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16. Abstract

The utilization of fly ash in concrete is advantageous for several reasons, including: (1) reduced need for the disposal of fly ash; (2) reduced cost of concrete; and (3) improved physical and mechanical properties of concrete. Improvements in the properties of concrete include improved workability, decreased temperature rise, increased long-term strength, and decreased long-term permeability.

Unfortunately, fly ash has variable effects on the sulfate resistance of concrete. Uncertainties concerning these effects have often limited its use.

This report describes a study in which researchers investigated the relationship between the composition of fly ash and the effects of fly ash on the sulfate resistance of concrete. Both the chemical and mineralogical compositions of fly ash were considered.

This study also included an investigation of the production of sulfate resistant concrete containing non-sulfate resistant fly ash. The purpose of this portion of the study was to facilitate the utilization of fly ash from Texas.

Methods for improving the performance of non-sulfate resistant fly ash concrete included both physical and chemical techniques. Physical techniques included increasing mixture design cement concrete and intergrinding fly ash with cement clinker and gypsum, as in the production of blended cements. These physical techniques were anticipated to decrease concrete permeability and thereby improve resistance to the ingress of harmful sulfate solution. Chemical techniques included adjustments in the gypsum content of blended fly ash cement and the utilization of sodium sulfate as a chemical additive in concrete. These chemical techniques were designed to optimize the sulfate and alkali contents of cement in order to account for the chemistry of fly ash.

Fly ash was obtained from 24 power plants within the U.S. and Canada. The mineralogy of fly ash was found to be significant in terms of the effects of fly ash on the sulfate resistance of concrete.

17. Key Words

fly ash, concrete, cement, sulfates, sulfate resistant, workability, strength, permeability, chemical, mineralogical, composition, performance

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OPTIMIZATION OF THE PHYSICAL AND COMPOSITIONAL CHARACTERISTICS OF FLY ASH CEMENT FOR THE PRODUCTION OF SULFATE RESISTANT CONCRETE

by

Reed B. Freeman
Ramon L. Carrasquillo

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Research Project 3-5/9-87-481

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in Hot Weather Concreting and Prestressed Concrete Girders

conducted for

Texas Department of Transportation

in cooperation with the

U. S. Department of Transportation
Federal Highway Administration

by the

CENTER FOR TRANSPORTATION RESEARCH

Bureau of Engineering Research

THE UNIVERSITY OF TEXAS AT AUSTIN

August 1992

NOT INTENDED FOR CONSTRUCTION,
PERMIT, OR BIDDING PURPOSES

Ramon L. Carrasquillo, P.E. (Texas No. 63881)
Research Supervisor

PREFACE

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

The study described in this report was part of Research Project 3-5/9-87-481, entitled "Durability and Performance of Concrete Containing Fly Ash." The study was jointly conducted by the Center for Transportation Research, the Bureau of Engineering Research, and the Ferguson Structural Engineering Laboratory at The University of Texas at Austin. The study was sponsored by the Texas Department of Transportation.

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

SUMMARY

The utilization of fly ash in concrete is advantageous for several reasons, including:

1) reduced need for the disposal of fly ash,
2) reduced cost of concrete, and
3) improved physical and mechanical properties of concrete.

Improvements in the properties of concrete include improved workability, decreased temperature rise, increased long-term strength, and decreased long-term permeability.

Unfortunately, fly ash has variable effects on the sulfate resistance of concrete. Uncertainties concerning these effects have often limited its use.

This report describes a study in which researchers investigated the relationship between the composition of fly ash and the effects of fly ash on the sulfate resistance of concrete. Both the chemical and mineralogical compositions of fly ash were considered.

This study also included an investigation on the production of sulfate resistant concrete containing non-sulfate resistant fly ash. The purpose of this portion of the study was to fascilitate the utilization of fly ash from Texas.

Methods for improving the performance of non-sulfate resistant fly ash concrete included both physical and chemical techniques. Physical techniques included increasing mixture design cement content and intergrinding fly ash with cement clinker and gypsum, as in the production of blended cements. These physical techniques were anticipated to decrease concrete permeability and thereby improve resistance to the ingress of harmful sulfate solution.

Chemical techniques included adjustments in the gypsum content of blended fly ash cement and the utilization of sodium sulfate as a chemical additive in concrete. These chemical techniques were designed to optimize the sulfate and alkali contents of cement in order to account for the chemistry of fly ash.

Fly ash was obtained from 24 power plants within the U.S. and Canada. Source coal types included bituminous, subbituminous, and lignite. Fly ash partially replaced 3 portland cements: an ASTM Type II cement and two ASTM Type I cements. Levels of replacement included 25, 35, and 45 percent by volume.

The mineralogy of fly ash was found to be significant in terms of the effects of fly ash on the sulfate resistance of concrete. A parameter termed Modified Calcium Aluminate Potential was offered as a method for predicting these effects on sulfate resistance. The Modified

Calcium Aluminate Potential model considers the average composition of amorphous phases plus reactive crystalline phases in fly ash.

Increased cement content and intergrinding fly ash improved the performance of Type II cement concrete containing moderately sulfate resistant fly ash, but did not significantly improve the performance of Type II cement concrete containing non-sulfate resistant fly ash.

Adjustments in the gypsum content of blended fly ash cement and the inclusion of sodium sulfate as a chemical additive in concrete significantly improved the performance of Type II cement concrete containing non-sulfate resistant fly ash.

IMPLEMENTATION

This report presents the results of a six-year study concerning the sulfate resistance of concrete containing fly ash. Several recommendations are made for improving the durability of fly ash concrete exposed to sulfate environments. Many of the recommendations from earlier parts of this study have already been implemented into TxDOT concrete construction practice and, hence, not repeated here.

A parameter termed Modified Calcium Aluminate Potential is presented as a criterion for selecting fly ash for sulfate resistant concrete. This parameter utilizes the chemical and mineralogical compositions of fly ash in order to estimate the potential for fly ash to contain reactive calcium aluminate phases. Construction specifications currently used by the Texas Department of Transportation would allow the use of certain sulfate-susceptible fly ashes to serve as partial replacements for Type II cement in concrete construction. The use of MCAP would prevent the use of these fly ashes in construction.

The effectiveness of using physical methods for improving the sulfate resistance of fly ash concrete is also discussed. These methods, which decrease concrete permeability, are effective in improving the performance of moderately sulfate resistant fly ash concrete. However, these methods do not significantly improve the durability of sulfate-susceptible fly ash concrete.

Chemical methods for improving the sulfate resistance of fly ash concrete are also presented. These methods involve the optimization of sulfate and alkali contents in cement in order to compensate for the inclusion of fly ash. Examples include adjustments in the gypsum content in blended fly ash cements and the utilization of sodium sulfate as a chemical additive. These methods are effective in improving the durability of concrete containing fly ash, including sulfate-susceptible fly ash, such as those which are predominantly produced in Texas. Above all, the benefits of intergrinding in the production of blended cements is demonstrated.

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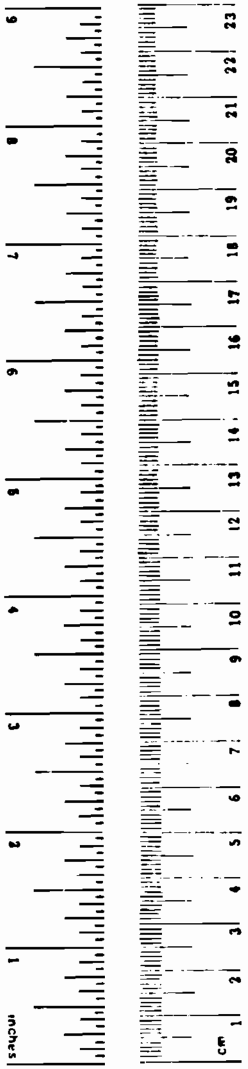
METRIC CONVERSION FACTORS

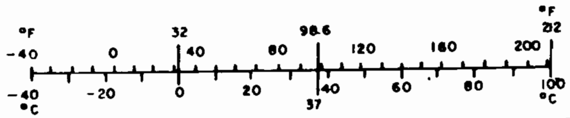
Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C



Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



CHAPTER 1

INTRODUCTION

1.1 GENERAL

1.1.1 FLY ASH

Fly ash is a by-product of the combustion of coal in power plants. It is removed from stack emissions by pollution control devices, such as fabric filters. Fly ash which is not used in some manner must be discarded. Discarding fly ash is expensive and potentially harmful to the environment. As an example, effluent from ash disposal ponds contains trace quantities of toxic elements (450,107).

According to the United States Department of the Interior, coal ash ranks sixth in terms of abundance of solid minerals (243). Recognition of fly ash as a solid waste problem prompted the Environmental Protection Agency to issue the "Guideline for Federal Procurement of Cement and Concrete Containing Fly Ash" (436). This guideline, which was issued in 1983, requires Federal agencies to permit the use of fly ash when procuring concrete. It also provides recommendations for controlling the quality of cement and concrete products which contain fly ash.

The use of fly ash as a partial replacement for cement, either as an admixture or interground, reduces energy consumption per ton of product and may increase cement plant capacity. Fly ash has also been found to provide benefits for the physical and mechanical properties of portland cement concrete. For example, fly ash can improve workability, decrease heat evolution during hydration, increase long-term compressive strength, and decrease long-term permeability. Consequently, cement producers and electric utilities have the opportunity to collaborate for mutual economic and environmental benefit (154).

Since almost one-half of total U.S. consumption of cement is in public construction projects and since federal funds account for nearly two-thirds of these projects, fly ash has recently been used extensively in concrete (154).

In 1987, fly ash production around the world totalled approximately 280 million tons. Twenty-four million tons of fly ash were used in the construction industry, approximately 88 percent of which was used in concrete: one million tons used as a cement raw material, 5 million tons used in blended cements, and 15 million tons used as a cement replacement (243). Fly ash has also been used as a fill material, a road stabilizer, an asphalt filler, and a constituent of bricks and ceramics (243).

1.1.2 SULFATE ATTACK

Sulfate attack is a widespread and common form of chemical-related deterioration of concrete. Sources of sulfates include alkali and gypsiferous soils, seawater, and some industrial wastes (295).

In the presence of moisture, sulfate ions and some constituents of hardened concrete can participate in expansive reactions. Constituents which can participate in these reactions include calcium hydroxide, unhydrated tricalcium aluminate, and various reactive alumina-bearing hydration products.

Initially, expansive reactions may densify the concrete without obvious damage. However, if expansions continue, internal stresses will develop and will eventually cause warping, cracking, and spalling of concrete. In addition to material deterioration, sulfate attack can cause structural problems. For example, the horizontal thrust of an expanding slab can displace walls (278).

The potential for sulfate attack in a particular geographical area can be measured by the concentrations of sulfate (SO_4) in water and water soluble sulfate in soil. The U.S. Bureau of Reclamation established a classification of four levels of exposure severity based on these concentrations of sulfates.

In order to ensure long-term concrete durability, the American Concrete Institute Building Code (7) includes requirements for cement type and water/cement ratio for each USBR level of sulfate exposure severity. The requirements for cement type are designed to minimize the potential for concrete constituents to participate in expansive reactions with sulfates. The requirements for water/cement ratio are designed to ensure that concrete has a sufficiently low permeability to resist the intrusion of aggressive solutions.

The requirements for cement type include provisions for the utilization of fly ash. The fly ash cements must be determined by exposure test or field record to be resistant to sulfate attack.

Standard Specifications for the Texas Department of Transportation do not differentiate between exposure severities. However, all substructure concrete must contain a moderately sulfate resistant cement (216).

1.2 STATEMENT OF PROBLEM

Although fly ash can improve many physical and mechanical properties of concrete, its effects on the resistance of concrete to sulfate attack are variable. These effects are primarily dependent on fly ash chemistry and mineralogy. Fly ash is a potential source of reactive calcium aluminates, which may participate in expansive reactions with sulfates after the concrete has hardened.

The chemical composition of fly ash is primarily dependent on the composition of the coal from which it was derived. The mineralogy of fly ash is dependent on the composition of the source coal and the burning conditions of the power plant. Fly ash derived from bituminous coals does not contain substantial proportions of calcium aluminates. However, fly ash derived from lignite and subbituminous coals may contain significant quantities of this sulfate-reactive material.

Portland cement is composed primarily of four crystalline compounds. Its potential for expansive sulfate reactions can be easily predicted by its tricalcium aluminate and tetracalcium aluminoferrite contents.

Contrarily, fly ash is partially amorphous and may contain a complex array of crystalline compounds. Therefore, predicting the potential for fly ash to promote expansive sulfate reactions is much more difficult.

1.3 JUSTIFICATION FOR RESEARCH

Approximately two-thirds of the fly ash produced by power plants in Texas is derived from lignite and subbituminous coals (112). Many of the lignite coals are mined in Texas and many of the subbituminous coals are mined in Wyoming. Due to the extensive use of these low-rank coals, a large portion of the readily available fly ash in Texas is potentially harmful for the sulfate resistance of concrete.

Producers and consumers of cement and concrete in Texas would like to know which fly ashes to avoid when concrete is to be placed in a sulfate exposure environment. The criterion for selecting fly ash for sulfate exposure environments should require only short-term tests because the physical and compositional characteristics of fly ash produced at a single plant may change with time. Long-term tests would provide results for fly ash which may no longer exist.

Since a large percentage of the readily-available fly ash in Texas may be susceptible to sulfate attack, members of the construction industry would also like to know if the sulfate resistance of mixtures containing these fly ashes can be improved to an acceptable level.

1.4 RESEARCH OBJECTIVES

The primary objectives of this study were:

1) to recommend a criterion, based on physical and compositional characteristics, for selecting fly ash to be used in concrete in sulfate exposure environments;
2) to recommend an exposure test for future studies on the sulfate resistance of concrete; and
3) to recommend alternatives for improving the performance of non-sulfate resistant fly ash concrete mixtures.

1.5 EXPERIMENTAL PROGRAM

The long-term sulfate resistance of concrete mixtures was evaluated with an accelerated sulfate exposure laboratory test. Accelerated sulfate exposure in the laboratory involved immersion of 3x6-inch concrete cylinders in 10 percent sodium sulfate solution.

In order to meet the objectives of this study, five series of immersion tests were implemented:

1) Series A - to study the relationship between fly ash composition and the sulfate resistance of fly ash concrete;
2) Series B - to study the effects of mixture design cement content;
3) Series C - to study the effects of intergrinding fly ash with cement clinker and gypsum;
4) Series D - to study the effects of high sulfate and/or high alkali contents in fly ash cements; and
5) Series E - to study the applicability of blended cements which contain large proportions of fly ash.

Unless otherwise specified, concrete was designed with 5½ sacks of cement per cubic yard of concrete. Mixing water was added until a fresh concrete slump of 5 to 7 inches was attained.

In order to study the relationships between fly ash composition, cement composition, and the resistance of concrete to sulfate attack, fly ash was added as a mineral admixture to concrete containing an ASTM Type II cement and two ASTM Type I cements, as shown in Table 1.1. Type I-L and Type I-H cements contain relatively low and high proportions of tricalcium aluminate, respectively. Twelve Texas Type A fly ashes and twelve Texas Type B fly ashes partially replaced cement at levels of 25, 35, and 45 percent by volume.

In order to study the effects of mixture design cement content on the sulfate resistance of fly ash concrete, several mixtures containing Texas Type B fly ash and ASTM Type II cement were produced with cement factors of 5½ sacks and 7 sacks per cubic yard. Six Type B fly ashes replaced cement as mineral admixtures at levels of 25, 35, and 45 percent by volume, as shown in Table 1.2. Decreased water/(cement+pozzolan) ratios were anticipated to decrease concrete permeability and to increase sulfate resistance.

Table 1.1. Test Series A

Cement	Type II	Type I-L	Type I-H
Fly Ash	12 Type A 12 Type B	5 Type A 5 Type B	6 Type A 7 Type B
Cement Replacement (vol.%)	0, 25, 35, 45	0 , 25, 35	0, 25, 35
Method of Fly Ash Inclusion	mineral admixture	mineral admixture	mineral admixture

Table 1.2 Test Series B

Cement	Type II
Fly Ash	6 Type B
Cement Replacement (vol.%)	0, 25, 35, 45
Method of Fly Ash Inclusion	mineral admixture
Cement Factor (sacks/cu.yd.)	5½, 7

In order to study the effects of intergrinding fly ash on the sulfate resistance of fly ash concrete, Texas Type A and Type B fly ashes were interground with ASTM Type I and Type II cement clinker. Six Type A fly ashes and 8 Type B fly ashes replaced cement at levels of 25 and 35 percent by volume, as shown in Table 1.3. Increased fly ash reactivity and cement homogeneity were anticipated to decrease concrete permeability and to increase sulfate resistance.

Table 1.3 Test Series C

Cement	Type I-H	Type II
Fly Ash	6 Type A 7 Type B	6 Type A 8 Type B
Cement Replacement (vol.%)	0, 25, 35	
Method of Fly Ash Inclusion	mineral admixture, interground	

In order to study the effects of high sulfate and/or high alkali contents on the sulfate resistance of fly ash concrete, additional gypsum, sodium hydroxide, and sodium sulfate were added. Additional gypsum was interground with blended fly ash cements, and sodium hydroxide and sodium sulfate were dissolved in concrete mixing water. Mixtures containing sodium sulfate included five Texas Type B fly ashes partially replacing an ASTM Type II cement at a level of 35 percent by volume, as shown in Table 1.4. Mixtures containing additional gypsum and sodium hydroxide included two Type B fly ashes partially replacing a Type II cement at a level of 35 percent by volume, as shown in Table 1.5. Increased reactivity of fly ash and the availability of sulfate during initial hydration reactions were anticipated to increase the long-term sulfate resistance of fly ash concrete.

In order to study the applicability of blended cements which contain large proportions of sulfate-susceptible fly ash, two Texas Type B ashes were interground with an ASTM Type II cement. Fly ash was interground at levels of 45 percent and 55 percent by volume, as shown in Table 1.6. The effects of high sulfate and high alkali contents were studied by dissolving sodium sulfate in the mixing water. Since the high fly ash contents increased the percentage of amorphous material in cements, the effects of sodium sulfate on both reactivity and composition of hydration products were anticipated to be intensified.

Table 1.4 Test Series D (Part 1)

Cement	Type II	
Fly Ash	5 Type B	
Cement Replacement (vol.%)	35	
Method of Fly Ash Inclusion	mineral admixture	inter-ground
Chemical Admixture Na_2SO_4 *	6 levels	7 levels

* dissolved in mixing water

Table 1.5 Test Series D (Part 2)

Cement	Type II
Fly Ash	2 Type B
Cement Replacement (vol.%)	35
Method of Fly Ash Inclusion	Interground
Additional Gypsum *	4 levels
Chemical Admixture NaOH **	4 levels

* Interground with clinker
** dissolved in mixing water

Table 1.6 Test Series E

Cement	Type II
Fly Ash	2 Type B
Cement Replacement (vol.%)	45, 55
Method of Fly Ash Inclusion	Interground
Chemical Additive Na_2SO_4 *	4 levels

* dissolved in mixing water

1.6 REPORT FORMAT

A review of literature concerning topics relevant to this study is presented. Topics include:

1) portland cement, including hydration reactions,
2) sulfate attack, including the effects of concrete mixture design variables,
3) fly ash, including its effects on the sulfate resistance of concrete,
4) blended fly ash cements, and
5) alkali-activated cements.

Materials and procedures used in this study are presented. Procedures include those for materials characterization, concrete mixing and casting, and tests performed on hardened concrete.

Results of this study are presented and discussed in the following order:

1) evaluation of the sulfate exposure test, including repeatability and duration requirements,
2) ASTM Type II cement mixtures containing fly ash as a mineral admixture,

3) ASTM Type I cement mixtures containing fly ash as a mineral admixture,

4) fly ash cement concrete with a high cement factor,

5) blended fly ash cement concrete,

6) fly ash cement concrete containing high sulfate and/or high alkali contents, and

7) blended fly ash cement concrete containing large proportions of fly ash.

In addition to presenting sulfate exposure results, fresh concrete properties, compressive strength developments, and permeabilities of hardened concrete are presented.

This report concludes with recommendations for the production and continued development of sulfate resistant fly ash concrete.

1.7 NOTATION

The oxides and compounds of portland cement are referred to by shorthand notation throughout this report. Typical oxides and compounds found in ordinary portland cement are shown in Tables 1.7 and 1.8, respectively.

Minerals found in fly ash are referred to by name in this study where possible. Due to space limitations in tables and figures, minerals are sometimes referred to by two-letter abbreviations, as shown in Table 1.9.

1.8 PROJECT SPONSORSHIP AND ADMINISTRATION

This project was sponsored by the Texas Department of Transportation. The Texas DOT Materials and Test Division provided technical expertise and guidance.

This project was administered by the Center for Transportation Research at The University of Texas at Austin. It was part of Study Number 3-5/9-87-481, "Durability and Performance of Concrete Containing Fly Ash Including Its Use in Hot Weather Concreting and Prestressed Concrete Girders."

This study was conducted at the Ferguson Structural Engineering Laboratory at The University of Texas at Austin.

Table 1.7 Shorthand Notation of Oxides in Ordinary Portland Cement

Shorthand Notation	Oxide	Common Name
C	CaO	lime
S	SiO_2	silica
A	Al_2O_3	alumina
F	Fe_2O_3	ferric oxide
M	MgO	magnesia
K	K_2O	alkalies
N	Na_2O	
$\bar{S}$	SO_3	sulfur trioxide
H	H_2O	water

Table 1.8 Shorthand Notation of Compounds in Ordinary Portland Cement

Shorthand Notation	Chemical Formula	Chemical Name
C_3S	$3CaO \cdot SiO_2$	Tricalcium Silicate
C_2S	$2CaO \cdot SiO_2$	Dicalcium Silicate
C_3A	$3CaO \cdot Al_2O_3$	Tricalcium Aluminate
C_4AF	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	Tetracalcium Aluminoferrite
$C\bar{S}H_2$	$CaSO_4 \cdot 2H_2O$	Calcium Sulfate Dihydrate (gypsum)

Table 1.9 Mineral Names, Abbreviations, and Chemical Compositions

Mineral Name (abbreviation)	Chemical Composition
Akermanite (Ak)	$Ca_2MgSi_2O_7$
Anhydrite (Ah)	$CaSO_4$
Bredigite (Bd)	$Ca_{1.75}Mg_{0.25}SiO_4$
Calcite (Cc)	$CaCO_3$
Calcium Monosulfoaluminate ($C_4A\bar{S}H_{12\text{-}18}$)	$Ca_4Al_2(SO_4)(OH)_{12} \cdot (6\text{-}12)H_2O$
Calcium Trisulfoaluminate (Ettringite: $C_6A\bar{S}_3H_{32}$)	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$
Dicalcium Silicate (C_2S)	Ca_2SiO_4
Ferrite Spinel (Sp)	$(Mg_{0.5}Fe_{0.5})Fe_2O_4$
Gehlenite (Geh)	$Ca_2Al_2SiO_7$
Hematite (Hm)	Fe_2O_3
Lime (Lm)	CaO
Magnetite	Fe_3O_4
Magnesioferrite	$MgFe_2O_4$
Melilite (Ml)	$Ca_2Mg_{0.5}AlSi_{1.5}O_7$
Merwinite (Mw)	$Ca_3Mg(SiO_4)_2$
Mullite (Mu)	$Al_6Si_4O_{13}$
Periclase (Pc)	MgO
Portlandite (Pl)	$Ca(OH)_2$
Quartz (Qz)	SiO_2
Sodalite Structure ($C_4A_3\bar{S}$)	$Ca_3Al_6O_{12} \cdot CaSO_4$
Thenardite (Th)	Na_2SO_4
Tricalcium Aluminate (C_3A)	$Ca_3Al_2O_6$

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter reviews topics relevant to this research project. Five topics are discussed in the following order:

1) portland cement,
2) sulfate attack,
3) fly ash,
4) blended fly ash cement, and
5) alkali activation.

2.2 PORTLAND CEMENT

2.2.1 INTRODUCTION

Manufacturing portland cement includes four principal steps (333, 295):

1) quarrying calcareous and argillaceous materials,
2) processing the raw materials, which involves grinding and blending in the required proportions,
3) heating these materials to a sufficient temperature to allow the formation of new compounds, and
4) kiln-product processing, which includes cooling and final grinding.

2.2.2 RAW MATERIALS AND PROCESSING

The most common form of calcareous deposits is limestone, although other forms of calcium carbonate such as chalk, shell deposits, and calcareous muds are used. Argillaceous materials are often iron-bearing aluminosilicates. Clays and silts are preferred since they are already in a finely divided state, but shales and schists are also used (295).

The purpose of grinding and blending raw materials is to ensure that the raw feed entering the kiln is of consistent composition and that the particles are small enough to allow complete chemical combination. Some cement plants perform these processes with the raw materials in a wet state because slurries are easily proportioned and blended. However, slurries are uneconomical for kiln operations because evaporation of slurry water consumes large quantities of heat.

Taking advantage of recent improvements in closed-circuit grinding mills, most modern cement plants economically employ dry grinding and blending procedures. A small amount of water may still be added to the ground raw materials in order to form nodules which are easily transported and stored (295).

2.2.3 HEATING

The majority of cement manufacturing companies heat their raw materials with a rotary kiln. The rotary kiln is a refractory-lined cylindrical shell which rotates slowly about a slightly-inclined longitudinal axis. The prepared raw materials are fed into the upper end of the kiln and are slowly transported by the slope and rotation of the kiln to the lower, hotter end (333).

Four distinct processes take place in the kiln, each occurring in a different range of kiln temperatures, as shown in Figure 2.1 (295):

1) evaporation, or loss of free water from the raw materials,
2) calcination, or decomposition of raw materials through the loss of bound water and carbon dioxide,
3) clinkering, or partial melting of the charge, and
4) cooling of the charge once it passes the flame.

The calcination zone occupies over one half the kiln length and transforms the charge into a reactive mixture that can enter into new chemical combinations. Chemical reactions take place in the melted fraction in the clinkering zone. The clinkering zone occupies about one-quarter of the length of the kiln.

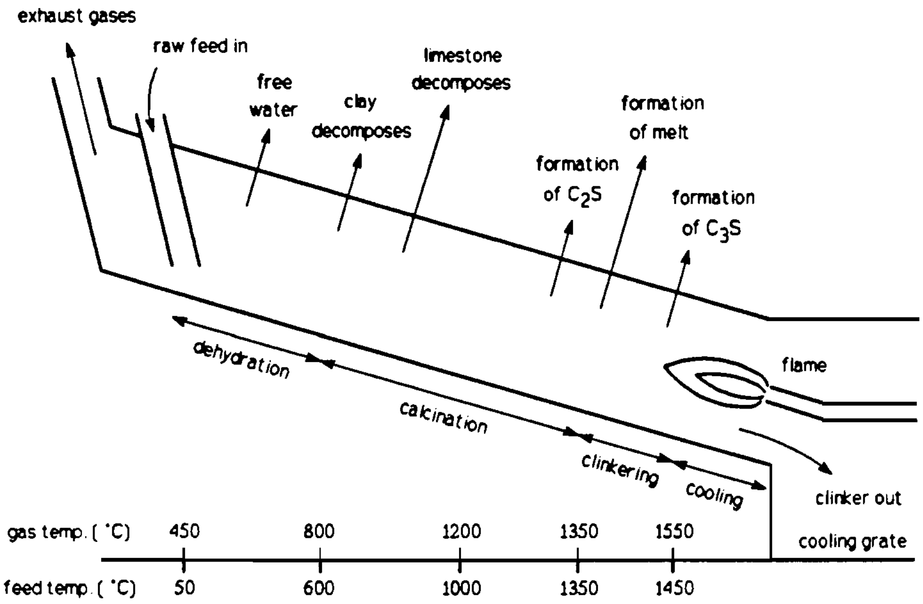


Figure 2.1 Conditions and Sequence of Reactions in a Typical Cement Rotary Kiln (Dry Process) (295)

2.2.4 COOLING AND GRINDING

The material which emerges from the kiln is termed portland cement clinker. It is composed of ¼-inch to 2-inch diameter dark gray porous nodules. Cooling of the clinker is fascilitated by air or water spray, typically on a moving grate (295). The rate at which clinker cools can significantly alter the properties of the final cement. For example, slow cooling permits the flux to crystallize and produces a highly inert form of C_2S. High levels of crystallinity for C_3A and MgO leads to setting difficulties and unsoundness, respectively. Rapid cooling preserves reactive C_2S and freezes the flux in a partially vitreous state, minimizing the size of C_3A and MgO crystals (333).

The cooled clinker is transported to a ball mill where it is ground to particle diameters mostly less than 75 micrometers. Approximately 5 percent gypsum (calcium sulfate) is usually interground with the clinker in order to retard the quick-setting tendencies of reactive C_3A (278). The grinding ball mill is a horizontal steel cylinder with orifices for feeding and discharging. The cylinder is lined with hardened steel and is normally loaded to one-third of the mill volume with wear-resistant steel balls. Rotation of the mill causes the balls to pound and abrade the clinker and gypsum (333).

2.2.5 COMPOSITION

The four primary oxides of a typical portland cement clinker are lime, silica, alumina, and ferric oxides. Minor constituents include magnesia, alkalies, and sulfur trioxide. Lime is generated by decarbonation of the calcareous materials, while alumina, silica, and ferric oxides are derived from the argillaceous materials (333). Alkalies of sodium and potassium are widely distributed elements in nature and are found in small amounts in all the materials used for manufacturing cement (218). The total amount of alkalies is usually expressed as an Na_2O molar mass equivalent $[Na_2O + (0.64)x(K_2O)]$. Sulfates and sulfides are usually derived from the clay components of the raw mix and also from the coal, oil, or natural gas used to fire the kiln. The high clinkering temperatures in the kiln promote the formation of sulfur trioxide.

The sulfur trioxide in clinker preferentially combines with alkalies to form alkali sulfates (405, 406, 407). During the formation of alkali sulfates, one mole of either Na_2O or K_2O is consumed for each mole of SO_3. Since the molar ratio, $(K_2O + Na_2O)/SO_3$, tends to exceed unity in clinker, the entire quantity of SO_3 is typically consumed. The molecular ratio of alkalies combining with SO_3 is typically $K_2O/Na_2O = 3$ (310).

Portland cement clinker consists primarily of four crystalline compounds: tricalcium silicate (C_3S), beta-dicalcium silicate (βC_2S; β is used indiscriminantly to represent two crystal forms), tricalcium aluminate (C_3A), and a phase approximating tetracalcium aluminoferrite (C_4AF). Calcium aluminates and ferrites form through solid-state reactions at the end of the calcination zone. These compounds then melt at approximately 1350 °C and act as the main fluxes in cement clinkering (278, 295, 309). Calcium silicates form in the liquid phase of the charge in the clinkering zone where the temperatures may reach 1600 °C (295). Without sufficient fluxing, the silicates would only form at much higher temperatures or after much longer durations (289).

The chemical compositions of the portland cement clinker compounds are not exact. For example, the ferrite phase, which exhibits hydration behavior typified by that of the C_4AF

composition, is actually a solid solution of composition lying between C_6AF_2 and C_6A_2F (218). Also, the high temperatures prevalent during clinker formation enables impurities to enter into solid solutions with each of the major compounds. Both C_3S and βC_2S invariably contain small amounts of magnesium, aluminum, iron, potassium, sodium, and sulfur ions. The impure forms of C_3S and βC_2S are known as alite and belite, respectively (278).

Silicate and aluminate phases are likely to contain K_2O and Na_2O, respectively. In conditions similar to cement clinker formation, Taylor (419, 420) reported the preparation of a compound $KC_{23}S_{12}$, optically similar to C_2S. Brownmiller and Bogue (43) reported the formation of a compound NC_8A_3, the x-ray pattern of which was similar to that of C_3A.

Small amounts of impurities in solid solution do not significantly alter the hydraulic properties of cement compounds, but larger amounts may contribute to the instabilities of compounds in aqueous environments (278). For example, C_3A and C_2S compounds containing large amounts of alkalies have complex crystal structures. These complex structures are characterized by large holes which increase the reactivities of these compounds. Upon wetting of cement, both NC_8A_3 and $KC_{23}S_{12}$ react quickly with $CaSO_4$ (218):

$$Na_2O \cdot 8CaO \cdot 3Al_2O_3 + CaSO_4 \rightarrow Na_2SO_4 + 3C_3A \text{ and}$$

$$K_2O \cdot 23CaO \cdot 12SiO_2 + CaSO_4 \rightarrow K_2SO_4 + 12C_2S\ .$$

Recently, due to increases in the use of impure raw materials in the production of cement, the effects of minor compounds has become a popular topic for research (278, 289).

After gypsum is interground with the clinker, ordinary portland cement has an oxide composition and a compound composition typified by Tables 2.1 and 2.2, respectively (295).

2.2.6 HYDRATION

2.2.6.1 Introduction

Portland cement is composed of a heterogeneous mixture of several anhydrous crystalline compounds. The hydration process of cement consists of many simultaneous reactions between these compounds and water.

Table 2.1 Typical Oxide Composition of a General-Purpose Portland Cement (295)

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO_3
Percent by Weight	63	22	6	2.5	2.6	0.6	0.3	2.0

Table 2.2 Typical Composition of an Ordinary Portland Cement (295)

Crystalline Compound	C_3S	C_2S	C_3A	C_4AF	$C\bar{S}H_2$
Percent by Weight	50	25	12	8	3.5

Portland cement compounds do not react at the same rate. The aluminates are known to react much faster than the silicates. The stiffening (loss of consistency) and setting (solidification) characteristics of a portland cement paste are, therefore, largely attributed to reactions involving aluminates. The hardening (strength development) characteristics of portland cement are largely attributed to reactions involving silicates (278).

2.2.6.2 Mechanism

Two mechanisms of hydration reactions have been proposed (278):

1) through-solution hydration and
2) topochemical hydration.

Through-solution hydration involves the dissolution of anhydrous compounds to their ionic constituents, the formation of hydrates in solution, and the eventual precipitation of the low-solubility hydrates from the supersaturated solution. Topochemical or solid-state hydration involves the reactions taking place at the surface of anhydrous cement compounds, without the compounds going into solution. It is generally accepted now that at least the early reactions of portland cement compounds with water are achieved by the through-solution mechanism (278).

2.2.6.3 Liquid Phase

Calcium hydroxide, calcium sulfate, and alkali sulfates are all present in portland cement as readily soluble solids. The liquid phase of hydrating portland cement is therefore initially abundant in ions from these compounds, tending towards the following equilibrium (217):

$$CaSO_4 \cdot 2H_2O + 2MOH \leftrightarrow M_2SO_4 + Ca(OH)_2 + 2H_2O,$$

where M is either K or Na or both.

The solution composition remains relatively constant for a period of several hours. As hydrated products are precipitated, additional anhydrous materials pass into solution. The precise composition of solution depends on the particular cement and the water/cement ratio (218).

Solid $Ca(OH)_2$ persists at all ages in portland cement and therefore maintains a supply of its ions. Sulfate ions have a limited supply from gypsum and alkali sulfates and they are quickly precipitated within insoluble hydrated calcium sulfoaluminates. Typically, nearly all of the sulfates are removed from solution within the first 24 hours of hydration (218). Alkali ions are initially supplied by the alkali sulfates and their supply is maintained by the release of alkali hydroxides from hydrating calcium aluminate and calcium silicate compounds (218). Typically, all or nearly all of the alkalies have passed into solution after 28 days of hydration (218).

The relative proportions of calcium, alkali, and sulfate ions in pore solution determines the nature of initial hydration products (137, 148, 351). Figure 2.2 indicates trends of calcium hydroxide solubility in solutions containing alkali hydroxides and alkali sulfates. The calcium ion content in solution decreases with increasing concentrations of alkali hydroxides. However, under the same OH^- concentration conditions, the calcium hydroxide appears to be more soluble in the presence of sulfates provided by alkali sulfates (351). This trend of higher Ca $^{2+}$ contents have also been observed when alkali hydroxides were used in combination with sulfates provided by gypsum (351).

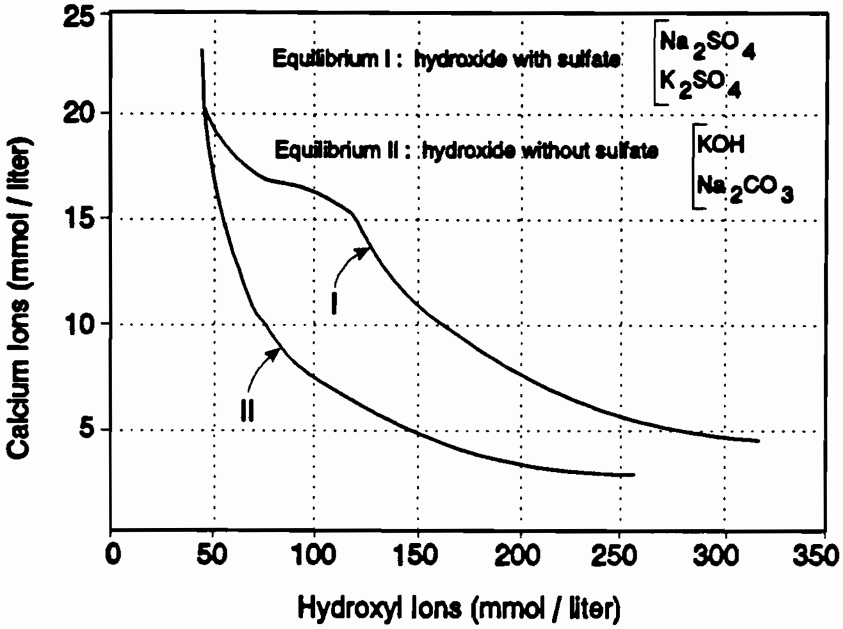


Figure 2.2 Dependencies of Calcium and Hydroxyl Ion Concentrations in Solution With and Without Sulfate Ions (137, 148, 351)

Decreasing calcium hydroxide solubility with increasing alkali hydroxide concentration has been attributed to a common ion effect (218). Alkali hydroxides are very soluble and therefore release hydroxide ions (OH$^-$) into solution quickly. Calcium hydroxide is then less able to dissolve in a pore solution which already contains hydroxide ions.

The apparent increased calcium hydroxide solubility in the presence of alkali sulfates is actually a result of the higher solubility of calcium sulfate and syngenite ($CaSO_4 \cdot K_2SO_4 \cdot H_2O$) under these conditions. Reactions between alkali sulfates and calcium hydroxide result in the formation of alkali hydroxide and calcium sulfate (and syngenite if potassium hydroxide is present). Calcium sulfate and syngenite then release higher concentrations of Ca $^{2+}$ ions into solution than would calcium hydroxide alone (351).

The same reasoning applies to solutions which initially contain calcium hydroxide, alkali hydroxide, and gypsum. However, the initial reaction between alkali sulfate and calcium hydroxide to form gypsum is not required (351). Since the two curves in Figure 2.2 converge, the solubilities of gypsum and syngenite must also decrease with increasing OH^- concentration (351).

2.2.6.4 Calcium Silicates

Tricalcium silicate reacts more rapidly than dicalcium silicate. The reactivity of C_3S is attributed to its irregular ionic packing which leaves large structural holes (218). Portland cements which contain large proportions of C_3S, relative to βC_2S, exhibit high early compressive strengths.

The hydration reactions of both C_3S and βC_2S produce a family of calcium silicate hydrates (C-S-H) and calcium hydroxide (CH). The members of the C-S-H family are all structurally similar but vary widely in calcium/silica ratios. On complete hydration, an average composition of the hydrates may be represented by $C_3S_2H_3$ (278, 295):

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH$$
$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH\ .$$

The C-S-H are poorly crystalline porous solids which exhibit the high surface area characterisitics of a rigid gel. Calcium hydroxide [$Ca(OH)_2$] is a compound of definite stoichiometry, tending to crystallize as large hexagonal plates and prisms (278).

Most of the strength of portland cement concrete is attributed to C-S-H, which bonds by Van der Waals forces over its extremely high surface area (278). Calcium hydroxide, which has a considerably lower specific surface area than C-S-H, does not contribute significantly to concrete strength.

Due to its solubility in acidic and sulfate waters, leaching of CH may increase concrete porosity and decrease concrete durability. Cements with relatively large proportions of βC_2S are conducive of low CH liberation and therefore contribute to strong and durable concrete (278).

2.2.6.5 Calcium Aluminates

The highly exothermic reactions of C_3A in water produce a mixture of hexagonal hydrates: $C_4AH_{(13\text{-}19)}$ and C_2AH_8. These hexagonal plate crystals are metastable and eventually transform into the cubic hydrate, C_3AH_6, which is less soluble (218, 278).

Although C_3A is initially highly reactive in water, its reactivity quickly decreases. Hexagonal hydrates form a diffusion barrier on the C_3A grain surface. Periodic breakdown of the protective hydrate layer, caused by crystal growth pressures, allows the C_3A to continue hydrating at a decreasing rate (175).

The ferrite phase, approximated by the composition C_4AF, reacts quickly in the presence of water, but not as quickly as C_3A. A solid solution of C_2AH_8 and ferric oxide is formed as hexagonal plates. At ordinary temperatures, the hexagonal solid solution phase readily converts into a cubic C_3AH_6-C_3FH_6 solid solution (60). These reactions are similar to the reactions involving C_3A and pure calcium aluminate hydrates.

The initial reaction of C_3A in water is so rapid that unless it is controlled by some means, cement will stiffen immediately (flash set) and will be useless for construction purposes. Immediate stiffening occurs as aluminum ions and silica ions coagulate to form a low-lime gel. The sources of aluminum ions and silicon ions include tricalcium aluminate and calcium silicates, respectively. The low-lime gel hinders the formation of normal C-S-H and therefore reduces concrete strengths (218). Prevention of the formation of the low-lime gel is accomplished by controlling the rate of hydration of C_3A. The rate of hydration of C_3A is generally controlled by intergrinding 1 to 10 percent gypsum with the cement clinker (334).

2.2.6.6 Effects of Gypsum

The morphology of hydration products of C_3S and βC_2S are slightly modified in the presence of gypsum because sulfate can enter the structure of the calcium silicate hydrate gel (218). Also, the rates of reaction of the calcium silicates are increased by the presence of gypsum, resulting in decreased final set times. In the absence of gypsum, ferric oxide produced during hydration of C_4AF can precipitate on cement particles and retard their hydration. When gypsum is present, C_4AF hydrates to form a solid solution of sulphoaluminate and sulphoferrite and there is no prolonged inhibiting effect on cement hydration (218).

