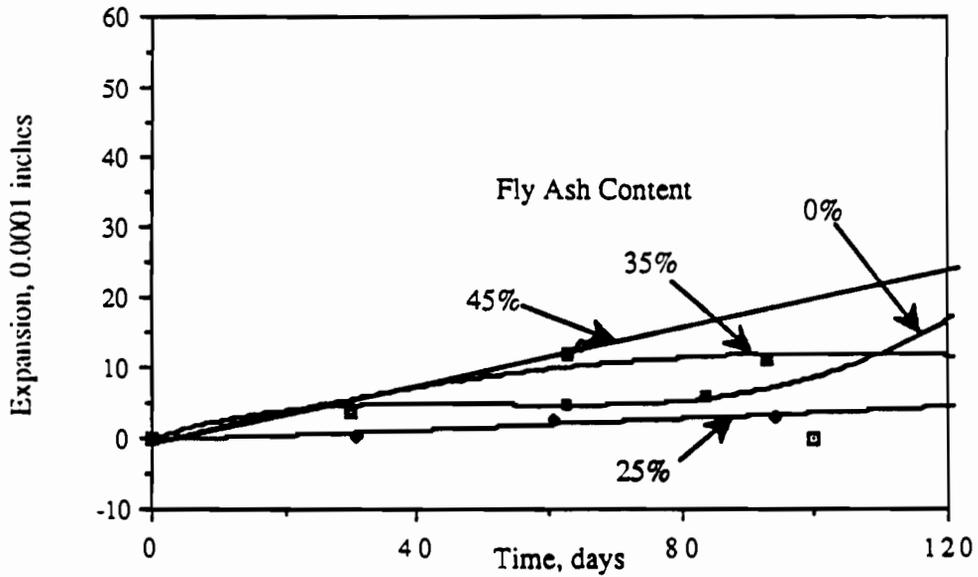


Fig. 5.21 Expansion of Concrete Concrete Containing Fly Ash R.

Expansion of Concrete Containing Fly Ash D

Slump: 2-3 in.; Type II Cement; 5.5 sks/cu.yd.

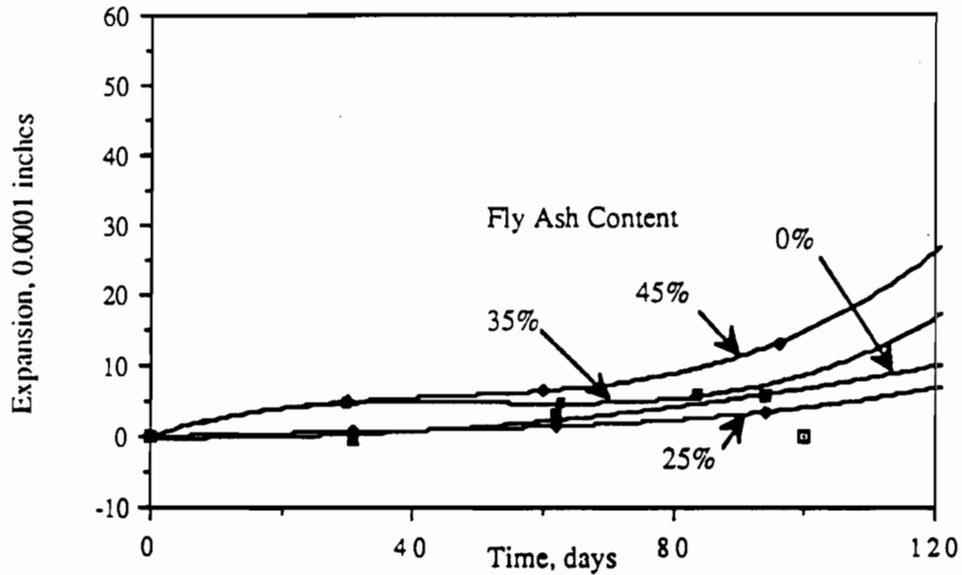


Fig. 5.22 Expansion of Concrete Concrete Containing Fly Ash D.

Expansion of Concrete Containing Fly Ash P

Slump: 2-3 in.; Type II Cement; 5.5 sks/cu.yd.

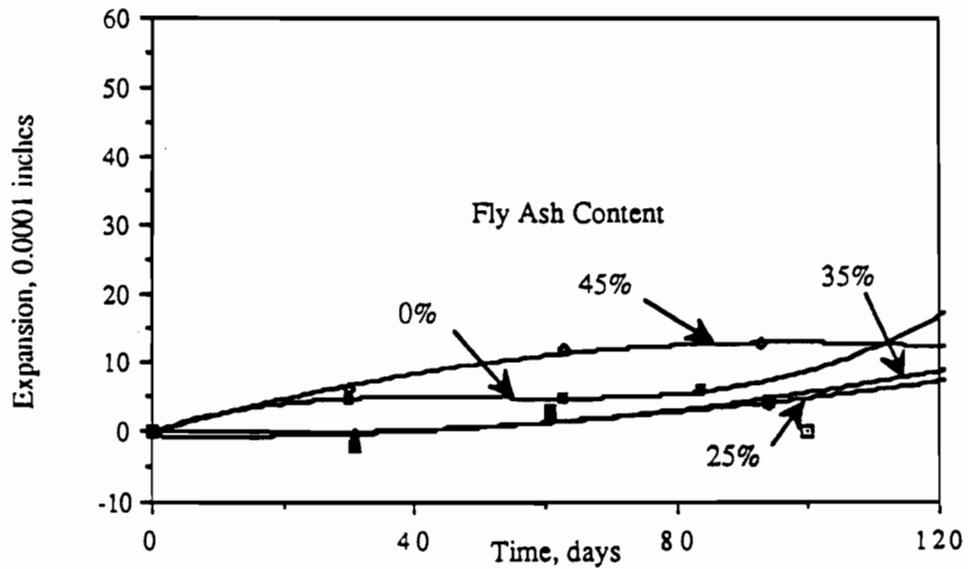


Fig. 5.23 Expansion of Concrete Concrete Containing Fly Ash P.