The hydration of C_3A is altered considerably by the presence of gypsum. Most importantly, hydration is retarded and portland cement concrete is provided with an extended time of plastic behavior. Forsen formed two theories for the mechanism of C_3A hydration retardation by gypsum (120): chemical repression and physical repression of the solubility of alumina. Chemical repression of alumina solubility is caused by gypsum releasing its calcium and sulfate ions into solution. A solution which contains an abundance of ions is less receptive of additional ions, including those from alumina-bearing compounds (218, 278). Physical repression of alumina solubility is caused by the formation of a film of insoluble hydration products around cement particles.

Calcium sulfoaluminate films which form around the anhydrous tricalcium aluminate compounds are theorized to be relatively impervious. Therefore, these films serve as diffusion barriers and retard further dissolution of aluminate compounds. The barriers are repeatedly formed and disrupted, allowing a slow supply of aluminum ions to enter the liquid phase. Disruption of barriers is caused by osmotic pressure and the transformation of trisulfoaluminate to monosulfoaluminate (217). The relative stabilities of trisulfoaluminate and monosulfoaluminate depends on the concentrations of aluminum and sulfate ions in solution (278).

Hydration of C_3A in the presence of gypsum can be considered to occur in three stages, as shown in Figure 2.3. During the first stage, there are sufficient sulfate ions supplied by the gypsum for the high-sulfate form of sulphoaluminate to precipitate (334). This hydrated compound is also known as ettringite, which is the name of the naturally occurring mineral of the same composition (295, 374):

$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32} .$$

The surfaces of C_3A particles act as catalysts for crystal nucleation. Therefore, ettringite crystals form near the surfaces of these particles and grow out into solution as fine needles (382). The rate of heat evolution gradually decreases as the ettringite barriers progressively obstruct water molecules from moving toward the surface of C_3A particles (334).

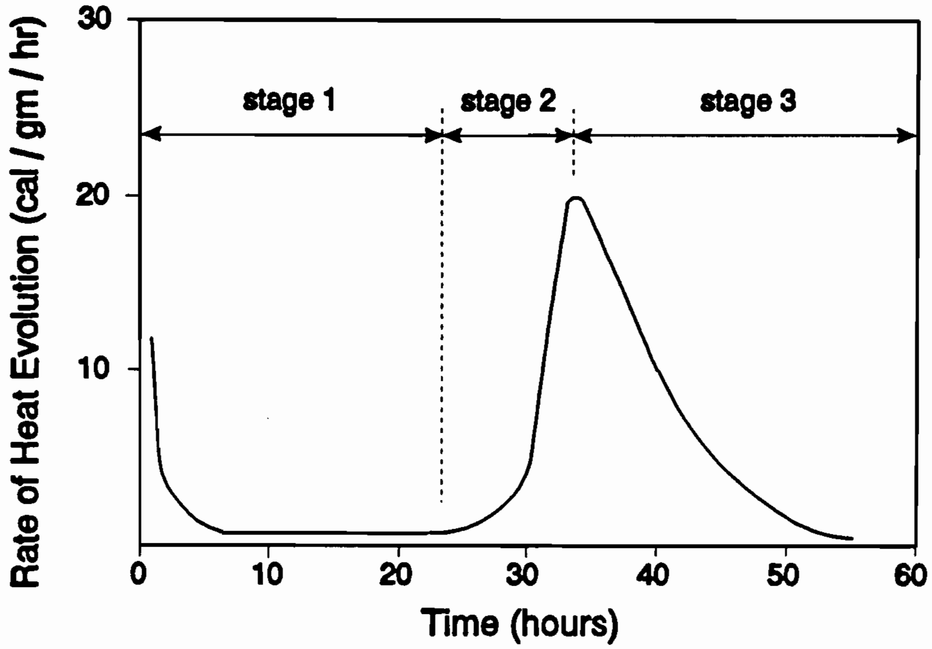


Figure 2.3 Calorimetric Curve for the Hydration of C_3A in the Presence of Calcium Sulfate (175)

Stoichiometry of ettringite formation suggests that when the initial molar ratio of gypsum to C_3A is less than three, all gypsum is eventually consumed. Depletion of gypsum is significant since ettringite is only stable while there is a sufficient concentration of sulfate ions in the liquid phase. If the concentration of sulfate ions nears depletion before all the C_3A has hydrated, ettringite begins the second stage of hydration. This stage involves massive conversion of ettringite to the low-sulfate sulfoaluminate, otherwise known as monosulfoaluminate hydrate or monosulfate hydrate (295, 374):

$$2C_3A + C_6A\bar{S}_3H_{32} + 4H \rightarrow 3C_4A\bar{S}H_{12}.$$

The second stage of hydration involves rapid consumption of C_3A and considerable heat evolution. Rate of heat evolution increases as the ettringite barrier is destroyed (334). Ghorab et.al. (127) believe monosulfoaluminate is also formed through-solution, as ettringite dissolves. This stage terminates when all ettringite has been converted or when the C_3A supply is depleted.

The third stage of C_3A hydration begins after total conversion of ettringite to monosulfoaluminate. The remaining C_3A reacts quickly with water in the presence of monosulfate to form a solid solution of monosulfate and hexagonal aluminate hydrates:

$$2C_3A + (21\text{-}27)H \rightarrow C_2AH_8 + C_4AH_{(13\text{-}19)}\ .$$

The hexagonal hydrates eventually convert to cubic hydrates, which are more stable (334):

$$C_2AH_8 + C_4AH_{(13\text{-}19)} \rightarrow 2C_3AH_6 + (9\text{-}15)H\ .$$

Some remaining C_3A may also be absorbed by the hydrous calcium silicate gel (374). During this third stage of hydration, the rate of heat evolution decreases as the remaining C_3A is consumed.

Exposure of C_3A to solution in the presence of monosulfoaluminate and in the absence of ettringite occurs only in cements with relatively low SO_3 contents. These low SO_3 contents correspond approximately to gypsum/C_3A molar ratios less than unity (334).

The reaction equations for ettringite and monosulfoaluminate are approximate; precipitates of variable chemical compositions have been found to be structurally similar. The notations AF_t and AF_m are often used to encompass all hydration products structurally similar to trisulfoaluminate (ettringite) and monosulfoaluminate, respectively (278).

2.2.6.7 Optimum Gypsum Content

Lerch (212) has investigated the influence of various proportions of gypsum on the initial rate of hydration of portland cement. He used a conduction calorimeter to record the rate of heat evolution during the exothermic cement hydration reactions, which provided insight into their nature and sequence (374, 385).

Lerch (221) studied four cements which were ground with the same clinker but with various levels of gypsum, producing SO_3 contents of 1.3, 1.9, 2.4, and 3.0 percent. Rate of heat evolution curves are shown in Figure 2.4. Heat of hydration within the first 30 minutes was ignored for clarity. Reactions causing initial heat evolution include the dissolution of alkalies and gypsum, the hydration of free lime, and the formation of ettringite. Peaks in Figure 2.4 which are labeled "C" represent heat released during the hydration of

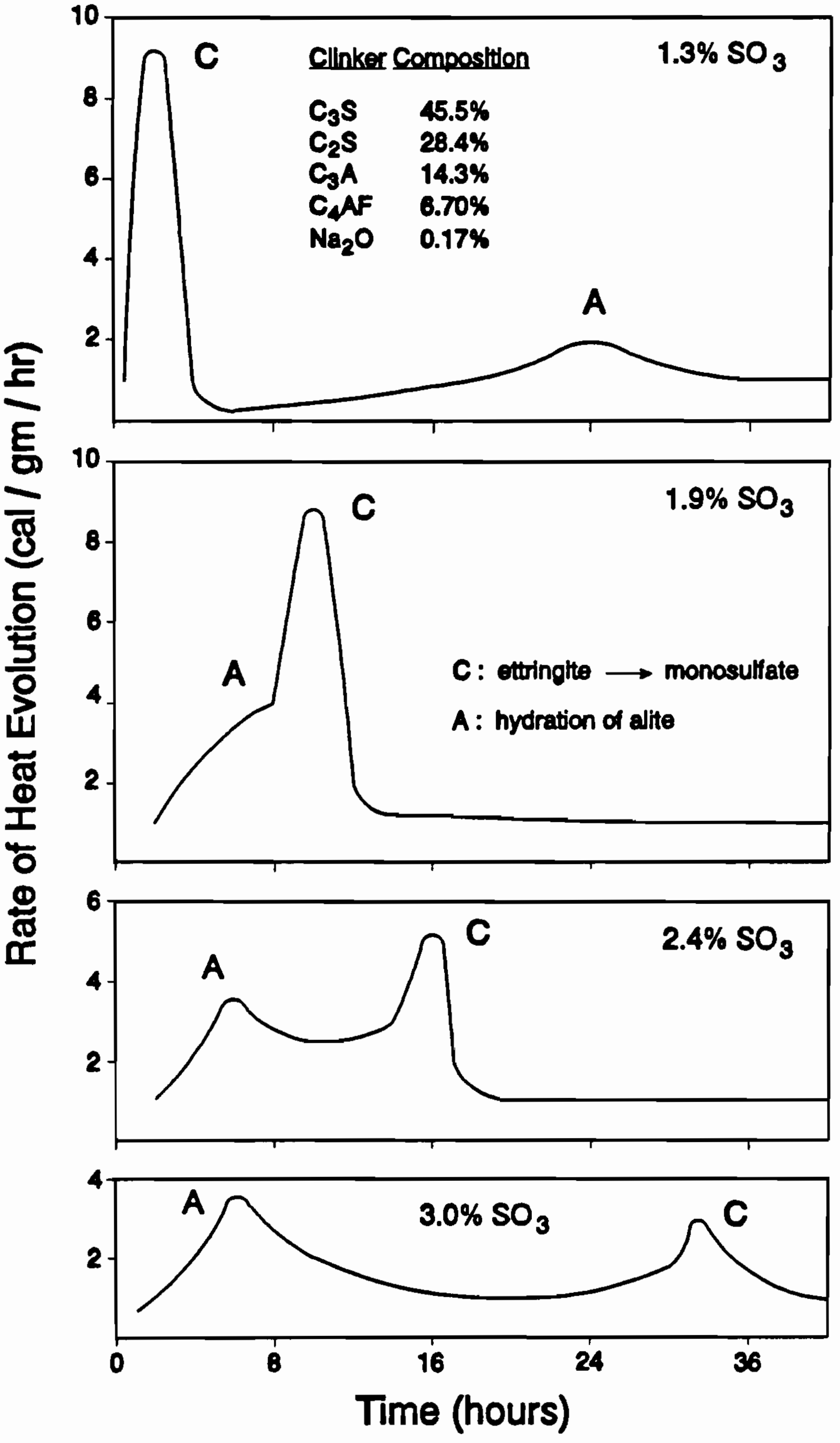


Figure 2.4 Calorimetric Curves for the Hydration of Ordinary Portland Cement with Varying Proportions of Gypsum (221)

C_3A or the conversion of ettringite to monosulfoaluminate. Peaks in Figure 2.4 which are labeled "A" represent heat released during the hydration of alite.

The lowest SO_3 content (1.3 percent) was insufficient to prevent rapid dissolution of C_3A and the formation of an alumina-silica gel. Alite hydration was delayed and hindered, as seen by its late occurence at 24 hours and its relatively low peak rate of heat evolution, respectively.

Higher gypsum contents delayed the dissolution of ettringite. As a result, the alite was able to hydrate properly. Lerch expected that there existed some SO_3 content higher than 3.0 percent which would have eliminated peak C altogether.

Lerch considered the optimum gypsum content to be that which is just sufficient to eliminate peak C. This level of gypsum supplies enough SO_3 to keep the ettringite stable until most C_3A is hydrated. The amount of gypsum required to eliminate peak C has been found to increase with increases in cement C_3A and alkali contents (221, 385).

Additional investigations on gypsum contents in cements have reported that cements exhibit the highest strengths and the lowest drying shrinkage approximately at their optimum gypsum content, as defined by Lerch (329). Gypsum contents lower than optimum impede proper alite hydration, while gypsum contents higher than optimum cause expansions which disrupt the hardened concrete. These expansions are due to the availability of sulfate ions after the concrete has hardened, which enables hydrating C_3A to continue to form ettringite.

Optimum gypsum contents cannot be determined by simply calculating a specified SO_3/C_3A ratio. Tricalcium aluminate compounds vary in reactivity, depending on their rate of cooling after firing, their impurity compositions, and the conditions within which the cement was stored (218). The rate of availability of sulfur trioxide in solution depends on whether the SO_3 is supplied by clinker, calcium sulfate hemihydrate, or calcium sulfate dihydrate (gypsum). Sulfur trioxide originating in clinker is readily soluble if it exists as exposed alkali sulfates, but it is slowly soluble if it is confined within cement compounds. Hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) is more soluble than gypsum and is produced when gypsum ($CaSO_4 \cdot 2H_2O$) is subjected to temperatures of 130 °C to 150 °C. If large proportions of hemihydrate are present in cement, the liquid phase may be supersaturated with calcium and sulfate ions. Subsequent precipitation of bulky gypsum crystals causes false set for the concrete mixture. False set can be remedied by vigorous mixing (223, 278, 381).

2.2.6.8 Effects of Alkalies

Modern cement processing technology and the use of impure raw materials have increased the proportions of alkali compounds which are typically found in portland cement (173). The effects of alkalies on cement hydration has therefore become a popular topic for research.

Spierings and Stein (390) compared the rates of heat evolution for C_3A pastes in water and in NaOH solutions of various concentrations. Heat evolution in the first 15 minutes decreased with increasing NaOH concentration, as shown in Figure 2.5. Decreased reactivity of C_3A was attributed to the formation of an efficient diffusion barrier. Alkalies increased the rate of conversion of hexagonal hydrates to the cubic hydrate, C_3AH_6, and decreased the size of these hydrates (140).

A portion of Na_2O in clinker is normally present within C_3A-like structures, forming solid solutions of the general formula: $(x)Na_2O \cdot (3\text{-}x)CaO \cdot Al_2O_3$ (230, 354). There is general aggreement that the initial hydraulic reactivity of C_3A increases as the Na_2O content in the crystal structure increases (35, 38, 39, 40, 352, 390, 391). However, as the Na_2O-doped C_3A hydrates, alkalies are released into solution. Once the alkalies are in solution, they have retarding effects similar to those found on the hydration of pure C_3A in NaOH solutions (390).

Decreased reactivity of C_3A has also been observed in the presence of gypsum and alkali sulfates (174). Jawed and Skalny (174) studied the heat evolution of C_3A hydration. Total heat evolved after 30 minutes was reduced slightly in the presence of gypsum alone and was reduced by more than 50 percent in the combined presence of gypsum and K_2SO_4, as shown in Figure 2.6. This severe retardation was presumed to be due to both the rapid formation of an ettringite film and to the decreased rate of hydration of C_3A in alkaline solutions (373, 381, 390).

The early hydration of C_3S has been found to be significantly accelerated by the addition of K_2SO_4 to mixing water. The presence of alkali sulfates removes Ca^{2+} ions from the aqueous phase by precipitating $Ca(OH)_2$ and $CaSO_4$. Since these phases precipitate in solution and not on the surfaces of C_3S particles, further dissolution of C_3S is enhanced (174).

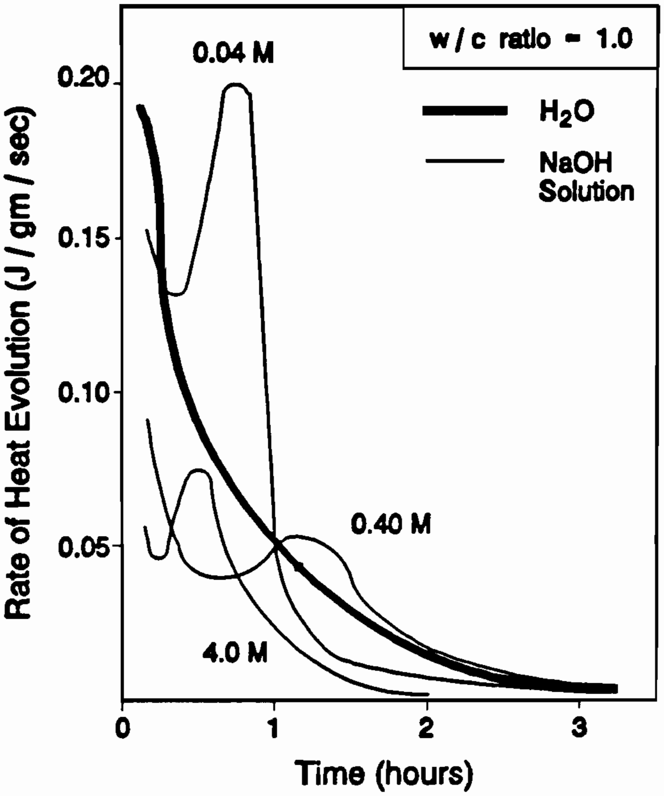


Figure 2.5 Calorimetric Curves for the Hydration of C_3A Pastes in Water and in NaOH Solution (390)

Jawed and Skalny (174) studied the effects of alkalies on the rate of heat evolution due to the hydration of C_3S. Inclusion of alkali sulfates with Type I cement decreased the time required for the peak rate of heat evolution to occur, as shown in Table 2.3. The decreased time-to-peak corresponded to increases in the rate of hydration of 6 percent to 32 percent (174).

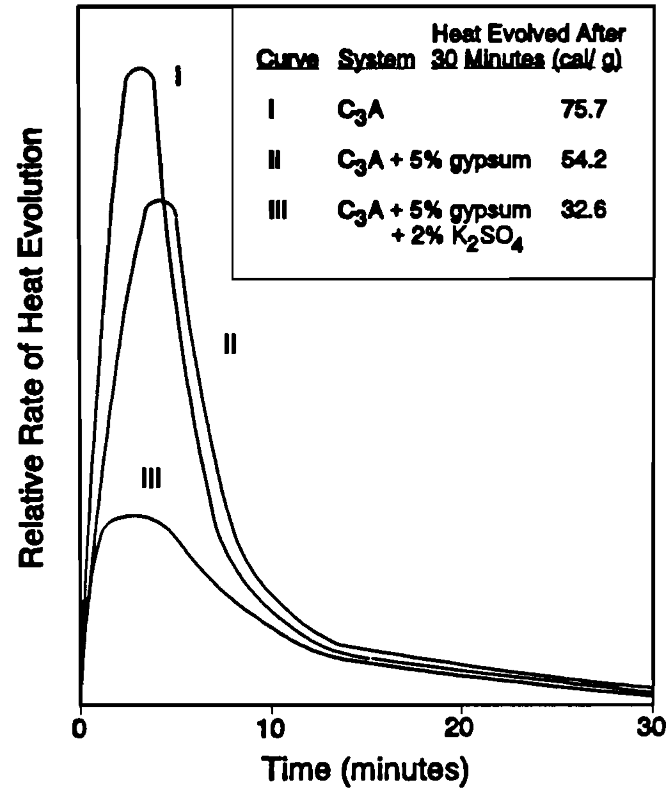


Figure 2.6 Early Heat Evolution of C_3A in the Presence of Gypsum and K_2SO_4 (174)

In general, the effects of alkalies on the hydration of calcium silicates results in increased early concrete compressive strengths (up to 7 days) and decreased 28-day compressive strengths (177). Increases in early strengths result from the increased rate of hydration of calcium silicates. Decreases in 28-day compressive strengths result primarily from changes in the morphology of hydration products (174). The changes in morphology result from two factors (174): increased rate of early hydration and increased water requirement for the same concrete slump. Rapid hydration reactions in the initial stages of calcium silicate hydration result in a coarser and more heterogeneous microstructure for the C-S-H gel. This microstructure leads to lower inherent strengths (303). The increased water requirement for cement paste which contains alkali sulfates has been attributed to early precipitation of gypsum and syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) in the liquid phase (357, 392).

Table 2.3 Heat Evolution Profile Characteristics for Cement Pastes with Potassium Sulfate Additive (174)

System	Heat Evolved at 30 minutes * (cal/ gm)	Time of Peak Maximum ** (hours)
Cement A	6.76	6.5
Cement A + 2% K_2SO_4	6.14	5.5
Cement A + 3% K_2SO_4	5.38	4.5
Cement B	6.88	8.5
Cement B + 2% K_2SO_4	5.90	8.0
Cement B + 3% K_2SO_4	4.87	6.0
Cement C	7.29	9.5
Cement C + 2% K_2SO_4	5.80	8.0
Cement C + 3% K_2SO_4	4.73	6.5

Note: water/cement ratio = 0.5, temperature = 30°C

* cumulative heat evolved after 30 minutes of hydration
** time for second heat evolution peak maximum

2.3 SULFATE ATTACK

2.3.1 DESCRIPTION OF PROBLEM

The action of sulfates is the most widespread and common form of chemical attack on concrete (295). Even as the most common form of chemical attack, Pierce (330) estimated that the proportion of concrete in the United States which is exposed to sulfates is probably less than 10 percent.

Sulfates originate from a wide range of sources. Seawater contains approximately 2700 mg/liter sulfates as SO_4^{2-}. Some groundwaters contain sulfates, particularly when the soil through which it flows consists of a high proportion of clay. High local concentrations of sulfates in groundwater may be found in the vicinity of industrial wastes such as mine tailings, slag heaps, and rubble fills. Rainwater may contain sulfates from air pollution, and sulfates may be produced by biological growths; these two sources of sulfates can cause deterioration of concrete above ground (278, 295).

Mineral sulfates within clayey soils are formed by the disintegration of rocks and are typically those of calcium, magnesium, sodium, and potassium. Clays containing these mineral sulfates are often referred to as alkali or gypsiferous soils (218).

Environmental conditions are important when considering the potential sulfate attack exposure of concrete. The solid salt content of surrounding soil alone does not provide an accurate indication of the severity of conditions. The solid salts require moisture in order to enter into a solution which can react with the hardened cement paste. A large amount of water accompanied by water movement, however, may leach the destructive salts away from the vicinity of the concrete. Regions in which alternate wetting and drying are fairly frequent, such as semi-arid regions in the western United States, are particularly conducive of sulfate attack (330).

Concrete which rests on wet, sulfate-bearing soils and which is subjected to surface drying is susceptible to deterioration. Evaporation on the top surface increases the volume of sulfate-bearing water which is drawn through the concrete. The concentration of sulfates inside the concrete may even exceed that of its subgrade (218).

The mobility of salts in solution causes variability in the sulfate contents of waters and soils between points close together. The irregular distribution exists between soil samples differing in horizontal location and also differing in depth. For example, due to gradual leaching by rainwater, the top 2 or 3 feet of soils may be relatively free from sulfates. Alternatively, in dry regions where rates of evaporation are high, large concentrations of salts may accumulate near the ground surface (218). Irregular distributions of salt concentrations make structures which cover large areas of land particularly susceptible to sulfate attack; scattered tests on soil samples may not reveal potential sulfate hazards for pavements or canals (330).

Sulfate attack has been a consistent topic of concrete durability research for the past 60 years. As early as 1936 a concrete construction manual published by the United States Bureau of Reclamation (USBR) warned that concentrations of soluble sulfates greater than 0.1 percent in soil (or approximately 150 mg/liter SO_4^{2-} in water) may be detrimental to concrete and that concentrations greater than 0.5 percent in soil (or greater than approximately 2000 mg/liter SO_4^{2-} in water) may have a significant damaging effect (278).

2.3.2 MECHANISM

Sulfate attack on concrete can be considered as a sequence of three processes which leads to cracking, expansion, and strength loss (295):

1) diffusion of sulfate ions into the pores of the concrete,
2) gypsum corrosion, and
3) sulfoaluminate corrosion.

The first step in the sulfate attack process requires moisture for the transport of SO_4^{2-} ions through solution (28). The rate of diffusion of sulfate ions into concrete depends on the permeability of concrete, the concentration gradient of sulfate ions, and the diffusion characteristics of the sulfate ions.

Gypsum and sulfoaluminate corrosion are both expansive reactions which cause the internal stresses responsible for concrete deterioration during sulfate attack.

Gypsum corrosion is a base exchange between calcium hydroxide and the sulfates entering the concrete pore solution. The calcium hydroxide is a product of the hydration of calcium silicates. The conversion of calcium hydroxide to gypsum more than doubles its solid volume; the respective molecular volumes of $Ca(OH)_2$ and $Ca_2SO_4 \cdot 2H_2O$ are 33.2 cc and 74.2 cc (218). The basic chemical reaction is:

$$Ca(OH)_2 + M_2SO_4 + 2H_2O \leftrightarrow CaSO_4 \cdot 2H_2O + 2MOH,$$

where M is usually K or Na or both.

The sulfate ions combine with calcium ions while the hydroxide ions combine with sulfate salt cations.

Increases in solid volume during transformations from calcium hydroxide to gypsum are only destructive when gypsum forms topochemically (80). Otherwise, gypsum formation encourages the penetration of additional sulfate ions into the concrete and concentrates them in a form in which they can react directly with alumina-bearing compounds (295).

The degree to which gypsum corrosion proceeds depends on the environmental conditions. If alkali hydroxides are removed by flowing waters and if alkali sulfates continue to be supplied, the conversion of calcium hydroxide to gypsum may proceed to completion. Alternatively, if the groundwater is stagnant, the alkali hydroxides accumulate in the concrete pores and an equilibrium is attained (28). For example, in stagnant 5 percent Na_2SO_4 solution, only about one-third of the sulfur trioxide is deposited as calcium sulfate when equilibrium is reached. In stagnant 2 percent Na_2SO_4 solution, only one-fifth of the sulfur trioxide is deposited as calcium sulfate (218).

The third step in the sulfate attack process, sulfoaluminate corrosion, involves reactions between gypsum and several alumina-bearing compounds: unhydrated tricalcium aluminates, hydrated calcium sulfoaluminates, and hydrated calcium aluminates. These reactions, in their respective order, proceed according to (65):

1) $C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_3A \cdot 3C\bar{S} \cdot H_{32}$,
2) $C_3A \cdot C\bar{S} \cdot H_{12\text{-}18} + 2C\bar{S}H_2 + (10\text{-}16)H \rightarrow C_3A \cdot 3C\bar{S} \cdot H_{32}$, and
3) $C_4AH_{13} + 3C\bar{S}H_2 + 14H \rightarrow C_3A \cdot 3C\bar{S} \cdot H_{32} + CH$.

These sulfate-induced expansive reactions are similar to some initial cement hydration reactions but they occur after the concrete has hardened. The product common to all reactions is trisulfoaluminate hydrate, or ettringite. The formation of ettringite may result in a large increase in solid volume as compared to its reactants. For example, the solid phase volume more than doubles during the transformation from monosulfoaluminate hydrate to trisulfoaluminate hydrate; their respective molecular volumes are approximately 313 cc and 715 cc (218).

Expansions may initially result in densification of concrete as crystals of gypsum and/or ettringite fill previously unoccupied pores (28). However, continued expansions lead to internal stresses, volumetric changes, and cracking in concrete. Cracks fascilitate the ingress of additional sulfate ions, thus accelerating the sulfate attack process.

An additional attack mechanism occurs in conditions where sulfate solutions are replenished. The supply of sulfate ions in concrete pore water solution is maintained, while the supply of aluminate ions is depleted by the formation of hydration products. Crystallization of gypsum, which does not require aluminates, must eventually replace that of ettringite. The source of calcium ions during gypsum formation, calcium hydroxide, may also eventually be exhausted resulting in decreased pore solution hydroxyl ion concentration. Low pH, high sulfate concentration solutions provide unstable environments for calcium silicate hydrates (65, 272):

1) sulfate adsorption on C-S-H surfaces is believed to reduce their adhesive properties and
2) in low pH environments, C-S-H gels release CH into solution in order to return the pH to a level which promotes its own stability.

Since calcium silicate hydrates are the primary binders within hydrated portland cement, this acidic form of sulfate attack results in the deterioration of cementitious properties. Surface-softening and decreased compressive strengths are often observed prior to any expansion (272).

2.3.3 SULFATE SALT TYPES

Sulfate salts are typically calcium, magnesium, sodium, or potassium sulfates. At relatively small concentrations, the nature of the cations accompanying the sulfate anions does not significantly affect the process of sulfate attack. However, at higher concentrations of sulfates, the type of salt present has significant effects on the severity of conditions (295).

Calcium sulfate, which is present in almost all soils, has the advantage of bypassing gypsum corrosion to proceed directly with sulfoaluminate corrosion. This difference is significant between sulfate ion (SO_4^{2-}) concentrations of approximately 600 mg/liter to 1400 mg/liter. At these sulfate ion concentrations, calcium sulfate is regarded as more aggressive than sodium or potassium sulfates (28). The contribution of calcium sulfate to the deterioration of concrete is less at sulfate ion concentrations greater than 1400 mg/liter (295). Calcium sulfate is limited by its solubility, which is approximately 1400 mg SO_4^{2-} per liter of clean water at normal temperatures (278).

Sodium and potassium sulfate solubilities are in excess of 10 percent at normal temperatures and are typically responsible for SO_4^{2-} concentrations in groundwater in excess of approximately 0.15 percent. In the alkali soils of North America, soil water has been found to contain up to 1.0% total sulfate salts (0.65 to 0.80% SO_4^{2-}) (28, 218, 409).

Magnesium sufates, which are also very soluble, initially cause damage to concrete by means similar to other sulfates: calcium sulfoaluminates and magnesium hydroxide are formed. However, magnesium sulfates may also attack the C-S-H gel directly. Magnesium and calcium ions have equal valence and similar ionic radii. Therefore, magnesium sulfate can react with the C-S-H gel to form gypsum, magnesium hydroxide, and a silica hydrate (57):

$$C_xS_yH_z + (x)M\bar{S} + (3x+0.5y-z)H \rightarrow (x)C\bar{S}H_2 + (x)MH + (0.5y)S_2H.$$

The gypsum formed may react with the calcium aluminates to produce additional ettringite. The magnesium hydroxide and silica hydrate react slowly to form a non-cementitious hydrated magnesium silicate (218, 250):

$$4MH + SH_n \rightarrow M_4SH_{8.5} + (n-4.5)H.$$

Magnesium hydroxide (or brucite) has a solubility of only 10 mg/liter and is thus an efficient remover of hydroxide ions from solution. During magnesium sulfate attack, the concrete pore solution may have a pH as low as 10.5 (28, 65, 218). Since calcium silicate hydrates are unstable in poorly alkaline solutions, the hydrates improve stability by releasing additional calcium hydroxide. The CH will contribute to the formation of additional gypsum if magnesium sulfate is available for reaction:

$$CH + M\bar{S} + 2H \rightarrow C\bar{S}H_2 + MH.$$

The gypsum will then be available for additional ettringite formation (65, 218).

Sodium and potassium sulfates are not able to attack the C-S-H gel directly because the Na^+ and K^+ ions are not of proper size or valence to displace the Ca^{2+} ions within the gel (65).

2.3.4 ETTRINGITE FORMATION

Two principal theories exist for the mechanism by which ettringite causes expansive stresses (64):

1) crystal growth theory and
2) swelling theory.

The crystal growth theory states that as soon as ettringite formation begins, the surfaces of the expansive particles (C_3A and $C_4A_3\bar{S}$) are covered with a dense coating of ettringite (355). Further hydration occurs topochemically, increasing the thicknesses of the ettringite coatings (373). The size of crystals eventually exceeds the space available, causing pressure and subsequent expansion (355).

The swelling theory states that ettringite particles form a gel by through-solution crystallization of colloidal-size particles. The gel tends to adsorb water and swell, which causes pressure and expansion (64).

Proponents of both ettringite formation theories generally agree that the presence or absence of $Ca(OH)_2$ results in the formation of two types of ettringite: expansive or non-expansive, respectively. In the presence of solid $Ca(OH)_2$ (Ca^{2+} and OH^- in solution) pore solution pH is generally 12.5 to 12.9. In the absence of solid $Ca(OH)_2$, pore solution pH is generally 11.5 to 11.8.

In solutions of relatively high pH, proponents of crystal growth theory propose that aluminates hydrate slowly and ettringite is formed topochemically (directly on the surface of C_3A without C_3A dissolving beforehand) (64, 373). The ettringite consists of small, rod-like crystals, typically 1 to 2 micrometers long and 0.1 to 0.2 micrometers thick (272). Proponents of the swelling theory propose that under these conditions the colloidal gel is formed by through-solution reactions. Proponents of both theories feel that under these conditions, ettringite is expansive.

In solutions of relatively low pH, aluminates hydrate rapidly and ettringite is formed by precipitation from solution phase (ions of calcium, aluminate, and sulfate first are dissolved from cement compounds) (64, 373). The ettringite consists of large lath-like crystals, typically 10 to 100 micrometers long and several micrometers thick. Advocates of the crystal growth theory state that these crystals do not form an efficient diffusion barrier on expansive particles, so ettringite continues to form through-solution. Advocates of the swelling theory state that these large crystals with their low specific surface area have reduced capabilities for adsorbing water molecules (64). Proponents of both theories feel that under these conditions, ettringite is not expansive.

Lafuma (210) has suggested that the combination of a cement compound in its solid state with a substance in solution always leads to expansion. However, if the cement compound passes into solution, reacts, and then precipitates as solid, no expansion occurs. The formation of calcium sulfoaluminates during sulfate attack on hardened portland cement is an action of the first type: the presence of free calcium hydroxide renders the hydrated calcium aluminates entirely insoluble during their reaction with sulfates. In some special cements with relatively low calcium hydroxide contents, however, the action of sulfate solutions is of the second type: the absence of lime allows the hydrated calcium aluminates to be slightly soluble during their reaction with sulfates (218).

Schwietz et al. (373) have suggested that ettringite which forms by precipitation from solution contributes to concrete strength, while ettringite which forms topochemically does not contribute to strength. These types of ettringite correspond to non-expansive and expansive, respectively.

Kalousek and Benton (190) reported an additional classification of ettringite types: aluminum-rich ettringite and iron-rich ettringite. Aluminum-rich ettringite is a product of the aluminate phase and is expansive by mechanisms discussed previously. Iron-rich ettringite is a product of the ferrite phase and expansion is small or non-existent. The ability of iron to reduce expansions has been attributed to two effects, neither of which is universally accepted:

1) iron-bearing ettringite resists conversion to monosulfoaluminate during hydration (284) and
2) iron-bearing monosulfoaluminate resists conversion back to ettringite, even in the presence of sulfates (295).

The ability of iron to affect the reactivity of alumina-bearing compounds has been linked to crystal morphology and the tendency for crystals to dispense ion or to cumulate ions from the surrounding solution (190).

The expansive potential of hydrated cement paste is not simply related to the amount of calcium sulfoaluminate present. It is also a function of the type of ettringite which is formed. The type of ettringite may even change with time. Changes in pore solution composition may cause non-expansive crystalline ettringite to transform into an expansive gel-like ettringite (1, 152).

2.3.5 SIGNS OF DISTRESS

Deterioration of concrete due to sulfate attack can be detected as changes in (65):

1) physical characteristics, including cracking, warping, mass loss, and expansion,
2) mechanical properties, including elastic modulus, compressive strength, and dynamic modulus,
3) chemical characteristics, including hydration product compositions and pore solution chemistry, and
4) microstructural properties, including shape and size of hydration products and pores.

Deterioration of concrete in the presence of sulfate solutions may involve several simultaneous processes. The prominent type of deterioration is affected by cement composition, concrete mixture design, and exposure solution chemistry. Therefore, several concrete properties should be monitored in order to make valid comparisons of sulfate resistance (65).

2.3.6 PHYSICAL TEST METHODS

2.3.6.1 Test Requirements

In order for a laboratory test method to provide a satisfactory assessment of sulfate resistance, it must meet the following criteria (281):

1) reliable and reproducible information should be obtained in a relatively short period of time,
2) natural sulfate attack processes should be reproduced as accurately as possible so that correlations with field experience may be developed, and
3) the test method should be applicable to a wide variety of cement types, including those which contain pozzolans.

2.3.6.2 Tests on Cement Pastes

Mehta (264, 276) utilized ½-inch cement paste cubes for comparing the resistance of cements to sulfate attack. The cubes were immersed in four percent Na_2SO_4 solution and were measured for retention of compressive strength after 28 days. Rapid and complete sulfate permeation was assured by using cement paste alone, by mixing paste at a water/cement ratio of 0.5, and by keeping specimen dimensions relatively small. A constant degree of sulfate exposure was maintained by automatic titration of 0.1N H_2SO_4. Solution pH was maintained within the narrow limits of 5.7 and 6.7. Since minor flaws in small specimens can lead to wide variabilities in mechanical properties, ten replicates were used for each strength test.

Cohen (65) utilized cement paste mixtures for sulfate tests on cubes and prisms. Water/solid ratios and flows were kept constant at 0.3 and 110 to 120 percent, respectively. In order to achieve both constants for various cement types, a high-range water reducing admixture was included. Cubes of dimensions 25x25x25 mm were monitored for changes in mass and compressive strength. Beams of dimensions 6x14x80 mm were utilized for monitoring changes in length and flexural elastic modulus. Specimens were cured for 28 days in saturated lime solution prior to exposure to sulfates.

Three replicates of each mixture were exposed to each of three solutions:

1) saturated lime-water solution,
2) 10 wt.% Na_2SO_4 solution (%SO_3 = 5.6), and
3) 8.5 wt.% $MgSO_4$ (20% bound water) solution (%SO_3 = 5.4).

Specimens in the saturated lime-water solution provided a control for comparisons with specimens in the sulfate solutions. Exposure solutions were covered to minimize evaporation and were replaced at least monthly. Durability characteristics were measured at 70 and 140 days after exposure, with long-term exposure conditions monitored as needed.

Stenzel (396) modified a paste slab test conceived by Merriman in order to standardize a method for rapid acceptance of cements to be exposed to sulfates. Slabs of dimensions 2x4½x1¼ inches were cast with paste consisting of 100 gm cement and 40 cc distilled water. After seven days of moist curing, the bottom of the slabs were coated with an impervious film and the slabs were placed in ten percent sodium sulfate solution. Since the slabs were attacked from one surface, they warped as sulfates caused expansive reactions. Warpage was measured at 21 days with a spherometer to provide an indication of sulfate-susceptibility.

A sulfate exposure test which was conceived by Le Chatelier and later modified by Anstett has been implemented in European communities (20, 147). Cements were ground to pass a sieve of 4900 openings per square centimeter. They were then mixed with 50 percent water by weight to form a paste. After 14 days of curing, the hardened pastes were crushed to a maximum size of 5 mm and were dried at a temperature of 40 °C. The dried powder plus an equal amount of gypsum by weight were ground to 100% passing the #200 sieve. The powder and gypsum were then mixed with 6 percent distilled water and were molded under pressure of 5 kg/(sq.cm.) into disks 80 mm in diameter and 30 mm high. After removal from the molds, the specimens were covered with filter paper which extended into distilled water. The specimens were monitored daily for changes in diameter.

This test was extremely severe and therefore provided rapid results. In order to make the test appropriate for cements containing mineral admixtures, the time allowed for hydration prior to the addition of gypsum would have to be extended.

Predictions on the resistance of concrete to sulfates, based on tests performed on cement paste, have to be used carefully. Cement paste and concrete respond differently to attack by sulfates. For example, paste can often withstand relatively large local tensile strains before cracking (67). Therefore, paste may expand due to the formation of ettringite and may not suffer a loss in strength. Also, paste/aggregate bonding in concrete influences permeability which, in turn, affects the rate of ingress of sulfate ions.

2.3.6.3 ASTM C-452: Potential Expansion of Portland Cement Mortars Exposed to Sulfate

This ASTM test method is based on measuring the length changes of portland cement mortars which contain relatively large proportions of sulfates. The portland cement to be tested is mixed with high-grade natural gypsum in order to obtain a total SO_3 content of seven percent by weight. The gypsum has a fineness of 90% passing the 45 micrometer sieve and is initially mixed directly with water to fascilitate dissolution. The water/(cement+gypsum) ratio is specified near 0.5 to assure high porosity.

Mortar bars of dimensions 1x1x11¼ inches are cast with a gage stud on each end. After moist curing for one day, the bars are removed from their molds and an initial length is obtained. Subsequent storage is in clean water of volume not more than five times the volume of the bars. The limitation on water volume is required to prevent excessive leaching. Lengths of mortar bars are measured again at 14 days and measurements at later ages are optional.

Expansions at 14 days have been found to correlate well with cement C_3A contents. However, three primary disadvantages limit the usefulness of this test (249, 281):

1) field conditions are not simulated because the anhydrous cement constituents, and not their hydrates, are exposed to sulfate attack,
2) resistance of cements to the surface-scaling type of sulfate attack is not evaluated, and
3) the initial chemical reactions of the aluminous constituents in slags and pozzolans are severely altered in the presence of high sulfate concentrations.

2.3.6.4 ASTM C-1012: Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution

This ASTM test method was developed primarily to satisfy the need for evaluating blended cements containing pozzolans and slags (249). Similar to ASTM C-452, mortar bars of dimensions 1x1x11¼ inches are cast with water/(cement+pozzolan) ratios near 0.5. However, the bars are moist cured until companion mortar cubes reach an average compressive strength of at least 2850 psi. Then the bars are immersed in aggressive sulfate solutions where the volume of solution is 4 ±0.5 times the volume of bars. Visual inspections and length measurements are conducted for one year at increasing time intervals (11).

During its development, this method was subjected to two rounds of cooperative testing. The first round included a test solution of 0.176 mol/liter of each of sodium and magnesium sulfates. The second round of tests included two exposure solutions: 0.303 mol/liter sodium sulfate with 0.407 mol/liter magnesium sulfate and 0.352 mol/liter sodium sulfate with no magnesium sulfate (11). The second round of testing permitted differentiation between sulfate attack and magnesium ion attack on C-S-H gel. Precision of the results and ranking of cements tested did not differ between solutions in the second test program, so the simpler exposure solution of plain sodium sulfate was selected as the standard. However, the composition and concentration of the exposure solution may be modified to simulate potential field conditions.