Effect of Curing Time on Sulfate Attack

Slump: 2-3 in.; Type II Cement; Fly Ash B

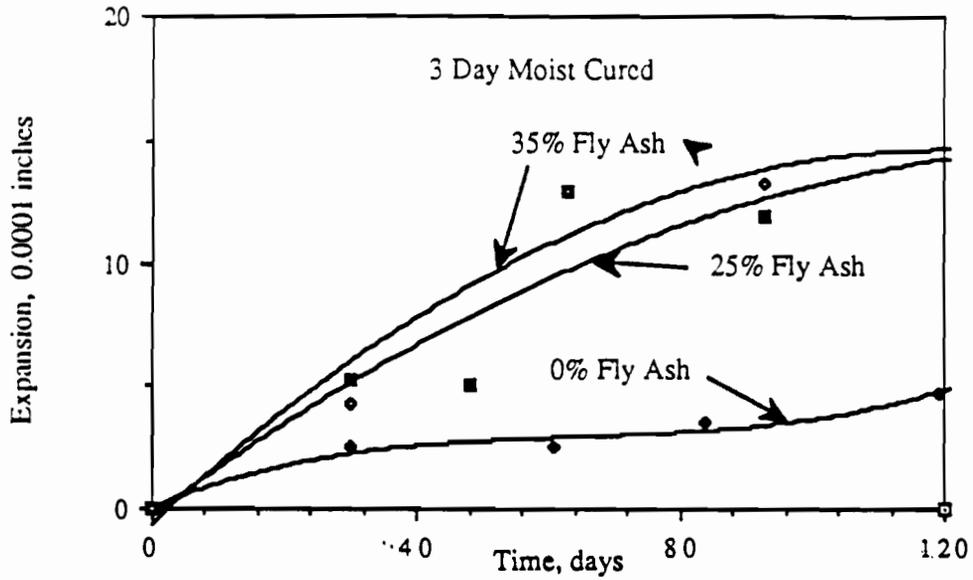


Fig. 5.24 Expansion in 3 day Moist Cured Concrete Containing Fly Ash B.

Effect of Curing Time on Sulfate Attack

Slump: 2-3 in.; Type II Cement; Fly Ash D

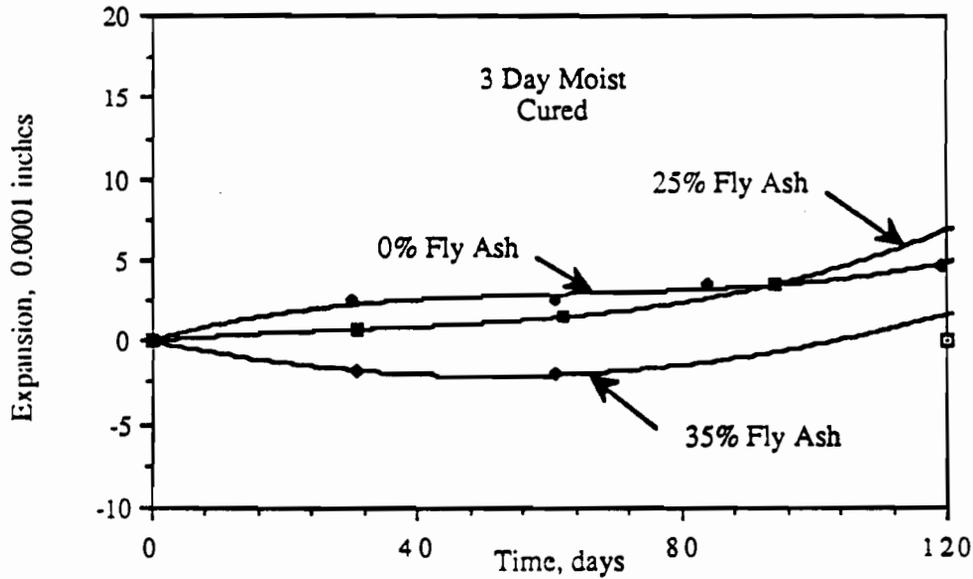


Fig. 5.25 Expansion in 3 day Moist Cured Concrete Containing Fly Ash D.

Effect of Curing Time on Sulfate Attack

Slump: 2-3 in.; Type II Cement; Fly Ash P

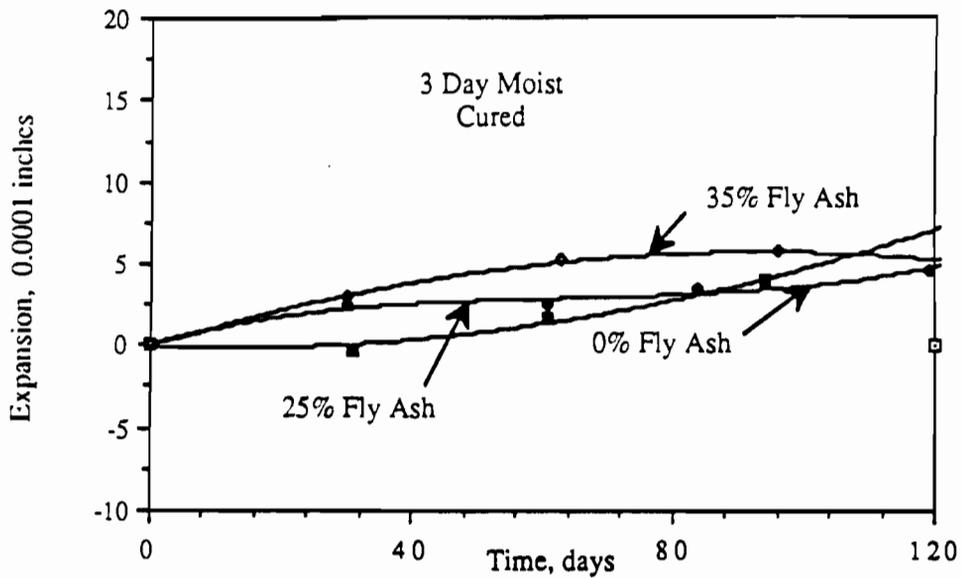


Fig. 5.26 Expansion in 3 day Moist Cured Concrete Containing Fly Ash P.

Effect of Curing Time on Sulfate Attack

Slump: 2-3 in.; Type II Cement; Fly Ash R

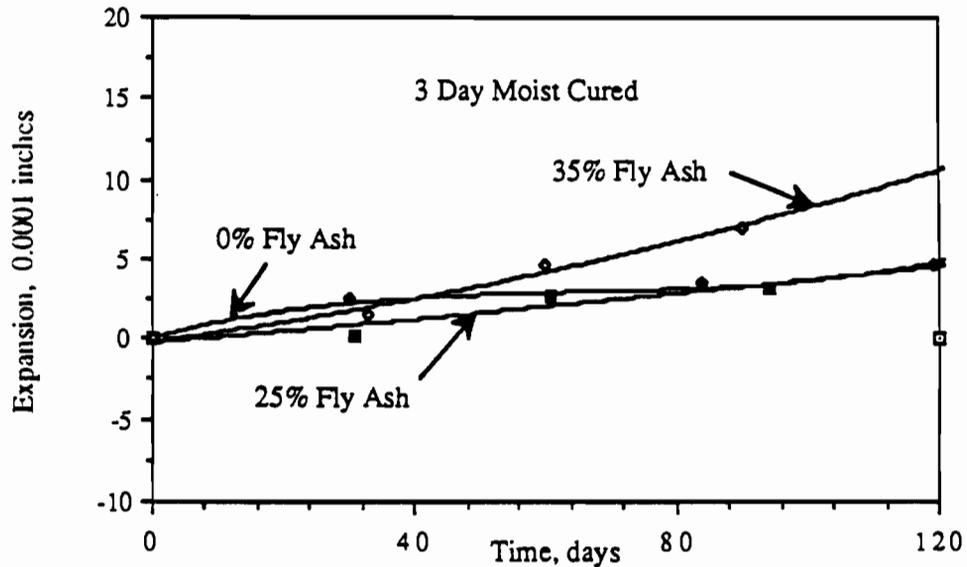


Fig. 5.27 Expansion in 3 day Moist Cured Concrete Containing Fly Ash R.

Expansion of Control Concrete

Slump: 6-7 in.; 5.5 sks/cu.yd.; 3500 psi

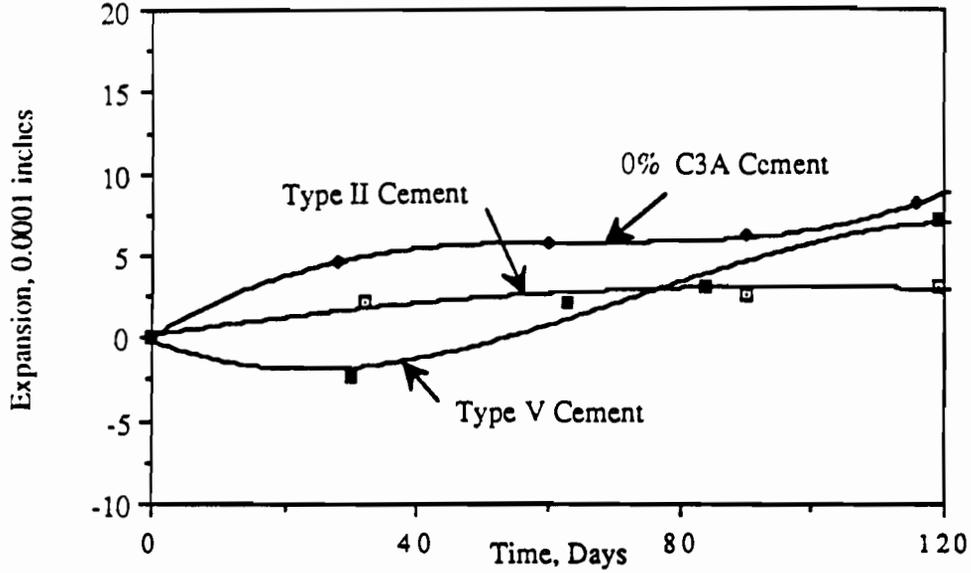


Fig. 5.28 Expansion of Control Concrete Mixes.

Expansion of 0% C3A Cement Concrete

Slump: 6-7 in.; 5.5 sks/cu.yd.; 35% Fly Ash

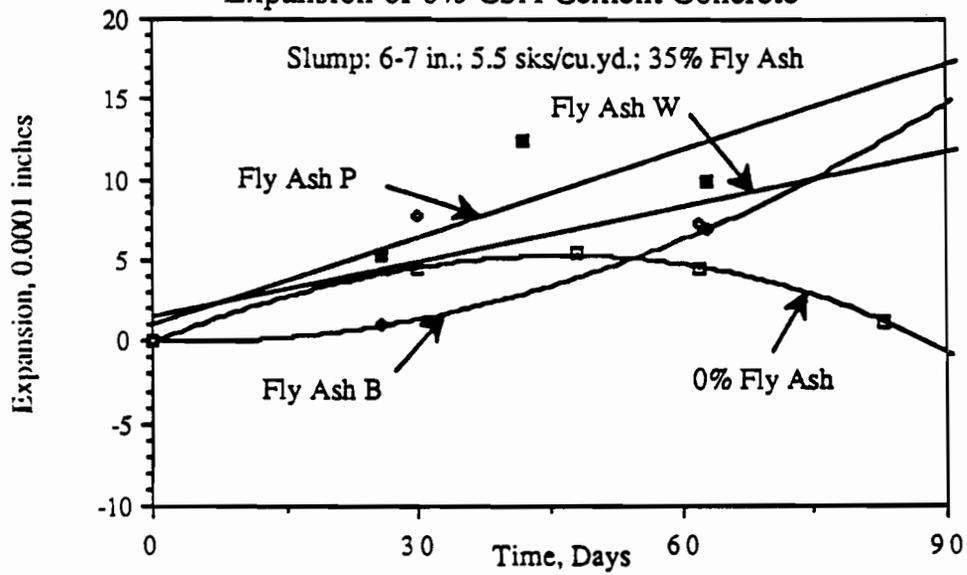


Fig. 5.29 Expansion of Concrete Containing Blue Circle Cement.

Effect of Curing Time on Sulfate Attack

Slump: 2-3 in.; Type II Cement; Fly Ash D

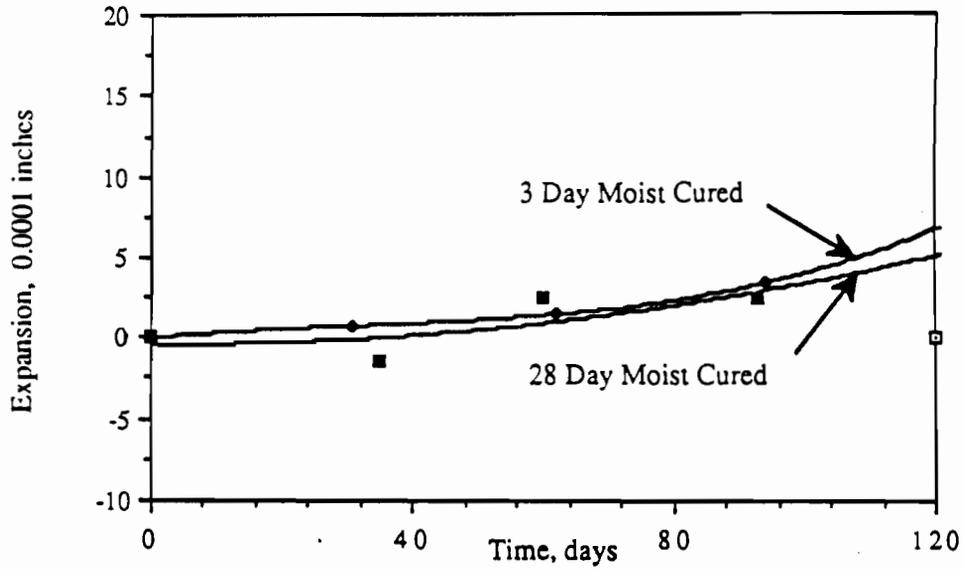


Fig. 5.30 Effect of Different Curing Times on Expansion.