This test method is generally too slow to be considered an accelerated test (281). Test periods of at least 180 days have been suggested for general testing (321), although 28 days has been found to be sufficient for the detection of cements with very low resistance to sulfate attack (448).

2.3.6.5 USBR 4908: Length Change of Hardened Concrete Exposed to Alkali Sulfates

This USBR test method was developed in order to provide a standard procedure for testing concrete, rather than paste or mortar. Similar to ASTM C-1012, it permits the evaluation of blended cements containing pozzolans and slags. Concrete cylinders of dimensions 3x6 inches are cast with ¾-inch maximum size aggregate and with a water/cement ratio of approximately 0.5 (158). The cylinders are immersed in sulfate solutions after 28 days of curing: 14 days of moist curing and 14 days of curing at 50 ±2 percent relative humidity. The test may be modified with any type of sulfate salt in the exposure solution, but sodium sulfate is recommended. Initial lengths of cylinders are measured prior to immersion and one day after immersion. The difference between these measurements provides an indication of initial absorption. The second measurement is used as the initial length for expansion calculations. Additional length measurements are taken after 30 days of immersion and every 3 months thereafter. If a mixture is seen to be particularly susceptible to sulfate attack, the frequency of measurements may be increased.

This standard provides three options for test procedures:

1) continuous soaking in a 2.1 percent sodium sulfate solution (Method A);
2) continuous soaking in a 10 percent sodium sulfate solution (Method B); and
3) alternately soaking for 16 hours in a 2.1 percent sodium sulfate solution and drying for 8 hours under a forced air draft of 130 °F (Method C).

One year of soaking/drying cycles has been reported to impose similar magnitudes of concrete deterioration as six to ten years of continuous soaking in 2.1 percent solution (192). Continuous soaking in 10 percent solution has been determined to be about as rigorous as the soaking/drying test (91). Continuous soaking in 10 percent solution has also been found to be a true acceleration of tests in more dilute solutions, with no apparent irregularities in the mechanism of sulfate attack (431).

2.3.6.6 Dynamic Tests for Monitoring Deterioration

Two test methods which utilize acoustic wave pulses have been implemented to monitor concrete deterioration due to actions of frost or chemicals: ultrasonic pulse velocity method and fundamental resonant frequency method. Both tests measure the dynamic modulus of elasticity of concrete, which is related to the compressive strength of concrete, as shown in Figure 2.7 (309). Dynamic modulus of elasticity is measured within a small range of stress and at low levels of stress. Therefore, it is approximately equal to the initial tangent modulus as determined by a static test (309). The initial tangent modulus is considerably higher than the chord modulus as determined under standard static test procedures (ASTM C-469) (295).

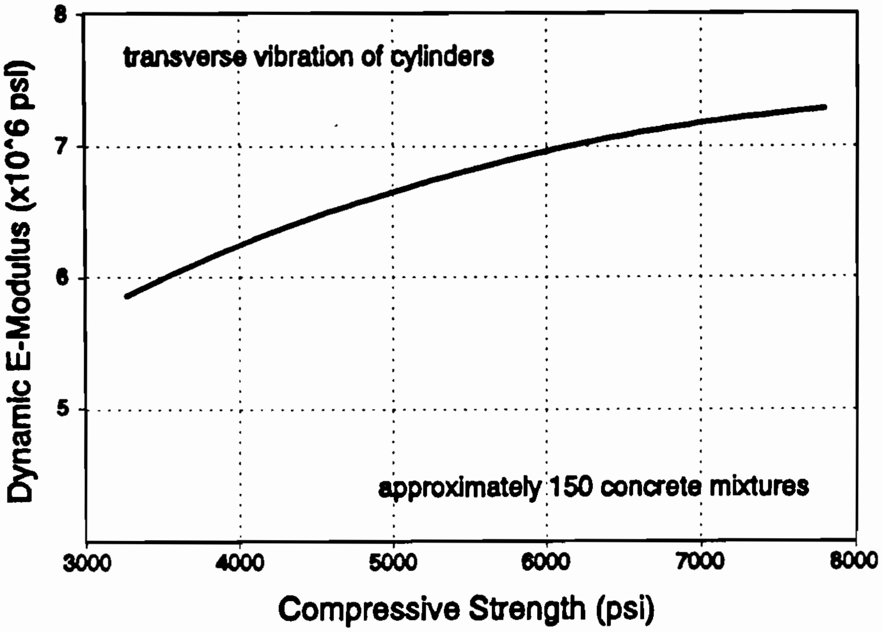


Figure 2.7 Relation Between the Dynamic Modulus of Elasticity and Compressive Strength of Concrete Cylinders (378)

The relationship between strength and modulus of elasticity depends on the aggregate used, mixture proportions, and curing conditions. Therefore, these dynamic test methods provide a good indication of changes in strength for a single concrete mixture, but should not be used to compare strengths of different mixtures (309).

The relationship between dynamic modulus of elasticity (E_d) and pulse velocity (V) in an infinite, homogeneous, isotropic, elastic media is (309, 356):

$$E_d = \rho V^2 \times \frac{(1+\mu)(1-2\mu)}{(1-\mu)}, \text{ where} \qquad (2.1)$$

ρ = density of concrete and

μ = Poisson's ratio of concrete.

The pulse velocity is calculated by simply dividing the distance between transducers by pulse transit time.

In bounded elastic media, such as cylindrical-shaped test specimens, lateral displacements occur freely. These conditions affect the relationship between pulse velocity and dynamic modulus of elasticity. However, provided the lengths of longitudinal waves are long in comparison with the cross-sectional dimensions of the rods, the inertial forces caused by the lateral motions of particles can be neglected. In these cases, the following solution is a reasonable approximation: $E_d = \rho V^2$ (356). This approximation neglects the effects of poissons ratio. The quotient in Equation 2.1, which accounts for the effects of Poisson's ratio, is nearly 1.0 for concrete.

Recommended test procedures for pulse velocity measurements are presented in ASTM Standard C-597. The standard recommends that the test not be considered as a means of establishing design compliance of field concrete for strength or modulus of elasticity.

Torii et al. (428) monitored longitudinal pulse velocity on 40x40x160 mm prisms, which were immersed in 10 percent Na_2SO_4 solution. They found that dynamic modulus of elasticity tended to increase with increases in mix design cementitious content and with fly ash content. However, measurements of dynamic modulus of elasticity did not detect concrete deterioration as readily as measurements of length, mass, or compressive strength. They attributed the lack of sensitivity of pulse velocity to the mismatch between the location of concrete deterioration and the location of wave travel. The rectangular beam specimens lost mass from surfaces and corners, but no large cracks had formed in the central portions of the beams, which is where acoustic waves travelled.

Three methods for evaluating fundamental resonant frequencies of concrete specimens are described in ASTM Standard C-215: longitudinal, transverse, and torsional. The relationship between dynamic modulus of elasticity (E_d) and fundamental resonant frequency (f_m) is (295):

$$E_d = WK(f_m)^2, \text{ where} \tag{2.2}$$

W = weight of specimen and

K = constant depending on direction of vibrations, specimen shape, and specimen dimensions.

Rosner and others (360) monitored deterioration of 1x1x11-inch mortar bars in 5 percent sodium sulfate solution by measuring expansions and transverse resonant frequencies. Initial lengths and resonant frequencies were recorded after 24 hours of curing. The specimens were then cured in saturated CH solution until they reached a strength of approximately 20.7 MPa, at which time they were exposed to sulfates. Two failure criteria were defined: expansion of 0.10 percent and dynamic modulus of elasticity falling below 120 percent of the initial value (initial value is measured 24 hours after casting). The measurements of resonant frequencies were discontinued after 150 days due to surface scaling of the mortar bars, which caused testing difficulty and variability. Therefore, they found linear expansion measurements better suited for monitoring deterioration in a sulfate environment.

The United States Bureau of Reclamation laboratories have reported an approximate relationship between expansions and reductions in dynamic moduli of elasticity (383):

$$x = \frac{(1.124)(1.108)^{y}}{100}\text{, where} \qquad (2.3)$$

x = percent expansion and

y = percent reduction in dynamic modulus.

This relationship was observed for 3x6-inch concrete cylinders which were soaking continuously in 2.1 percent sodium sulfate solution. The relationship is linear on a semi-log plot, as shown in Figure 2.8 (383).

2.3.6.7 Permeability Tests

Traditionally, permeability has been a concern for designers of hydraulic structures who required information on the rate of passage of water through concrete under the influence of high hydraulic heads (447). Testing often involved pressure produced by standpipes of mercury. Outflow of water through hardened cement paste samples is measured in a calibrated, vertical capillary tube. The change in position of the meniscus in the capillary tube is measured with respect to time (338). In such instances, flow of water through concrete can be adequately described by Darcy's Law (77):

$$Q = \frac{k}{\mu} \times A \times \frac{dp}{ds}\text{, where} \tag{2.4}$$

Q = volume outflow (cm^3/sec),
A = area (cm^2),
μ = viscosity of fluid (centipoise),
dp/ds = pressure gradient (atm/cm), and
k = Darcy's permeability constant.

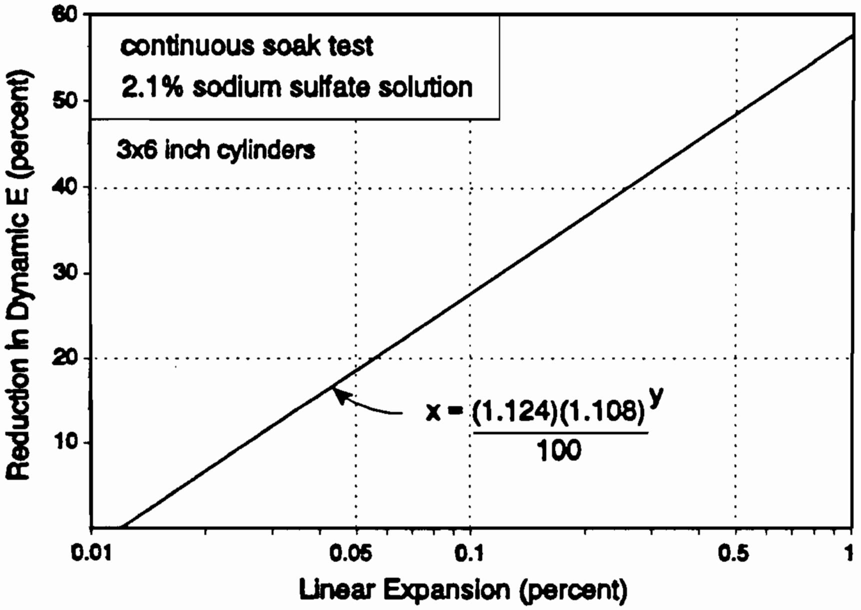


Figure 2.8 Relationship Between Linear Expansion and Dynamic Modulus of Elasticity (383)

For those concerned with concrete durability, the term "permeability" has been associated with more than saturated flow under a hydraulic gradient. Permeability is often considered the ability of concrete to resist the penetration of a particular substance. As examples, corrosion of reinforcement and sulfate attack depend on the ingress of chloride ions and sulfate ions, respectively (447). Concrete durability problems may often be minimized by decreasing concrete permeability and thus resisting the penetration of deleterious substances.

Under conditions other than those of saturated fluid flow, transport of substances through concrete can occur by a variety of mechanisms (447): capillary action, vapor transmission, and ionic diffusion. Within nearly saturated concretes, ions migrate primarily through diffusion processes which are modeled by Fick's Second Law (447):

$$\frac{\partial C}{\partial t} = D \times \frac{\partial^2 C}{\partial x^2}\text{, where} \qquad (2.5)$$

C = concentration at distance x (cm) from a boundary,
t = time (sec), and
D = effective diffusion coefficient (cm^2/sec).

The rate of diffusion of chloride or sulfate ions through hardened cement paste is a function of both its chemical and physical microstructures. While fluid will not flow through saturated discontinuous pores, chloride or sulfate ions may diffuse between these pores, depending on the chemical microstructure. These ions may also react with hydration products to form new compounds. Physical microstructure may be characterized by pore size distribution which is commonly measured by mercury intrusion porosimetry (MIP).

Pores in normal-weight concrete are considered part of the paste fraction and cover a large range of sizes. Voids with diameters less than 10,000 nm are generally labeled "pores" and voids with diameters larger than 10,000 nm are generally labeled "air voids". The traditional classification of pores, as suggested by Powers and Brownyard (337), includes two classes, as shown in Figure 2.9 (451):

1) capillary pores, which are remnants of water-filled space, and
2) gel pores (intrinsic porosity), which are associated with the morphology of hydration products.

The capillary pores form a continuum which can be measured by MIP. Sorption techniques are required to investigate the finer gel pores (451).

Mehta (270) has suggested that measurements of pore structures of blended cement pastes are likely to yield the best predictions of durability. However, measurement techniques which use pressure differentials, such as MIP, should be avoided. The pore structure developed by blended cement pastes is particularly susceptible to damage during testing (116).

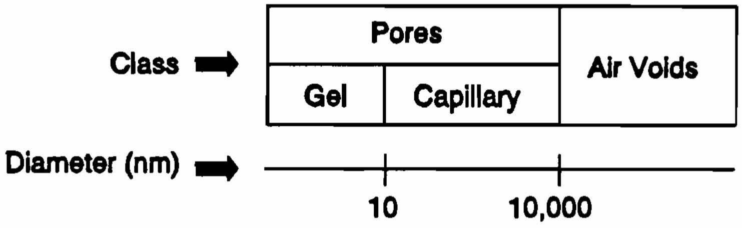


Figure 2.9 Classification of Pore and Void Sizes for Cement Paste (337)

The resistance of concrete to the intrusion of chloride ions has received considerable attention due to the influence of chloride ions on the corrosion of reinforcing steel. Until recently, ponding tests such as AASHTO Standard T-259 have been relied upon to assess chloride permeability characteristics of concrete. Small concrete slabs are ponded with 3 percent sodium chloride solution for 90 days. Samples are then removed from the slabs at various depths and are pulverized. Chloride contents of solutions containing the samples are determined by laboratory titration procedures (299).

In 1983, AASHTO adopted a rapid method for assessing chloride ion permeabilities of concrete. Testing Standard T-277 involves the use of electric potential to drive chloride ions through concrete samples. The total electric charge passed during a 6-hour period has been shown to correlate well with chloride ion profiles after 90-day ponding tests (446).

2.3.7 EFFECTS OF MIX DESIGN VARIABLES

2.3.7.1 Cement Composition

In the year 1919, D.G. Miller (292, 293) began an investigation with the objective of correlating sulfate resistance of concrete with portland cement compounds. Concrete cylinders of dimensions 2x4 inches were cast with 122 portland cements from 85 mills.

Some specimens were immersed in Medicine Lake, South Dakota, which averaged five percent total sulfates and companion specimens were stored in tap water. Compressive strengths of cylinders in the lake and in tap water were monitored; the ratio of strengths [f_c(lake)/f_c(tap water)] provided an indication of concrete deterioration due to sulfates.

Companion cylinders from all concrete mixtures were also immersed in two solutions prepared in the laboratory: one percent magnesium sulfate solution and one percent sodium sulfate solution. These cylinders were monitored for linear expansion.

Tricalcium aluminate was the cement compound which exhibited the best correlation with concrete sulfate resistance. Sulfate resistance generally increased as the cement C_3A content decreased, as shown in Table 2.4. Tricalcium aluminate contents were calculated from bulk chemical analyses utilizing Bogue equations (147).

Thorvaldson (114) studied various mixtures of the four major compounds of cement clinker. His conclusions aggreed with Miller, but he also found that substitutions of C_4AF for C_3A increased the resistance of cement to sulfate attack; decreasing Al_2O_3/Fe_2O_3 ratios in bulk chemical compositions generally resulted in decreasing sulfate-related expansions. When the Al_2O_3/Fe_2O_3 ratio of a cement was low, ettringite formed as a solid solution: $C_3A \cdot 3C\bar{S} \cdot H_{32}$ -$C_3F \cdot 3C\bar{S} \cdot H_{32}$. As discussed previously, iron-bearing ettringite tends to be less expansive than ettringite without iron (193).

Tetracalcium aluminoferrite, however, is not immune to sulfate attack. Bogue (37) compared the sulfate resistance of cements which contained 5 percent C_3A and proportions of C_4AF ranging from 6 to 25 percent. He used mortars with a cement/sand ratio of 0.5 and a water/cement ratio of 0.35. Mortar bars were exposed to 2 percent Na_2SO_4 solution. The rate of expansion increased as C_4AF contents exceeded ten percent, as shown in Figure 2.10.

The susceptibility of high C_4AF content cements to sulfate attack offers a partial explanation to the erratic behavior of zero percent C_3A cements. Cements which do not contain any C_3A may still be susceptible to sulfate attack due to the presence of high proportions of C_4AF. In fact, the Bureau of Reclamation has consistently reported superior sulfate resistance for cements which contain small amounts of both C_3A and C_4AF (193).

Table 2.4 Effect of Portland Cement C_3A Content on Its Resistance to Sulfates (292, 293)

Cement Group	C_3A (%)	Average Strength Ratio *		Months to 0.01% Expansion	
	Min. - Max.	1 year	5 years	1% $MgSO_4$	1% Na_2SO_4
1	4.4 - 5.4	92	82	220	260
2	4.1 - 6.7	92	69	160	190
3	5.9 - 9.7	90	56	130	150
4	7.4 - 9.5	87	45	97	122
5	8.1 - 10.3	83	29	79	106
6	8.7 - 9.7	85	28	68	71
7	9.2 - 10.9	85	8	58	55
8	9.0 - 11.6	79	0	46	51
9	9.9 - 13.5	76	0	36	29
10	10.6 - 14.1	72	0	29	24
11	11.1 - 13.4	62	0	29	20
12	11.9 - 14.2	50	0	18	13

Note: All data was obtained from 2x4-inch concrete cylinders.

* Medicine Lake storage / laboratory water storage

Variations in C_3S/C_2S ratios may also contribute to variabilities in the resistance of 0% C_3A cements to sulfate attack (193, 295). During hydration, tricalcium silicate liberates a large proportion of calcium hydroxide relative to that which would be liberated by dicalcium silicate. In the process of sulfate attack, calcium hydroxide permits the formation of gypsum. Calcium hydroxide is also relatively soluble and therefore may be leached out into solution, leaving the concrete more permeable and less durable.

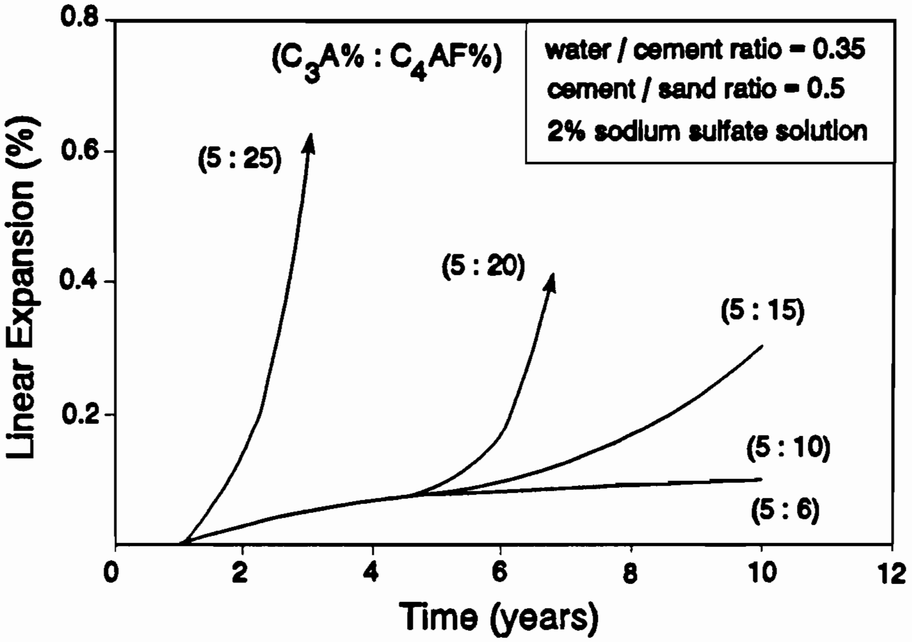


Figure 2.10 Effect of Portland Cement C_4AF Content on Its Resistance to Sulfates (37)

The proportions of anhydrite and/or gypsum added to cement are largely determined by optimizing strength and shrinkage characteristics. However, relatively high SO_3 contents in cement may be beneficial for sulfate resistance. Concrete pore solutions with high SO_3 contents promote rapid ettringite formation and keep ettringite stable while the calcium aluminates continue to hydrate. Budnikov and Grachera (46) conducted a study involving two cement clinkers (5.0 and 10.9 percent C_3A) and three percentages of added anhydrite (3.0, 5.0, 10.0 percent). By increasing the total SO_3 for cement, the percentages of combined SO_3 within six hours of hydration increased and the durations for the presence of uncombined SO_3 increased, as shown in Table 2.5.

Budnikov and Grachera (46) tested these cements for resistance to sulfates by monitoring the flexural strength of mortar bars in 5 percent Na_2SO_4 solution. The low-C_3A clinker was resistant to sulfate attack at all three percentages of added anhydrite, as shown in Table 2.6. The sulfate resistance of the high-C_3A clinker increased with increasing percentages of anhydrite.

Table 2.5 Rate of Combination of SO_3 from Anhydrite with Two Cements (46)

Clinker C_3A (%)	Added Anhydrite		Total SO_3 in Cement (%)	Uncombined SO_3 in Hydrated Cement Paste (%)				
	Total (%)	SO_3 (%)		6 hrs	1 day	3 days	7 days	28 days
5.0	3.0	1.76	2.05	0.780	0.170	0	—	—
	5.0	2.95	3.24	1.390	0.083	0	—	—
	10.0	5.88	6.17	3.070	2.220	1.380	1.170	0.308
10.9	3.0	1.76	2.18	0.041	0	—	—	—
	5.0	2.95	3.37	0.632	0	—	—	—
	10.0	5.88	6.30	1.660	1.310	1.545	0.222	0

The proportion of SO_3 in cements also affected the flexural strength of mortar bars stored in water, as shown in Table 2.6. Increases in added anhydrite from 5 to 10 percent decreased the 28-day flexural strengths of mortars for both clinker types by approximately 40 percent.

Alkalies in cement are limited to prevent flash setting and alkali-aggregate durability problems. However, high alkali contents have yielded some interesting results concerning sulfate attack. Heller and Ben-Yair reported that C_3A reacts differently with calcium sulfate in relatively concentrated solutions of alkali hydroxides than it does in the normal liquid phase of portland cement pastes. They proposed that in highly alkaline solutions, crystalline calcium sulfoaluminate is formed through-solution and therefore does not cause expansion (189, 191).

Table 2.6 Effects of Added Anhydrite on the Strength and Sulfate Resistance of Mortars (46)

Clinker C_3A (%)	Added Anhydrite (%)	Flexural Strengths (kg/cm^2)		
		Water	5% Na_2SO_4	
		28 days	28 days	3 months
5.0	3.0	53.0	42.0	45.0
	5.0	48.0	47.8	47.0
	10.0	28.8	32.4	35.0
10.9	3.0	46.2	36.6	0
	5.0	50.6	50.0	12.2
	10.0	30.0	26.8	26.4

Notes: 1:3 (cement:sand) mortar mixtures
1x1x3-cm mortar bar specimens

Van Aardt and Visser (438) studied the effects of alkali and sulfate contents on the sulfate resistance of mortars containing a low-alkali, low-sulfate Type I portland cement (11.8 percent C_3A). Alkali and sulfate contents of the cement were increased individually with additions of sodium hydroxide and gypsum, respectively. Alkali and sulfate contents of the cement were increased simultaneously with additions of sodium sulfate.

Table 2.7 shows calculated Na_2O equivalent and SO_3 contents of the cements; additives were considered as part of the cements. Mortar bars of dimensions 1x1x11 inches were moist cured for 28 days and were then immersed in 5 percent sodium sulfate solution. Specimens were monitored for both dynamic modulus of elasticity (E_d) and linear expansion. Increasing sulfate or alkali contents individually were in some cases able to decrease rates of deterioration, however, no significant improvements were observed, as shown in Figure 2.11. When Na_2SO_4 was used to increase both sulfate and alkali contents, expansions were significantly reduced and loss of dynamic modulus of elasticity was prevented.

Table 2.7 Modification of the Alkali and Sulfate Contents of a Low-Alkali Portland Cement (438)

Mortar Mixture	Cement Modification	Na_2O eq.(%)	SO_3 (%)	$\frac{C_3A\%}{SO_3\%+Na_2O\text{ eq.}\%}$	$\frac{SO_3\%}{Na_2O\text{ eq.}\%}$
U	Unchanged	0.16	1.65	6.52	10.31
N1	NaOH	0.32	1.65	5.99	5.16
N2	NaOH	0.64	1.65	5.16	2.58
N3	NaOH	1.28	1.65	4.03	1.29
N4	NaOH	2.56	1.65	2.81	0.64
C1	$CaSO_4 \cdot 2H_2O$	0.16	1.86	5.85	11.63
C2	$CaSO_4 \cdot 2H_2O$	0.16	2.27	4.86	14.19
C3	$CaSO_4 \cdot 2H_2O$	0.16	3.09	3.63	19.31
C4	$CaSO_4 \cdot 2H_2O$	0.16	4.75	2.41	29.69
S1	Na_2SO_4	0.32	1.86	5.42	5.81
S2	Na_2SO_4	0.64	2.27	4.06	3.55
S3	Na_2SO_4	1.28	3.09	2.70	2.41
S4	Na_2SO_4	2.56	4.75	1.62	1.86

Based on the sufate resistance of mortar mixtures containing cement with 11.8 percent C_3A and various proportions of sulfate and alkali, Van Aardt and Visser (438) formulated two cement composition criteria. In order to resist attack by sulfates, cements should satisfy both requirements:

$$\frac{C_3A\%}{SO_3\% + Na_2O\text{ eq}\%} < 3 \quad \text{and} \tag{2.6}$$

$$1 < \frac{SO_3\%}{Na_2O\text{ eq}\%} < 3.5\ . \tag{2.7}$$

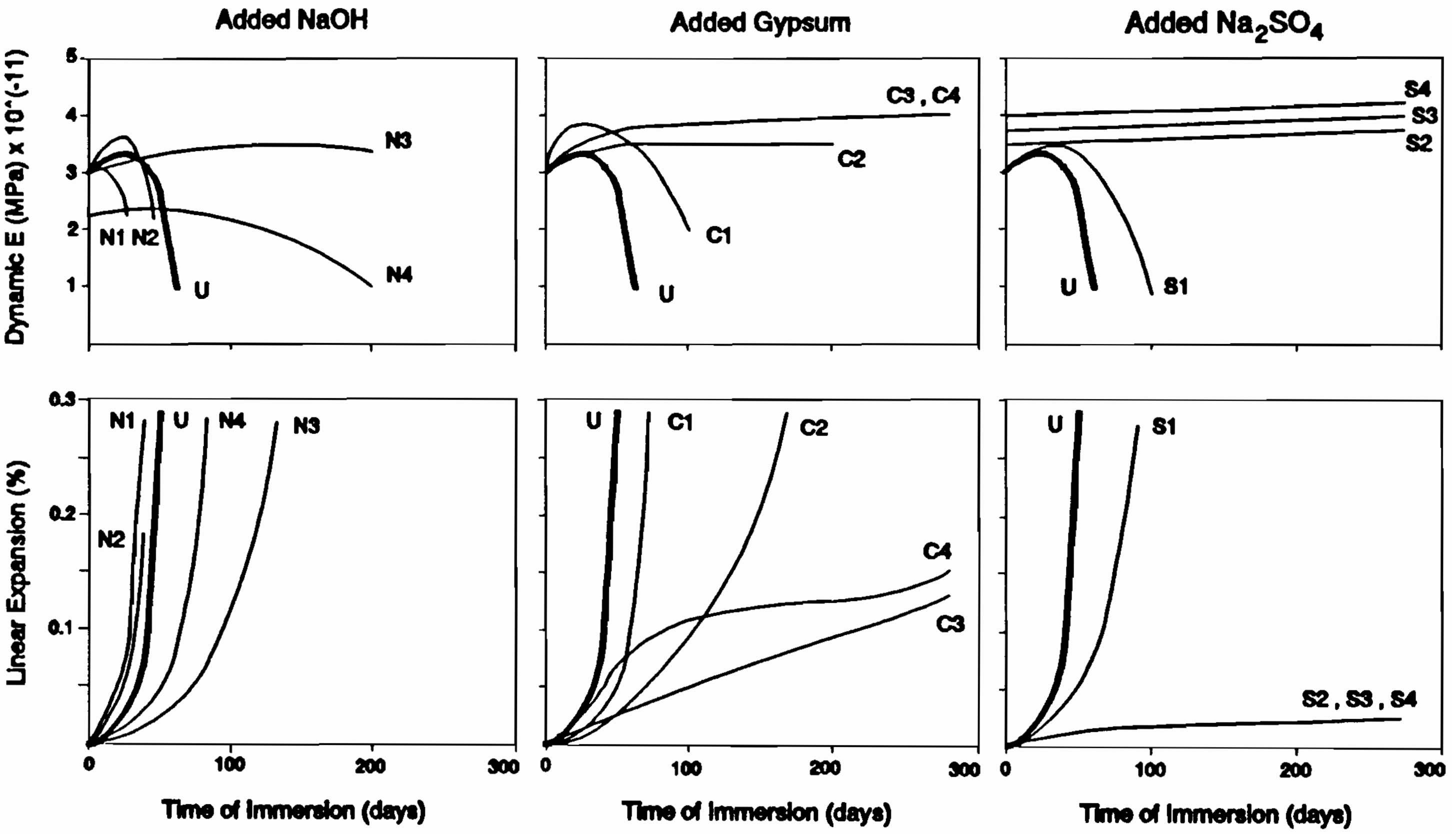


Figure 2.11 Sulfate Resistance of Portland Cement Mortar with Additional Alkalies and Sulfates (438)

2.3.7.2 Specialized Non-Portland Cements

Two types of cement have been developed specifically for the purpose of being resistant to the action of sulfates: calcium aluminate cement and supersulfated cement.

Calcium aluminate cement (CAC) contains monocalcium aluminate (CA) as its principal cementitious compound. Calcium aluminate cements typically contain 50 to 60 percent by weight CA and 10 to 17 percent by weight Fe_2O_3, with the remainder varying considerably. The large proportion of iron (as Fe_2O_3) comes from the use of bauxite, a hydrated alumina mineral, as the raw material source of alumina. Bauxite ores typically contain considerable amounts of iron as an impurity (278).

Although CAC products have setting times comparable to ordinary portland cement, the rate of water consumption and the rate of strength gain at early ages are both high due to the reactivity of CA. Thermal gradients may cause problems as the rate of heat liberation at early ages may be as high as three times the rate for high-early strength portland cement (278).

Under ordinary temperature conditions, the performance of CAC in the presence of sulfates or seawaters is unequalled by any other construction cement (218). The extraordinary resistance to sulfates is attributed to the absence of calcium hydroxide in set cement, which is beneficial for at least two reasons (218):

1) there are no reactions between CH and sulfates to form gypsum and
2) the absence of CH permits the formation of non-expansive calcium sulfoaluminates.

Failure to achieve long-term stability has precluded the use of CAC as a general construction cement (295). Low-temperature (< 50 °F) hydration products, hexagonal CAH_{10} and C_2AH_8, are thermodynamically unstable. Under warm and humid conditions, they convert to the more stable calcium aluminate hydrate, cubic C_3AH_6. This conversion reduces the volume of solids by more than 50%, which causes a significant loss in strength for the hardened cement paste (278).

The second non-portland cement which is highly resistant to sulfate attack is supersulfated cement. This cement is produced by intergrinding 80 to 85 percent granulated slag, 10 to 15 percent anhydrite or hard burnt gypsum, and about 5 percent portland cement. The product is ground more finely than typical portland cement; specifications in Great Britain require a specific surface area of not less than 4000 $(cm_2)/gm$ (218).

Slags to be used in slag cements are chilled very rapidly from their molten state, which prevents crystallization and promotes solidification as glass. These glassy slags are very reactive (218). The composition of slags typically range from 30 to 50 percent lime, 28 to 38 percent silica, 8 to 24 percent alumina, 1 to 18 pecent magnesia, and 1 to 2.5 percent sulfur (218).

German specifications require that slags to be used in supersulfated cement must contain Al_2O_3 contents greater than 13 percent and must conform to the compositional formula (218):

$$\frac{CaO + MgO + Al_2O_3}{SiO_2} \geq 1.6 \; . \tag{2.8}$$

Similar to calcium aluminate cement, supersulfated cement combines chemically with more water than is required for the hydration of ordinary portland cement. The curve for strength versus water/cement ratio has been observed to be unusually flat (309). Contrary to calcium aluminate cement, supersulfated cement has a low heat of hydration: 40 to 45 cal/gm in 7 days and 45 to 50 cal/gm in 28 days (218). A typical ASTM Type I cement will produce 80 to 90 cal/gm in 7 days and 90 to 100 cal/gm in 28 days (278). Despite their low evolution of heat, supersulfated cements harden at a rate which is comparable to that of ordinary portland cement. The quality of concrete containing supersulfated cement, however, is more sensitive to early curing conditions (218).

The setting and initial hardening of supersulfated cement is attributed to the formation of calcium sulfoaluminates. Alumina is provided by slag, sulfate is provided by calcium sulfate, and calcium is provided by all constituents (295).

Ettringite formation only occurs within a range of solution calcium hydroxide contents. In saturated lime solution (high pH), the unstable monosulfoaluminate phase forms. In water which contains no calcium hydroxide (low pH), no calcium sulfoaluminates form. Budnikov found the optimum concentration of calcium in solution to be from 0.15 to 0.5 grams CaO per liter (45). The correct lime content for the formation of ettringite in supersulfated slag cement pore solution is ensured by the small addition of portland cement (218).

The resistance of supersulfated cement to sulfate attack is attributed to both the retention of ettringite and the absence of calcium hydroxide in the set cement (295). The significant effect of blast furnace slag/portland cement ratios on the calcium hydroxide content in hardened cement pastes is displayed in Figure 2.12 (204).

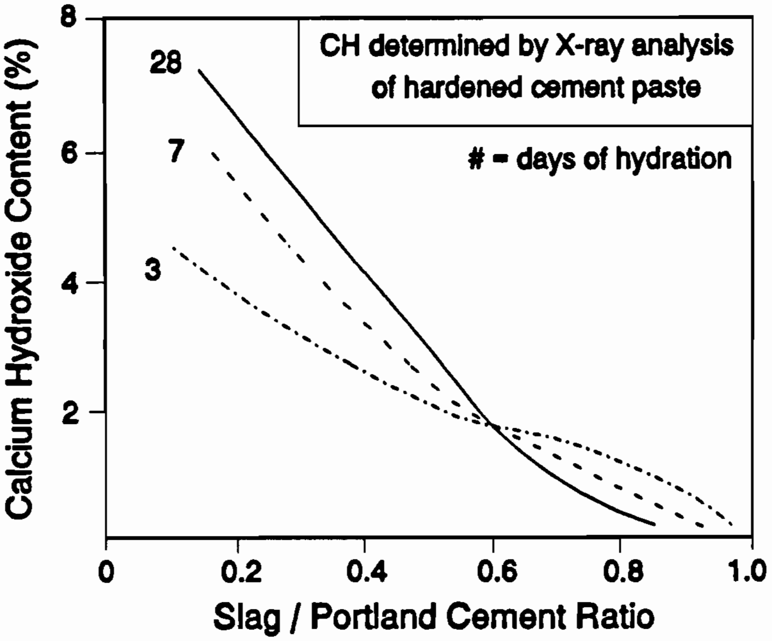


Figure 2.12 Calcium Hydroxide Content of Set Blastfurnace Cements (204)

2.3.7.3 Water/Cement Ratio

Decreasing the water/cement ratio in concrete mixture design generally results in more durable concrete (295). Ouyang and others (316) exposed mortars containing a high C_3A cement (12.0 percent) and various proportions of water to ASTM C-1012 sulfate environment conditions. Decreasing the water/cement ratio delayed expansion, but did not eliminate expansion, as shown in Figure 2.13. This delay was attributed to decreased matrix porosity and increased concrete strength.

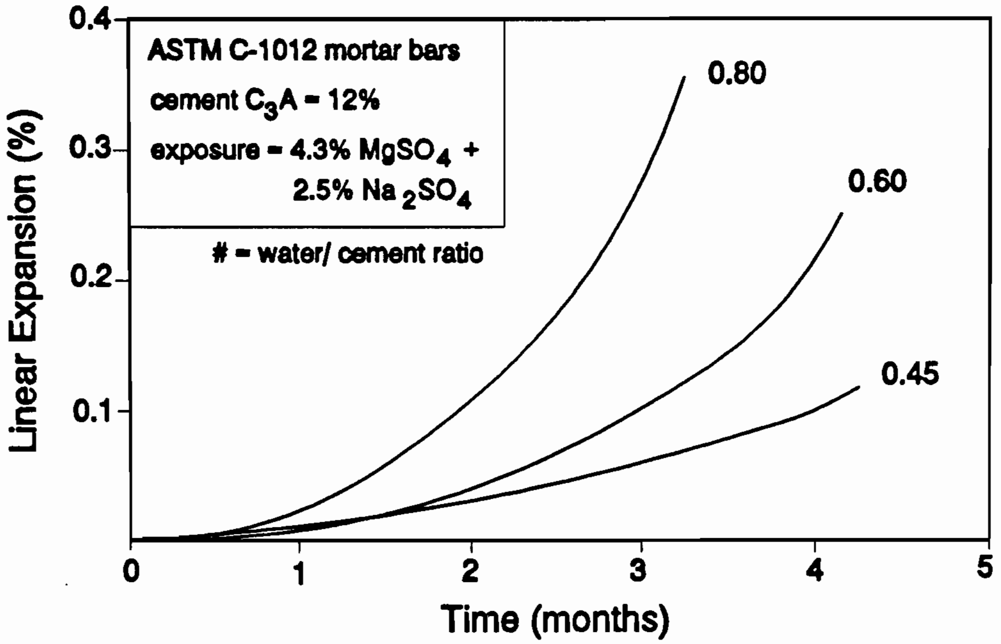


Figure 2.13 Effect of Water/Cement Ratio on the Sulfate Resistance of Mortar (316)

2.3.7.4 Proportion of Cement

The Bureau of Reclamation subjected numerous concrete mixtures to sulfate exposure field testing in 1945 (158). Eighteen cement types of various C_3A contents were cast in a number of forms, including 3x3x16¼-inch prisms. The prisms were immersed in a basin of 4 to 5 percent sulfate solution (predominantly sodium sulfate) and were monitored for changes in length. Figure 2.14 displays the results of seven years of testing. Sulfate resistance increased with decreasing C_3A contents and with increasing mix design cement factors, where cement factor represents the quantity of 94 lb sacks of cement per cubic yard of concrete. As cement factors increased, the time to 0.05 percent expansion increased slightly for cements with high C_3A contents and increased significantly for cements with low C_3A contents (less than approximately 6 percent C_3A). Improvements in the resistance of concrete to sulfate attack, due to increased cement factors, are most likely related to decreased concrete permeabilities.

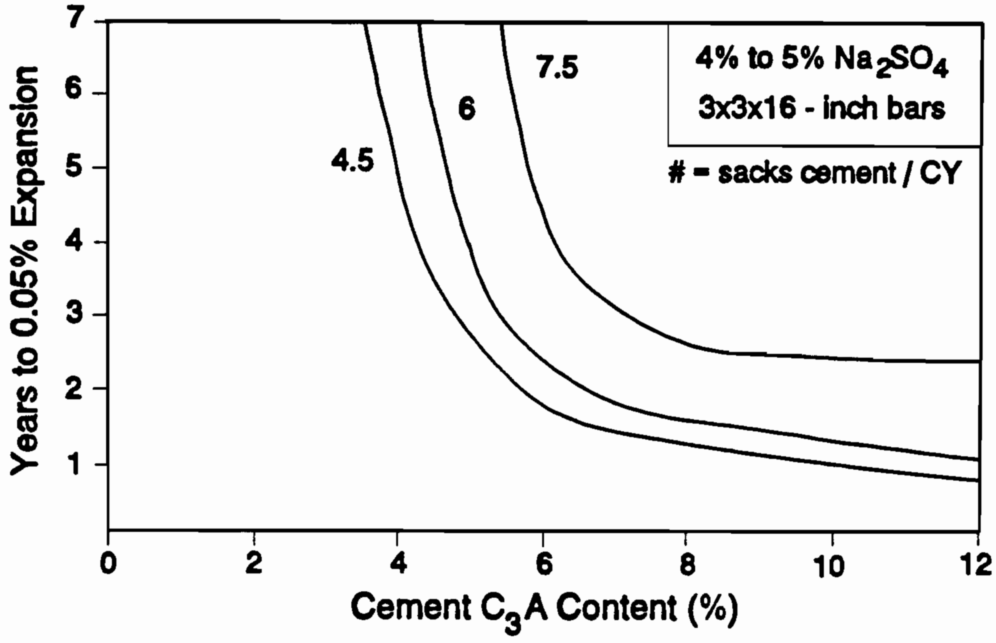


Figure 2.14 Effects of C_3A Content of Cement and Richness of Concrete Mixtures on Sulfate Resistance (158)

2.3.7.5 Aggregates

Katharine Mather (252) has suggested that aggregate particles in portland cement concrete should not be regarded as completely inert, especially when the concrete is stored in a moist environment. Although aggregate type is typically less significant than other factors when designing concrete for resistance to sulfates, its influence should not be ignored.

Piasta et al. (328) conducted mortar and concrete sulfate exposure tests in order to investigate the effects of fine and coarse aggregate types. Fine aggregates in mortars included a low porosity (5.5 percent pores by volume) crushed limestone, a high porosity (36.0 percent pores by volume) crushed limestone, and a natural quartz sand. Coarse aggregates in concrete included the same two crushed limestones, and a crushed granite with 2.5 percent pores by volume. The fine aggregate in concrete was quartz sand for all mixtures. Cement type, C_3A = 8.6 percent, remained constant. Mortar samples contained no fly ash while 40 percent by weight of the cement in concrete samples was replaced by a low calcium fly ash.