Effect of Curing Time on Sulfate Attack

Slump: 2-3 in.; Type II Cement; Fly Ash R

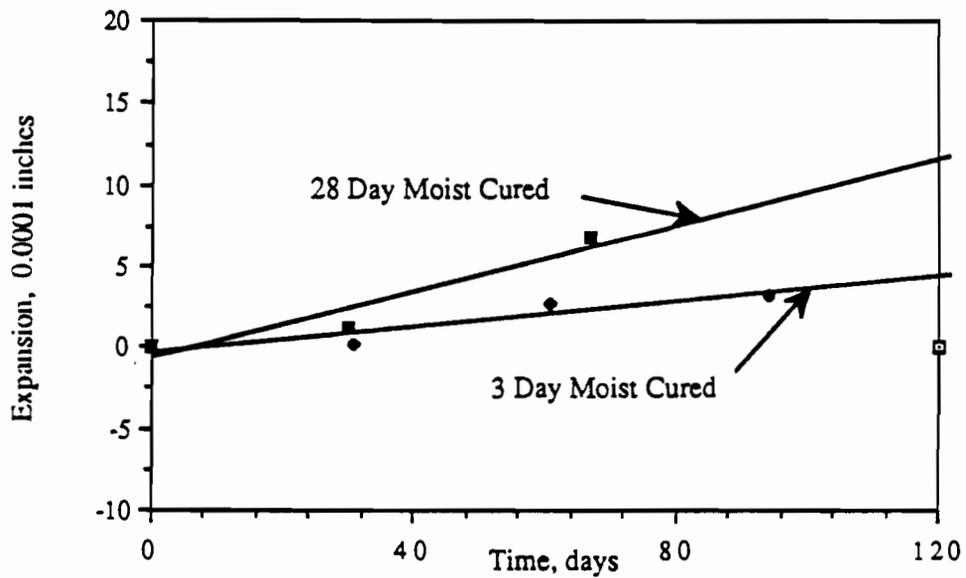


Fig. 5.31 Effect of Different Curing Times on Expansion.

Effect of Curing Time on Sulfate Attack

Slump: 2-3 in.; Type II Cement; Fly Ash T

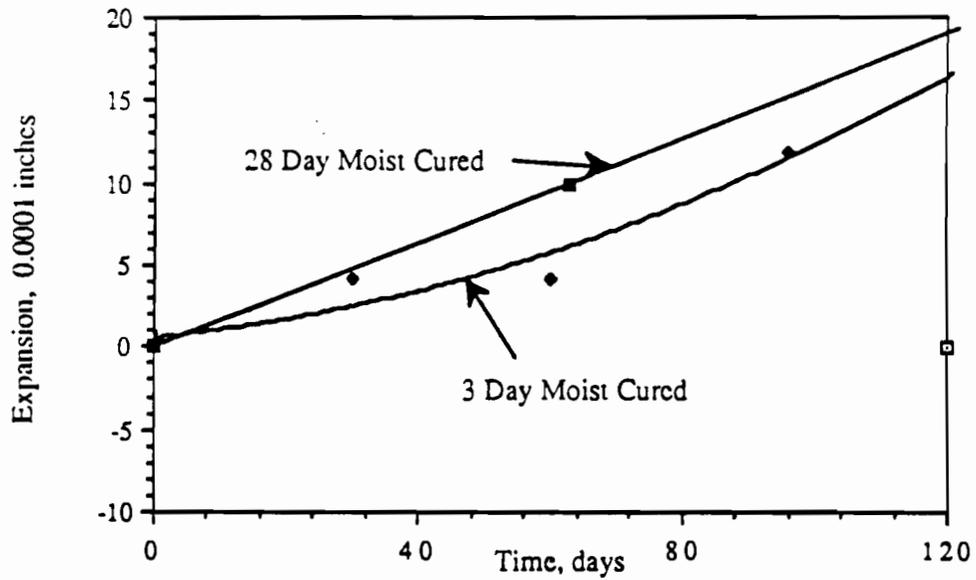


Fig. 5.32 Effect of Different Curing Times on Expansion.

Effect of Curing Time on Sulfate Attack

Slump: 2-3 in.; Type II Cement; Fly Ash W

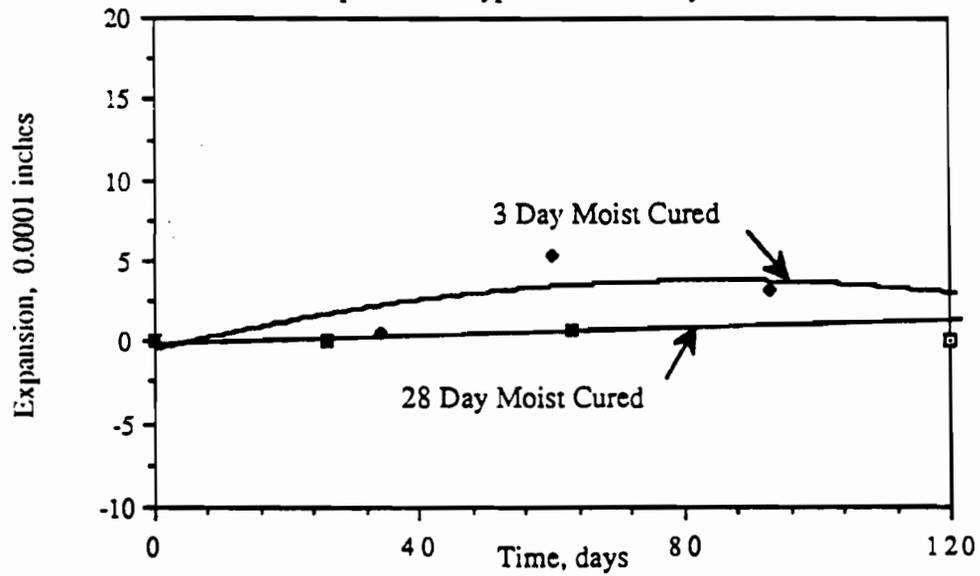


Fig. 5.33 Effect of Different Curing Times on Expansion.

results. However, radial cracking is present in some of these specimens and expansions are being monitored.

Photos 5.1 through 5.15 show the physical condition of specimens containing each type of fly ash after soaking in the sodium sulfate solution. Photos 5.16 and 5.17 display the effect of fly ash content on the degradation of concrete. Photo 5.18 shows the four phases of degradation from sulfate attack through a cross sectional view of the specimens. The specimen on the bottom right is undamaged, while the one on the bottom left shows small radial cracks around the outside rim of the specimen. The top left specimen displays spalling and large radial cracking. The specimen shown in the top right has failed and falls apart at the touch.

Figures 5.2 and 5.3 show the the R factors and OD factors, respectively, of the fly ashes used in this study. The MinChem R factor will be investigated more thoroughly in the next stage of the study.

The expansion behavior of the 6-7 inch slump series is reported in Figures 5.4 through 5.17. These figures also summarize the chemical and crystalline phase characteristics of the fly ash. Figures 5.18 and 5.19 compare the expansions of three different fly ashes, but the same cement replacement level of fly ash. The expansion of concrete with 2-3 in. slump containing fly ashes T, R, D, and P are shown in Figures 5.20 through 5.23, respectively. Figures 5.24 through 5.27 show the effect of curing time on the sulfate expansion of concrete containing fly ash. Figure 5.28 is a plot of the expansions of the control specimens. Figure 5.29 shows the expansions of the concrete proportioned with Type II cement with 0 percent C_3A and fly ash. The effect of curing time is shown in Figures 5.30 through 5.33.

The mass change of concrete subjected to the 10 percent sulfate solution is shown in Figures 5.34 and 5.35. In addition to the results presented in this section, the strength and curing information is presented in Table B-5 of Appendix B.

5.4 Discussion of Test Results.

The test results from the first year are largely inconclusive. The expansion tests require more time to develop a decisive trend

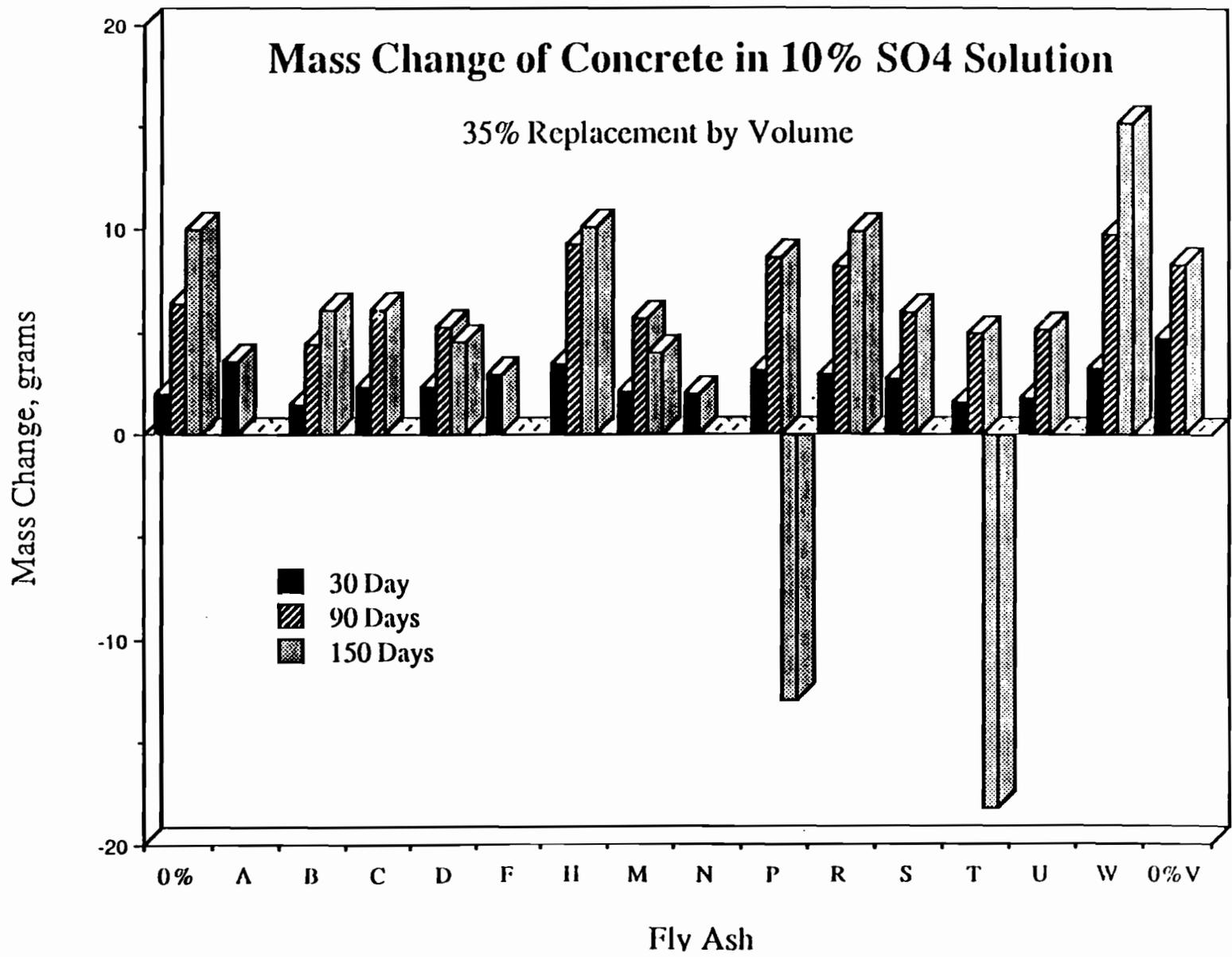


Fig. 5.34 Mass change of concrete containing 35 percent fly ash

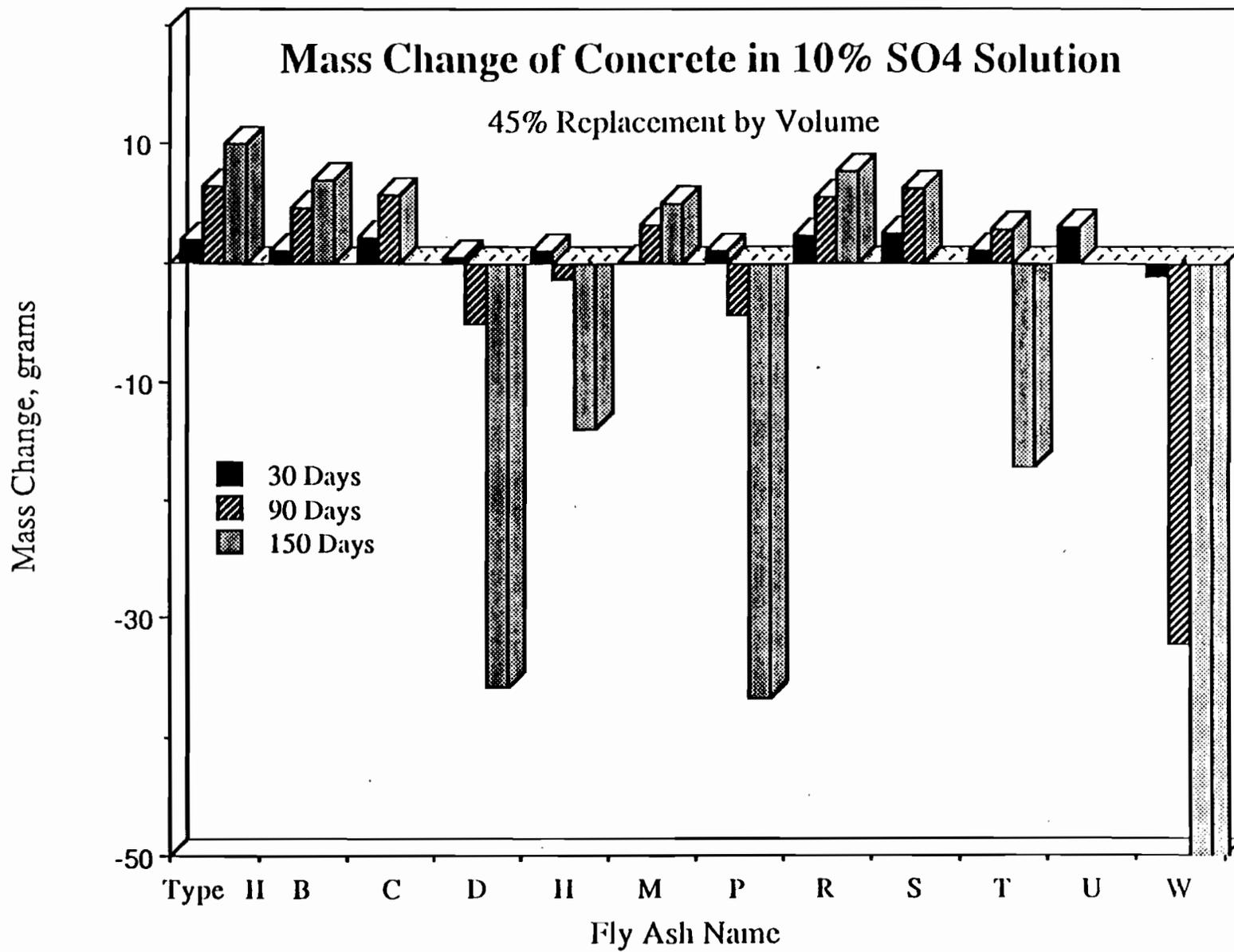


Fig. 5.35 Mass change of concrete containing 45 percent fly ash

in the data. However some concrete has shown physical deterioration and excessive expansions during the 180 days of exposure testing. In addition, several comparisons to the OD and R factors are possible based on test results to date.

The low calcium fly ashes from lignite and bituminous coal sources, B, C, M, N, S, and U, have performed well in the sulfate environment. Specimens cast with these fly ashes, regardless of the percent replacement or workability, show no signs of cracking, loss of mass or expansive damage. These fly ashes had the lowest R and OD factors and are characterized by low calcium contents, and low free lime contents, with the exception of fly ash U. Fly ash U had a free lime content over 2.0 percent according to the ASTM C114 $\text{Sr}(\text{NO}_3)_2$ Method and the second highest OD factor. This is the highest free lime content of all of the fly ashes in this study. The crystalline phases of these six fly ashes were characterized by little or no anhydrite, melilite or tricalcium aluminate and the presence of mullite, quartz and magnetite. The significance of these compounds will be more thoroughly investigated in the second year of the study.

The results of the concrete containing high calcium fly ashes from subbituminous coal sources is less clear. The eight high calcium fly ashes used in this study showed a range of physical deterioration from no damage to complete failure. Failure was judged by both exceeding 0.1 percent expansion and by the inability to measure the specimen for mass loss or expansions due to deterioration. Typically, the specimens cracked radially in the first stage of deterioration and failed by a horizontal through crack in the middle section of the cylinder. The specimens made with fly ash W showed very poor resistance to sulfate attack, with those specimens containing a higher percentage of fly ash deteriorating at a higher rate than those with less fly ash, as shown in Figure 5.17. Fly ash T also performed poorly when proportioned with a 2-3 in. slump, as shown in Figure 5.20. Why the 6-7 in. slump concrete proportioned with fly ash T did not deteriorate at the same or faster rate is being studied more closely. Fly ash W and T were characterized as having a highest calcium oxide contents of the fly ashes in this study and the highest free lime contents of the fly ashes from subbituminous coal sources. The crystalline phases of these two fly ashes indicate a strong presence of tricalcium aluminate, hematite and periclase

and a diminished presence of magnetite. Fly ash A shows these same characteristics, but the specimens are too young to draw any conclusions. In addition to the composition characterization already stated, fly ash W contains a strong presence of anhydrite, melilites, mullite and quartz; whereas fly ash T and A had less intense peaks of anhydrite, melilites and quartz and a diminished presence of mullite. The R and OD factors would both indicate poor performance of these fly ashes in sulfate environments.