All samples were cured at 100% relative humidity prior to immersion in sulfate solutions. Both mortar and concrete specimens were immersed in 4.5% Na_2SO_4 solutions at 28 days. Deterioration due to sulfate attack was monitored as the ratio of flexural strength to the 28-day flexural strength. This ratio was expressed as Relative Flexural Strength.

Mortar bars containing quartz sand suffered a slow but steady loss in flexural strength, as shown in Figure 2.15. This was attributed to the dissolution of quartz in the alkali environment, which caused deterioration of the sand-cement paste interface (21, 328).

Concrete containing both limestone coarse aggregates suffered losses in flexural strength, while the concrete containing granite aggregate continued to gain strength, as shown in Figure 2.16. X-ray diffraction analyses detected much larger amounts of ettringite and gypsum and lower amounts of calcium hydroxide in the limestone mixtures compared to the granite mixtures. Porosity of aggregates and aggregate influence on water/cement ratio may have affected concrete permeability and thus, the rate of ingress of sulfate ions.

An additional characteristic of aggregates which could influence the durability of concrete is their sulfate content. Recently, for reasons of economy and ecology, sulfate-bearing aggregates have been utilized as concrete constituents: gypsum contaminated aggregates in the Middle East and by-product gypsum (phosphogypsum) in the United States (316). If a large proportion of unreacted C_3A is present after the concrete has hardened and if the aggregates maintain a supply of sulfate ions, sulfate-related expansive reactions may cause deterioration of concrete. This durability problem is an example of internal sulfate attack.

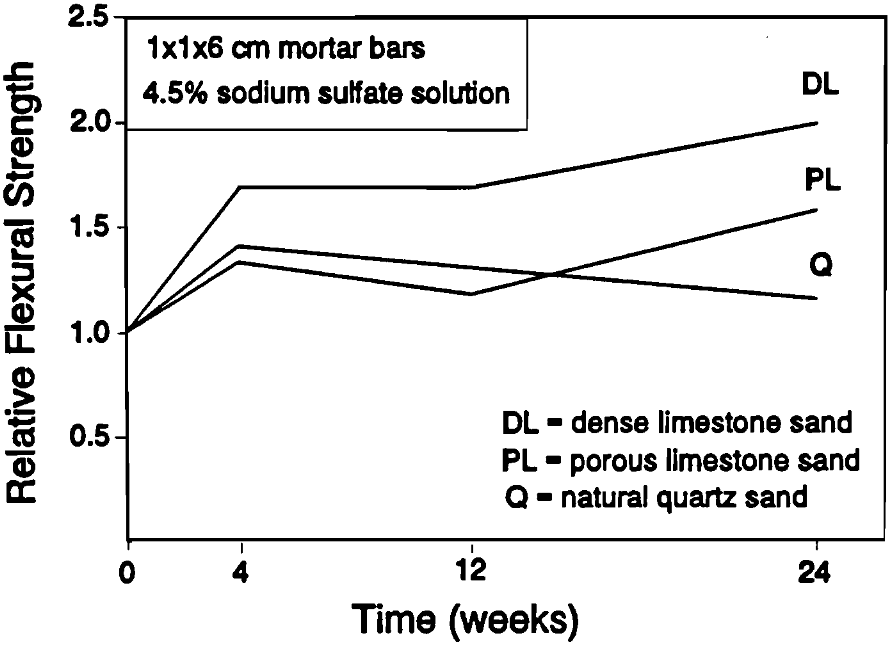


Figure 2.15 Effect of Type of Sand on Sulfate Resistance of Mortars (328)

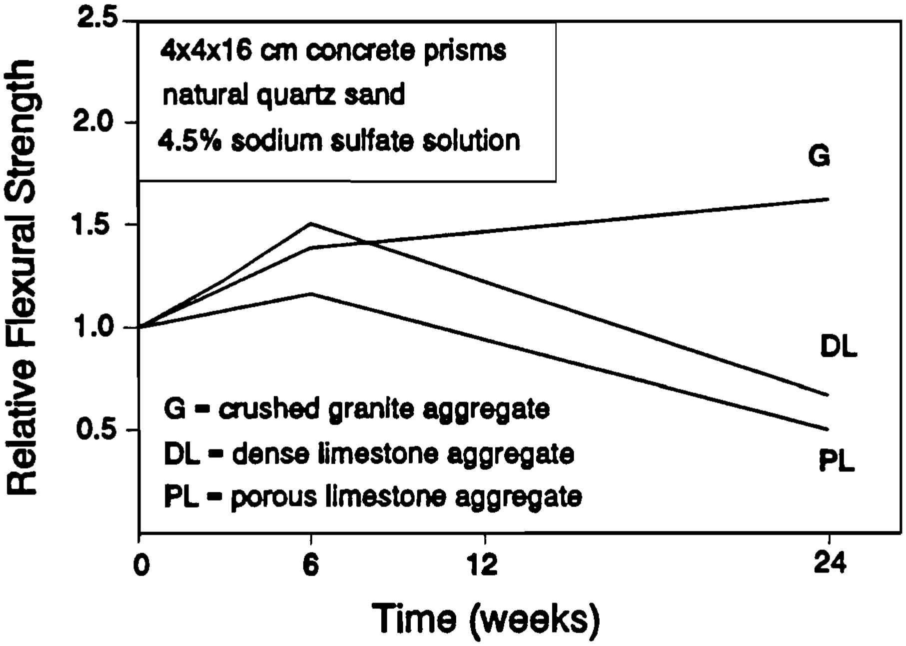


Figure 2.16 Effect of Coarse Aggregate Type on Sulfate Resistance of Concrete (328)

2.3.8 SPECIFICATIONS

2.3.8.1 ASTM Portland Cements

Specific cement types are often designated by designers when specific cement properties are required, including resistance to sulfate attack. ASTM Standard C-150 provides chemical and physical requirements for five non-air entrained cement types:

1) Type I cement for use when the special properties specified for any other type are not required,
2) Type II cement for general use, more especially when moderate sulfate resistance and/or moderate heat of hydration is desired,
3) Type III cement for use when high early strength is desired,
4) Type IV cement for use when a low heat of hydration is desired, and
5) Type V cement for use when high sulfate resistance is desired.

Type I cement offers no special advantages, so no limits are imposed on any of the principal oxides or compounds. Limitations on minor constituents such as magnesium oxide, sulfur trioxide, and alkalies are required to ensure proper setting and soundness characteristics.

Moderate sulfate resistance of Type II cement is ensured by the requirement that it contain no more than 8 percent C_3A. Moderate heat of hydration is ensured if the optional requirement [$(C_3S + C_3A) \leq 58$ percent] is enforced. Both C_3S and C_3A are primarily responsible for early heat evolution.

High-early strength characteristics of Type III cement is ensured by its meeting the physical requirements of one and three day compressive strengths. High-early strengths for cements are generally achieved through high C_3S contents and/or high cement fineness. To ensure that the high-early strength is not due mainly to alumina-bearing hydration products, C_3A content is limited to 15 percent (278, 295). If high-early strengths and moderate or high sulfate-resistance is desired, ASTM C-150 includes 8 percent and 5 percent C_3A limitations as optional chemical requirements.

Low heat of hydration for Type IV cements is obtained by limiting C_3S and C_3A contents to 35 percent and 7 percent, respectively. Since C_2S can provide long-term strength with low early heat evolution, Type IV cements must contain a minimum C_2S

content of 40 percent. The limitation of C_3A makes Type IV cement moderately sulfate-resistant. However, relative to Type II cement, the additional restrictions on calcium silicates makes Type IV cement more expensive to produce and more difficult to obtain in most areas.

The high sulfate-resistance of Type V cement is ensured by limiting its C_3A content to a maximum of 5 percent. Since studies have indicated that cements with high C_4AF contents are susceptible to sulfate attack, the proportion of this compound is also limited. The sum $[(C_4AF + 2(C_3A)]$ or the solid solution $(C_4AF + C_2F)$, whichever is applicable, is limited to 25 percent. Since aluminates act as fluxing agents in the cement manufacturing process, Type V cements with low proportions of aluminates are relatively expensive to produce.

2.3.8.2 Exposure Conditions/ Cement Requirements

The United States Bureau of Reclamation (USBR) recognizes four classes of sulfate exposure severity, as shown in Table 2.8 (193). Classification may be determined by water soluble sulfates in soil samples or by sulfates in water samples. The table includes USBR recommendations for a cement type for each exposure condition. Utilization of pozzolans as mineral admixtures is an option for severe and very severe exposures.

The American Concrete Institute (ACI) based their sulfate exposure specifications on those originally developed by the USBR. The four categories of sulfate exposure severity remained unchanged, but cement type requirements were modified and water/cement ratio and strength requirements were added, as shown in Table 2.9. The following terms facilitate understanding the recommendations for blended cement types (16):

1) I(PM) - pozzolan-modified portland cement in which the pozzolanic constituent is less than 15 percent by weight of the blended cement,
2) IP - portland-pozzolan cement in which the pozzolan constituent is between 15 and 40 percent by weight of the blended cement,
3) P - portland-pozzolan cement in which the pozzolan constituent is more than 40 percent by weight of the blended cement,
4) I(SM) - slag-modified portland cement in which the slag constituent is less than 25 percent by weight of the blended cement,

5) IS - portland blast-furnace slag cement in which the slag constituent is between 25 and 70 percent by weight of the blended cement, and
6) (MS) - moderate sulfate resistance.

In order for a blended cement to be specified as moderately resistant to sulfate attack, it must be tested in accordance with ASTM C-1012 procedures. Mortar bar expansion must be less that 0.10 percent at 180 days.

Table 2.8 United States Bureau of Reclamation Classification for Sulfate Attack Severity (435)

Relative Degree of Sulfate Attack	Water-Soluble Sulfate (as SO_4) in Soil Samples (%)	Sulfate (as SO_4) in Water Samples (ppm)
Negligible	0.00 to 0.10	0 to 150
Positive *	0.10 to 0.20	150 to 1,500
Severe **	0.20 to 2.0	1,500 to 10,000
Very Severe †	> 2.0	> 10,000

* use Type II cement

** use Type V cement or an approved portland-pozzolan cement providing comparable sulfate resistance when used in concrete

† use Type V cement plus an approved pozzolan which has been determined by test to improve sulfate resistance when used in concrete

Blends, as defined by ASTM C-595, consist of intimate mixtures of portland cement and fine granulated blast-furnace slag or pozzolan. Blends may be produced by either intergrinding portland cement clinker and slag or pozzolan, by intimately mixing portland cement and slag or pozzolan, or by a combination of the two procedures (16).

The specified maximum water/cement ratios and minimum compressive strengths promote desireable durability characteristics for concrete, including low permeability. Minimum levels of compressive strength are specified for lightweight concrete because accurate calculations of water/cement ratios are difficult. Lightweight aggregates are typically porous and have high absorption capacities (7).

Construction specifications written by the Texas Department of Transportation (Texas DOT) do not include classes of sulfate exposure. However, general design guidelines are offered (216):

1) Item 421 of the Texas DOT Standard Specifications requires the use of ASTM Type II cement for substructure concrete and
2) a special provision for Item 421 states that Texas Type B fly ash may not be used in conjunction with ASTM Type II cement.

Table 2.9 American Concrete Institute Requirements for Concrete Exposed to Sulfate-Containing Solutions (7)

Sulfate Exposure	Water Soluble Sulfate (SO_4) in Soil (%)	Sulfate (SO_4) in Water (ppm)	Cement Types *	Normal Weight Aggregate Concrete	Lightweight Aggregate Concrete
				maximum w/c ratio **	minimum f'_c (psi) **
Negligible	0.00 to 0.10	0 to 150	—	—	—
Moderate †	0.10 to 0.20	150 to 1,500	II,IP(MS),IS(MS), P(MS),I(PM)(MS), (SM)(MS)	0.50	3750
Severe	0.20 to 2.0	1,500 to 10,000	Type V	0.45	4250
Very Severe	> 2.0	> 10,000	Type V plus a pozzolan ‡	0.45	4250

* Descriptions of blended cements may be found in ASTM Standard C-595.

** A lower water/cement ratio or higher strength may be required for low permeability or for protection against corrosion of embedded items or freezing and thawing.

† including seawater

‡ a pozzolan that has been determined by test or service record to improve sulfate resistance when used in concrete containing Type V cement

2.4 FLY ASH

2.4.1 INTRODUCTION

In 1987, the United States ranked fourth in production of fly ash (38 million tons), second in total utilization of fly ash (8 million tons), and first in utilization of fly ash in concrete (4.3 million tons) (243). However, if total utilization of fly ash is calculated as a percentage of fly ash produced, the United States ranks far below some European countries. The United States used only 18 percent of its fly ash while the United Kingdom and France used 57 and 58 percent, respectively. The effectiveness of the ash utilization programs in France and the United Kingdom has been partially attributed to the nationalization of their power plants. Meanwhile, private electric utilities throughout the United States are not synchronized in their ash marketing techniques (243).

In 1984, Gaynor (124) surveyed concrete producers in order to obtain an estimate of the extent of fly ash utilization. The survey was sent to 330 concrete producers, accounting for more than 18 percent of all the producers in the United States. Gaynor reported that fly ash was used by 39 percent of concrete producers and that for companies which used fly ash, an average of 42 percent of their concrete contained fly ash. For concrete produced with fly ash, an average of 20 percent by weight of cement was replaced with the mineral admixture.

2.4.2 ORIGIN

2.4.2.1 Coal

Coal fields originate from peat swamps, which are abundant in plant matter. Over millions of years, the swamps subside and are buried by increasing depths of soil and rock deposits from the surrounding area. Coal is gradually formed by the decomposition of plant matter under conditions of extreme pressure and temperature, accompanied by moisture and in the absence of air (325, 441). Degree of coalification, which is a function of time, temperature, and pressure, affects the chemical composition of the coal.

Coal deposits are ranked by The American Society for Testing and Materials (ASTM D-388), according to their degree of coalification, as shown in Table 2.10. As coalification progresses, chemical changes produce compounds of lower oxygen and hydrogen contents and of higher carbon contents (154). These changes result in decreasing proportions of volatile matter and increasing calorific value (Btu/lb coal), which is a measure of energy production efficiency (154). The common names and physical characteristics of the ASTM classes of coal, listed in order of increasing coalification, are (154):

1) lignitic coal, which is usually brown in color and is composed of consolidated, but easily recognizable, metamorphosed plant matter;
2) subbituminous coal, which is black and crumbly;
3) bituminous coal, which is dark brown to black in color and does not disintegrate on exposure as readily as subbituminous coals; and
4) anthracitic coal, which is hard and black with a semi-metallic luster.

Table 2.10 ASTM D-388 Coal Classification (19)

Class	Fixed Carbon * (%)	Calorific Value ** (Btu/lb)
Anthracitic	≥ 86	—
Bituminous	—	≥ 10,500 †
Subbituminous	—	≥ 8,300
Lignitic	—	‡

* dry, mineral-matter-free basis
** moist, mineral-matter-free basis

† agglomerating
‡ must be consolidated coal

Coal is composed mainly of carbon, hydrogen, and oxygen, with inorganic mineral constituents accounting for the remaining 3 to 30 percent (154, 427). The inorganic mineral matter in coal is incorporated by three mechanisms (154):

1) deposition of loose soil and rock fragments during early coal field formation,
2) crystallization of soluble minerals from water which permeated the coal seams, and
3) collection of impurities during coal mining operations.

The most common sedimentary minerals are aluminum, iron, and magnesium silicates derived from clays. The most common soluble minerals are kaolinite, calcite, pyrite, and gypsum (154).

2.4.2.2 Coal Combustion

A schematic diagram of a typical pulverized coal boiler is shown in Figure 2.17. Large bunkers feed coal to a pulverizer where the coal is crushed to approximately 70 percent finer than 75 μm (#200 sieve) (154). The fine coal powder is mixed with preheated air and is blown into a combustion zone where temperatures may exceed 1600 °C (156). Large fans force air in the combustion zone upwards through a pollution control device and out the exhaust stack. Various gases and a portion of the noncombustible ash residue travel with the draft (72, 154, 156).

The ash residue created during coal combustion consists of the inorganic coal constituents and any unburned carbon (427). The residue is collected at two locations, providing two forms of by-product (427):

1) bottom ash, which is collected from the bottom of the boiler unit and is comprised primarily of the coarse, heavy particles; and
2) fly ash, which is collected by air pollution control equipment and is comprised of particles that are light enough to be transported by the stack gases.

Generally, bottom ash and fly ash together make up 3 to 30 percent by weight of the coal (427). Most pulverized coal-firing methods yield by-product proportions of 65 to 85 percent fly ash and 15 to 35 percent bottom ash (154).

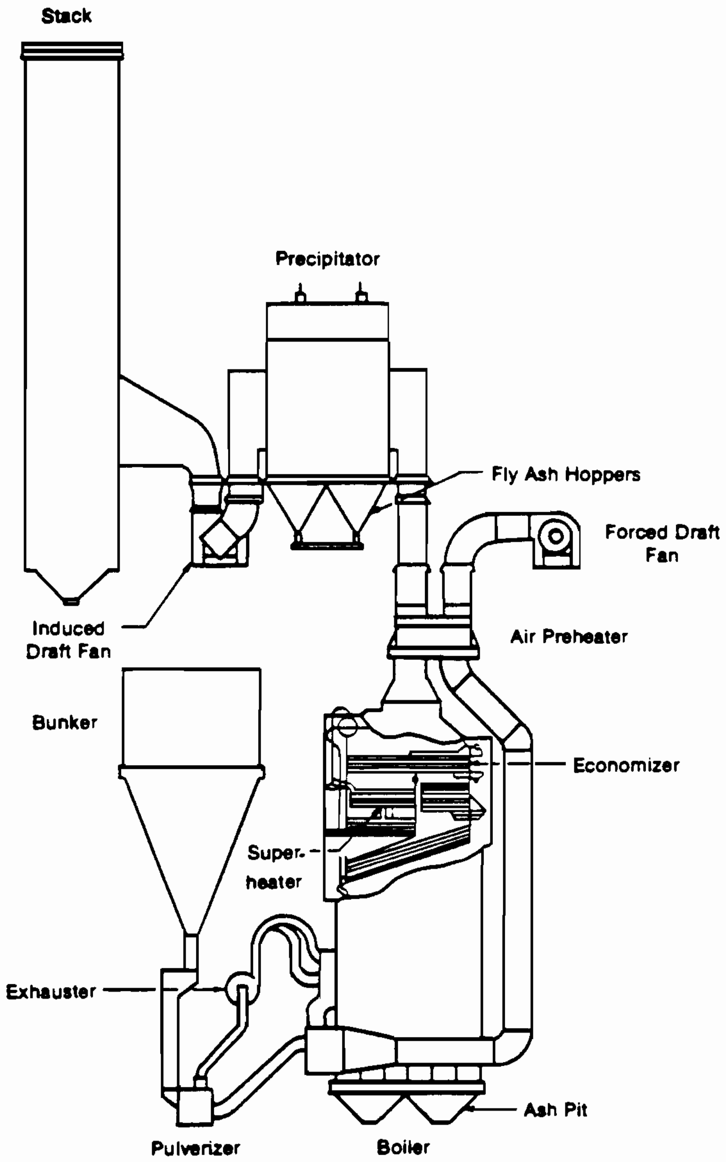


Figure 2.17 Pulverized Coal Boiler (22)

2.4.2.3 Fly Ash Collection

Four types of particulate control devices are available (109):

1) electrostatic precipitators (ESPs),
2) fabric filters,
3) wet scrubbers, and
4) mechanical collectors (cyclones).

Electrostatic precipitation is the most common method of controlling pollution; ESPs are used by over 95 percent of U.S. power plants (109). An ESP unit is equipped with electrodes and collecting plates carrying DC charges of opposite polarity, as shown in Figure 2.18. The electrodes impress a charge on particles in the flue gas, so the particles are attracted to the collecting plates. The plates are periodically shaken, causing the fly ash particles to fall into collection hoppers (72, 109).

In additon to removing more than 99 percent of fly ash particles from stack gases, ESPs offer the advantage of collecting the coarsest particles first and progressively finer particles thereafter (287). Fly ash is collected in several hoppers (typically 5 to 7) which yield different particle ranges. Fly ash from the separate hoppers may then be combined for use in any desired proportions (154).

Fabric filters are becoming increasingly popular for two reasons (109, 442):

1) their initial costs are less than those of ESP units and
2) they are more efficient than ESPs at removing particles smaller than 10 micrometers.

Fabric filters are installed in enclosures commonly referred to as bag houses, as shown in Figure 2.19. Flue gases travel through the fabric from inside to outside. Fly ash is trapped by the fabric and by the layer of previously collected ash. Efficiency of particle removal increases as the layer of previously collected ash increases in thickness. The bags are periodically cleaned by simultaneously reversing air flow and shaking the bags. Fly ash is collected in hoppers which are located beneath the fabric filters (109).

Wet scrubbers are no longer used as primary fly ash removal systems because scrubber sludge is difficult to handle and wet fly ash is difficult to market. However, wet scrubbers are effective for secondary particulate removal when preceded by an ESP unit (109).

Mechanical collectors (or cyclones) are obsolete. They are inefficient collection systems, particularly for very small particle sizes (< 1.5 μm) (304).

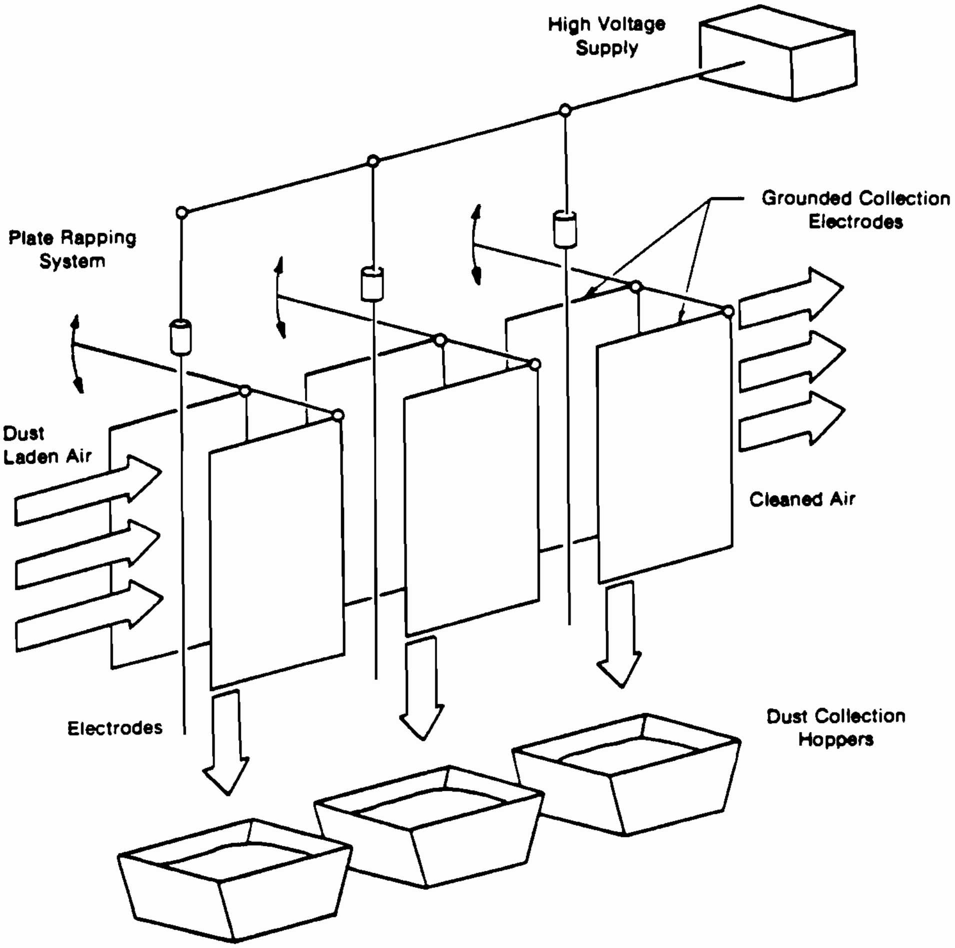


Figure 2.18 Electrostatic Precipitator (314)

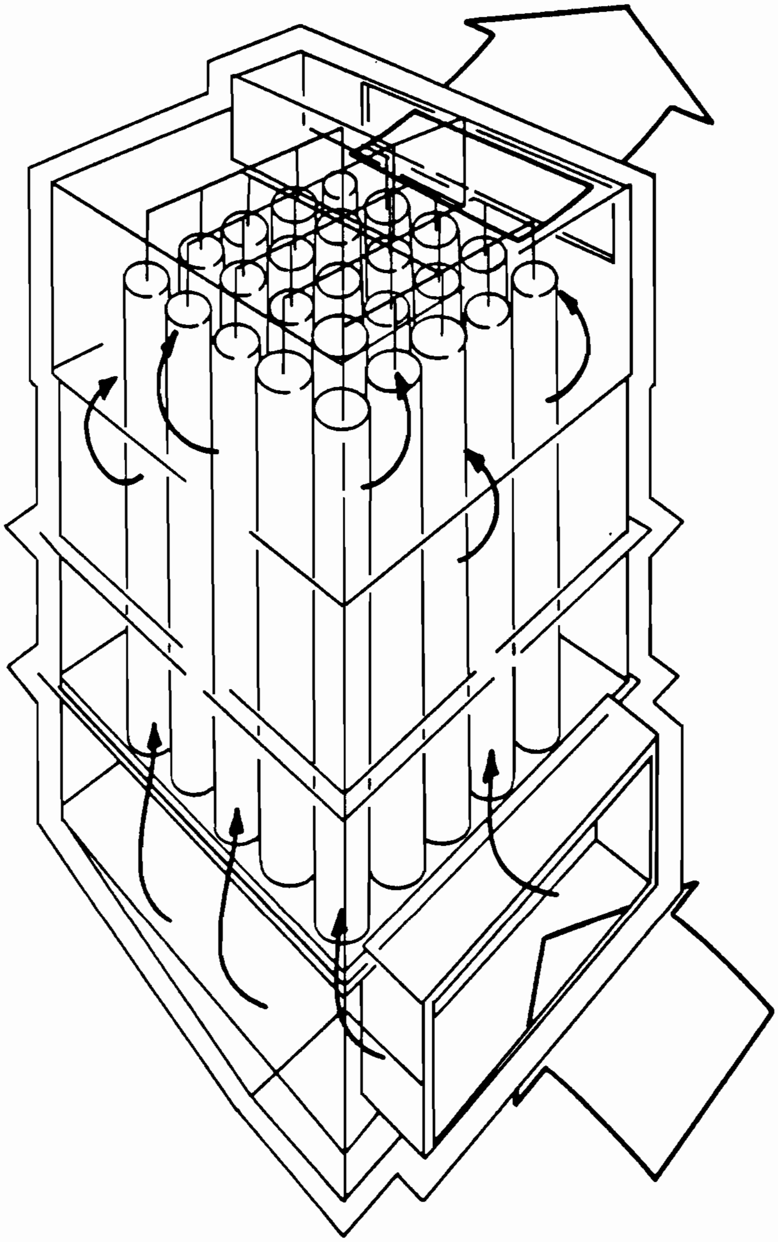
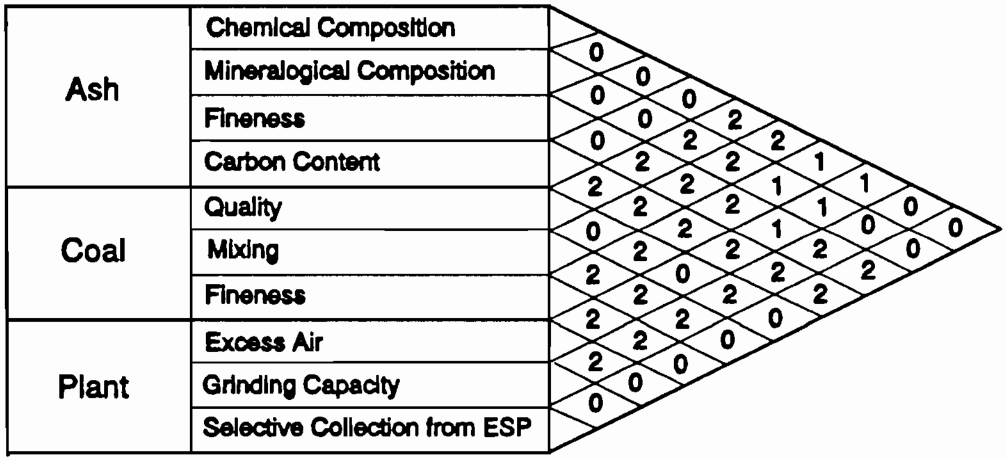


Figure 2.19 Gas Flow Through a Bag House Particle Collector (113)

2.4.2.4 Quality Control

Fly ash quality is affected by variables in coal composition and power plant operations (176). Coal varies in the compositions of inorganic constituents and in the proportions of volatile matter and ash. Power plant operations vary in conditions of grinding and combustion of coal and in the method of collecting fly ash. Variables in grinding conditions include mill capacity and control and adjustment of fineness. Variables in combustion conditions include load level, adjustment of excess air, procedures for periodic start-up, and source of energy for combustion (oil and/or gas).

Correlations between power plant operation conditions and measures of fly ash quality are shown in Figure 2.20 (176). The requirement of cooperation between the power plants and fly ash consumers is evident. For example, plants with multiple or nonuniform coal sources have to mix coals in order to produce fly ash with a homogeneity approaching that of a plant with a single uniform coal source (176).



0 : no correlation / no relevance
1 : uncertain correlation
2 : good correlation

Figure 2.20 Correlations Between Coal Characteristics, Power Plant Parameters, and Fly Ash Quality (176)

Pattern of boiler operation is also important for fly ash quality. Some power plants operate continuously, while others operate intermittently to serve peak power demands. Each start-up operation may require the use of oil to stabilize the boiler flame. Fly ash particles produced while oil and coal are burning simultaneously may be coated with hydrocarbons from the oil and may not be of sufficient quality for use in concrete. Intermittent operations, therefore, require careful control over fly ash collection (287).

Slight malfunctions in the sequence of coal combustion and fly ash collection can also affect the quality of fly ash. A malfunction in the electrostatic precipitators may allow fine particles to exit throught the stack. Decreases in the proportion of fine fly ash particles can cause reductions in pozzolanic activity. A malfunction in the coal pulverizers can result in higher proportions of coarse fly ash particles, including unburnt carbon. High proportions of these fly ash particles may cause concrete air-entraining difficulties and may increase concrete water demand (72).

In order to prevent users of fly ash from receiving shipments of inadequate quality, ASTM C-618 specifies chemical and physical requirements for fly ash. Also, ASTM C-311 specifies sampling methods, test methods, and test frequencies.

2.4.3 CHARACTERIZATION

2.4.3.1 Variability/ Heterogeneity

The manner in which fly ash is produced and collected results in a material with variable physical, chemical, and mineralogical properties. In this respect, fly ash is a unique mineral admixture; other mineral admixtures tend to be relatively homogeneous. Ground granulated blast furnace slag and natural pozzolans are products ground from quasi-homogeneous masses. Silica fume is collected in particulate form, but is generally found to be composed of particles that are morphologically and compositionally nearly identical (87). Fly ash exhibits heterogeneity at three levels:

1) between source power plants,
2) between particles from a single power plant, and
3) within single particles of fly ash.

Variabilities in morphology and composition of fly ash particles between sources are primarily the result of different coal sources and different coal combustion and fly ash collection configurations (365). Variabilities between fly ash particles from a single source are the result of the nature of coal combustion. Fly ash constitutes the residue of combustion of many small particles of coal. Each particle is heated and undergoes changes independently of neighboring particles. Therefore, the composition of each fly ash particle reflects that of the inorganic portion of the particular coal fragment from which it originated (87, 88). Inhomogeneities within single particles of fly ash can be partially attributed to their incomplete crystallinity. Fly ash particles consist of crystalline precipitates within otherwise glassy matrices. Even the glassy phases themselves exhibit inhomogeneities in the form of phase separations (156).

The intrinsic variability of fly ash, coupled with the complexity involved in its characterization, have hindered its use as a mineral admixture in concrete (365).

2.4.3.2 Morphology

All fly ash particles can be classified as "fine" since they must be small enough to be carried by flue gases. However, particle diameters (or widths) vary from several tenths of a micrometer to several hundred micrometers (365). The largest fly ash particles are often bulky agglomerates of smaller particles or rough fragments of unburnt coal. Small fly ash particles, however, are typically spherical. Warren and Dudas (444) have presented a model for the microstructure of a typical small-sized fly ash particle, as shown in Figure 2.21. The spherical shape of small particles results from the rapid cooling and solidification of molten droplets while they are suspended in air (365). The smaller spheres are typically solid while the larger spheres may be hollow and empty (cenospheres) or hollow with smaller spheres inside (plerospheres). Vesicles within spheres are formed when particles solidify around trapped gas bubbles (365).

Most crystalline material is incorporated within the glassy matrix. However, alkali-rich (less viscous) melt solidifies from vapor on and slightly under particle surfaces (255). The surface salts and very rapid cooling history of glass near particle surfaces make it the most reactive glass.

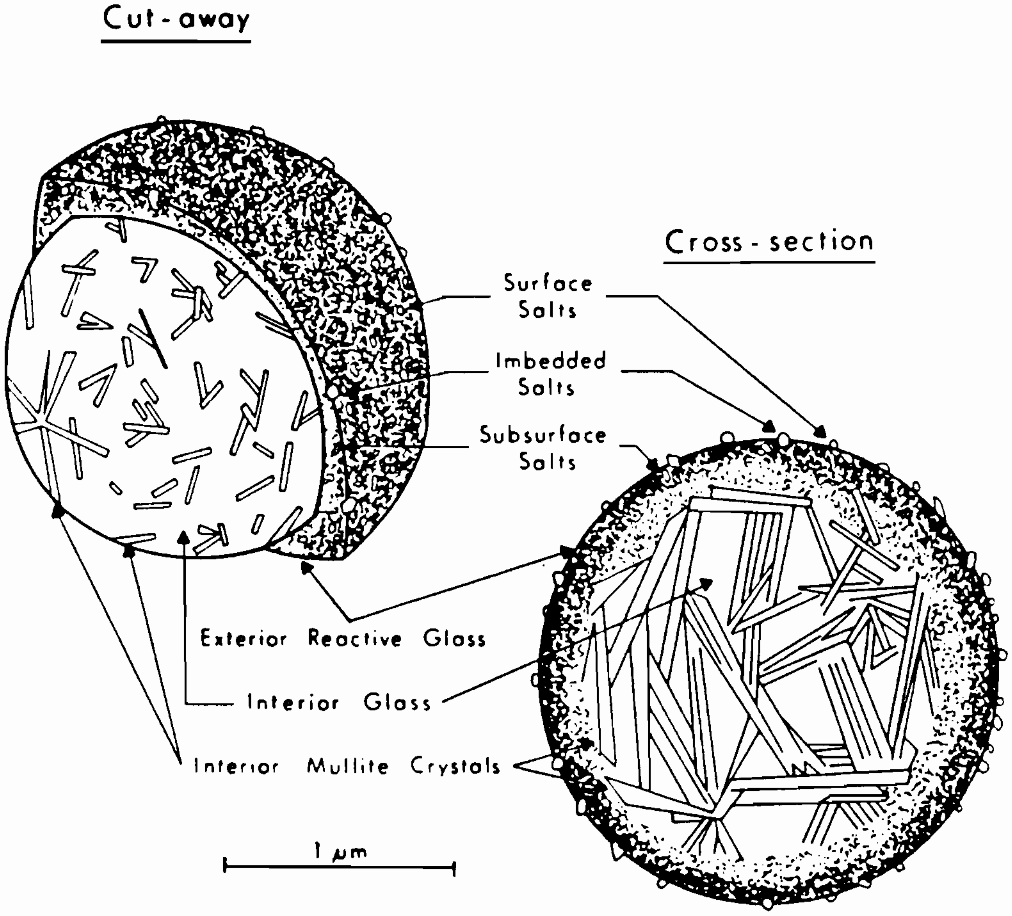


Figure 2.21 Structure of a Typical Fly Ash Particle (444)

2.4.3.3 Physical Properties

Specific gravities of fly ash particles vary considerably, ranging from approximately 1.6 to 2.8 (365). Minnick et al. (298) performed statistical regression analyses between fly ash specific gravities and fly ash bulk chemical compositions; iron oxide contents yielded the highest direct correlations with specific gravities. Fly ashes with low specific gravities have often been found to contain high carbon contents (365).

The range of typical particle size distributions for fly ashes is displayed in Figure 2.22 (30). These distributions are assumed to be measured by hydrometer (ASTM D-422) and are assumed to include both Class F and Class C fly ashes. The range of particle distributions which includes 60 percent of samples is a good approximation of a typical particle distribution for ordinary portland cement. Portland cement, however, typically has a lower proportion of particles larger than 45 μm.

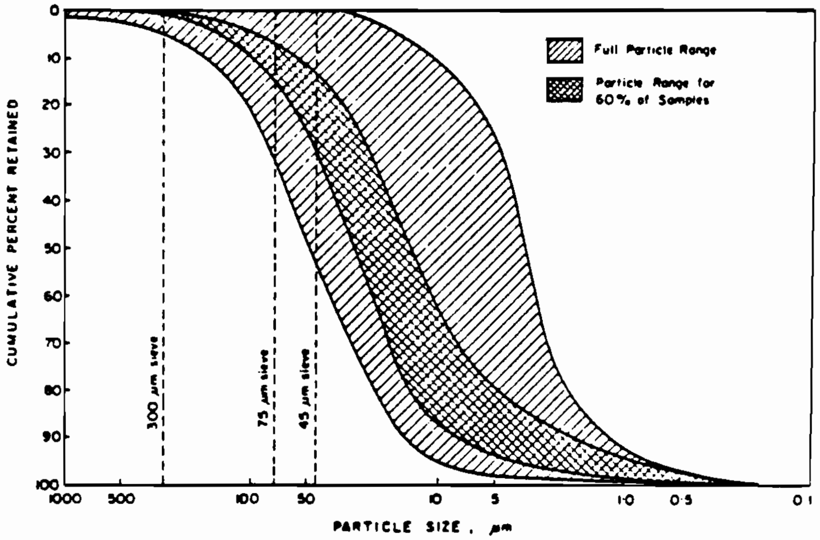


Figure 2.22 Particle Size Analyses of Fly Ash, Including Both High-Calcium and Low-Calcium Ash (30)

Two single-value measures of fly ash fineness have commonly been used: percent retained on the #325 sieve and specific surface area. Each method has limitations: percent retained on #325 sieve provides limited information and the reliability of specific surface area measurements is questionable. The reliability of specific surface area measurements has been questioned because of discrepancies between measuring techniques, including Blaine air permeability, nitrogen adsorption, and Wagner turbidimeter (154). Chopra and Narain (63) reported that the presence of fly ash particles larger than the #325 sieve and unburned carbon particles are primarily responsible for these discrepancies. Increased surface areas due to internal fissures and pores in particles affect adsorption measurements but do not significantly affect air permeability measurements.

2.4.3.4 Chemical Composition

Although several dozen minerals are present in coals, most occur only in trace amounts. The majority of coal minerals that influence fly ash composition may be classified into five groups (119, 133): aluminosilicates (clays), carbonates, sulphides, chlorides, and silica (quartz). With the exception of quartz, all other minerals are substantially decomposed during coal combustion. Chemical reactions at high temperatures result in the formation of new glassy and crystalline phases (156, 343). The bulk chemical composition of fly ash glassy and crystalline phases consists mainly (95 percent to 99 percent by weight) of oxides of silica, aluminum, iron, and calcium with smaller amounts (0.5 percent to 3.5 percent by weight) of magnesium, sulfur, sodium, and potassium (154, 427).

ASTM Standard C-618 specifies two classes of fly ash based on chemical composition. Class F fly ashes, which were at one time the only class, are required to have a minimum sum of three major oxides ($SiO_2+Al_2O_3+Fe_2O_3$) of 70 percent by weight. This requirement was designed to ensure adequate pozzolanic reactivity. Class F fly ashes are typically derived from burning anthracitic and bituminous coals.

Fly ashes derived from burning lignitic and subbituminous coals were found to enhance concrete quality even though their silica, aluminum, and ferric oxide contents were relatively low. Therefore, an additional fly ash class was added, Class C. Class C fly ashes are required to have a sum of three major oxides ($SiO_2+Al_2O_3+Fe_2O_3$) of 50 to 70 percent by weight.

Since Class C fly ashes have relatively low proportions of silica, aluminum, and ferric oxides, they have relatively high proportions of the fourth major oxide, calcium. Class C fly ashes are often referred to as high-calcium ashes while Class F fly ashes are often referred to as low-calcium ashes.

A compilation of reported chemical compositions of Class F and Class C ashes is shown in Table 2.11 (365). In addition to high calcium contents relative to Class F fly ashes, Class C fly ashes typically have higher magnesium oxide, sulfur trioxide, and alkali contents

(259). Differences in the bulk chemical compositions of fly ashes are reflections of the different glassy and crystalline compound compositions. The composition of glass and the types and proportions of crystalline compounds influence fly ash reactivity.

Table 2.11 Range of Bulk Chemical Compositions of Fly Ash (365)

Oxide	Range of Chemical Compositions (wt.%)	
	Class F Fly Ash	Class C Fly Ash
SiO_2	38 - 65	33 - 61
Al_2O_3	11 - 33	8.0 - 26
Fe_2O_3	3.0 - 31	4.0 - 10
CaO	0.6 - 13	14 - 37
MgO	0.0 - 5.0	1.0 - 7.0
Na_2O	0.0 - 3.1	0.4 - 6.4
K_2O	0.7 - 5.6	0.3 - 2.0
SO_3	0.0 - 4.0	0.5 - 7.3
LOI *	0.1 - 12	0.2 - 1.4

* loss on ignition

2.4.3.5 Mineralogy

Quantifying the crystalline compositions of fly ashes is difficult for three primary reasons:

1) crystalline phases are typically not pure,
2) crystalline particles are non-discrete, and
3) the background components of X-ray diffractograms interfere with analyses.