Three of the remaining five high calcium fly ashes, D, H, and P, have shown signs of physical degradation when used at higher volume replacement levels. Radial cracking and minor spalling is evident in these specimens, but expansions have not approached failure. This is evident from the changes in mass shown in Figures 5.34 and 5.35. These three high calcium fly ashes are characterized as having calcium oxide and free lime contents in the mid-range of the subbituminous based fly ashes, i.e. 23 to 28 percent and 0.10 to 0.60, respectively. The crystalline phase identification of these fly ashes reveal the presence of tricalcium aluminate, melilites, anhydrite, hematite, periclase, mullite and quartz; except in fly ash H which had strong peaks of quartz and anhydrite. Both the R and OD factors would predict marginal to poor performance of these fly ashes in sulfate environment. It is too soon to evaluate the results of concrete cast with fly ash F, but this fly ash has much the same chemical and crystalline characterization as fly ashes D, H, and P with the exception that shows a diminished presence of quartz and free lime. The R and OD factors would predict a marginal performance for fly ash F in sulfate environments.

Fly ash R has shown good performance in the first part of this study. There are small radial cracks in the specimens containing 45 percent fly ash, but no mass loss or physical deterioration is noted on any of the other specimens containing fly ash R. The R and OD factors would predict marginal performance. The calcium oxide and the free lime contents of both fly ashes are at the lower end of the range for subbituminous coal fly ashes. The crystalline phase analysis shows a diminished presence of hematite, mullite and quartz and the presence of tricalcium aluminate, anhydrite, magnetite, melilites and periclase.

The meaning of the first years results are still unclear because of the long term nature of the sulfate attack mechanism. A more thorough discussion will be possible when the next stage of this experimental program is complete. However, there is enough conclusive evidence based on the observed deterioration of the specimens to implement restrictions stated in the next section.

CHAPTER 6

SUMMARY

6.1 Summary of First Year Results.

Work during the first year of this study concentrated on setting up and starting the implementation of the sulfate expansion experiment. Over 200 of the 600 long term specimens have been soaking in the 10 percent solution of Na_2SO_4 solution for over 150 days. Of these specimens only one set of specimens have reached the 0.1 percent expansion limit. Four specimens have been rendered unmeasurable because of the physical damage, however many specimens are showing physical distress.

At 150 days, the control Type II portland cement along with a Type V and two 0 percent C_3A cements have shown no excessive expansions or cracking from the sulfate environment. The TSDHPT Type A fly ashes which include fly ashes from bituminous and lignite sources have performed very well, even when used at replacement levels as high as 45 percent by volume of Type II portland cement. The TSDHPT Type B fly ashes have shown varied amounts of expansion. The tendency is to have more physical damage when a Type B fly ash is used at higher replacement levels.

The Type B fly ashes with a strong presence of crystalline C_3A have been the most severely damaged by expansions. An analysis of the validity of the R and OD factors show that they generally indicate the trends of expansive concrete containing fly ash, however they are oversimplified by not considering the supersulfating mechanism, or inert crystalline compounds in fly ash. The MinChem R factor, in its present form, has not accurately predicted the expansive damage in concrete containing fly ash. However, this factor is still being developed and may be more applicable with modifications.

The second year will be dedicated to performing quantitative analysis on the concrete containing fly ash in the sulfate environment. Ion permeability of the concrete, XRD on the hydration products, petrographic analysis are among the tests to be performed. In addition, several more fly ashes will be brought

into the study and further development of a prediction method will be pursued.

The advisory panel for this study has provided valuable technical and material assistance. In the second year we hope to draw on information from other studies to better understand the problem of sulfate attack on concrete containing fly ash.