Many of the crystalline phases in fly ash contain substantial amounts of impurities and some phases are members of complete solid solutions (254). Individual crystalline particles are not ordinarily present in fly ashes; crystalline material is either embedded within glass or is deposited as a film on the surface of particles (44, 85, 142, 143, 163, 259, 339). The total Bragg scattering of crystalline phases is reduced by a broad background feature on the baseline of diffractograms. The background feature is caused by the glassy component of fly ash, which typically accounts for over 50 percent of fly ash composition (254).

The mineralogy of low-calcium fly ashes consists primarily of four crystalline phases: quartz, mullite, hematite, and magnetite (or ferrite spinel) (254). These crystalline phases are relatively inert during cement hydration and during glassy ash/water reactions (154, 259).

The mineralogy of high-calcium fly ash is more complex. In addition to the previously mentioned crystalline phases, the higher calcium concentrations during coal combustion induce the formation of lime, C_3A, merwinite, melilite, and C_2S. If both calcium and sulfur are present in high concentrations, anhydrite and sodalite structures are also formed (254). The chemical compositions and X-ray diffractogram reference peaks of the common crystalline phases formed in fly ashes are presented in Table 2.12 (254).

Quartz is found in all fly ashes and usually accounts for the most intense XRD reflection. It originates as quartz in coal and survives combustion without melting (254).

Mullite is found in most fly ashes. It is not a naturally-occurring mineral in coal, but it forms during the decomposition of alumino-silicates, particularly clays (155, 254). Mullite is often difficult to identify because its strongest XRD reflections are close to those of quartz (259).

Hematite and a spinel structure result principally from the oxidation of pyrite in coal. Hematite is present in all fly ashes, but is difficult to detect because its XRD peak overlaps with merwinite and C_3A. Most fly ashes contain a spinel structure oxide with an X-ray pattern similar to magnetite (Fe_3O_4) and magnesioferrite ($MgFe_2O_4$). This solid solution phase contains partial Mg and Al substitutions for Fe. Treatment of a fly ash sample with a hand magnet provides a sub-sample rich in hematite and ferrite spinel (254).

Crystalline CaO (lime) is found in virtually all high-calcium lignite and subbituminous fly ashes, typically accounting for 2 percent to 5 percent of overall analytical CaO (365). Lime results from the decomposition of calcite and/or gypsum (254). Dissolved CaO is capable of reacting with the glass phase in a relatively slow "self-pozzolanic" reaction (259, 365). When crystalline CaO is not reactive upon first contact with water (highly sintered large grains), it can remain to cause unsoundness problems due to its transformation to portlandite (259, 371).

Table 2.12 Fly Ash Crystalline Phases (254)

Short-hand	Name	Nominal Composition	XRD 2Θ °(CuKα)
Ah	Anhydrite	$CaSO_4$	25.4
As	Alkali Sulfates	$(N,K)_2SO_4$	32.2
C_3A	Tricalcium Aluminate	$Ca_3Al_2O_6$	33.2
C_2S	Dicalcium Silicate	Ca_2SiO_4	**
Hm	Hematite	Fe_2O_3	33.2
Lm	Lime	CaO	37.5
Ml	Melilite	$(Ca,Na)_2(Mg,Al,Fe)(Si,Al)_2O_7$	31.3
Mu	Mullite	$Al_6Si_2O_{13}$	26.2
Mw	Merwinite	$Ca_3Mg(SiO_4)_2$	33.3
Pc	Periclase	MgO	42.9
Pl	Portlandite	$Ca(OH)_2$	34.1
Qz	Quartz	SiO_2	26.7
So	Sodalite Structure	$Ca_2(Ca,Na)_6(Al,Si)_{12}O_{24}(SO_4)_{1-2}$	23.7
Sp	Ferrite Spinel*	$(Mg,Fe)(Fe,Al)_2O_4$	35.6

* Including magnetite
** C_2S exhibits may X-ray diffraction patterns

The relative proportions of tricalcium aluminate and merwinite are difficult to determine in x-ray diffractograms because their reference peaks overlap. However, the proportion of merwinite, a Ca-Mg silicate, is known to increase with increasing fly ash MgO contents (254). For purposes of quantitative XRD analysis, the intensity of the composite peak is typically attributed equally to C_3A and merwinite (256).

Tricalcium aluminate is often present in substantial amounts in high calcium fly ashes. This compound can react rapidly with anhydrite to generate ettringite (259). Self-cementing high calcium fly ashes are known to contain ettringite rods which link and bind adjacent particles (365). Contrarily, merwinite is not reactive at normal temperatures and pressures. Experiments of fly ash with water and gypsum showed C_3A to be very reactive and merwinite to be nonreactive through several weeks of setting (259).

Melilite is a mineral group term encompassing akermanite ($Ca_2MgSi_2O_7$), gehlenite ($Ca_2Al_2SiO_7$), and sodium-melilite ($NaCaAlSi_2O_7$). Iron commonly substitutes for portions of Mg or Al. Formation of melilite and merwinite requires substantial MgO and CaO contents in fly ash (254). Melilite solid solutions (Ca, Mg, Al pyrosilicates) are not ordinarily very reactive (365).

Dicalcium silicate and even tricalcium silicate are occasionally detected in high calcium fly ashes, but only in amounts of less than one percent by weight. Their eventual hydration may contribute slightly to the formation of cementitious products (259, 365).

Periclase, crystalline MgO, is found in most subbituminous and lignite coals. It originates from dolomite or from the oxidation of organic magnesium (254). The total analytical MgO content of fly ashes is limited to 5 percent or less in specification ASTM C-618. This requirement is based on experience with portland cement in which the formation of $Mg(OH)_2$ has resulted in unsoundness. However, MgO in fly ashes is often present as periclase, merwinite, and in glass. Fly ashes with high MgO contents routinely show no expansions during autoclave tests (365).

Anhydrite is found in fly ashes with high calcium and high sulfur trioxide contents. Calcium oxide acts as a "scrubber" for SO_2 during coal combustion and in the exhaust stack. As a "scrubber", CaO combines with SO_2 and with excess O_2 to form anhydrite ($CaSO_4$).

Sodalite is a calcium-bearing sodium aluminosilicate mineral found in high-calcium, high-sulfate fly ashes. Its name is used for a group of isostructural phases, including hauyne ($Ca_2(NaAlSiO_4)_6(SO_4)_2$) and calcium aluminosulfate ($Ca_4Al_6O_{12}SO_4$). The composition of this phase in fly ash is typically closer to $C_4A_3\bar{S}$ than to hauyne (254).

Many fly ashes contain alkali sulfates as surface deposits. These crystalline species include potassium sulfate (α-K_2SO_4), sodium sulfate (thenardite), and mixed sulfates. The mixed sulfates include aphthitalite ($(Na,K)_2SO_4$) and potassium-calcium sulfates (365).

McCarthy et al. (245, 259) have studied numerous fly ashes from North Dakota, Wyoming, and Montana subbituminous and lignitic coals sources. Based on their data and data from literature on bituminous coal ashes, they reported trends of fly ash chemical and mineralogical compositions, as shown in Table 2.13 (245).

Table 2.13 Trends of Fly Ash Characteristics Based on Source Coal Type (245)

Component	Low Calcium	High Calcium	
	Bituminous	Lignite	Subbituminous
Al_2O_3	23 - 35%	< 16%	16 - 25%
MgO	< 2%	> 4%	2 - 4%
Na_2O - K_2O	$K_2O > Na_2O$	$Na_2O > K_2O$	$Na_2O > K_2O$
Lime	Very Rare	Common	Common
C_3A	No	Common	Common
Periclase	No	Yes	Yes
Anhydrite	Very Rare	Yes	Yes
Alkali Sulfates	No	Common	No

2.4.3.6 Glass

Fly ash particles are produced by melting and subsequent quenching of the inorganic material present in coal. The cooling rate of fly ash leaving the combustion zone, as it is transported by stack gases, has been reported to be as quick as 1500 °C to 200 °C in 4 seconds (154). This results in glass as the predominant phase, constituting 50 to 90 percent of fly ash particles (427).

Fly ash contains modified siliceous glasses. Fly ash with total calcium oxide contents of 20 percent by weight or less contain mainly aluminosilicate glass. Fly ash which contains total calcium oxide contents greater than approximately 20 percent by weight may also contain calcium aluminosilicate glass (156).

A useful model for describing complex glass systems such as those found in fly ash was pioneered by Zachariason in the 1930s (452). The glass network theory proposes structural disorder in terms of three influencing factors: rapid quenching, network isomorphic substitution, and cation modification.

In ordered crystalline silica, silica tetrahedra form a three-dimensional network by sharing oxygen atoms at their corners (452), as shown in the two-dimensional schematic representation, Figure 2.23(a). Quenching results in a loss of long-range order. However, short-range order in the form of Si^{4+} and O^{2-} relationships remains intact, as shown in Figure 2.23(b).

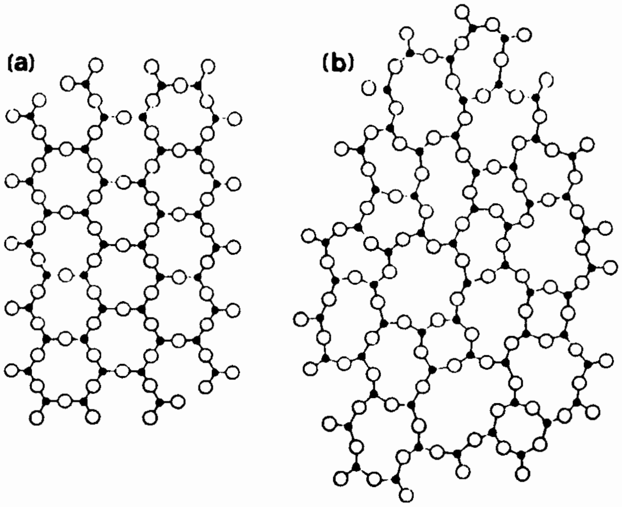


Figure 2.23 Schematic Representation in Two Dimensions of the Structure of (a) Crystalline Silica and (b) Glassy Silica (452)

Short-range order is disrupted by isomorphic substitution and cation modification. Ions Al^{3+}, Fe^{3+}, and other cations of similar size and valence may substitute for silicon within the tetrahedra, while Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, and other relatively small cations may be incorporated in the holes between tetrahedra. These two groups of cations are termed substitutes and modifiers, respectively (350).

Network isomorphic substitution introduces two forms of disorder to the already distorted glass network (156):

1) a chemical disorder through the random substitution of network-forming atoms and
2) subsequent depolymerization of the three-dimensional structure.

Depolymerization is the result of tetravalent silicon ions being replaced by lower valence elements such as trivalent aluminum ions. The continuous polymeric network is disrupted and the excess negative charge supplied by the oxygen must be neutralized by the inclusion of an additional cation, (such as Na^{+}), as shown in Figure 2.24 (156).

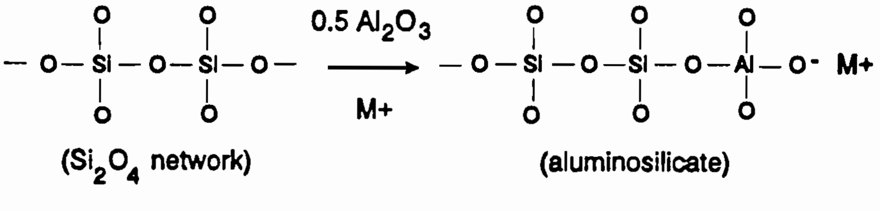

$$-O-\underset{O}{\overset{O}{Si}}-O-\underset{O}{\overset{O}{Si}}-O- \xrightarrow[M+]{0.5\,Al_2O_3} -O-\underset{O}{\overset{O}{Si}}-O-\underset{O}{\overset{O}{Si}}-O-\underset{O}{\overset{O}{Al}}-O^{-}\ M+$$

Figure 2.24 Network Isomorphic Substitution (156)

In addition to supplying neutralizing cations for Si substitution, modifiers may also depolymerize a pure vitreous silica network on their own. Incorporation of modifying cations induces breakage of Si-O-Si bonds to preserve electroneutrality, as shown in Figure 2.25, the two-dimensional schematic representation of a sodium silicate glass (156). Higher concentrations of network modifiers result in increased depolymerization; as Na_2O (or K_2O, CaO, MgO, etc.) is added, the glass network is composed of increasingly smaller silicate or aluminosilicate polymeric units, with an increasing number of non-bridging oxygens (156).

Comparisons of typical proportions of network formers and modifiers for mineral admixtures and commercial glasses are presented in Table 2.14. Fly ashes have compositions which are ranked between the highly disordered blast furnace slags and the scarcely modified silica fumes.

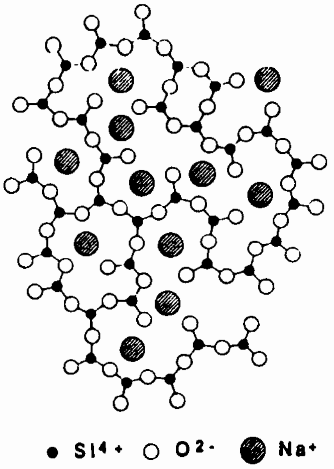


Figure 2.25 Schematic Representation in Two Dimensions of the Structure of a Binary (e.g. sodium) Silicate Glass (452)

Fly ash glass compositions are an approximate reflection of fly ash bulk chemical compositions. Class F fly ashes have relatively high Si and Al contents and relatively low Ca and alkali contents. Therefore, they are composed of alumino-siliceous glasses with relatively low modifier contents. These high-silica glass phases originate from the thermal dissociation and fusion of lime-deficient clay particles (155).

Lignite ashes typically contain higher modifier contents than bituminous or subbituminous ashes. As fly ash modifier content increases, the modifiers are incorporated into the alumino-siliceous glass network. High calcium contents result in the formation of calcium aluminosiilcate glass. These glass phases may be formed by reactions between clay minerals and closely associated limestone, or by the thermal dissociation and fusion of calcareous shale particles (155).

The X-ray diffraction response to the glass phases present in fly ashes is a broad elevation through a range of diffraction angles. The highest point of this background is often termed the "broad diffuse maximum" or the "halo". The position of the diffuse maximum reflects the position of the main peak of the crystalline compound that the glass would have formed had it devitrified (88). For example, pure silica glass shows a halo close to the position of cristobalite (22° 2Θ to 23° 2Θ, Cu radiation), which is the high-temperature crystalline form of SiO_2 (88).

Table 2.14 Typical Compositions of the Glassy Components of Some Mineral Admixtures and Commerial Glasses (439)

Material	Network Formers * (%)	Network Modifiers ** (%)
Silica Fume	> 90	< 10
Bituminous Fly Ash	84 - 90	10 - 16
Subbituminous Fly Ash	81 - 84	16 - 19
Lignite Fly Ash	72	28
Blast Furnace Slag	47	52
Pyrex Glass	96	4
Container Glass	76	24
Window Glass	74	26

* $SiO_2 + Al_2O_3 + Fe_2O_3$
** $Na_2O + K_2O + CaO + MgO$

The position of the diffuse maximum shifts as the fly ash glass is modified. Diamond (88) found an approximately linear relationship between diffuse maximum and analytical calcium oxide percentage of fly ash (Figure 2.26). At calcium contents approaching zero, the halo position was at approximately 23° 2Θ (Cu radiation). This is also the Bragg angle where pure silica glass shows its maximum. As analytical calcium oxide percentage increased to approximately 20 percent by weight, the halo position increased to approximately 27° 2Θ; increasing Bragg angles correspond to decreasing interplanar spacings. For analytical calcium oxide contents greater than 20 percent by weight, the halo positions jumped abruptly to a 2Θ of approximately 32 degrees. This abrupt change indicated a transition from modified alumino-silicate glasses to calcium aluminate glasses.

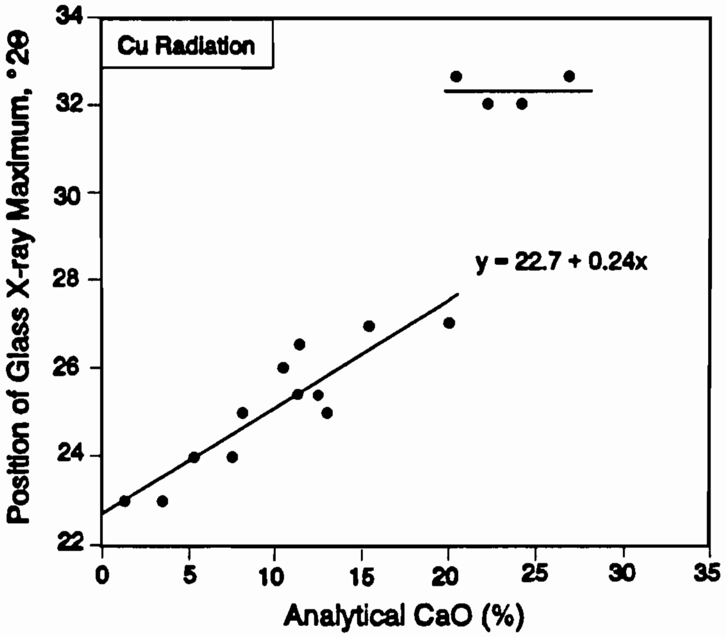


Figure 2.26 Glass X-Ray Maxima Versus Analytical CaO Contents of Fly Ash (88)

Rawson (349) supported the theory of the transition of glass types in fly ashes as calcium contents increase. He prepared $C_{12}A_7$ by mixing proper proportions of $Ca(OH)_2$ and $Al(OH)_3$. He then heated the mixture to 1450 °C and quenched it to retain a glassy structure. X-ray diffraction of the material then resulted in a glass halo at approximately 31.5° 2Θ (Cu radiation), which is the approximate position produced by very high calcium fly ashes.

McCarthy et al. (255) explored these effects further by measuring the positions of diffuse maximums for 80 fly ash samples. The resulting trend of diffuse maximum versus analytical CaO is shown in Figure 2.27. The curve drawn through the data points is a third order regression with a correlation coefficient of 0.81 (255).

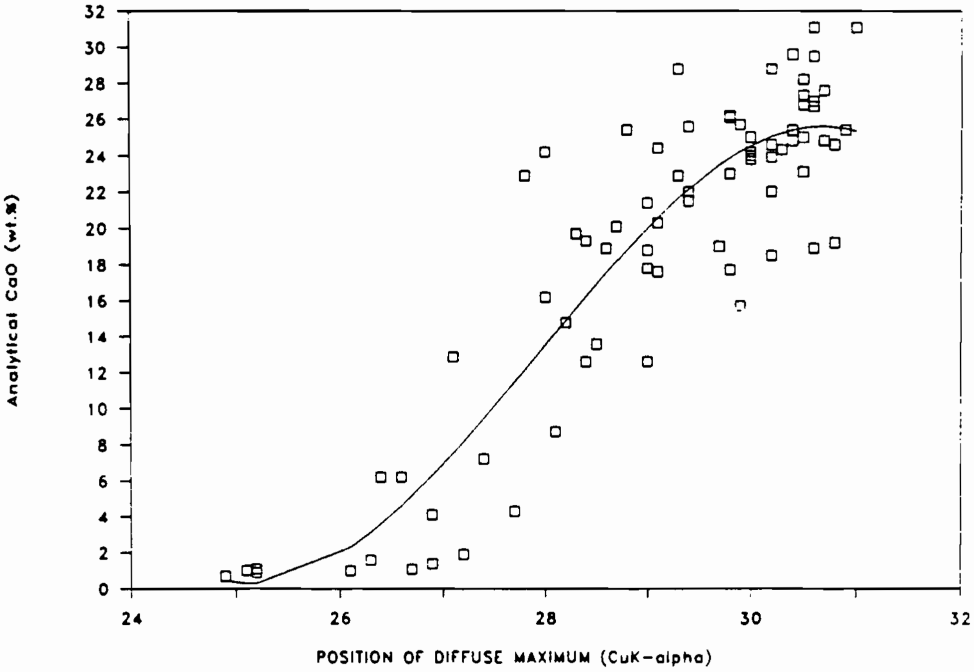


Figure 2.27 Glass X-Ray Maxima Versus Analytical CaO Contents of Fly Ash (255)

Although there is a general trend in changing glass compositions with increasing CaO contents, the relationship should not be viewed as strict. Diffuse maximum versus total CaO content plots include the following sources of error (156):

1) the XRD halo represents glass composition, while bulk analytical CaO contents include both CaO in glass and CaO in crystalline compounds and
2) other modifiers such as magnesium, sodium, and potassium, which may be present in the glass, are neglected.

Diamond provided an example of the first source of error by analyzing two fly ashes with similar bulk CaO contents (89). These fly ashes had bulk CaO contents of 25.8 percent and 28.7 percent by weight and halo positions of 32° and 27° 2Θ, respectively. The difference in halo positions was related to fly ash mineralogy. The fly ash with the aluminosilicate glass had a significant portion of its CaO content present as crystalline CaO and as crystalline anhydrite. The fly ash with the calcium aluminosilicate glass had only a few percent of its calcium content tied up in calcium-bearing crystalline components.

Therefore, nearly all of the CaO was available for glass formation. Cement pastes were mixed with partial replacement by each fly ash type. The paste which contained the fly ash with the reactive calcium aluminate glass was found to set more quickly and to gain a compressive strength of 3500 psi at 28 days. The paste which contained the fly ash with the high crystalline CaO content was slow-setting and exhibited unsoundness (89).

An example of the second source of error was provided by van Roode and Hemmings (439), who studied the effects of alkalies on glass structures. Sodium silicate model glasses were examined with sodium contents ranging from 0 to 50 percent Na_2O by weight. The glass structures became progressively depolymerized as measured by ratios of non-bridging oxygen atoms to silicon atoms (NBO/Si ratios). Non-bridging oxygen atoms were defined as oxygen atoms which were no longer shared by more than one silica tetrahedra. As sodium contents increased, the NBO/Si ratios increased from approximately 0 to 2 and halo positions in XRD patterns shifted to higher $2\Theta_{max}$ angles, as shown in Figure 2.28 (156).

2.4.4 HYDRATION AND POZZOLANIC REACTIONS

2.4.4.1 Reaction Mechanisms

The products of pozzolanic reactions consist of CSH-gel-like structures (84, 432, 437). The formation of CSH-gel is only possible when the fly ash has dissolved into solution. The dissolution of the glassy portion of fly ash is strongly dependent on the alkalinity of the pore water; glass structures break down substantially beyond a pH of approximately 13 (121).

During the first few days, the pH of pore water remains relatively low (<13) and the fly ash particles hardly dissolve. As cement hydration continues, the amount of pore water decreases and the concentrations of Ca^{2+}, Na^+, K^+, and OH^- increase. After approximately one week, the pH increases beyond 13 (123).

In a high pH solution, such as that produced in the presence of calcium hydroxide, the SiOH groups on the surfaces of fly ash particles are dissociated to SiO^- and H^+. The SiO^- ions cause surface grains to be negatively charged, which attracts calcium ions (Ca^{2+}) from solution. As calcium ions are adsorbed, a thin amorphous Si- and Al-rich layer developes on the surfaces of particles. The amorphous layer releases SiO_4^{4-} and AlO_2^- ions into solution where they combine with Ca^{2+} ions to form solid hydrates (412).

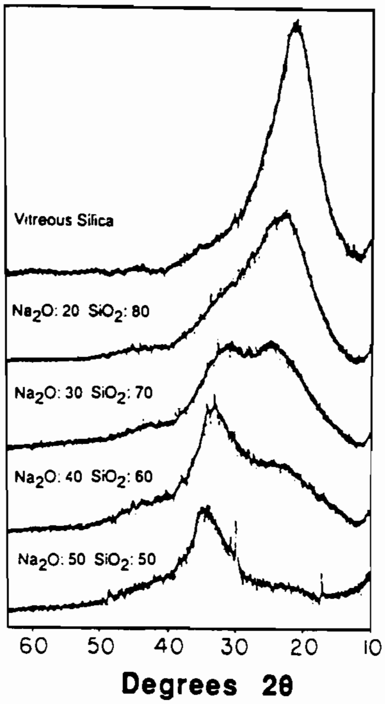


Figure 2.28 X-Ray Diffraction Patterns for Na_2O-SiO_2 Model Glasses (439)

Alumina diffuses more rapidly than silica and generally requires a higher calcium ion concentration for the formation of hydrates. Therefore, the calcium silicate hydrates tend to form next to glassy surfaces, while the aluminate hydrates tend to form at some distance (412). The C-S-H structures which precipitate near the surfaces of fly ash particles can slow down further dissolution of the glass network. As pore water pH increases with age, however, the Ca^{2+} concentration decreases and precipitation of the CSH occurs farther away from the fly ash particles (121). Urhan (437) reported that Na^+ and K^+ ions neutralize the negative charge of the dissolved silica, enabling their movement in pore water.

2.4.4.2 Reaction Products

For pure materials, the reaction between silica and calcium hydroxide to produce calcium silicate hydrates can be represented as (201, 238, 248, 375, 430):

$$xCH + yS + zH \rightarrow C_xS_yH_{x+z}$$

Studies of many lime-pozzolan systems have indicated the C-S-H to be a poorly crystalline form with a relatively low CaO/SiO_2 molar ratio of approximately 0.8 to 1.5 (154).

Pozzolan reactions involving impure fly ash are not as simple. The calcium silicate hydrate gels may incorporate additional anions and cations. The alumina supplied by fly ashes may also yield a variety of hydrates: calcium aluminate hydrates (C_4AH_{19}), gehlenite hydrates (C_2ASH_8), ettringite ($C_3A \cdot 3C\bar{S} \cdot H_{32}$), and calcium monosulfoaluminate hydrate ($C_3A \cdot C\bar{S} \cdot H_{12}$).

As an example of the more complex reactions of fly ash with calcium hydroxide, both C-S-H and gehlenite hydrate may be formed (171):

$$AS_2 + 3CH + zH \rightarrow CSH_{z-5} + C_2ASH_8$$

Sersale and Orsini (376) reported that the main compounds formed in lime-pozzolan pastes are C-S-H and C_2ASH_8 as long as the alumina and silica contents in pozzolan glasses are high while the calcium content is relatively low. If the calcium content in pozzolan glass is high, C-S-H and solid solutions of C_3AS_3-C_3AH_6 (garnet-hydrogarnet) are likely to form. In the presence of gypsum, these reaction products may be replaced or accompanied by ettringite and monosulfate hydrate.

Marsh and Day (246) have reported distinct differences in the manner in which low- and high-calcium fly ashes hydrate. They performed thermogravimetric and compressive strength tests on hardened fly ash cement pastes in which the cement was partially replaced by each fly ash at levels of 30 percent and 50 percent by weight. Specimens were cast at a constant water/solids ratio of 0.47. Calcium hydroxide contents were determined by thermal analyses; weight loss near 450 °C was attributed to dehydration of CH (290). The variations of calcium hydroxide contents with age for plain cement pastes and for cement pastes containing fly ash are shown in Figure 2.29. Calcium hydroxide content is stated as a weight percent of anhydrous cement (or fly ash cement). Neither fly ash at 30 percent or 50 percent replacement had a significant effect on calcium hydroxide content up to one month. However, at later ages, both fly ashes showed significant reaction as indicated by the depletions in CH contents. Depletions did not appear to depend on fly ash type but were larger for the mixtures containing larger proportions of fly ash (246).

Despite the similarities between fly ash types in rates of calcium hydroxide consumption, mortars consisting of 50 percent replacement of the same cement with the same two fly ashes revealed very different strength gaining characteristics. The mortar which contained the high-calcium fly ash gained strength more rapidly at early ages when compared to the mortar containing the low-calcium fly ash.

Marsh and Day (246) also reported non-evaporable water contents of the paste mixtures at various ages; non-evaporable water is a measure of chemically combined water. A portion of the non-evaporable water, termed "H-water", was defined as a measure of the amount of hydrates due to both the reactions of cement and the reaction of fly ash, excluding crystalline calcium hydroxide. "H-water" was calculated from thermal analyses data as the total weight loss between 105 °C and 850 °C minus the water lost from the dehydration of calcium hydroxide (at approximately 450 °C). At both replacement levels, the high-calcium fly ash showed higher "H-water" contents at all ages when compared to the low-calcium fly ash. Results for 50 percent fly ash replacement for cement are shown in Figure 2.30.

The researchers concluded that the high-calcium fly ash participated in both cementitious activity with water and pozzolanic reactivity with calcium hydroxide while the low-calcium fly ash participated only in pozzolanic reactions (246).

2.4.5 EFFECTS ON FRESH AND EARLY-AGE CONCRETE

There seems to be a general aggreement in literature that low-calcium fly ashes retard cement setting characteristics (154). Experiments conducted at The Canada Centre for Mineral and Energy Technology (CANMET) included mixtures which contained eleven Class F fly ashes with total CaO contents ranging from 1.4 to 13.0 percent and a cement

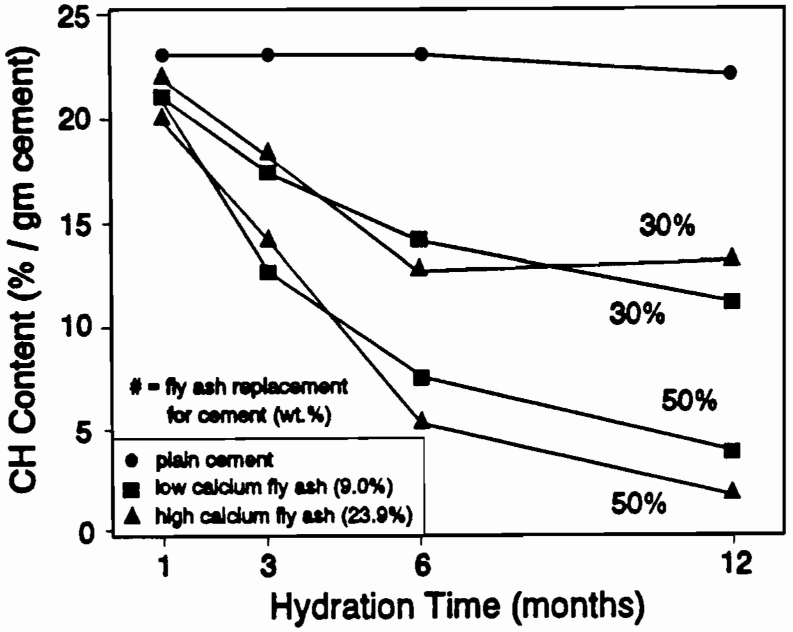


Figure 2.29 Effect of Fly Ash on the Calcium Hydroxide Content of Hydrating Cement Pastes (246)

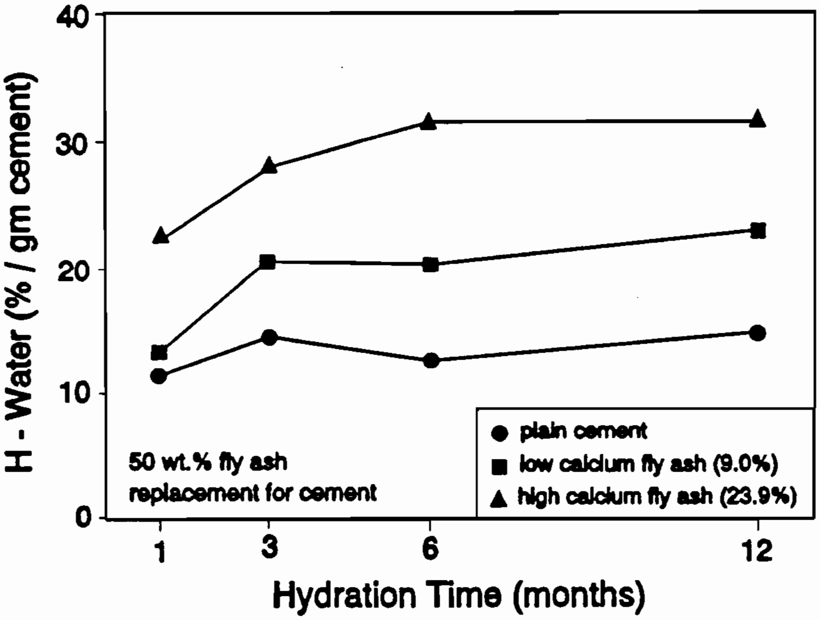


Figure 2.30 Effect of Fly Ash on the H-Water Content of Hydrating Cement Pastes (246)

replacement of 20 percent by mass. The researchers found significant increases in both initial and final set times (59).

The effects of Class C fly ashes on setting times appears to be more variable. Ramakrishnan et al. (345) reported on a fly ash containing 20.1 percent CaO which increased initial and final set times for fly ash concretes containing both Type I and Type III cements. However, Dodson (92) reported on a fly ash containing 25.5 percent CaO which reduced setting times when used as a partial cement replacement in concrete.

Wei et al. (115) reported that high-calcium fly ashes tend to retard C-S-H formation to a greater extent than low-calcium fly ashes, but that early stiffness and strength are obtained through the formation of calcium aluminates. They proposed that during early hydration reactions, fly ash is a source of soluble alumina as well as a nucleation site for ettringite. The formation of ettringite depresses the concentration of calcium and sulfate ions in solution, which decreases the rate of precipitation of $Ca(OH)_2$ and thus, prolongs the induction period of C-S-H hydration. Relative to low-calcium fly ashes, high-calcium fly ashes were more efficient retarders of CH precipitation due to their higher solubilities and reactivities.

Hydration of cement is accompanied by evolution of heat, which causes a temperature rise in concrete. Replacement of cement with fly ash results in a reduction in this temperature rise. Maximum temperature rise is of particular importance in mass concrete where thermal gradients and cooling after a large temperature rise can lead to cracking (33).

Grutzeck et al. (138) monitored rates of heat evolution of hydrating cement and fly ash/cement samples in an isothermal calorimeter. A Type I cement was partially replaced by both a Class F and a Class C fly ash at a level of 40 percent by weight. Two gram samples were mixed with 0.8 ml of deionized water. Rates of heat evolution throughout the first 24 hours of hydration, excluding first peaks for clarity, are shown in Figure 2.31. Both fly ashes extended the time to reach the second exothermic peak and decreased the rates of heat evolution at the second peaks. Therefore, both fly ashes prolonged the induction period of hydration. The high-calcium fly ash is shown to prolong the induction period to a greater extent than the low-calcium fly ash, which agrees with the observations of Wei et al. (115).

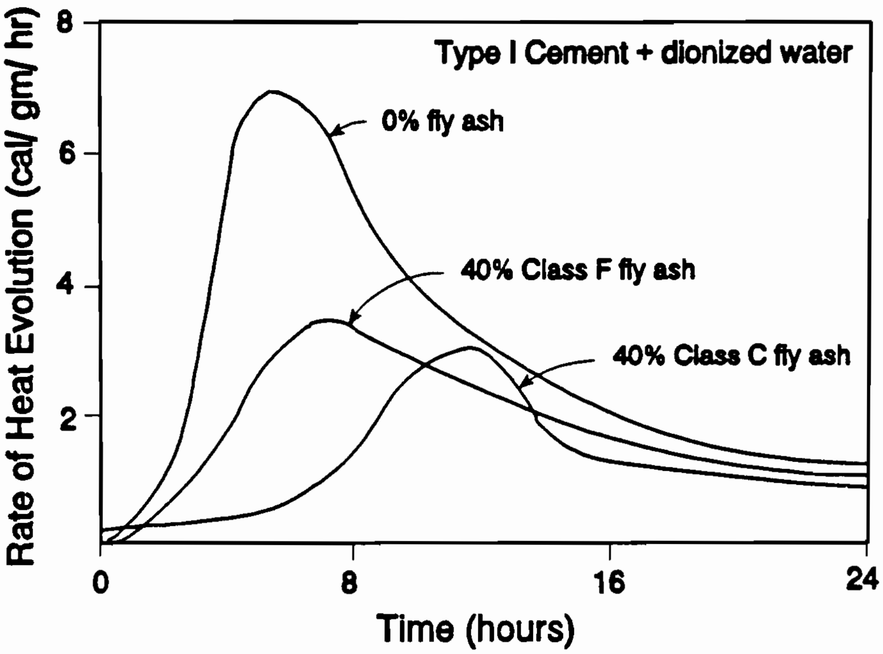


Figure 2.31 Rate of Heat Evolution for Plain Cement and Fly Ash Cement (138)

Low-calcium and high-calcium fly ashes generally reduce the amount of water required to achieve a degree of workability equivalent to that of a paste without fly ash (33, 126). The small size and essentially spherical form of fly ash particles and their tendency to disperse cement flocs have been credited with this effect (33, 131, 363).

Fly ashes which do not reduce the water demand of concrete mixtures are often found to contain large proportions of coarse material (> 45 μm) (317). Increasing proportions of coarse particles has the general effect on workability shown in Figure 2.32 (33). Fly ashes with high carbon contents have also been found to increase water requirements of mortars (41). High carbon contents and coarse particle sizes are often both found in fly ashes produced at relatively old power plants (33).

Fly ash concretes generally exhibit reduced segregation and bleeding relative to plain concrete, particularly during concrete pumping operations (33).

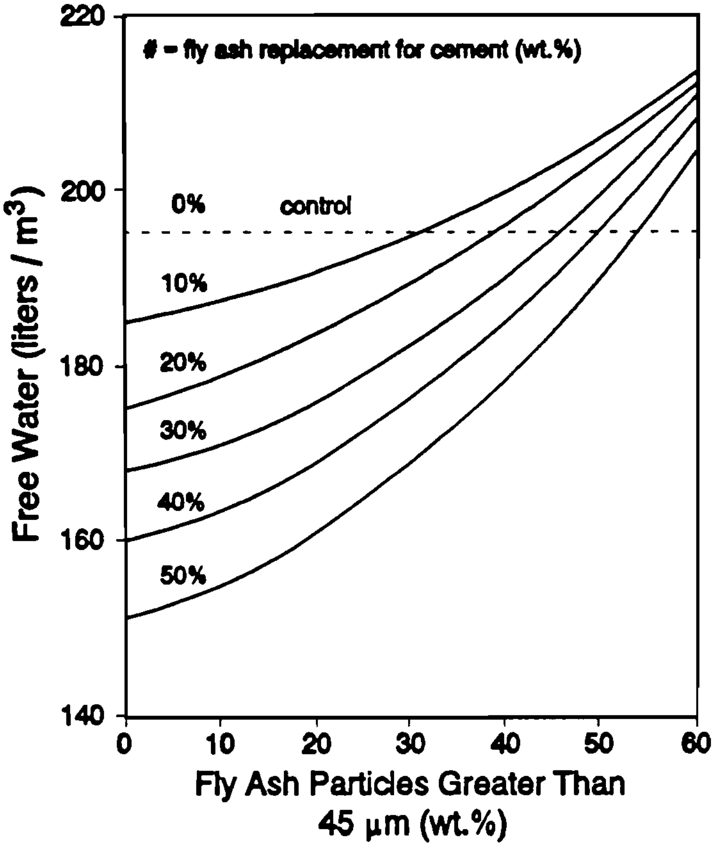


Figure 2.32 Influence of the Coarse Particle Contents of Fly Ash on the Water Required for Equal Workability in Concrete (317)

2.4.6 EFFECTS ON CONCRETE PERMEABILITY

The primary factors which influence the hydraulic permeabilities of plain concretes are water/cement ratio and age (130, 367).

At early ages, fly ash concretes have been observed to behave as lean, permeable concrete mixtures, but permeability is reduced as the pozzolanic reactions proceed (194). The use of silica fume, blast furnace slag, and fly ash in portland cement systems reduces permeabilities and reduces the rate of diffusion of fluids or ions through the matrix (161, 206, 282, 319, 364). Manmohan and Mehta (239) indicated that pozzolanic reactions transform large pores within cementitious systems to fine pores. Calcium-silica reactions take place within the existing pore structure (123). Mehta (270) has also suggested that the measurement of pore structures of blended cement pastes is likely to yield the best estimate of durability.

Short and Page (379) have studied the diffusion of chloride ions (in solution) into portland cement pastes and blended cement pastes. They reported the chloride ion diffusion coefficients shown in Table 2.15 and concluded that slag cements and fly ash cements were more effective in limiting the diffusion of chloride ions into paste than were normal and sulfate-resisting cements.

Table 2.15 Diffusion of Chloride Ions in Solution in Portland and Blended Cement Pastes (379)

Type of Cement	$D_c \times 10^9$ (cm^2/ sec)*
Normal Portland	44.7
Sulfate Resisting	100.0
Fly Ash / Portland	14.7
Slag / Portland	4.1

* D_c calculated with Fick's Second Law

Tikalsky and Carrasquillo (426) studied the effects of two fly ashes on the permeabilities of concretes, as measured by AASHTO T-277 (Rapid Determination of the Chloride Permeability of Concrete). A Class F fly ash and a Class C fly ash were each combined with a Type I cement. Fly ash replacements for the cement included 25 and 35 percent by volume and water was added until the desired slump of 5 to 7 inches was achieved. The Class C fly ash increased permeabilities at 10 days relative to the control mixture without fly ash, as shown in Figure 2.33. However, the Class C fly ash decreased permeabilities at ages of 56 days and later. The permeabilities of mixtures containing Class F fly ash were lowest at all ages. Decreased water/(cement+pozzolan) ratios due to the incorporation of fly ash may have contributed to the decreased permeabilities.