6.2 Implementation.

This report summarizes the findings of the first year of a three year study on the effects of fly ash on the sulfate resistance of concrete containing fly ash. The preliminary findings show that there is a relationship between fly ash composition and sulfate resistance.

This interim report is an overview of the complete experimental project on the sulfate resistance of concrete containing fly ash. The first year's results indicate that the use of high calcium fly ash increase the potential for sulfate attack of concrete. Some lignitic fly ashes add to the sulfate resistance of concrete. On the basis of results to date, recommendations have been made to TSDHPT officials and these recommendations have been incorporated into job concrete specifications to allow only TSDHPT Type A fly ash for the use of concrete exposed to sulfate environments. Until further research produces a means of ensuring adequate sulfate resistance of concrete containing TSDHPT type B fly ash, their use should be restricted to concrete not subjected to sulfate attack.

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APPENDIX A

TABLE A-1
CEMENT CHEMISTRY SHORTHAND NOTATION

<u>Symbol</u>	<u>Chemical Compound</u>
A	Al ₂ O ₃
C	CaO
F	Fe ₂ O ₃
H	H ₂ O
K	K ₂ O
M	MgO
N	Na ₂ O
S	SiO ₂
\bar{S}	SO ₃

APPENDIX B

Table B-1

Chemical and Physical Properties of Portland Cements

	Type II	Type V	Incor	Blue Circle
Physical Data				
Specific Surface				
Blaine	3350	—	—	3625
Compressive				
Strength (psi)				
1-day	2030	—	—	1850
3-day	3670	—	—	3960
7-day	4670	—	—	5069
28-day	—	—	—	6438
Setting Time				
Vicat Test				
Initial Set	132 min.	—	—	140 min.
Final Set	244 min.	—	—	305 min.
Chemical Composition				
SiO ₂	21.8	22.0	21.3	21.8
Al ₂ O ₃	4.2	3.4	2.8	2.5
Fe ₂ O ₃	3.2	3.2	4.8	3.8
CaO	64.7	64.9	64.4	64.8
MgO	0.6	3.3	3.9	1.3
SO ₃	2.9	2.5	3.0	2.3
LOI	0.90	0.56	0.70	1.27
Insol. Residue	0.30	0.19	0.17	0.44
Free Lime	0.90	—	—	1.61
C ₃ S	54	62	66	70
C ₃ A	6.0	3.6	0.0	0.0
Total Alkali	0.63	0.52		0.54
C ₄ AF + C ₂ F		9.8	14.6	11.6
C ₂ S		16.2	11.27	9.6

Table B-2

FLY ASHES USED IN THIS STUDY

3 Bituminous Coal Ashes (B)
 3 Lignite Coal Ashes (L)
 8 Subbituminous Coal Ashes (S)

Fly Ash	Location	Coal Type		CaO (%)	Fe ₂ O ₃ (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	Sum of Metal Oxides (%)
A	TEXAS	S	B	29.9	5.0	32.2	22.2	59.4
B	TEXAS	L	A	9.5	9.0	52.9	17.9	79.8
C	N.M.	L	A	10.1	6.0	42.5	24.1	72.6
D	TEXAS	S	B	28.0	5.0	31.3	22.5	58.8
F	TEXAS	S	B	26.3	5.8	33.3	24.1	63.2
H	OK	S	B	22.8	5.2	33.7	24.8	63.7
M	TEXAS	L	A	7.0	4.3	55.6	18.6	78.5
N	GA	B	A	1.6	16.1	43.0	27.4	86.5
P	TEXAS	S	B	23.1	5.1	35.6	22.4	63.1
R	TEXAS	S	B	22.4	6.7	34.5	23.8	65.0
S	UTAH	B	A	3.7	4.7	45.9	24.1	74.7
T	TEXAS	S	B	31.3	4.7	30.8	21.9	57.4
U	UTAH	L	A	8.8	5.6	50.9	18.6	75.1
W	TEXAS	S	B	33.9	4.9	28.4	20.2	53.5

Table B-2 (Cont.)

Fly Ash	MgO (%)	SO ₃ (%)	LOI (%)	S.G.	<u>Fineness</u>		Av. Alk. (%)	Pozz. Act.
					R#325	Blaine		
A	5.6	2.5	.03	2.70	18.9	4220	1.67	91.6
B	1.7	0.9	.19	2.43	23.8	2560	0.57	90.9
C	1.6	0.5	.93	2.28	16.6	4325	—	103.3
D	4.3	2.3	.45	2.70	17.0	3925	1.56	100.1
F	4.2	—	.46	2.60	14.3	4560	4.35	—
H	5.7	—	.06	2.59	8.20	—	0.86	—
M	0.8	0.3	.04	2.32	13.3	2520	0.31	97.1
N	0.0	1.2	.90	2.43	15.4	2430	—	86.0
P	4.3	2.1	.52	2.58	22.0	3820	2.04	100.0
R	3.9	2.0	.28	2.57	17.3	4365	2.35	—
S	0.0	0.4	1.62	2.18	18.2	4030	—	97.2
T	6.1	2.0	.17	2.73	15.7	3935	1.67	105.4
U	0.5	0.7	3.90	2.23	46.3	2875	—	74.1
W	8.4	4.5	.25	2.79	10.4	3510	1.54	91.5

Table B-3

FLY ASH CRYSTALLINE PHASE RANKING

Fly Ash	CaSO ₄	C ₃ A	Hem	CaO	Mag	Mel	Mul	MgO	SiO ₂	Sp
A	7	1	3	5	—	6	—	4	2	8
B	—	—	5	—	4	—	3	2	1	—
C	—	—	3	7	2	4	—	5	1	6
D	8	2	4	5	—	3	6	7	1	9
F	3	4	9	8	10	1	6	5	2	7
H	7	2	5	4	8	6	10	3	1	9
M	—	—	5	—	4	6	3	2	1	—
N	—	—	3	5	2	—	7	6	1	4
P	5	2	6	10	8	4	7	3	1	9
R	6	2	7	—	5	3	—	4	1	—
S	9	—	5	2	3	7	6	4	1	8
T	7	1	3	5	8	6	—	4	2	9
U	—	2	7	8	4	—	6	3	1	5
W	7	2	5	4	11	6	8	3	1	9

Small amount of alkali sulfate were identified in fly ashes C, D, P, R, and U.