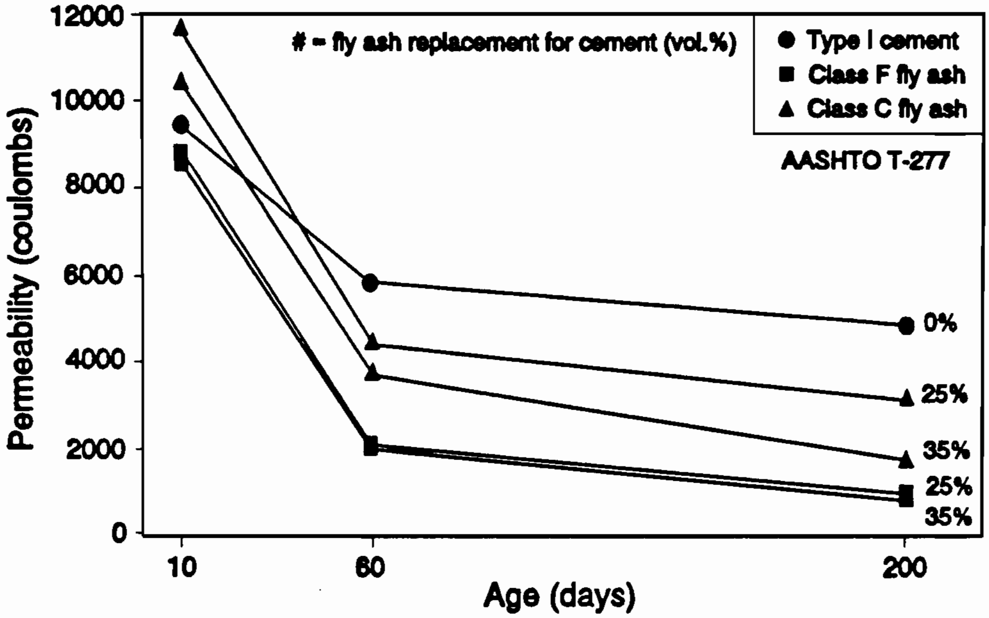


Figure 2.33 Effect of Fly Ash on the Permeability of Concrete (426)

Ozyildirim and Halstead (318) studied the effects of a Class F fly ash on the permeability of Type II cement concrete with water/(cement+pozzolan) ratios remaining constant. Permeability was measured by AASHTO T-277. Cement replacements included 15 percent and 25 percent by mass of cement where the mass of fly ash added was 1.2 times the mass of cement being replaced. A high-range water-reducing admixture was used to achieve workable concretes at water/(cement+pozzolan) ratios of 0.35, 0.40, and 0.45. Permeabilities were measured at 28 and 90 days. After 28 days of moist curing and with the exception of the highest water/(cement+pozzolan) ratio, the fly ash concretes had comparable permeabilities with the control mixture without fly ash, as shown in Figure 2.34. At the highest water/(cement+pozzolan) ratio, the permeability of the concrete containing the highest percentage of fly ash was significantly greater than the permeability of the control mixture without fly ash. After 90 days of moist curing, all the fly ash concretes had equal or lower permeabilities relative to the control mixture without fly ash, as shown in Figure 2.35.

2.4.7 EFFECTS ON THE RESISTANCE OF CONCRETE TO SULFATES

2.4.7.1 J.T. Dikeou

Dikeou (91) investigated the sulfate resistance of concrete in order to recommend design requirements for concrete drain pipes for the United States Department of the Interior. The pipes were to be buried in soils where soluble sulfate concentrations were as high as 5 to 6 percent and where concentrations of soluble sulfates in ground waters were as high as approximately 150,000 ppm. Dikeou chose fly ash additions as an alternative because examinations of previous test results indicated that inclusion of fly ash consistently improved the sulfate resistant properties of concrete over similar concrete.

Dikeou studied 30 concrete mixtures, including 8 portland cements and 12 fly ashes. Cement replacements by fly ash ranged from 15 percent to 25 percent by weight. Concrete cylinders of dimensions 3x6 inches were cured for 28 days: 14 days at 100 percent relative humidity and 14 days at 50 percent relative humidity. Specimens were subjected to one of two tests: continuous soaking in 10 percent sodium sulfate solution and accelerated testing in a 2.1 percent sodium sulfate solution. The accelerated test consisted of wet-dry cycles, including 16 hours soaking at 73 °F and 8 hours drying in air at 130 °F. Specimens were monitored for linear expansions.

Dikeou (91) reported that all fly ashes improved the resistance of concrete to sulfate attack, regardless of the type of cement used. Complete chemical analyses of fly ashes were not reported by Dikeou, but Dunstan (99) indicated that the ashes were obtained from power plants burning hard bituminous coals. Therefore, Dikeou's ashes were most likely low-calcium ashes, similar to ashes which meet modern ASTM C-618 specifications for Class F fly ashes.

The effectiveness of fly ash in improving the sulfate resistance of concrete generally decreased in the order of the following cements: Type I, Type V, and Type II. The degree of sulfate resistance of concrete in both the continuous soak test and the accelerated test generally decreased in the following order of cements and fly ash cements:

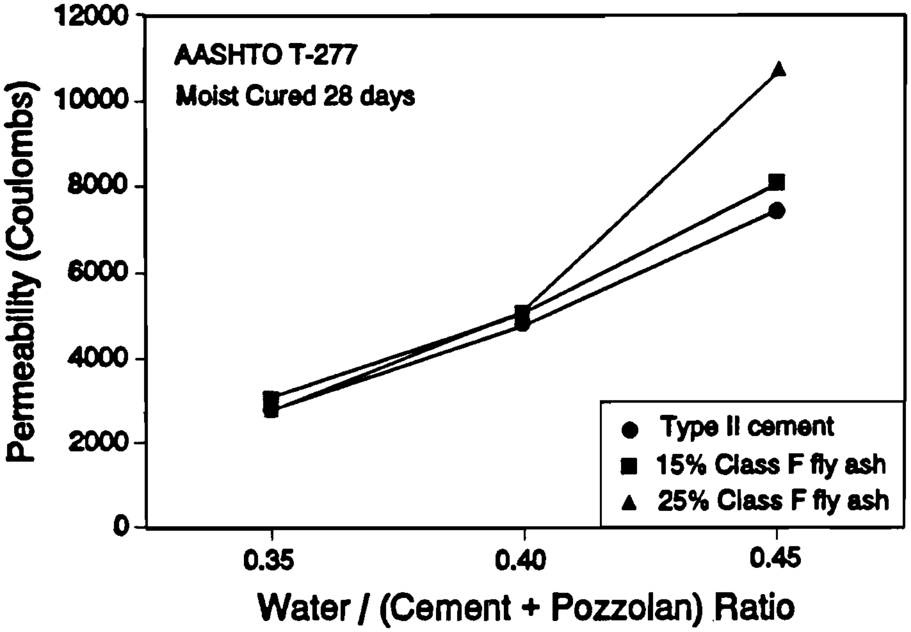


Figure 2.34 Effect of Fly Ash on the Permeability of Concrete After 28 Days of Moist Curing (318)

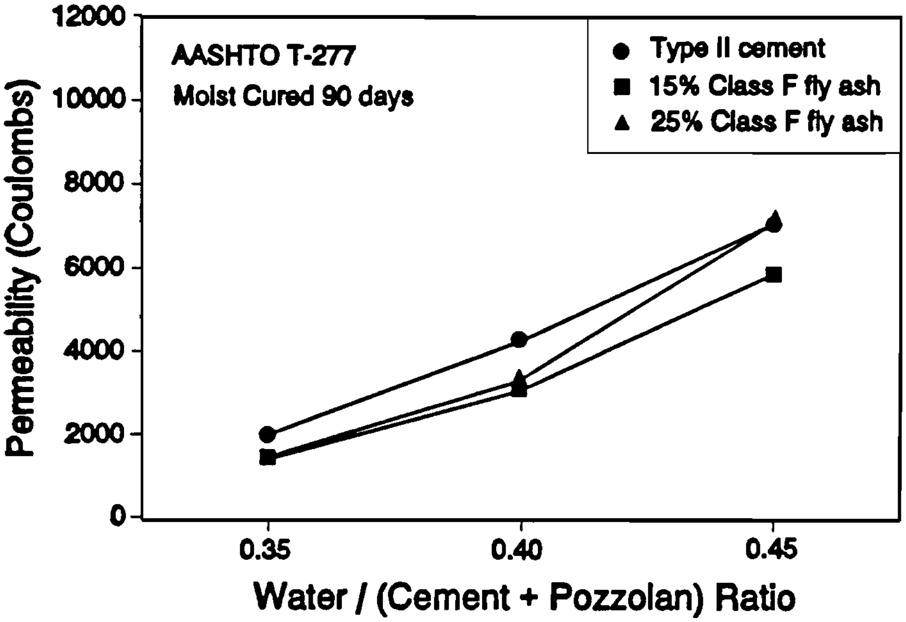


Figure 2.35 Effect of Fly Ash on the Permeability of Concrete After 90 Days of Moist Curing (318)

1) Type V cement with fly ash,
2) Type II cement with fly ash,
3) Type V cement,
4) Type II cement,
5) Type I cement with fly ash, and
6) Type I cement.

Dikeou (91) offered explanations for the improvements in the resistance of concrete to sulfates, as a result of the incorporation of fly ash. He reported a physical improvement and a chemical improvement, both of which involved decreased calcium hydroxide contents in hardened concretes. Calcium hydroxide is a soluble product of the hydration of portland cement. Fly ash constituents react with calcium hydroxide to form relatively insoluble cementitious compounds. The physical improvement was decreased permeability. Calcium hydroxide, which would otherwise be present, could be leached out of concrete, leaving voids. The chemical improvement was the reduction in available calcium hydroxide which would otherwise be available for reaction with sulfates to form gypsum. This reaction is expansive and is one of the mechanisms of sulfate attack.

2.4.7.2 K. Torii et al.

Torii et al. (428) studied the effects of a fly ash on the chemical and physical properties of concrete, including resistance to sulfate attack. Their results substantiate Dikeou's reasoning for the improvements in concrete sulfate resistance, which were obtained by the incorporation of fly ash.

A detailed chemical analysis of the fly ash was not reported, but the high SiO_2 content (54.7 percent) provides evidence that the fly ash was probably a low-calcium ash, similar to fly ashes which meet present ASTM C-618 specifications for Class F fly ashes. A general-purpose portland cement was replaced by the fly ash at levels of 30 and 50 percent by weight. Mixture designs included cement plus fly ash contents of 300 and 400 kg/m^3.

Cylinders of dimensions 7.5x15 cm were immersed in ten percent sodium sulfate solution after curing in water for 14 days and curing in 90 percent relative humidity for an additional 14 days. Attack by sulfates was monitored by periodically testing cylinders for compressive strengths. Microstructural changes were monitored by mercury porosimeter and chemical changes were monitored by DSC-TG analyses.

Increasing cement content from 300 kg/m ^{3} to 400 kg/m ^{3} without adding fly ash decreased the rate of strength loss, as shown in Figure 2.36. Replacing 50 percent of the cement with fly ash in the 400 kg/m ^{3} mixture eliminated strength loss completely.

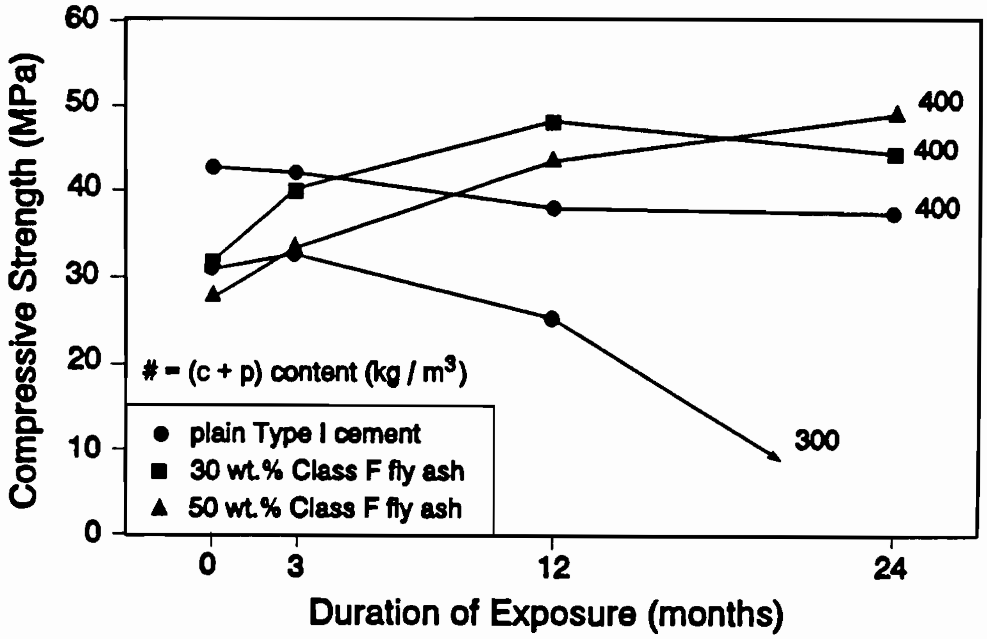


Figure 2.36 Sulfate Resistance of Concrete as Measured by Compressive Strength (428)

The Differential Thermal Analyses (DTAs), shown in Figure 2.37, were performed on two types of hardened concrete: a plain concrete which was not resistant to sulfates and a fly ash concrete which was resistant to sulfates. The DTA curves permit comparisons between the ettringite, gypsum, and calcium hydroxide contents of these concrete mixtures as they were immersed in sodium sulfate solution. The height of peaks approximate the relative proportions of crystalline compounds in hardened concrete. The plain concrete started with larger proportions of the three compounds and the proportions increased for 6 months as the specimens were immersed. From 6 to 12 months, the proportions of ettringite and gypsum continued to increase while the proportion of calcium hydroxide decreased due to its conversion to gypsum. In the sulfate resistant fly ash concrete, ettringite and gypsum proportions increased at a much slower rate through 12 months and did not appear to increase at all between 12 and 24 months. With the absence of gypsum formation between 12 and 24 months, the diminishing calcium hydroxide content was reported to be due to pozzolanic reactions with fly ash (428).

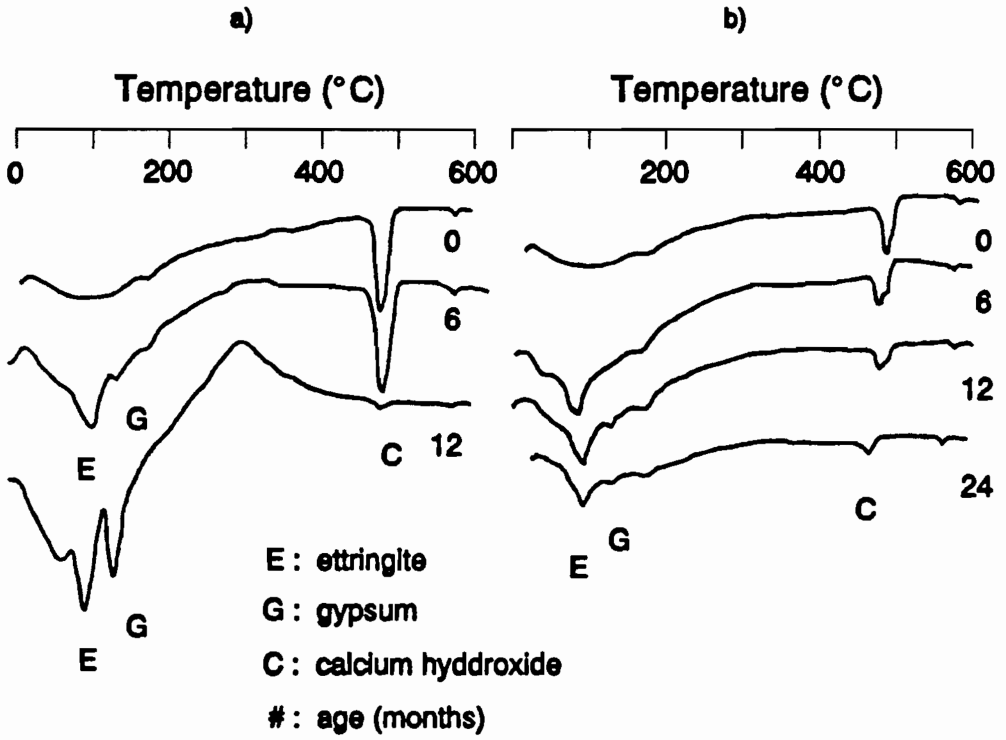


Figure 2.37 Differential Thermal Analyses for a) Plain Concrete (c = 300 kg/m^3) and b) Concrete with Fly Ash (c+f = 400 kg/m^3, f/(c+f) = 50%) (428)

Mercury porosimeter results shown in Figures 2.38 and 2.39 permit comparisons of pore size distributions between a sulfate susceptible plain concrete and a sulfate resistant fly ash concrete. The distributions of pore diameters and total pore volumes (TPV) were measured after 28 days, 6 months, and 24 months of hydration; immersion in sulfate solution began at 28 days. Although the TPV for the two mixtures were initially approximately equal,

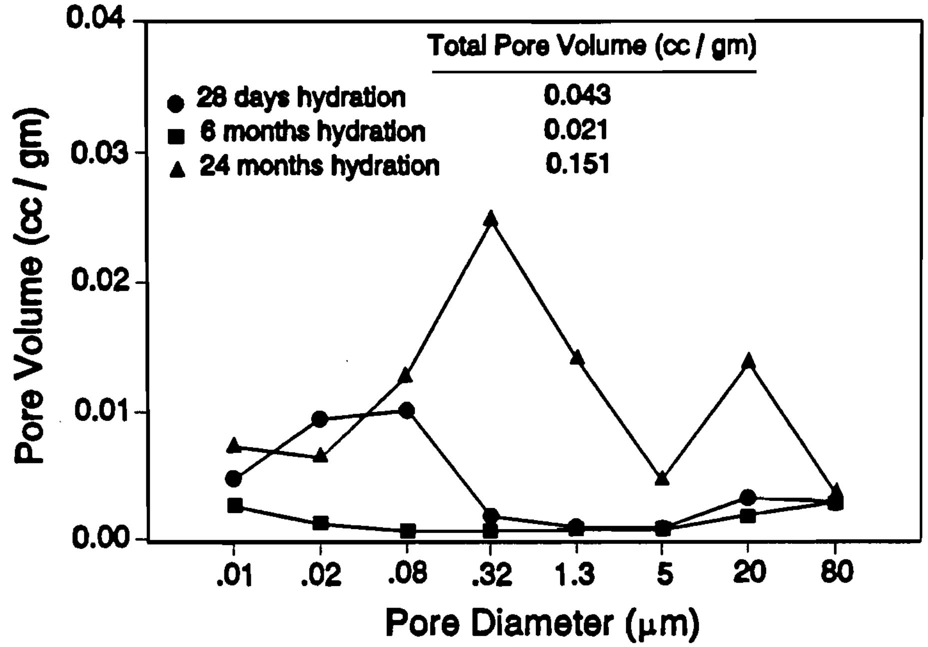


Figure 2.38 Pore Size Distributions Over Time for Type I Cement Concrete (300 kg/m^3) (428)

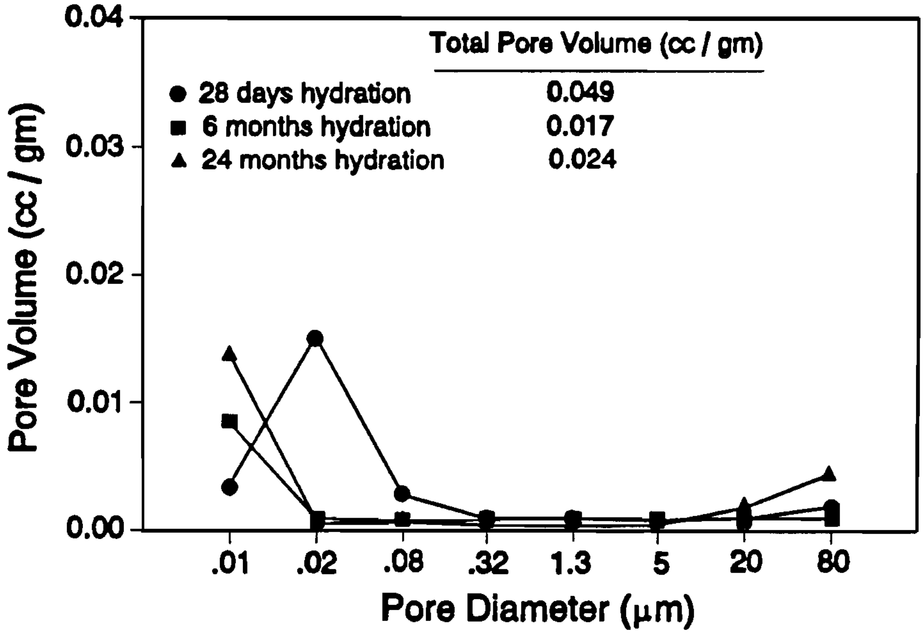


Figure 2.39 Pore Size Distributions Over Time for Concrete with 50 wt.% Class F Fly Ash (c+p = 400 kg/m^3) (428)

the TPVs were much different by the end of the sulfate exposure test. The TPV of the plain concrete increased by approximately 350 percent, while the TPV of the fly ash concrete decreased by approximately 50 percent. It is also apparent that, during sulfate exposure, the plain concrete suffered increases in its volume of pores larger than 0.1 um in diameter. Meanwhile, the peak of the pore size distributions for the fly ash concrete shifted toward finer diameter pores. Mehta (269) has indicated that pores larger than 0.1 μm in diameter are significant in terms of the permeability of cement paste and thus, the chemical durability of concrete.

The plain concrete mixture exhibited a temporarily low TPV at 6 months. Gypsum and ettringite crystals may have densified the concrete by filling voids prior to the development of interior stresses and cracking.

2.4.7.3 E.R. Dunstan

In 1973, the Water and Power Resources Service began an investigation to evaluate the performance of concrete containing fly ash from western United States. These new power plants were burning lignite and subbituminous coals (99). Contrary to bituminous coal ashes, all of these ashes did not improve the resistance of concrete to sulfate attack. Dunstan (99) proposed a fly ash sulfate resistance factor, based on the chemical compositions of fly ashes, in order to predict the effects on the sulfate resistance of concrete.

The total alumina content of portland cement is not the determining factor for its sulfate-resistance; it is the relative amounts of alumina combined into compounds C_3A and C_4AF. Similarly, the total alumina content of fly ash is not the determining factor for its sulfate resistance. Fly ashes from bituminous coals typically contain higher alumina contents than the cements they replace, although the bituminous coal ashes have been found to improve the sulfate resistance of concrete (91). Also, high-calcium fly ashes from low-rank coals typically contain lower alumina contents than fly ashes from bituminous coals, although they often do not improve the sulfate resistance of concrete (99).

The principal alumina-bearing phase in fly ash from bituminous coals is mullite (A_3S_2) (97, 200, 445). Crystalline mullite is highly nonreactive, so alumina combined in this phase is not available for reactions in concrete (99). Additional alumina-bearing phases which may be found in high-calcium fly ashes include $C_4A_3\bar{S}$ and C_3A. Both of these phases are reactive and are susceptible to expansive reactions in the presence of sulfates.

Dunstan used bulk chemical analyses to characterize the compositions of fly ash glasses. Calcium oxide, aluminum oxide, and silicon dioxide were plotted on a ternary diagram. The same ternary diagram had been used to characterize the composition of another glassy material, blast furnace slag (218, 222). The compositions of Dunstan's fly ashes plotted in the ternary regions of mullite (A_3S_2), anorthite (CAS_2), and gehlenite (C_2AS), as shown in Figure 2.40 (99).

The compositions of crystalline compounds and glass were assumed to follow the general trends of the ternary diagram. For example, fly ashes in the mullite field were anticipated to contain relatively large proportions of crystalline mullite and an aluminosilicate-type glass. Fly ashes in the gehlenite field were anticipated to contain crystalline compounds of calcium and relatively large proportions of calcium aluminosilicate glass (99).

Crystalline compounds and glasses of compositions approximating gehlenite were believed to be more reactive with sulfates than those in the mullite field. Hydration products of fly ashes in the gehlenite field were also believed to be susceptible to sulfate attack (99). This is significant because a substantial amount of cement/fly ash hydration may occur before concrete is exposed to sulfates.

Dunstan partially replaced a low-alkali Type II cement with 8 fly ashes. Replacement levels included 15 and 25 percent by weight. Total CaO contents of fly ash ranged from 7.0 to 32.0 percent. Mixture designs included 5 percent entrained air and water/(cement+pozzolan) ratios of approximately 0.45. Concrete cylinders of dimensions 3x6 inches were cured for 14 days at 100 percent relative humidity and for an additional 14 days at 50 percent relative humidity, prior to sulfate exposure. Sulfate exposures consisted of continuous soaking in 10 percent sodium sulfate solution and an accelerated test in 2 percent sodium sulfate solution. The accelerated test was a cyclic test of wetting and drying, consisting of 16 hour soaking periods at 73 °F and 8 hour drying periods at 130 °F. Deterioration of specimens was monitored by changes in length.

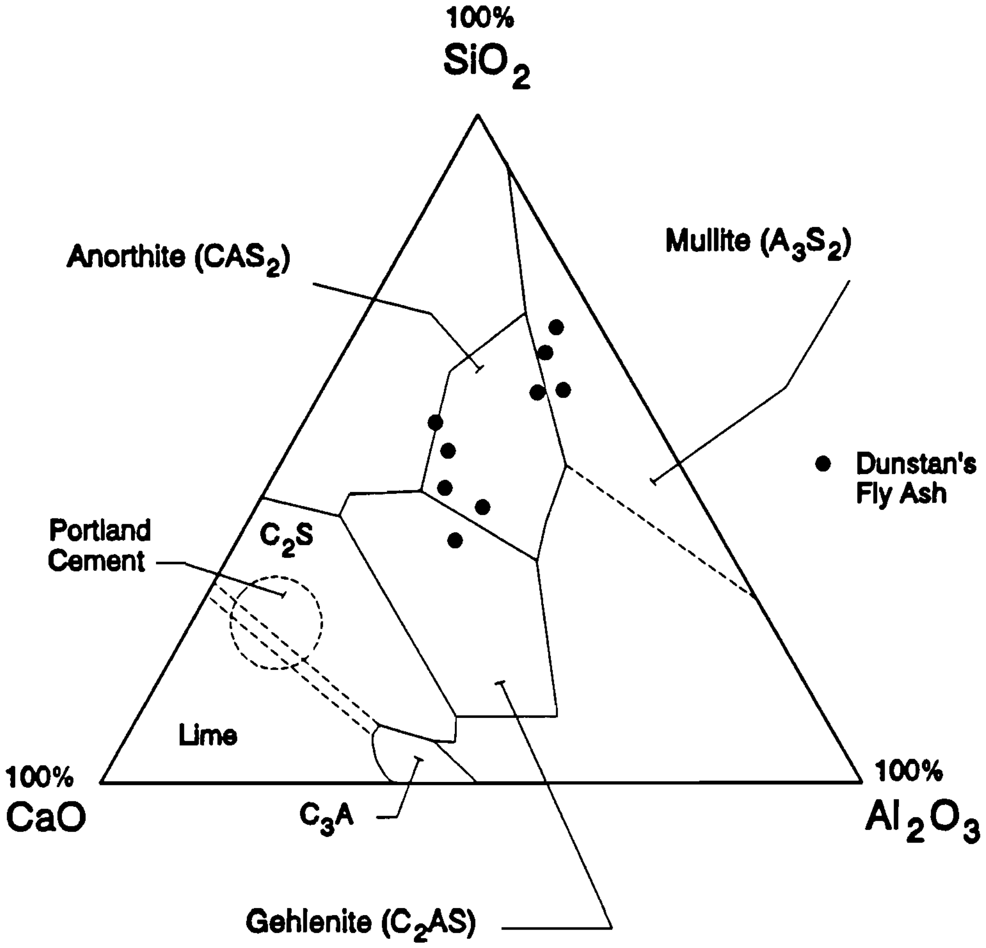


Figure 2.40 Ternary (SiO_2-CaO-Al_2O_3) Compositions of E.R. Dunstan's Fly Ash (99)

The fly ashes which had compositions approximating the mullite field typically improved the resistance of concrete to sulfate attack. These fly ashes contained approximately 5 percent calcium or less. Therefore, the calcium oxide content in excess of 5 percent was believed to be directly related to decreasing sulfate resistance (99).

Fly ashes which contained the highest proportions of ferric oxide (18.6 and 7.9 percent, respectively) performed well in the sulfate exposure tests. The iron in fly ash was believed to promote the formation of iron-rich ettringite, which has been shown to cause minimal expansions (190).

Based on bulk chemical analyses of fly ashes, Dunstan developed a parameter termed Resistance Factor in order to characterize the potential effects of the fly ashes on the sulfate resistance of concrete:

$$\text{Resistance Factor, } R = \frac{(C-5)}{F}\text{ , where} \qquad (2.9)$$

C = total calcium oxide content (percent) and

F = total ferric oxide content (percent).

As the ferric oxide content approaches zero, the resistance factor approaches infinity. Therefore, a suggested lower limit for the ferric oxide content is 2 percent.

Based on comparisons between fly ash resistance factors and the performances of fly ash concretes in the sulfate exposure tests, Dunstan classified R-factors according to anticipated effects on sulfate resistance, as shown in Table 2.16.

These classes of resistance factors were determined with a single Type II cement, a limited number of fly ash samples, a single cement replacement level, and a single water/(cement+pozzolan) ratio. These limitations should be realized when considering the resistance factor for practical applications.

The United States Bureau of Reclamation adopted the Resistance Factor as its method of specifying fly ash for use in concrete to be exposed to sulfates. Recommended types of cement and types of fly ash cement are shown in Table 2.17, along with the classes of potential sulfate exposure, which are described in Table 2.16.

2.4.7.4 P.K. Mehta

Mehta (276) proposed that rather than the chemical composition or the Resistance Factor of a fly ash, it is the mineralogical compositions of the cement-fly ash interaction products that control sulfate resistance. He compared the resistance of fly ash cement pastes to sulfates with the mineralogical compositions of their hydration products before immersion.

Table 2.16 Proposed Limits for R-Factors for Concrete Containing Fly Ash at 25 Percent Replacement by Weight (99)

R - Factor Limits *	Sulfate Resistance **
< 0.75	greatly improved
0.75 - 1.5	moderately improved
1.5 - 3.0	no significant change
> 3.0	reduced

* for very severe conditions of cyclic wetting and drying or $MgSO_4$ solution, reduce R-factor by 0.50

** compared to a Type II cement without fly ash at a water/cement ratio of 0.45

Mehta (276) partially replaced a Type I cement (11 percent C_3A) with 5 Class F fly ashes and 11 Class C fly ashes. Cement replacements consisted of 25 and 40 percent by weight. Pastes were mixed at water/(cement+pozzolan) ratios of 0.5 and were moist cured for 14 days at 104 °F. Mineralogical analyses of hydrated cement pastes were performed by X-ray powder diffraction using Cu $K\alpha$ radiation. Sulfate exposure consisted of immersing ½-inch paste cubes in four percent sodium sulfate solution. Solution pH was maintained at 7 ± 0.5 by automatic titration of dilute sulfuric acid. Susceptibilities to sulfates were measured as percentages of lost compressive stength after 28 days of exposure. Due to the small-sized test cubes and the potential for experimental error, ten replicates were tested for each compressive strength measurement.

Comparisons were made between the principal alumina-bearing phases in fly ash, the principal alumina-bearing hydration products, and the resistance of cements containing fly ash to sulfate attack, as shown in Table 2.18 (276).

Fly ashes 1 through 5 were bituminous ashes with calcium contents less than or equal to 10.5 percent. Despite low Resistance Factors for fly ashes 2 and 3, they did not perform satisfactorily in the sulfate exposure test. Cement pastes incorporating these fly ashes contained monosulfate hydrate ($M\bar{S}H$), rather than ettringite, prior to immersion in the sulfate solution. Monosulfate hydrate became unstable in the presence of additional sulfate ions. The cement pastes which contained ettringite prior to immersion performed satisfactorily because ettringite remained stable in the sulfate environment.

Table 2.17 United States Bureau of Reclamation Recommendations for the Production of Sulfate Resistant Concrete (330)

Relative Degree of Sulfate Attack *	Cement Types
Positive	Type II cement
	Type II cement plus Class F or C pozzolan with R-factor < 2.5
	Type IP (MS) cement with R-factor < 2.5
Severe	Type V cement
	Type V cement plus Class F or C pozzolan with R-factor < 2.5
	Type II cement plus Class F or C pozzolan with R-factor < 2.5
	Type IP (MS) cement with R-factor < 2.5 (cement C_3A < 5.0%)
	Type IP (MS) cement with R-factor < 1.5 (cement C_3A 5.0% to 8.0%)
Very Severe	Type V cement plus Class F or C pozzolan with R-factor < 1.5
	Type II cement plus Class F or C pozzolan with R-factor < 0.75
	Type IP (MS) cement with R-factor < 1.5 (cement C_3A < 5.0%)
	Type IP (MS) cement with R-factor < 0.75 (cement C_3A 5.0% to 8.0%)

* refer to Table 2.8 for limitations on sulfate contents in soils and groundwater

Fly ashes 1 and 2 consisted of similar chemical compositions, but they promoted the formation of different alumina-bearing hydration products. Mehta indicated that this was the result of their different mineralogical compositions. The respective amounts of quartz, mullite, and aluminosilicate-type glass in fly ash number 1 were 8 percent, 19 percent, and 73 percent. The respective amounts of the same constituents in fly ash number 2 were 3 percent, 2 percent, and 95 percent. Fly ash number 2 contained a smaller proportion of its

Table 2.18 Influence of the Composition of Fly Ash on the Sulfate Resistance of Blended Cements (276)

Ash Number	R - Factor	Principal Alumina-Bearing Phases in Fly Ash	Alumina-Bearing Hydration Products *	Performance in Sulfate Test
1	-0.9	mullite, A-S glass	ettringite	satisfactory
2	-0.1	> 90% A-S glass	$M\bar{S}H$	poor
3	-0.01	A(F)-S glass	$M\bar{S}H$	very poor
4	0.3	A-S glass	ettringite	satisfactory
5	1.1	A-S glass	ettringite, $M\bar{S}H$	satisfactory
6	4.0	N-C-A-S glass, $C_4A_3\bar{S}$	ettringite	excellent
7	4.0	N-C-A-S glass, $C_4A_3\bar{S}$	ettringite	satisfactory
8	4.0	N-C-A-S glass, $C_4A_3\bar{S}$	ettringite	satisfactory
9	4.5	C_3A, $C_4A_3\bar{S}$, C-A-S glass	$M\bar{S}H$ and C-A-H	very poor
10	3.5	C_3A, $C_4A_3\bar{S}$, C-A-S glass	$M\bar{S}H$ and C-A-H	very poor
11	3.0	C_3A, $C_4A_3\bar{S}$, C-A-S glass	$M\bar{S}H$ and C-A-H	very poor
12	2.6	C_3A, C-A-S glass	$M\bar{S}H$ and C-A-H	very poor
13	1.8	C_3A, C-A-S glass	$M\bar{S}H$	poor
14	1.5	A-S & C-A-S glass	ettringite, $M\bar{S}H$	satisfactory
15	1.2	C_3A, $C_4A_3\bar{S}$, C-A-S glass	$M\bar{S}H$ and C-A-H	poor
16	0.5	A-S & C-A-S glass	ettringite	excellent

* 40 percent by weight of cement was replaced by fly ash

alumina in the nonreactive form of mullite. Therefore, the cement containing fly ash number 2 had a high available alumina content and an alumina/sulfate ratio which favored the formation of $M\bar{S}H$.

Fly ash number 3 provided evidence that high iron contents in fly ash are not always beneficial for sulfate resistance. Although this fly ash consisted of a low alumina content (12.3 percent) and a high iron content (39.0 percent), the paste in which it was included performed very poorly in the sulfate exposure test. Mehta suspected that a considerable proportion of the total iron content was present in glass and became available for the formation of an iron-substituted $M\bar{S}H$ phase ($C_4A(F)\bar{S}H_{12}$).

Fly ashes 6 through 8 were all derived from lignite coals. Pastes containing these ashes performed satisfactorily or excellent even though their total CaO contents were 19.2 percent, 23.6 percent, and 25.0 percent, respectively. Mehta attributed these performances to the high available sulfate contents (7.8 percent, 9.6 percent, and 16.6 percent, respectively) of the fly ashes. The alumina/sulfate ratios during hydration favored the formation of ettringite as the primary alumina-bearing hydration product. Large proportions of alkalies were also present in glass, which promoted rapid hydration of aluminates before the concrete hardened.

Fly ashes 9 through 16 were all derived from subbituminous coals. Fly ashes 13, 14, and 15 yielded comparisons which were particularly interesting. These fly ashes had similar Resistance Factors (1.8, 1.5, and 1.2, respectively) and similar total CaO contents (15.8 percent, 12.9 percent, and 16.2 percent, respectively). However, they did not perform similarly in the sulfate exposure test. Pastes containing fly ashes 13 and 15 performed poorly in the sulfate solution and the paste containing fly ash 14 performed satisfactorily. Mehta attributed the different performances to different fly ash mineralogical compositions. Fly ashes 13 and 15 contained C_3A as their principal alumina-bearing phase, while fly ash 14 contained inert mullite. These phases and their effects on the alumina/sulfate ratios during hydration determined whether $M\bar{S}H$ or ettringite was formed.

2.4.7.5 Manz, McCarthy, et al.

Manz and others (245) utilized both the mineralogy and the chemistry of fly ashes in their development of a method for rating the potential effects of fly ash on the resistance of concrete to sulfate attack. This method of rating fly ashes, termed the MinChem Resistance Factor, is an evolution of ideas presented by Dunstan (99) and Mehta (276). It takes advantage of quantitative X-ray diffraction characterizations of fly ashes to estimate relative proportions of reactive and nonreactive crystalline phases and to estimate average glass compositions.

The basis of the MinChem Resistance Factor is that calcium and aluminum that are present in non-reactive crystalline phases or in phases that react completely during initial set, will not contribute to the proportion of calcium aluminates that may react with sulfate solution after the concrete has hardened (245). It is also proposed that in high- and intermediate-calcium fly ashes, available sulfates may enhance the sulfate resistance of concrete. During initial set, sulfates react with hydratable CaO and CH to produce $C\bar{S}$. High levels of available gypsum ($C\bar{S}$) promoted the formation of ettringite rather than $M\bar{S}H$ during initial set, minimizing subsequent expansive reactions of $M\bar{S}H$ to ettringite after the concrete has hardened (245).

Manz and others (245) proposed the following assumptions for the development of their MinChem Resistance Factor:

1) minerals of quartz, mullite, ferrite spinel (magnetite), hematite, periclase, melilite, and merwinite are fly ash constituents which do not participate in expansive reactions related to sulfate attack;
2) iron oxides which are not present as ferrite spinel or hematite may participate in expansive reactions through $C_4A(F)\bar{S}H_{12}$ reacting with sulfates to form iron-substituted ettringite;
3) calcium oxides which are present as crystalline lime, portlandite, anhydrite, and calcium silicates are typically reactive during initial hydration and, therefore, do not participate in expansive reactions related to sulfate attack; and
4) the total sulfur trioxide content, as determined by the bulk chemical analysis, is reactive during the initial hydration period.

Utilization of the MinChem Resistance Factor involves the calculation of two parameters (245, 253):

1) Calcium Aluminate Potential (CAP), which measures the potential for a fly ash-cement to contain unreacted calcium aluminates (C-A-H, C_3A, or C-A-rich glass) after initial hydration reactions are complete, and
2) Calcium Sulfate Equivalent ($C\bar{S}E$), which measures the potential for a fly ash to mitigate the effects of a high CAP by promoting the formation of ettringite during the initial hydration period.

Calcium Aluminate Potential is calculated as follows:

$$CAP = \frac{CaO'' + Al_2O_3' + Fe_2O_3'}{SiO_2}\text{, where} \tag{2.10}$$

(oxide)' = proportion of bulk oxide in reactive components
= (weight percent in bulk chemical analysis) -
(weight percent fixed in inert crystalline phases) and
(CaO)" = (CaO)' - (weight percent CaO which is reactive during early hydration) .

Oxides fixed in inert phases include:

1) SiO_2 in quartz,
2) SiO_2 and Al_2O_3 in mullite, melilite, and merwinite,
3) Fe_2O_3 (FeO) in ferrite spinel and hematite, and
4) CaO in melilite and merwinite.

Phases of CaO which are assumed to be reactive during early hydration or to not participate in sulfate-related reactions include: lime, portlandite, anhydrite, C_2S, and C_3S.

Calcium Sulfate Equivalent is calculated as follows:

$$C\bar{S}E = \text{Anhydrite} + 1.69 \times (SO_3)\ . \tag{2.11}$$

The constant 1.69 is a gravimetric factor for the formation of additional anhydrite from reactions between SO_3 and calcium hydroxide. Sulfur trioxide content is calculated as the bulk chemical SO_3 remaining after accounting for SO_3 already present in anhydrite.

Utilization of the MinChem Resistance Factor is completed by defining a curve on a scatter plot of fly ash CAP versus fly ash C$\bar{S}$E, as shown in Figure 2.41. The points on the scatter plot are labeled with results from a sulfate exposure test. Then the curve defines a boundary separating satisfactory and unsatisfactory fly ashes, with respect to their effects on the resistance of concrete to sulfate attack (245).

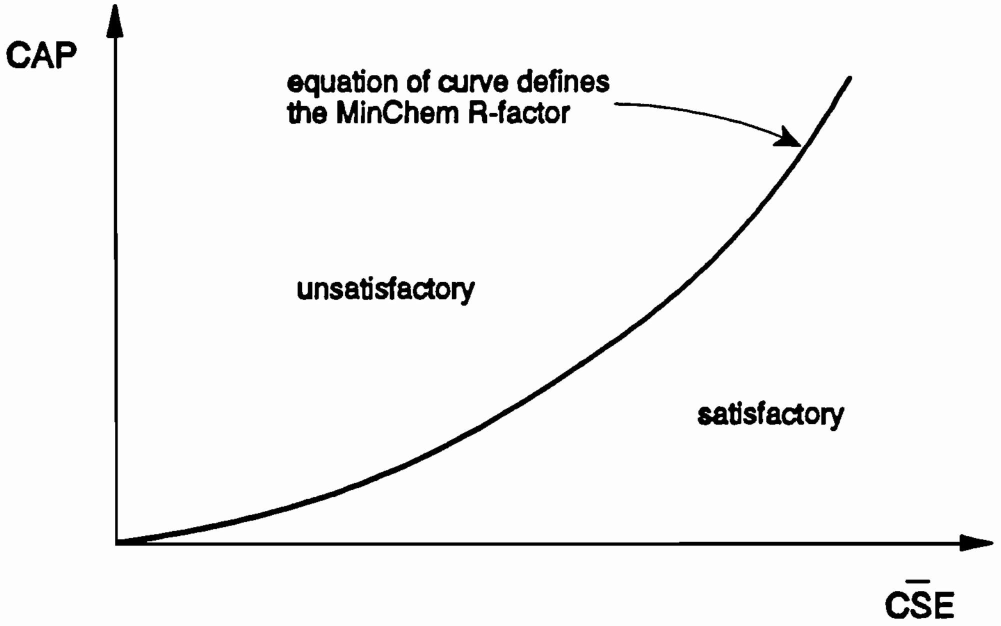


Figure 2.41 Minchem R-Factor as Defined by the Calcium Aluminate Potential and the Calcium Sulfate Equivalent (245)

Manz and others (245) performed some sulfate exposure tests on fly ash concretes while developing the MinChem Resistance Factor. Concrete beams of dimensions 3x3x12 inches were immersed in ten percent sodium sulfate solution. Test results yielded some interesting trends relating compositions of fly ashes to the resistance of fly ash concretes to sulfate attack.