Table B-4

CONCRETE MIX PROPORTIONS

(per cubic yard at SSD)

Mix No.	Cement	Fly Ash	Stone	Sand	Water	Admixture
CNTL 45	565.4	0.0	1613.7	1499.7	246.8	none
CNTL 55	580.5	0.0	1657.0	1387.5	267.0	none
CNTL 45-2	558.7	0.0	1591.2	1534.9	248.8	none
CNTL 55-2	568.2	0.0	1607.9	1357.9	301.9	none
CNTL 53	516.2	0.0	1565.7	1519.1	274.5	none
CNTL 47	508.9	0.0	1543.6	1586.0	260.0	none
CNTL 49	519.8	0.0	1662.9	1662.9	242.8	none
CNTL 46	505.8	0.0	1590.1	1590.1	263.7	none
TYPEV 7	522.1	0.0	1536.6	1536.6	258.8	none
TYPEV 3	511.1	0.0	1550.1	1605.7	249.6	none
ZERO 7	507.3	0.0	1530.5	1492.6	301.5	none
ZERO 3	516.2	0.0	1565.7	1621.9	235.5	none
T25-7	390.6	114.6	1579.5	1532.5	262.4	none
T35-7	335.5	159.0	1585.5	1519.1	274.6	none
T45-7	284.9	205.2	1570.9	1524.4	269.8	none
W25-7	387.2	116.1	1565.9	1519.8	274.1	none
W35-7	337.6	163.6	1575.1	1528.8	266.0	none
W45-7	286.7	211.3	1575.3	1534.0	263.4	none
H25-7	369.9	111.0	1576.7	1529.9	264.8	none
H35-7	341.1	157.0	1591.1	1543.8	252.2	none
H45-7	296.1	201.0	1582.3	1535.8	256.0	none
P25-7	388.8	107.8	1572.6	1525.9	268.5	none
P35-7	337.5	151.3	1574.5	1527.8	266.7	none
P45-7	287.3	195.7	1584.7	1537.7	257.8	none
B25-7	391.6	102.3	1583.6	1536.7	258.8	none
B35-7	347.3	146.5	1619.9	1516.6	248.0	none
B45-7	283.9	182.0	1585.6	1519.0	274.6	none
M25-7	391.7	97.7	1584.1	1537.2	258.3	none
M35-7	342.1	137.9	1595.7	1548.4	248.1	none
M45-7	288.5	176.7	1591.0	1543.8	252.3	none
D25-7	389.1	113.0	1573.7	1525.9	267.5	none
D35-7	338.1	158.6	1577.2	1530.4	264.3	none
D45-7	289.1	205.9	1594.2	1545.9	249.5	none
R25-7	394.9	109.2	1596.8	1549.4	247.3	none
R35-7	335.7	149.9	1558.1	1519.5	277.2	none
R45-7	285.0	193.3	1563.9	1525.1	272.3	none
S25-7	380.1	89.2	1537.3	1491.6	299.3	none
S45-7	289.4	166.5	1595.9	1548.5	248.0	none
C25-7	387.1	94.9	1565.6	1519.1	274.6	none
C45-7	283.8	170.9	1565.5	1519.0	274.6	none
U25-7	389.3	93.25	1574.4	1527.6	256.9	none
U45-7	286.0	168.4	1577.5	1530.6	264.1	none

Table B-4 (cont)

Mix No.	Cement	Fly Ash	Stone	Sand	Water	Admixture
T25-3	387.1	113.7	1585.6	1621.9	235.6	POZZ 300R
T35-3	331.3	157.1	1545.6	1601.3	253.5	POZZ 300R
T45-3	280.0	201.9	1544.5	1600.1	254.6	POZZ 300R
W25-3	388.5	116.5	1571.2	1637.1	227.0	POZZ 300R
W35-3	336.7	163.2	1571.1	1637.1	227.0	POZZ 300R
W45-3	285.0	209.7	1571.2	1637.1	227.0	POZZ 300R
H25-3	385.7	109.9	1559.8	1625.3	237.2	POZZ 300R
H35-3	331.6	152.6	1547.4	1612.4	248.4	POZZ 300R
H45-3	285.0	199.3	1571.1	1637.1	227.0	POZZ 300R
P25-3	388.6	101.8	1571.3	1627.8	230.4	POZZ 300R
P35-3	337.9	151.4	1576.3	1633.0	225.9	POZZ 300R
P45-3	283.2	193.3	1585.6	1621.9	235.6	POZZ 300R
B25-3	389.2	101.7	1573.8	1630.4	228.2	POZZ 300R
B35-3	339.0	143.2	1579.7	1636.8	222.5	POZZ 300R
B45-3	284.0	182.1	1565.6	1621.8	235.6	POZZ 300R
M25-3	391.8	98.0	1588.8	1644.8	215.5	POZZ 300R
M35-3	339.5	136.8	1584.3	1641.3	218.8	POZZ 300R
M45-3	288.4	176.5	1589.9	1647.1	213.7	POZZ 300R
D25-3	383.4	111.3	1550.6	1607.5	248.7	POZZ 300R
D35-3	335.6	157.4	1585.6	1623.0	235.1	POZZ 300R
D45-3	278.8	198.9	1537.8	1594.2	250.2	POZZ 300R
R25-3	387.1	107.0	1595.6	1621.9	235.6	POZZ 300R
R35-3	335.5	149.9	1585.5	1621.9	235.6	POZZ 300R
R45-3	283.8	192.6	1585.6	1621.9	235.6	POZZ 300R
A35-7	337.15	158.20	1573.13	1526.44	267.88	none
F35-7	338.13	152.68	1577.67	1530.86	263.94	none
N35-7	336.05	141.84	1567.99	1521.45	272.40	none
BLUE-7	510.51	0.0	1548.57	1502.55	289.42	none
BBLUE-7	337.12	142.29	1573.07	1526.32	268.00	none
DBLUE-7	335.49	157.41	1565.47	1518.95	274.61	none
NBLUE-7	335.50	141.60	1565.49	1518.98	274.62	none
PBLUE-7	336.52	150.87	1570.28	1523.62	270.41	none
TBLUE-7	339.11	160.75	1582.22	1535.27	259.98	none
WBLUE-7	335.49	162.62	1565.48	1518.96	274.61	none
CNTL-7A9	483.19	0.0	1465.55	1422.06	252.42	MB - VR
CNTL-7A7	506.83	0.0	1537.39	1434.44	245.07	MB - VR
CNTL-7A5	513.45	0.0	1587.47	1453.18	261.50	MB - VR
D35-7A	335.14	157.25	1563.72	1517.32	242.40	MB - VR
T35-7A	334.09	158.37	1568.82	1512.56	250.96	MB - VR
W35-7A	339.39	164.52	1583.68	1477.63	247.36	MB - VR
P35-7A	346.05	155.14	1614.81	1506.68	271.13	MB - VR

Table B-5
CURING INFORMATION FOR PRIMARY STUDY

<u>Fly Ash</u>	<u>Content</u>	<u>Days to 3500</u>	<u>28 Day Fc'</u>
Type II		5	5120
A	35%	20	-----
B	25%	19	-----
	35%	12	4112
	45%	26	3657
C	25%	14	4204
D	25%	3	5376
	35%	5	6126
	45%	8	5939
F	35%	20	-----
H	25%	9	5007
	35%	9	5053
	45%	11	5032
M	25%	7	5007
	35%	19	-----
	45%	23	3757
N	35%	28	2700
P	25%	3	4384
	35%	4	4622
	45%	13	5016
R	25%	3	5870
	35%	5	5144
	45%	10	5680
S	25%	28	3465
T	25%	3	4720
	35%	7	4710
	45%	10	5475
U	25%	14	4284
W	25%	10	5220
	35%	10	3951
	45%	10	4578