Four fly ashes, which were derived from Wyoming subbituminous coals, partially replaced a Type I cement at a level of 20 percent by weight. All fly ashes significantly reduced expansions compared to the control mixture without fly ash. However, two of the fly ash concrete mixtures experienced cracking within three years of exposure. The subbituminous coal ashes which were susceptible to sulfate attack were reported to have relatively high ($CaO+Al_2O_3$) contents (46.0 percent and 42.7 percent), resulting in relatively high C_3A contents. They also contained large proportions of quartz (14.5 percent and 10.2 percent), resulting in reduced availability of SiO_2 for glass. Tricalcium aluminates and glasses rich in calcium and alumina are susceptible to sulfate-induced expansions (276).

A lignite fly ash from Spain partially replaced a general purpose portland cement at a level of 30 percent by weight. Mortar mixtures were tested in accordance with ASTM Standard C-1012; the exposure solution contained 0.176 molarity Na_2SO_4 and 0.176 molarity $MgSO_4$. After six months of exposure, the control mortar without fly ash failed the ASTM C-1012 failure limit of 0.1 percent while the mortar containing fly ash exhibited minimal expansions. The fly ash was reported to contain only a moderate amount of Al_2O_3 (16.2 percent) and a relatively large proportion of SiO_2 (42.0 percent), a portion of which would be available for the formation of glass. A large proportion of total CaO was present as crystalline lime (8.3 percent), which limited the amount of CaO which was available for the formation of C_3A or C-A-rich glass. The fly ash also contained a relatively large amount of anhydrite (5.1 percent), which would promote the formation of ettringite during early hydration (245).

2.4.8 SPECIFICATIONS

2.4.8.1 Introduction

ASTM C-618, "Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for use as a Mineral Admixture in Portland Cement Concrete," is the prevalent standard specification for controlling the quality of fly ash in the United States. This specification includes standard and optional requirements for both chemical and physical fly ash characteristics. These requirements provide guidelines for determining whether mineral admixtures are of a minimum acceptable quality. However, they provide little guidance for evaluations of the relative performances of two or more products (277).

The original ASTM specification for fly ash was adopted in 1954. Its development was based primarily on bituminous coals, so all the fly ash studied fell into a narrow range of compositions. Therefore, only one class of fly ash was specified, Class F. This single class was required to distinguish fly ash from natural pozzolans, Class N.

As power plants were constructed in the Western United States, some fly ashes were derived from lignite and subbituminous coals. These ashes did not meet the chemical requirements specified for Class F fly ash, but they were shown to be suitable for use in concrete. Therefore, in 1977, another class of fly ash was added to the ASTM specification, Class C. The Class C fly ashes were typically higher in calcium and were recognized as having some cementitious properties.

In ASTM C-618, Class F and Class C fly ashes are defined as follows:

1) Class F fly ash has pozzolanic properties and is normally produced from burning anthracite or bituminous coal.
2) Class C fly ash has pozzolanic properties and some cementitious properties; it is normally produced from burning lignite or subbituminous coal.

The references to coal source types often cause confusion because many fly ashes produced from lignite and subbituminous coals meet the Class F requirements (241, 326).

2.4.8.2 Chemical Requirements

Fly ash classes F and C are differentiated by the sum of silica, alumina, and ferric oxides, as shown in Table 2.19. Class F and Class C fly ashes are required to contain 70 percent and 50 percent of this sum of oxides ($SiO_2+Al_2O_3+Fe_2O_3$), respectively. Initially, these limits were defined to ensure fly ash pozzolanic activity. However, these oxides only exhibit pozzolanic activity when present in non-crystalline form (glass). Minerals such as quartz, mullite, and hematite do not react with calcium hydroxide at ordinary temperatures (277). Since most fly ashes are partially crystalline, the accuracy with which this sum of oxides measures pozzolanicity is often debated.

Calcium contents have a significant influence on fly ash behavior. The presence of high CaO contents modifies the mineralogical characteristics and reactivity of fly ash. Aluminosilicate glasses become more reactive as they are modified by calcium and calcium-bearing crystalline compounds, such as C_3A, $C\bar{S}$, and $C_4A_3\bar{S}$, are highly reactive and are cementitious (277).

Consequently, some researchers feel that fly ash classification should be based on calcium contents (277). Manz has suggested a fly ash classification based on the 3-day compressive strengths of cubes without cement (241). Butler has suggested a fly ash classification based on a knife-cut setting test used in the gypsum plaster industry (48).

Limits on fly ash sulfur trioxide content are intended to prevent difficulties with setting of fly ash cement and to reduce the possibility of expansive deterioration of hardened concrete due to the formation of ettringite (33, 277). However, Butler suggests that the presence of lime in fly ash influences the optimum level of sulfates in concrete and provides for larger acceptable ranges of sulfate contents than is currently recognized (48).

Table 2.19 ASTM C-618 Chemical Requirements for Fly Ash to be Used as a Mineral Admixture in Portland Cement Concrete (17)

Chemical Requirements	Mineral Admixture Class	
	F	C
SiO_2 + Al_2O_3 + Fe_2O_3 (min.%)	70.0	50.0
Sulfur Trioxide, SO_3 (max.%)	5.0	5.0
Moisture Content (max.%)	3.0	3.0
Loss on Ignition (max.%)	6.0 *	6.0
Optional Chemical Requirements **		
Available Alkalies, as Na_2O (max.%)	1.5	1.5

* Class F pozzolan containing up to 12.0 percent loss on ignition may be approved by the user if acceptable performance records or laboratory test results are made available.

** Applicable only when specifically required by the purchaser and when the mineral admixture is to be used in concrete containing alkali-reactive aggregate.

Limits on moisture content are required to protect the purchaser from receiving fly ash in a wet state (33). Moist fly ash is difficult to handle and some active cementitious constituents may get deactivated in the presence of water (277).

Specifications for loss on ignition are intended to limit the carbon content of fly ash. Unburnt carbon, which has a high surface area, has been associated with increased mixing water requirements for a given workability of concrete. It has also been associated with increased air-entrainment dosages for a given air content of concrete (33, 277). Unfortunately, loss on ignition may not provide a reliable estimate of unburnt carbon due to the presence of salts which also volatize at ignition temperature (48).

A limit on available alkalies is provided as an optional chemical requirement for fly ash. If certain reactive aggregates are to be used in concrete, this requirement may be imposed to limit the alkalies which may be available for expansive alkali-silica reactions (48).

Dunstan (100), however, reported that some alkalies in fly ash may not increase the dangers of alkali-silica reaction. An example is sodium sulfate, which is often present because of its use as a precipitator agent. Also, partial replacement of cement with fly ash has been shown to decrease expansions related to alkali-silica reactions, even when total alkali contents of mortars were kept constant by additions of potassium sulfate (125).

Additonal reasons that users of fly ash may choose to limit alkali contents are noteworthy. Fly ashes containing high contents of both alkalies and sulfates tend to accelerate the setting and hardening characteristics of concrete. Also, fly ash with high alkali contents may increase the possibility for concrete efflorescence (277).

The suitability of the method for measuring alkalies in fly ash has been questioned. The alkali content measured is "available" alkalies, rather than total alkalies. The test, included in ASTM C-311, involves reacting a sample of the fly ash with calcium hydroxide and water for 28 days. The concentration of "available" alkalies is determined with flame photometry (220). Lee and others (220) have reported that, under ASTM C-311 test conditions, significant proportions of alkalies are released after 28 days. Also, Butler (52) has reported that the rate and amount of extraction of sodium and potassium ions increases as the mass ratio fly ash/$Ca(OH)_2$ decreases. Therefore, the available alkali test may not be equally severe for all fly ashes. Fly ashes which contain large proportions of calcium may change the effective fly ash/$Ca(OH)_2$ mass ratio during the test (220).

2.4.8.3 Physical Requirements

Requirements for fly ash fineness are specified by weight percentages retained on a 45 μm (#325) sieve, as shown in Table 2.20. High proportions of particles larger than 45 μm decrease fly ash reactivity and increase concrete mixture water requirements. Other options that are available for characterizing fly ash fineness, including particle size distribution and specific surface area, have been determined to be unsuitable. Measurements of particle size distributions are inappropriate for routine quality control because measurement techniques are complex and expensive equipment is required (277). Specific surface area measurements have been determined to be significantly influenced by fly ash carbon content (361).

Strength activity indices are attempts to ensure that fly ash does not significantly decrease concrete strength. Three options for testing are provided. Two options involve comparisons between the compressive strength of fly ash/portland cement mortars and the strength of cement mortars without fly ash. The third option involves testing fly ash/hydrated lime mortars for compliance with a specified strength.

The strength activity index utilizing lime is no longer an option for Class C fly ashes. It has been determined to be unsuitable for use with high-calcium ashes because of the unrealistically high fly ash/lime ratio of 2.0 (48). During the ASTM C-311 lime test, the reactivity of Class C fly ash is limited by this lime-deficient, silica-rich environment. Under these circumstances, low-lime hydrates are produced within the 7-day test duration. These low-lime hydrates yield lower strengths than the hydration products expected in fly ash cement concrete (154).

Fly ash/portland cement mortars for strength activity indices are proportioned to meet consistency requirements (277). Therefore, they are tested at different water/(cement+pozzolan) ratios. Since the workability of mortars is not directly related to the workability of concrete, strength activity indices have been found to not always reflect the strength that will develop in fly ash/portland cement concrete (17, 240). These indices

Table 2.20 ASTM C-618 Physical Requirements for Fly Ash to be Used as a Mineral Admixture in Portland Cement Concrete (17)

Physical Requirements	Mineral Admixture Class	
	F	C
Retained on 45 μm Sieve (#325) (max.%)	34	34
Strength Activity Index:		
with portland cement at 7 days (min.% of control)	75	75
with portland cement at 28 days (min.% of control)	75	75
with lime at 7 days (min. psi)	800	—
Water Requirement (max.% of control)	105	105
Autoclave Expansion or Contraction (max.%)	0.8	0.8
Uniformity Requirements: *		
specific gravity (max.% variation from average)	5	5
retained on 45 μm sieve (#325) (max.% variation)	5	5
Optional Physical Requirements **		
Multiple Factor (max.%) †	255	—
Increase in drying shrinkage of mortar bars at 28 days (max.%)	0.03	0.03
Uniformity Requirements: *		
air entraining agent (max.% variation from average)	20	20
Reactivity with Cement Alkalies:		
mortar expansion at 14 days (max.%)	0.020	0.020

* average is established by ten preceding tests, or by all preceding tests if the quantity is less than ten

** applicable only when specifically required by the purchaser

† calculated as the product of loss on ignition and amount retained on the #325 sieve (wet-sieve analysis)

should be viewed as fly ash acceptance requirements which represent mimimum acceptable performances.

The water requirements of fly ash/portland cement mortars are limited by a maximum percentage with respect to mortars containing portland cement alone. The water requirements are obtained from the strength activity tests. Mehta (277) has suggested that this specification may be overly restrictive. He suggested that an excessive water requirement can be mitigated by the use of a water-reducing agent and that the decision of whether or not to reject such a fly ash should be left to the user.

Maximum percentages of expansion are specified for fly ash/cement mixtures subjected to autoclaving conditions. The test method was originally developed for evaluations of soundness for portland cements, which show excessive expansion and cracking when large amounts of crystalline MgO (periclase) or free CaO are present (277). The necessity of the expensive autoclave test for fly ashes has been questioned. Class F fly ashes rarely contain any crystalline MgO (periclase) or free CaO (277). Lignite and subbituminous ashes, which often contain magnesium oxides, rarely contain these oxides in the form of periclase (240). In order to monitor the few subbituminous and lignite fly ashes which may contain significant amounts of crystalline CaO, a simple, less expensive test such as the Le Chatelier test may be appropriate (277, 361).

Fly ash physical requirements include limits concerning the uniformity of two physical properties: specific gravity and percent retained on the 45 μm sieve. These properties, as measured from each sample, shall not vary from the average of ten preceding samples by more than five percent. This specification protects fly ash users from source power plants which do not provide a reliable product.

An optional physical requirement for Class F ashes is the "Multiple Factor", which is the product of loss on ignition and fineness (percent retained on 45 μm sieve). A maximum of 255 percent is defined, in order to control the deleterious effects of both high carbon contents and high proportions of coarse particles (361).

Additional optional physical requirements include a limit for drying shrinkage of mortar bars, a uniformity requirement for the amount of air entraining agent required to achieve a specified air content in mortar, and a limit for mortar bar expansions during an alkali-aggregate test.

2.4.8.4 Test Frequency

In addition to specifying procedures for testing fly ash for conformance with ASTM C-618, ASTM C-311 specifies fly ash sampling techniques and test frequencies. Two levels of testing are specified: samples representing each 400 tons of fly ash produced and composite samples representing each 2000 tons of fly ash produced. Composite samples are prepared by combining equal parts of five consecutive samples, each representing 400 tons of fly ash (15).

Samples representing each 400 tons of fly ash are tested for fineness (percent retained on 45 μm sieve), moisture content, specific gravity, loss on ignition, and soundness. All chemical and physical tests are performed on the composite samples (15).

2.4.8.5 Texas Specifications

The Texas Department of Transportation (Texas DOT) provides their own fly ash specifications: Departmental Materials Specification D-9-8900. Although the test methods for determining chemical and physical properties of fly ashes are in accordance with ASTM procedures, the fly ash requirements are modified slightly from ASTM Specification C-618. The Texas specification classifies fly ashes as Types A and B, approximating ASTM Classes F and C, respectively. Also, Texas Specification D-9-8900 requirements for fly ash quality are generally more stringent:

1) chemical and physical requirements which are optional in the ASTM specification are mandatory in the Texas specification;
2) loss on ignition (LOI) may not exceed 3.0 percent;
3) retention on #325 sieve may not exceed 30 percent;
4) total MgO content may not exceed 5.0 percent; and
5) a uniformity requirement is included for calcium oxide content: calcium oxide content shall not deviate from the average of the previous 10 samples by more than 4.0 percent.

The Texas specification allows for MgO contents higher than 5.0 percent if the fly ash passes the autoclave expansion limit. This condition was included because MgO in fly ash is typically present in several nonreactive forms, including merwinite and melilite. The uniformity requirement for calcium content was included because of the significant effects of CaO on fly ash reactivity and cementitious characteristics.

Additional minor modifications include a reduction in maximum moisture content to 2.0 percent and a reduction in maximum water requirement to 100 percent.

2.5 BLENDED FLY ASH CEMENTS

2.5.1 PRODUCTION

There are three principal methods for producing fly ash cements (401):

1) mixing unground, unclassified fly ash with cement,
2) separate grinding or classifying of fly ash and subsequent mixing with cement, and
3) intergrinding fly ash with cement.

Fly ash cements in which fly ash is interground with portland cement clinker and gypsum are often referred to as blended cements. They have become the standard cements in Denmark and Norway (403, 151).

The typical system for grinding cements in Norway is shown in Figure 2.42 (401). The ball mill consists of two compartments. The first compartment contains steel balls with a maximum diameter of 90 mm. The second compartment, often referred to as the finishing compartment, contains steel balls with diameters of approximately 17 mm to 50 mm. After grinding, a mechanical air separator redirects coarse particles back to the ball mill (401). In addition to ensuring sufficient product fineness, the separator improves product uniformity; recirculating 1/5 to 1/3 of total mill load effectively dampens slight feed variations (29).

When intergrinding fly ash with portland cement clinker and gypsum, several options exist for the location of fly ash interjection, as shown in Figure 2.42 (401):

1) introduce fly ash into the first compartment of the ball mill (location "a"),
2) introduce fly ash into the finishing compartment (location "b"), and
3) introduce fly ash into the separator (location "c").

Introducing fly ash into the finishing compartment has been found to be the most desirable option; fly ash acts as a grinding aid for relatively small clinker particles (400). When fly ash is added to the first ball mill compartment, it dampens the comminution of large clinker lumps. Introducing fly ash into the separator causes a quality risk because hollow and porous particles tend to leave the separator with the finished cement particles (400).

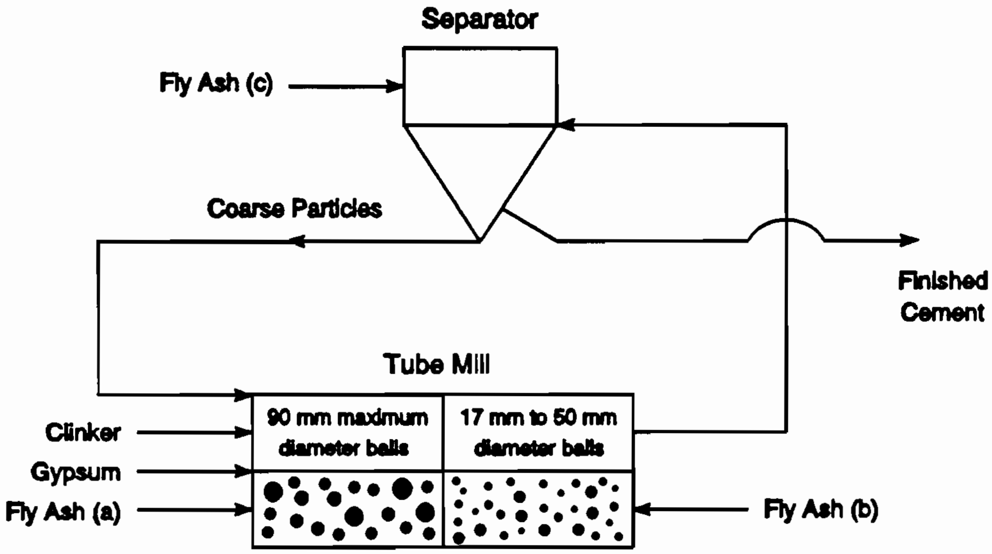


Figure 2.42 Three Methods for Producing Interground Fly Ash Cements (401)

2.5.2 COST EFFECTIVENESS

The portland cement production industry is among the top six energy consumers in the United States (267). Energy consumption accounts for approximately 40 percent of portland cement manufacturing costs. The most energy-efficient plants consume approximately 4.3×10^6 Btu of fossil fuel energy per ton of portland cement produced. However, many obsolete plants require approximately 7.4×10^6 Btu per ton of cement (267).

Decreased manufacturing costs are a principal incentive for the use of fly ash in cement production. Savings are accomplished through reduced kiln operations required per ton of product. Kiln operations account for most of cement manufacturing energy consumption (165).

Stoltenberg-Hansson (401) reported a case of cost savings when a Danish fly ash was utilized by a Norwegian cement company. The Class F fly ash replaced an ordinary portland cement at a level of 20 percent by weight. The fly ash was interground with cement clinker and gypsum to a Blaine fineness of 430 m^2/kg, which was finer than the ordinary portland cement (320 m^2/kg). The increased fineness enabled the blended cement to provide 3 and 7 day mortar strengths equal to those of the ordinary portland cement.

Energy consumptions per ton of product for the ordinary portland cement and the blended cement are shown in Figure 2.43. The use of fly ash decreased thermal energy consumption by 21 percent; thermal energy accounted for coal firing during cement kiln operations. The use of fly ash decreased electrical energy consumption (excluding grinding) by 21 percent; electrical energy accounted for electricity required for clinker cooling systems and kiln operations. The use of fly ash increased grinding costs by 23 percent as a result of the increased fineness of the blended cement. The transportation cost for the blended cement accounted for the costs of shipping the fly ash from power plant to cement plant. This cost included estimates for transportation by ship (0.1 kwh/ton-km), by road (0.5 kwh/ton-km), and by rail (0.15 kwh/ton-km). The total energy costs for the production of the blended cement was 17 percent less than the total energy costs for the production of the ordinary portland cement (401).

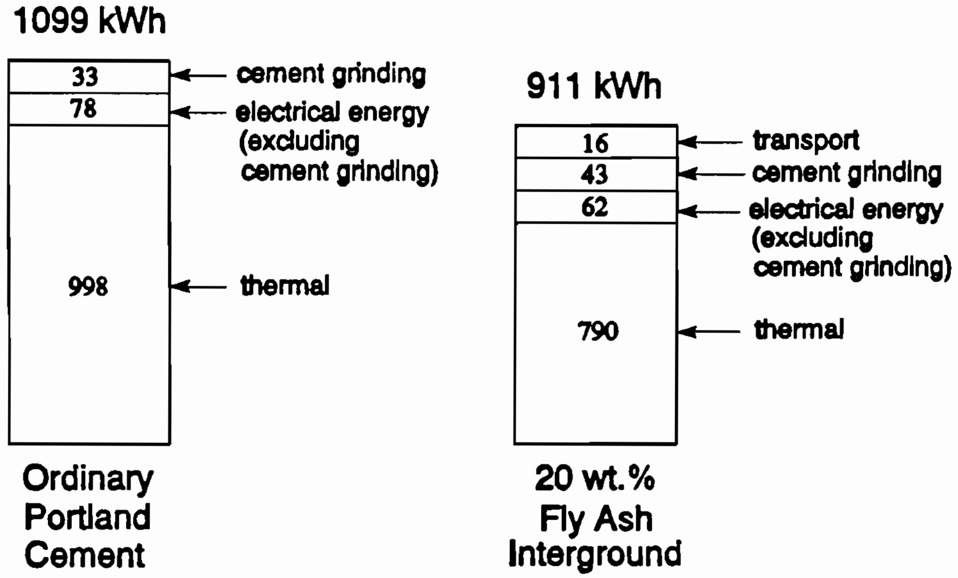


Figure 2.43 Thermal and Electrical Energy Consumption Per Ton of Cement (401)

2.5.3 EFFECTS OF GRINDING FLY ASH

Increasing the fineness of fly ash by grinding individually or by intergrinding with cement clinker and gypsum increases fly ash reactivity through morphological, chemical, and physical changes (29):

1) agglomerates are dispersed,
2) partially crystalline shells, which surround glass and restrict its ability to react, are crushed,
3) the glass itself is crushed, increasing available soluble silica and alumina, and
4) specific gravity is increased through the destruction of porous and/or hollow particles.

These effects of grinding fly ash have been confirmed with SEM photomicrographs (401).

A comparison between some physical characteristics of unground and ground fly ashes is shown in Table 2.21 (401). The five fly ash samples were obtained from various deliveries (3000 to 5000 tons) from the same source. Vigorous grinding decreased the proportions of coarse particles, as indicated by increases in percent passing the 32 μm sieve. Grinding crushed some porous and hollow particles, as indicated by increases in specific weights (401).

Intergrinding fly ash with clinker and gypsum, as opposed to adding fly ash at the time of batching concrete, provides two additional benefits for the quality of concrete (29).

1) intergrinding fly ash with cement clinker will result in a degree of homogeneity and proximity between fly ash and cement particles that cannot normally be achieved by mixing fly ash and cement at the time of batching concrete and
2) during production of blended cements, the quantity of added gypsum can be adjusted for an SO_3 content which optimizes cement performance.

While adding fly ash at the time of batching concrete, the SO_3 content can only by chance be at optimum.

2.5.4 QUALITY CONTROL

Fly ash quality is typically ensured with specifications on chemical composition, loss on ignition, pozzolanic activity, fineness, and residue on the 32 μm sieve (358). When Norwegian fly ash suppliers use coal of relatively consistent quality, modern boilers, and an advanced selection system, cement producers shift their quality control efforts toward the physical characteristics of fly ash. In these cases, quality is more easily ensured by monitoring specific weight, particle size distribution, and degree of agglomeration (401).

Grinding fly ash decreases variabilities in the physical properties which are considered significant in terms of quality control. Variations in specific weight are a frequent weakness in fly ash quality (401). Grinding can decrease the coefficient of variation of fly ash specific weights, as shown in Table 2.21.

Concern has been expressed that the compressive strengths of blended fly ash cements are more variable than those of ordinary portland cements. Bernshausen (29) compared 3-, 7-, and 28-day compressive strengths for an ordinary portland cement (OPC) and a blended cement containing the same clinker and 15 percent fly ash by weight, as shown in Table 2.22 (29). Compressive strengths up to 28 days were slightly lower for the blended cement, so within-month variabilities were compared by coefficients of variation (COV). Average variabilities of compressive strengths for concrete with the same curing durations are shown to be similar.

2.5.5 MORTAR AND CONCRETE PROPERTIES

Dhir and others (82) studied the effects of grinding fly ash on the workability and compressive strength of concrete. They added four fly ashes, each from a different source, to concrete which contained ordinary portland cement. The fly ashes differed in their coarse particle contents; retention on the 45 μm sieve ranged from 5.2 percent to 25.7 percent by weight. All fly ash concretes contained 300 kg/m^3 of cement and 130 kg/m^3 of fly ash. Mixture design water contents were fixed, so measured concrete slumps provided comparisons of workability. Each fly ash was added to two concrete mixtures: once in its original state and once after being ground separately to a fineness of less than one percent retention on the 45 μm sieve.

Table 2.21 Physical Characteristics of Unground and Ground Fly Ash (401)

Shipment Number	Unground		Ground	
	Specific Weight (gm/cm^3)	Passing 32 μm Sieve (%)	Specific Weight (gm/cm^3)	Passing 32 μm Sieve (%)
1	2.11	69.3	2.40	96.2
6	2.19	69.2	2.43	89.4
3	2.24	70.0	2.52	91.6
4	2.25	76.4	2.51	91.4
2	2.26	68.6	2.46	90.1
5	2.28	63.1	2.53	82.2
Average	2.22	69.4	2.48	90.2
Standard Deviation	0.05	4.24	0.04	4.56
Coefficient of Variation (%)	2.37	6.10	1.82	5.06

Comparisons of concrete slumps and compressive strengths are shown in Table 2.23. As the proportion of coarse particles in fly ashes increased, workability (as measured by slump) and compressive strength decreased. After grinding fly ashes to a constant fineness, the concrete workabilities and compressive strengths were very similar. Improvements due to grinding were largest for the fly ashes with high proportions of coarse particles (82).

Increases in concrete strength due to grinding of fly ash has been attributed more to decreased air content than to increased fly ash surface area or pozzolanic activity (315). Air content decreases with grinding as a result of the crushing of hollow and porous particles.

Giergiezny and Werynska (128) studied the effects of grinding fly ash on mortar properties. A low-calcium and a high-calcium fly ash were each ground in a ball mill to three

Table 2.22 Concrete Compressive Strength and Coefficient of Variation for Strength for a Blended Cement and an Ordinary Portland Cement (29)

Type of Cement	Month	Concrete Compressive Strength (MPa) *			Compressive Strength Coefficient of Variation (%) **		
		3 days	7 days	28 days	3 days	7 days	28 days
Blended Cement, 15% Fly Ash	May	21.7	29.3	40.9	4.15	3.41	3.18
	June	21.5	29.8	41.0	4.65	3.02	3.41
	July	20.3	28.4	39.6	4.93	3.17	2.02
	Aug.	20.6	28.0	38.3	5.83	6.07	6.01
	Sept.	20.3	27.7	38.6	4.93	3.97	3.11
	Oct.	19.4	27.5	39.1	3.61	3.64	3.58
	Nov.	19.8	27.7	39.0	3.54	3.61	3.33
	Dec.	18.2	26.5	39.3	4.40	3.40	2.80
Average †		20.2	28.1	39.5	4.50	3.79	3.43
Ordinary Portland Cement	May	27.4	37.2	45.9	5.11	3.76	3.49
	June	26.2	36.2	45.3	4.96	4.14	2.87
	July	25.0	35.7	45.6	5.20	3.36	3.95
	Aug.	25.7	35.1	45.4	6.61	5.41	3.52
	Sept.	25.6	34.4	45.0	3.91	2.91	3.33
	Oct.	24.9	34.3	44.7	3.61	3.50	3.58
	Nov.	25.5	34.9	45.7	4.71	4.87	4.16
	Dec.	23.7	34.1	46.4	6.75	4.11	3.66
Average		25.5	35.2	45.5	5.11	4.01	3.57

* monthly averages
** within-month test data
† average of eight months

levels of fineness. After grinding, the fly ashes were mixed thoroughly with cements, replacing 30 percent by weight of cement. Mortars were mixed with a fixed water/(cement+pozzolan) ratio of 0.5 (128).

Table 2.23 Effect of Grinding Fly Ash on Concrete Workability and Compressive Strength (82)

Fly Ash Concrete Mixture *	Retained 45 µm Sieve (%)	Slump (mm)	Compressive Strength (MPa)			
			7 days	28 days	6 months	18 months
#1 orig.	5.2	120	29.5	46.5	73.0	79.5
#1 ground	< 1	125	31.0	47.5	74.5	82.0
Increase	—	5	1.5	1.0	1.5	2.5
#2 orig.	5.4	100	30.0	47.5	72.0	78.0
#2 ground	< 1	110	31.0	51.5	75.5	82.5
Increase	—	10	1.0	4.0	3.5	4.5
#3 orig.	17.0	90	30.5	44.5	69.5	75.5
#3 ground	< 1	120	32.0	47.5	72.0	80.0
Increase	—	30	1.5	3.0	2.5	4.5
#4 orig.	25.7	45	29.0	45.5	61.0	70.0
#4 ground	< 1	100	30.5	50.0	71.5	81.0
Increase	—	55	1.5	4.5	10.5	11.0

* fly ash source number and condition (original or ground)

Specific gravities and specific surfaces (Blaine fineness) of unground and ground fly ashes are shown in Table 2.24. For both fly ashes, specific gravity and fineness both increased with increasing grinding times (128).

Table 2.24 Physical Properties of Fly Ash With Various Durations of Grinding (128)

Type of Fly Ash	Grinding Duration (min)	Specific Gravity (gm/cm^3)	Specific Surface * (m^2/kg)
Low Calcium	0	2.03	295
	15	2.27	388
	30	2.38	543
	60	2.56	640
High Calcium	0	2.29	233
	15	2.32	464
	30	2.38	559
	60	2.44	744

* Blaine air-permeability

The highest compressive strengths for moist-cured mortars containing low-calcium and high-calcium fly ash were obtained when fly ashes were ground for 30 minutes, as shown in Figures 2.44 and 2.45, respectively. Blaine finenesses for this low-calcium ash and this high-calcium ash were 543 m^2/kg and 559 m^2/kg, respectively. At optimum fineness, the mortar containing the high-calcium ash exhibited strengths comparable to the control mixture without fly ash at all ages and the mortar containing the low-calcium ash exhibited a strength comparable to the control mixture without fly ash only at 90 days. The 7-day and 28-day strengths of the low-calcium fly ash mortar were 32 percent and 23 percent lower than the control mixture strength, respectively (128).

Schiebl and Hardtl (368) performed workability and compressive strength tests on mortars in order to study the effects of fly ash particle size and particle shape. Granulometric properties of the cement and the two Class F fly ashes, in "as received" condition, are shown in Table 2.25. The two fly ashes were chosen because they had different granulometric properties but similar bulk chemical compositions. A sample of

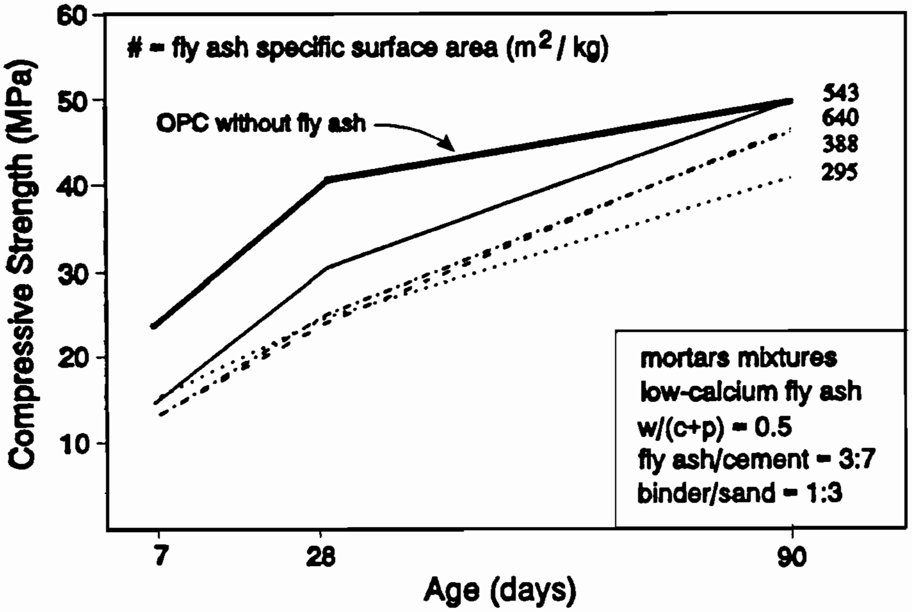


Figure 2.44 Development of Compressive Strength for Mortar Containing Low-Calcium Fly Ash in Both Unground and Ground Conditions (128)

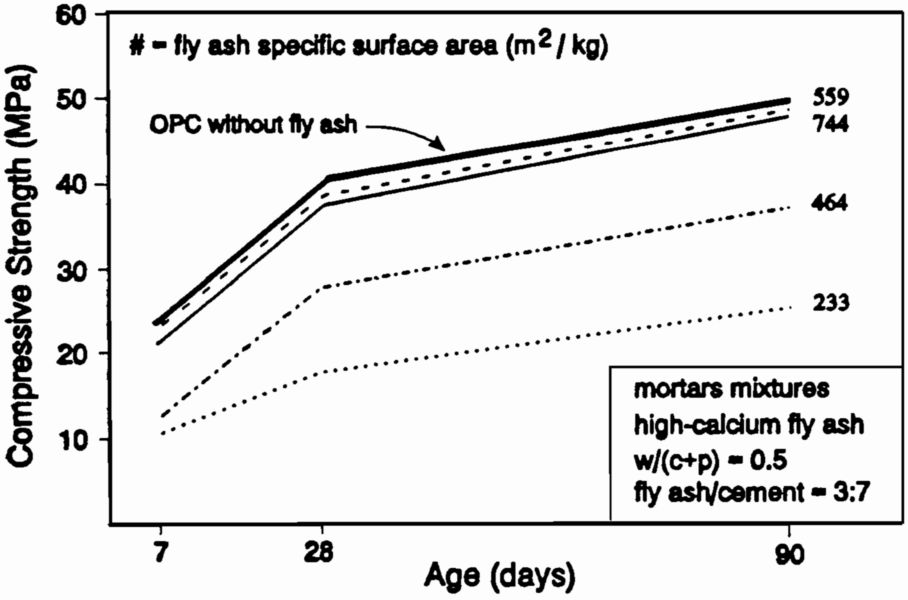


Figure 2.45 Development of Compressive Strength for Mortar Containing High-Calcium Fly Ash in Both Unground and Ground Conditions (128)

fly ash number 1, which was the coarsest ash, was ground thoroughly. Similar particle size distributions to the ground ash were then obtained from each of the two original fly ash samples through classification and remixing procedures. These classified ashes are labelled "selected" in Table 2.25 and in following figures. The cement was partially replaced by fly ash at levels of 20, 40 and 60 percent by volume. Weight of water in mixture designs was kept constant. The workability of mortars was measured by mortar spread on a flow table and compressive strength was measured by mortar cube tests.

Table 2.25 Physical Characteristics of Original Fly Ash, Ground Fly Ash, and Classified Fly Ash (368)

Material	Density (gm/cm^3)	d_{50} * (μm)	Particles Passing (wt.%)				
			5 μm	10 μm	20 μm	40 μm	90 μm
Cement	3.10	17.8	18.2	33.6	54.1	78.8	96.2
Fly Ash #1 (as received)	2.32	14.7	15.9	36.4	60.2	82.1	94.4
Fly Ash #2 (as received)	2.38	10.2	28.3	49.3	70.6	87.4	95.0
Fly Ash #1 (ground)	2.67	8.3	33.2	55.7	76.7	94.1	100
Fly Ash #1 (selected)	2.39	8.8	35.7	55.2	77.2	95.7	100
Fly Ash #2 (selected)	2.48	7.6	37.9	58.7	79.0	94.9	100

* median particle diameter

The relative spreads of mortar mixtures on the flow table increased with increasing fineness of fly ash and with increasing volume percentage of fly ash, as shown in Figure 2.46. Mixtures containing ground fly ash number 1 exhibited higher flow values than mixtures containing unground fly ash number 1. However, the mixture containing ground fly ash number 1 (fly ash/cement = 0.4) did not flow as easily as similar mixtures containing classified samples of ashes 1 and 2, even though all the fly ash particle size distributions were similar. This was attributed to the changes in particle shapes for fly ash number 1 during grinding procedures; scanning electron photomicrographs revealed splintered and shell-shaped particles (368).

Compressive strengths of mortars containing fly ash at a cement replacement of 40 percent by volume, are shown in Figure 2.47. Grinding fly ash number 1 increased the compressive strength of mortar at all ages, relative to the mortar containing an unground sample. Increases in two-day and seven-day strengths, as a result of grinding fly ash, were attributed to a physical filler effect in the hardening cement paste structure. The physical filler effect includes densification (filling of voids) of the aggregate-cement-additive system. This was verified by partially replacing cement with inert quartz which was ground to the same fineness as the ground fly ash; similar two and seven day strengths were obtained. Increases in strengths after 28 days, as a result of grinding, were at least partially attributable to the increased fly ash surface area which was available for reactions (368).

Mortars containing classified ashes 1 and 2 attained similar long-term compressive strengths as the mortar containing ground fly ash 1. Strengths at 7 days and 28 days, however, were highest for the mortar containing ground fly ash 1. This effect was attributed to a chemical phenomenon without further explanation.

Bissat (36) compared the permeabilities of concretes in which fly ash was interground with cement clinker with those in which fly ash was added as a mineral admixture at the time of batching. A Class F fly ash partially replaced a Type I cement at levels of 20, 25, 30, and 35 percent by weight. Concrete slump remained constant at 4 to 6 inches. Permeabilities were measured according to procedures of AASHTO T-277, which is a rapid chloride ion test. Permeabilities were compared on the basis of total electric charge passed (coulombs). Intergrinding the fly ash reduced permeabilities by up to more than 50 percent, as shown in Figure 2.48.

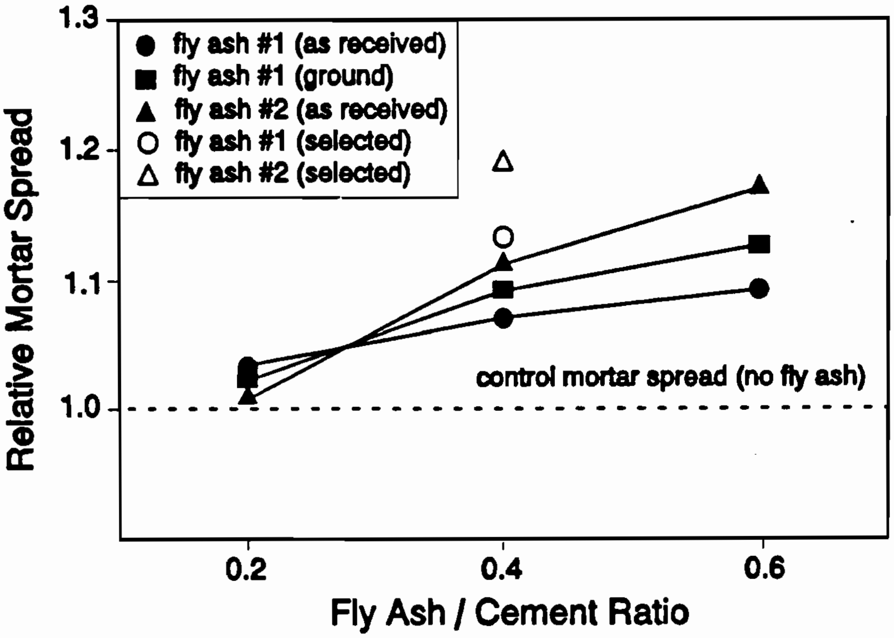


Figure 2.46 Relative Flow Table Spreads of Mortar Containing Original Fly Ash, Ground Fly Ash, and Classified Fly Ash (368)

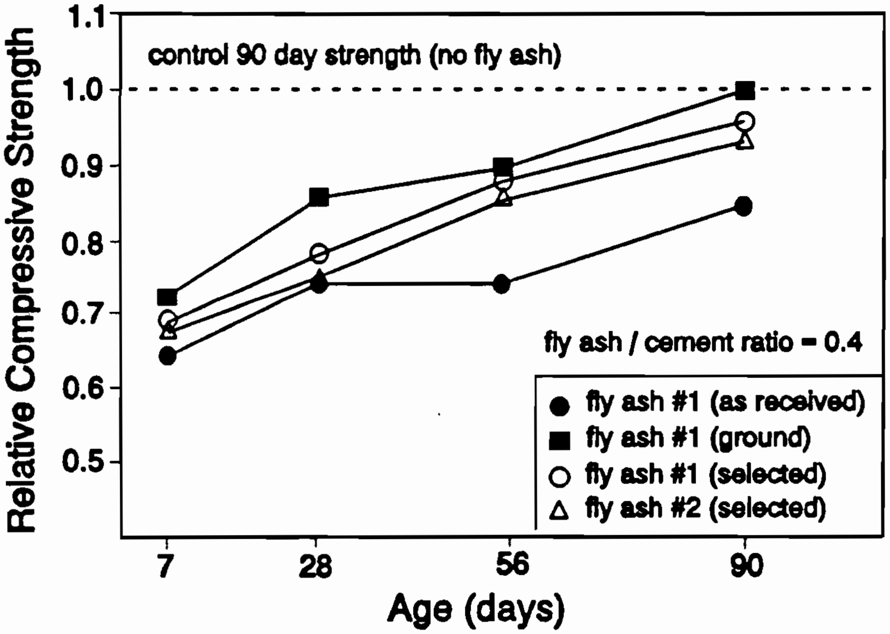


Figure 2.47 Relative Compressive Strength of Mortars Containing Original Fly Ash, Ground Fly Ash, and Classified Fly Ash (368)

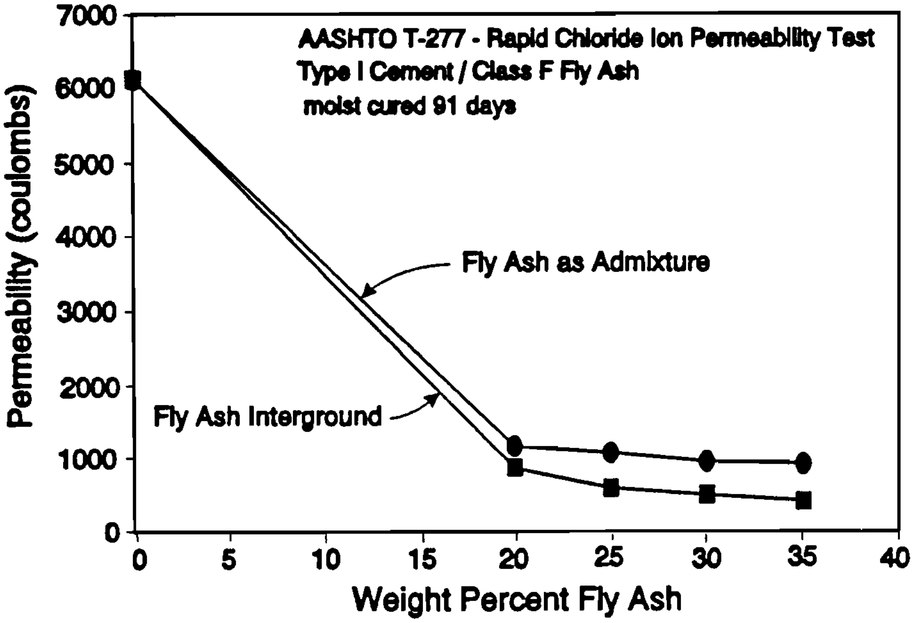


Figure 2.48 Rapid Chloride Ion Permeabilities of Concrete Containing Fly Ash as a Mineral Admixture and Fly Ash Interground (36)

2.5.6 SPECIFICATIONS

Fly ash to be used in blended cements (interground with cement clinker and gypsum) must meet the requirements specified in ASTM C-595, "Standard Specification for Blended Hydraulic Cements." Blended cements, as defined by ASTM C-595, consist of intimate and uniform blends of portland cement and pozzolan. Blended cement may be produced either by intergrinding portland cement clinker and pozzolan, by thoroughly mixing portland cement and finely divided pozzolan, or by a combination of intergrinding and mixing.

Fly ash requirements include fineness (percent retained #325 sieve), alkali reactivity, and strength activity, as shown in Table 2.26. Prior to testing for conformance to these requirements, fly ash shall be ground in the laboratory to a fineness at which it is believed to be present in the finished blended cement. Alkali reactivity tests are performed in accordance with ASTM C-227 test procedures and are performed at cement replacement levels of 2.5, 5.0, 7.5, 10.0, 12.5, and 15.0 percent by weight (16).

Standard Specification ASTM C-595 also includes definitions for types of blended cements and chemical and physical requirements for final blended cement products.

Table 2.26 Requirements for Pozzolan for Use in Blended Cements (16)

Fineness: retained on 45 µm (#325) sieve (max.%)	20.0
Alkali Reactivity *: mortar bar expansion at 91 days (max.%)	0.05
Activity Index: with portland cement at 28 days (min.%)	75

* required for pozzolans to be used in Types I(PM) and I(PM)-A cements

2.6 ALKALI-ACTIVATED CEMENTS

2.6.1 INTRODUCTION

Increasing fuel costs required for the production of conventional cement and increasing availability of aluminosilicate dusts and ashes from air pollution control equipment make alkali-activated aluminosilicate binders economically attractive (237). Alkali-activated aluminosilicate binders are formed by reacting fine-grained silica- and alumina-rich solids with a solution of alkali or alkali salts to produce a series of cementitious gels and crystalline compounds (237). Blast furnace slags are the most widely used material for the production of alkali-activated binders, but clays (both natural and fired), furnace dust, and industrial ash have also been shown to be potentially reactive fine-grained aluminosilicates (237).

During the hardening process of alkali-activated binders, the role of the alkaline component is basically to create high pH conditions under which the anhydrous slag can hydrate to form low-basic calcium silicates (413). While a pH of 12.6 is typical of portland cement due to the presence of calcium hydroxide, pH in alkali-activated slag (AAS) systems typically exceed 13.5. The high concentration of OH^- ions disintegrates the vitreous slag, releasing silicate and aluminate ions into solution (414). The predominant hydration products are calcium silicate hydrates and calcium aluminate hydrates (237, 340).

2.6.2 DISSOLUTION OF GLASS

2.6.2.1 Solubilities of Silica and Alumina

The reaction rate between slags (or fly ash) and $Ca(OH)_2$ has been reported to be limited by the dissolution rate of silica from slags (or fly ash) (185, 186, 323). The overall mechanism may be represented by a sequence of reactions (323):

$$Ca(OH)_2\ (s) \leftrightarrow Ca^{2+} + 2OH^- \qquad \text{(fast)}$$

$$\text{FlyAsh (s)} \leftrightarrow \text{silica (aq)} \qquad \text{(slow)}$$

$$Ca^{2+} + \text{silica (aq)} \leftrightarrow \text{calcium silicates} \qquad \text{(fast)}$$

Silica dissolves in water according to the following hydration reaction, which forms monosilicic acid (169, 323):

$$SiO_2 + 2H_2O \rightarrow Si(OH)_4 .$$

Silica is most soluble when present in its vitreous (glassy) or amorphous (colloidal) state. Stöber (399) and Kopeikin et al. (203) investigated the solubilities of several modifications of silica in water. Solubilities reported from the two sources were slightly different due to variable testing conditions, however, reported trends were similar: solubility decreased with increased crystallinity, as shown in Table 2.27.

Table 2.27 Solubilities of Various Modifications of Silica (203, 399)

Modification	Limiting Silica Concentration (ppm)	
	Stöber	Kopeikin et al.
Amorphous (colloid)	not reported	120
Vitreous (glass)	39	88
Cristobalite	6	12
Tridymite	4.5	16
Quartz	2.9	7

Iler (169) reported that the mechanism of dissolution of silica in water involves a catalytic depolymerization through hydrolysis. The "catalyst" is a material which can be chemisorbed to glass surfaces. Chemisorption increases the coordination number of silicon atoms to more than four, thus weakening the underlying oxygen bonds. Iler proposed that hydroxide ions may act as catalysts, as shown in Figure 2.49 (169, 323).

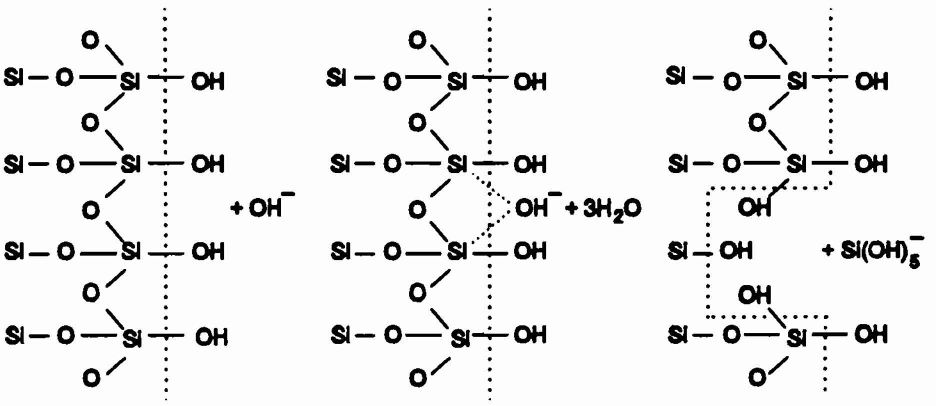


Figure 2.49 Mechanism for the Dissolution of Silica in the Presence of Hydroxyl Ions (169, 323)

The solubility of amorphous silica increases with temperature and pH of solution, as shown in Figure 2.50 (134). Solution pH increases solubility by causing the conversion of monosilicic acid to an ionic species (169, 323):

$$\mathrm{Si(OH)_4 + OH^- \rightarrow Si(OH)_5^-}.$$

The consumption of monosilicic acid permits the dissolution of additional silica (169, 323).

Aluminum, which is another major constituent of fly ash, can react with calcium hydroxide to form calcium-aluminate compounds. Peterson (323) reported that in comparison to research on the solubility of silica, much less work has been published on the reactivity of aluminum in aqueous, alkaline solutions. However, it is well known that aluminum is readily soluble at both very high pH and very low pH. Aluminum exists as $\mathrm{Al(OH)_4^-}$ and $\mathrm{Al^{3+}}$ at the two conditions of pH, respectively (323).

The presence of aluminum in an amorphous silica system is known to reduce the rate of dissolution of silica and to reduce the solubility of silica at equilibrium. Iler (168) reported that occupation by aluminum of only five percent of the silica surface was sufficient for drastic reductions in solubility. The addition of silica to a suspension of alumina is also known to depress the solubility of alumina. Iler (169) theorized that a surface layer containing both SiO_2 and Al_2O_3 forms and that the solubility of the surface layer is lower than either individual oxide.

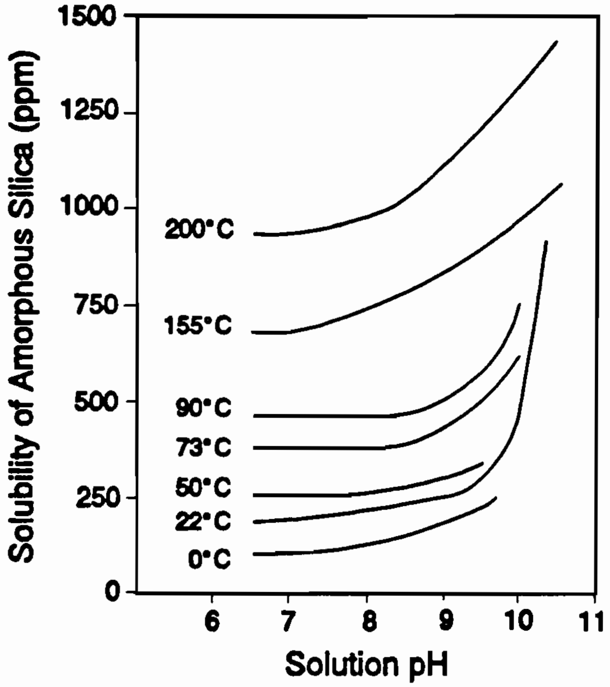


Figure 2.50 Effect of Solution pH and Temperature on the Solubility of Amorphous Silica in Water (134)

2.6.2.2 Glassy Component of Fly Ash

The mechanism for the dissolution of fly ash is probably similar to the mechanism by which pure silica dissolves. However, the siliceous glass in fly ash is impure: silicon atoms are partially substituted by aluminum (and other metals) and the glass network is further modified by small cations.

Peterson (323) studied the effects of hydroxide concentration and temperature on the dissolution of fly ash. Ten types of fly ash were studied, with total CaO contents ranging from 2 percent to 34 percent. Experiments were performed in NaOH solutions in a temperature controlled, 500 ml, stainless steel autoclave. Sodium hydroxide concentrations ranged from 0.0 to 0.5 molarity and slurry temperatures ranged from 25 to 90 ± 1.0 °C.

Slurries included 500 mg of fly ash, 400 ml of distilled water, and 2.0 gm of Na_2EDTA. The EDTA (ethylene-diamene-tetraacetate) was included to complex the calcium that dissolved from the fly ash, thus preventing the precipitation of calcium silicate diffusion barriers. The NaOH concentrations were adjusted with 5 normality NaOH solution prior to the additions of fly ash. Solutions were stirred at 1000 rpm for up to 24 hours as the fly ash dissolved (323). Dissolution was monitored by measuring silicon and aluminum metal ion concentrations in solution.

The rate of dissolution of fly ash was found to be strongly dependent on NaOH concentration. Dissolved silica increased with time and with solution NaOH concentration for both low- and high-calcium fly ashes, as shown in Figure 2.51 and 2.52, respectively. The dissolution of aluminum from fly ashes also increased with solution NaOH concentration, but the effects were less substantial.

Initial rates of dissolution of both silica and alumina were found to be strongly dependent on fly ash calcium content, as shown in Figures 2.53 and 2.54, respectively. In a 0.1 molarity NaOH solution, an average of approximately 25 percent of the high-calcium fly ash silica contents dissolved instantly, while an average of only 10 percent of the low-calcium fly ash silica contents dissolved instantly. In the same solution concentration, an average of 50 percent of high-calcium fly ash alumina contents dissolved instantly, while an average of only 15 percent of the low-calcium fly ash alumina contents dissolved instantly. After the initial period of rapid dissolution, the high- and low-calcium fly ashes dissolved at similar rates (323).

The reactive nature of high-calcium fly ashes, relative to low-calcium fly ashes, has been attributed to differences in the structures of glass components (280, 323). High calcium fly ash glass contains larger proportions of cation modifiers (Ca^{2+}, Na^+, and K^+), which break the aluminosilicate chains into shorter, more reactive units (88, 156).

Both silica and alumina dissolved more rapidly as slurry temperatures increased from 25 °C to 90 °C, which is in agreement with Iler's results for pure amorphous silica (Figure 2.50).

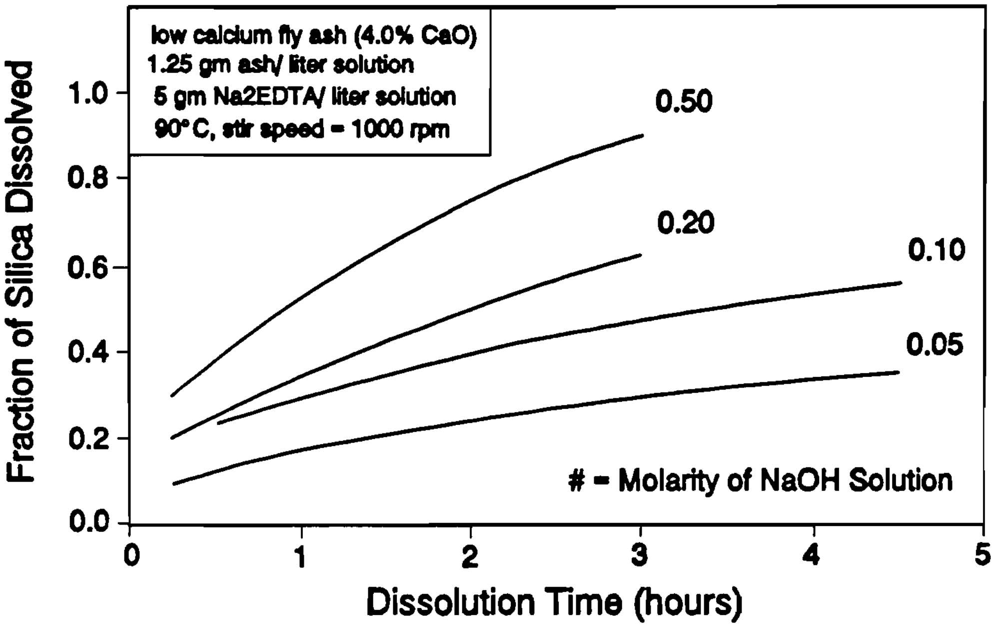


Figure 2.51 Effect of NaOH on the Dissolution of Silica from Low-Calcium Fly Ash (323)

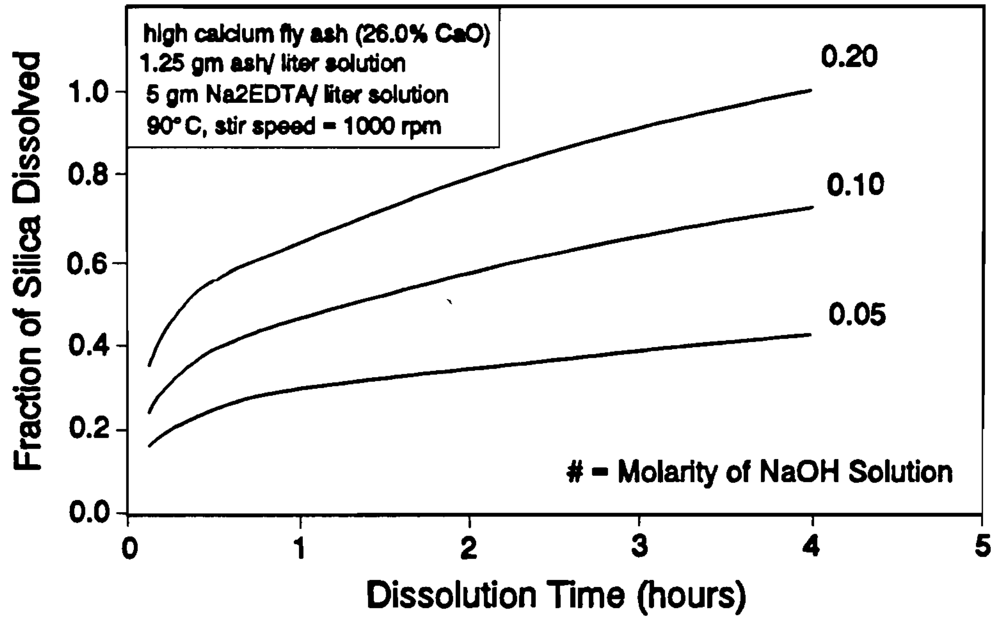


Figure 2.52 Effect of NaOH on the Dissolution of Silica from High-Calcium Fly Ash

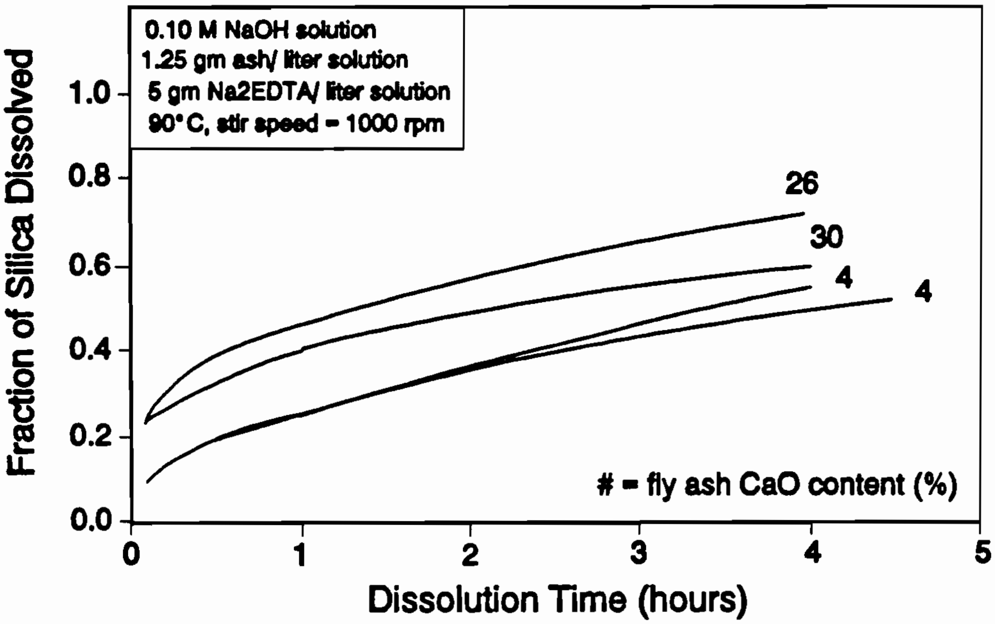


Figure 2.53 Effect of Fly Ash Calcium Oxide Content on the Dissolution of Silica from the Fly Ash (323)

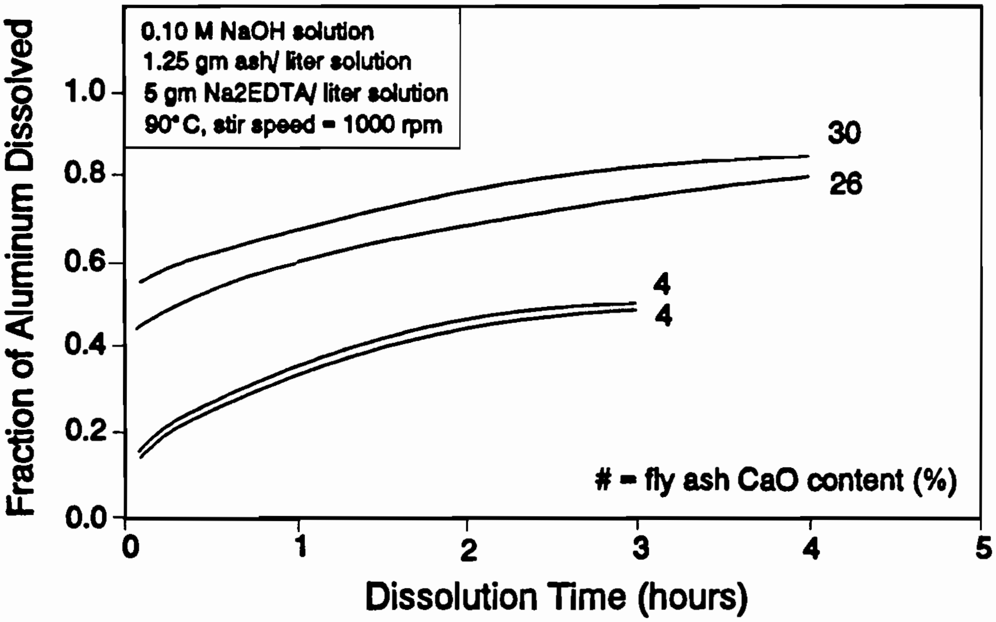


Figure 2.54 Effect of Fly Ash Calcium Oxide Content on the Dissolution of Aluminum from the Fly Ash (323)

Peterson (323) also studied the effects of fly ash fineness on the rate of dissolution. Fineness of a single fly ash was increased by grinding from 1.8 m^2/g to 25.6 m^2/g, as measured by specific surface area. Silica dissolved more rapidly as fly ash fineness increased, but the rate of dissolution of aluminum was not a function of the initial surface area of fly ash. Petersen (323) explained these different behaviors with the help of a fly ash glass model proposed by Hemmings and Berry (156). When aluminum is substituted into the polymeric silica network, the network is broken into silica chains which are occupied at their ends by aluminum atoms. The aluminum atoms are therefore exposed to potential hydroxide attack, even in unground fly ash. The grinding process may increase the exposure of silica more than it increases the exposure of aluminum (323).

2.6.3 FLY ASH/PORTLAND CEMENT

Fraay et al. (123) studied various alkali-activated fly ash-portland cement mixtures for use as stabilization mixtures in road construction. Mixtures included Class F fly ashes from five sources and five concentrations of NaOH, which was dissolved in the mixing water. Mixing water consisted of NaOH solutions of concentrations 0, 0.1, 1.0, 2.5, and 5.0 percent. Mixture proportions included 100 parts fly ash, 6 parts portland cement, and enough mixing water to achieve a desired paste consistency.

Compressive strengths of cylindrical paste specimens at 28 days and pore water pH at 40 days are shown in Table 2.28. The 2.5 percent NaOH mixing solution resulted in the highest compressive strengths for mixtures containing fly ashes from sources 1, 3, 4, and 5. For the mixture containing fly ash from source 2, the 5.0 percent NaOH mixing solution produced the highest strength. Relative to the other fly ash mixtures, the mixture with fly ash 2 required least mixing water (NaOH solution) for the desired paste consistency. Therefore, the total proportion of NaOH in the mixture containing fly ash 2 was not significantly different than the total proportions of NaOH in the other fly ash cement mixtures.

Pore water pH was measured by microtitration of solutions which were squeezed out of hardened specimens. Pore water pH increased with mixing water NaOH concentration. Mixtures which obtained optimum 28-day compressive strengths had 40-day pore water pH ranging from approximately 13.0 to 13.3.

Table 2.28 Effect of Sodium Hydroxide on Compressive Strength and Pore Water pH of Fly Ash Cement Pastes (123)

Fly Ash	Physical Parameters	Concentration of NaOH in Mixing Water (wt.%)				
		0.0	0.1	1.0	2.5	5.0
1	Mixing Water (%) *	16				
	Compr. Strength at 28 days (MPa)	4.4	4.7	4.9	6.1	7.3
	pH **	12.85	12.90	13.00	12.95	†
2	Mixing Water (%) *	20				
	Compr. Strength at 28 days (MPa)	3.2	3.5	4.7	5.5	5.0
	pH **	12.80	12.80	12.90	13.20	13.50
3	Mixing Water (%) *	22				
	Compr. Strength at 28 days (MPa)	3.7	4.1	5.3	5.7	5.1
	pH **	12.80	12.80	12.90	13.15	13.45
4	Mixing Water (%) *	24				
	Compr. Strength at 28 days (MPa)	3.0	2.9	4.3	4.8	4.2
	pH **	12.25	12.35	12.60	12.95	13.50
5	Mixing Water (%) *	30				
	Compr. Strength at 28 days (MPa)	1.3	1.5	3.4	4.6	2.8
	pH **	12.75	12.80	12.90	13.25	13.60

* percent by weight

** pH determined from OH^- concentration (titration)

† a sufficient amount of pore water could not be collected

2.6.4 BLAST FURNACE SLAG

2.6.4.1 Introduction

Blast furnace slag is the most widely used material in alkali-activated binders. Slag, which is a by-product obtained in the manufacture of pig-iron, is formed by the combination of the earthy constituents of iron ore and a limestone flux. Granulated blast furnace slag is obtained by rapid chilling of the basic (high-lime) slag as it emerges from the blast furnace. Granulated slag is a light, porous, and friable product (218).

The extent to which slag is used in cements varies between countries; it is particularly well developed in western Europe. There exist several methods for its use (218):

1) as a raw material for the manufacture of portland cement,
2) interground with portland cement clinker, and
3) interground with a small proportion of anhydrite and an even smaller proportion of cement or lime (supersulfated cements).

The compositions of slags vary over a wide range, depending on the type of iron being made and on the compositions of the iron ore and limestone flux (218). Slag typically contains oxides of lime, silica, alumina, magnesia, sulfur, iron, and manganese in proportions shown in Table 2.29 (218).

2.6.4.2 Criteria for Slags

Granulated slags to be used as cementitious components, typically are required to meet the following chemical composition criteria:

1) a CaO/SiO_2 ratio between 0.5 and 2.0 and
2) an Al_2O_3/SiO_2 ratio between 0.1 and 0.6.

If alkaline activators are used, basic (high lime) slags are the most hydraulically active. If sulfate activators are used, slags with high lime contents and at least moderate alumina contents are desireable (218). Slags with low Fe_2O_3 contents are preferred because iron tends to decrease the reactivity of slags (414).

Slags which contain high proportions of glass and which are finely ground are also desireable because these characteristics contribute to high reactivity. Crystalline slags must be ground to a fineness of approximately 5000 cm^2/g to be useful (237).

Table 2.29 Range of Compositions of Typical Blast-Furnace Slag (218)

Oxide	Typical Proportion (%)
Lime	30 - 50
Silica	28 - 38
Alumina	8 - 24
Magnesia	1 - 18
Sulfur	1 - 2.5
Ferrous and Manganese	1 - 3.0

German standards specify that slags to be ground with portland cement must meet the following requirement for proportions of oxides (218):

$$\frac{CaO + MgO + Al_2O_3}{SiO_2} \geq 1.6 \,. \tag{2.12}$$

2.6.4.3 Types of Activators

Ground blast furnace slag can be slightly hydraulic, but without an activator the development of strength is extremely slow (197). The most widely used slag activator is portland cement. Other traditional activators include lime, calcium sulfate, calcium chloride, and phosphogypsum (414). Recent attention has been directed towards slag activation with sodium and potassium compounds. Sodium or potassium hydroxides, sodium carbonate, sodium or potassium sulfates, and sodium chloride are more soluble than corresponding calcium compounds (414).

Metso and Kajaus (288) compared the effects of various activators in blast furnace slag mortars. Based on visual assessment, demoulding characteristics, and compressive strength, the following rankings of activators:

1) very good: portland cement, NaOH, and (Na_2CO_3 + NaOH);
2) good: (phosphogypsum + NaOH), (cement + NaOH), and (fly ash + NaOH);
3) moderate: $Ca(OH)_2$ and (gypsum + NaOH); and
4) poor: fly ash, Na_2CO_3, gypsum, phosphogypsum, and $CaCl_2$.

Tashiro and Yoshimoto (417) compared various alkali activators for their effects on the rate at which blast furnace slag in slag cement hydrated. Quantitative determination of the degree of reaction of slag was performed by the salicylic acid-methanol solution method. The degrees of reaction measured on 3- and 28-day pastes are shown in Table 2.30. The ranking of accelerating effects on slag after 3 days of hydration, in decreasing order, were NaCl, NaOH, Na_2CO_3, and Na_2SO_4. After 28 days of hydration, NaCl accelerated the rate of reaction of slag, NaOH and Na_2CO_3 had net negligible effects, and Na_2SO_4 had a net retarding effect. The authors theorized that the effects of Na_2SO_4 on reaction rates may have been influenced by aluminum components dissolved from slag and calcium aluminates from cement. The formation of sulfoaluminate compounds may have increased early strengths but impeded ionic mobility at later ages.

2.6.4.4 Reaction Products

The first reaction products in alkali-activated slag binders are weakly crystalline calcium hydrosilicates of the tobermorite group. The general formula for tobermorite is $Ca_{10}(Si_{12}O_{31})(OH)_6 \cdot 8H_2O$, but these phases may also contain alumina and magnesia in solid solution. While tobermorites continue to form, hyrogarnets (or calcium aluminosilicate hydrates) of approximate composition $3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, begin to crystallize. Later reaction products include sodium zeolites and the tobermorite mineral, foshagite ($Ca_8(Si_6O_{17})(OH_6)$) (135, 237).

Variabilities in reported reaction products during the hardening of alkali-activated binders are primarily related to variabilities in the reacting materials; slag, fly ash, ground rock, and other materials can be used as the source of silica and alumina and a variety of alkaline solutions (or salts) can be used to produce the hardening reactions. For example, formation of zeolites is not favored in slags containing relatively small proportions of aluminum and/or relatively large proportions of calcium. Aluminum is a necessary structural component in most zeolite minerals and high calcium contents favor the formation of tobermorites over zeolites (237).

Table 2.30 Comparison of Alkali Activators Based on Degree of Reaction (417)

Additive	Degree of Reaction of Slag (%)	
	3 days	28 days
no addition	19.1	28.1
NaF	22.5	24.2
NaCl	32.6	38.2
NaBr	29.7	33.6
NaI	25.3	32.4
NaOH	26.0	27.8
Na_2CO_3	22.7	27.2
Na_2SO_4	21.7	22.9

Schröder (380) reported additional hydration products for mixtures containing slag and portland cement. The presence of sulfates promoted formations of mono- and tri-calcium sulfoaluminates, with partial substitutions of iron for aluminum. Calcium hydroxide was present in proportions which varied with the portland cement/slag ratio. Mixtures which contained low proportions of portland cement did not contain calcium hydroxide at later stages of hydration (204).

Examination of a hydrated alkali-activated slag matrix by optic microscopy has revealed no large crystalline structures. Analysis of the same matrix by X-ray diffraction revealed mainly calcium silicate hydrates and calcium aluminate hydrates with short-range ordering (413).

High strengths of slag-alkali systems have been attributed to the strong crystallization contacts between zeolites and calcium hydrosilicates. Also, the amount of fine-grained, unreacted silicates that can interfere with bonding to aggregate is minimal (132, 135, 237).

2.6.4.5 Paste, Mortar, and Concrete Properties

Gjorv (129) compared the heat development of various concretes under adiabatic conditions. Concrete mixtures containing slags from a single source, ground to various levels of fineness, were compared to a mixture containing a blended cement with 10 percent fly ash. The slags were activated with a combination of alkaline chemicals and sodium lignosulfonate. After 72 hours, the slag mixtures developed approximately 60 percent of the heat of hydration as compared to the blended cement, as shown in Figure 2.55.
Despite its low evolution of heat, the mixture in which slag was ground to a fineness of 640 m^2/kg exhibited compressive strengths similar to those of the blended cement mixture. The coarser slags, 540 m^2/kg and 420 m^2/kg, exhibited 28-day strengths approximately 15 percent and 22 percent less than the finest slag (640 m^2/kg), respectively.

Toshiro and Yoshimoto (417) compared the strength development of slag cement mortars with various alkali additives. The control mixture contained only slag and portland cement. Additional alkali activators, including NaCl, NaOH, and Na_2SO_4, were added in the amounts of 0.25, 0.5, 1.0, 1.5, and 2.0 mole percent of Na_2O equivalent (cement basis). Additions of sodium chloride increased strengths at all ages, particularly at early ages. Early age compressive strengths increased as NaCl dosage increased. Sodium hydroxide imposed negligible effects at low concentrations and decreased strengths at high concentrations. Sodium sulfate increased compressive strengths at early ages and imposed negligible effects at 91 days; strengths at early ages increased with increasing Na_2SO_4 dosages. The effectiveness of additives in accelerating the reaction of slags was reported to be dependent on the ionic mobility of activators. Differences in long-term compressive strengths were attributed to variations in reaction products and in the compactness of hydrated pastes (417).

Talling (413) studied the effects of various curing conditions on the performance of alkali-activated slag pastes, mortars, and concretes. Sodium silicate solutions were used as the activating agents. Curing temperatures ranged from -15 °C to 105 °C and the curing humidities included 50 percent, 70 percent, and 100 percent. Talling reported that heat-treating the alkali-activated slag mixtures immediately after casting resulted in increased early strengths without any significant losses in later strengths as long as the specimens were stored in polyethylene bags to prevent loss of moisture. At high temperatures, smaller proportions of activators were required for high early strengths (413).

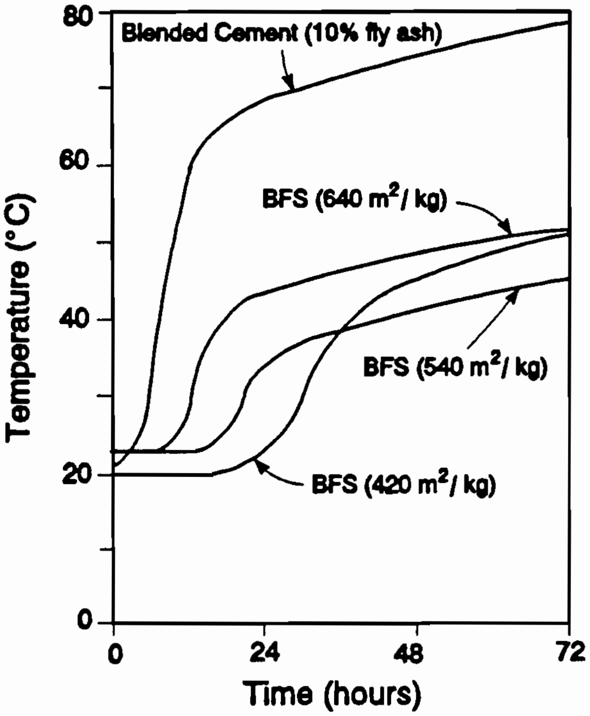


Figure 2.55 Adiabatic Heat Development of Concrete Containing Blended Fly Ash Cement and BFS of Varying Fineness (129)

At normal temperatures, alkali-activated slag concretes cured at 70 percent relative humidity performed as well as specimens cured at 100 percent relative humidity. However, concrete specimens cured at 50 percent relative humidity stopped gaining strength after approximately 28 days (413).

The alkali-activated slag mortars were reported to have hardened under freezing conditions (413). Mortars which were cured at -15 °C exhibited strengths at 1 day and 28 days of 0.5 to 2.2 MPa and 4.5 to 13.5 MPa, respectively. The mortars contained a slag of fineness 450 m^2/kg and an activator contributing 4 percent equivalent Na_2O by weight of slag. Low-temperature reactions were attributed to electrolyte concentrations of 25 percent to 30 percent in pore solutions, which prevented frost damage.

Other researchers (209) have reported relatively low strengths of NaOH-activated slag mortars which were heat-cured, followed by curing in dry conditions. Mortar specimens were cured under two conditions: 6 hours at 90 °C, followed by air-curing at relative humidity 60 percent and continuous curing in water at 20 °C. Although, the 1-day strengths were improved by heat-curing, the 7- and 28-day strengths were decreased by more than 50 percent. In the same study, heat curing an ordinary portland cement mixture improved its 1-day strength, had negligible effects on its 7-day strength, and slightly decreased its 28-day strength. Alkali-activated slag concretes were reported to be particularly susceptible to poor curing conditions.

Tashiro and Yoshimoto (417) compared porosities of slag cement mortars with various alkali activators. The control mixture contained only slag and portland cement. Activators NaCl, NaOH, and Na_2SO_4 were added to additional mixtures at proportions of 1.0 mole percent of Na_2O equivalent. Porosities were measured by mercury porosimeter after 3 days of curing. All alkali activated mixtures contained lower total volumes of pores than the control mixture, as shown in Figure 2.56. The largest reductions in pore volume occured for pores of relatively large radius. The mixture with activator NaCl contained the lowest total volume of pores.

Alkali-activated slag binders exhibit desireable durability characteristics. The alkali activator ensures long-term alkalinity on the surfaces of reinforcing steel, which keeps the rate of corrosion at a very low level (54). Rates of chloride diffusion in alkali activated slag pastes have been reported to be 30 to 40 times slower than that of ordinary portland cement paste when compared at similar water/binder ratios (54).

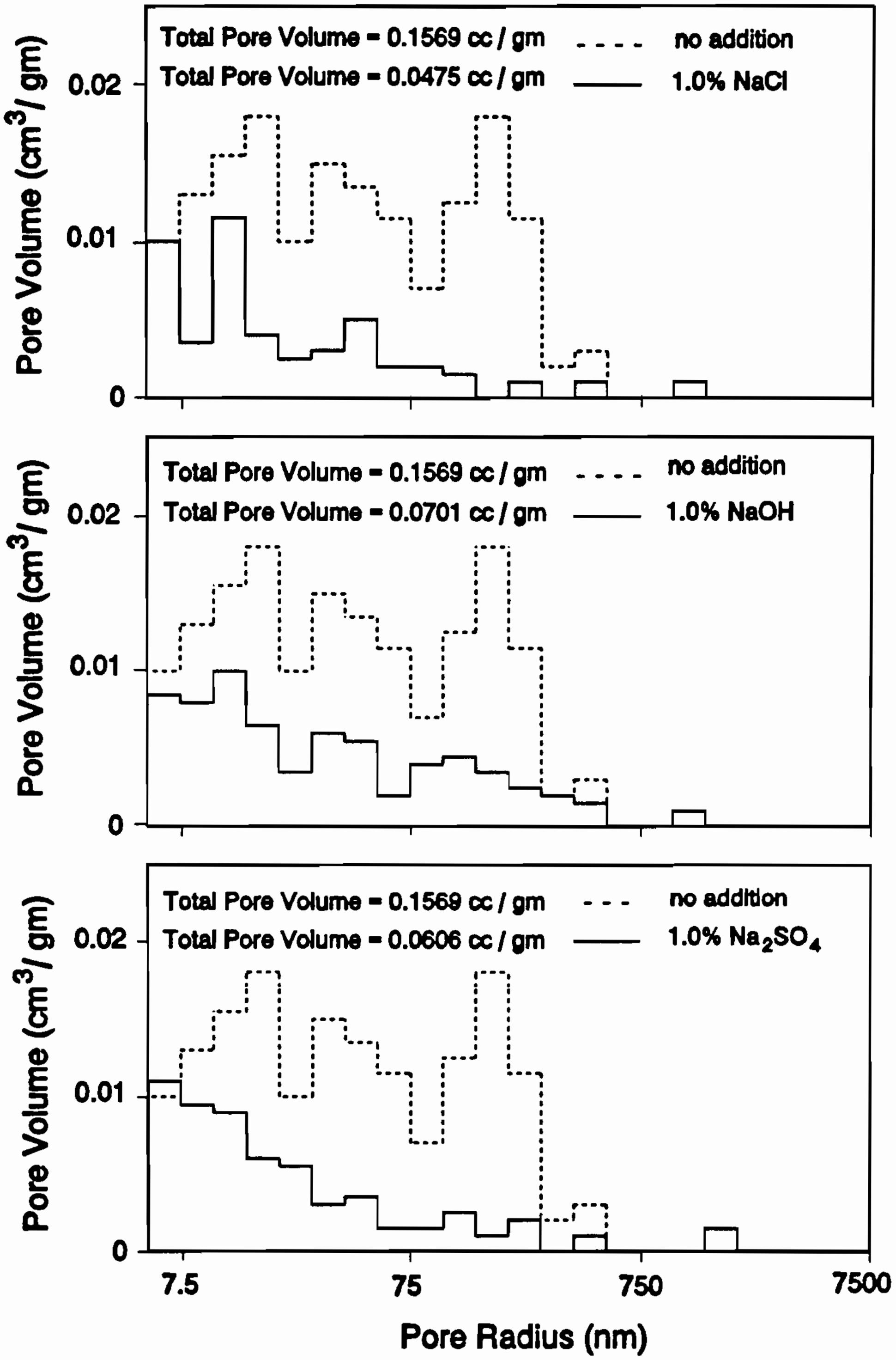


Figure 2.56 Pore Size Distributions of BFS Cement Pastes After 3 Days of Hydration (417)

Alkali-activated slag products most often have higher chemical resistance than portland cement products (54). The resistance to deterioration has been attributed to small pore sizes and to suppression of capillaries. These characteristics hinder the migration of destructive solutions within the concrete (414). The absence of calcium hydroxide also contributes to its resistance to chemicals. In ordinary portland cement concrete, it is a soluble constituent which may be leached out and thus, increase permeability. Calcium hydroxide may also react with sulfates in solution to cause destructive expansions (414).

Freeze-thaw cycle resistivity for alkali-activated slag concrete has been reported to be 10 times greater than portland cement concrete of comparative strength (307).

Rates of carbonation, however, have been reported to be higher for alkali-activated slag mortars than for portland cement mortars of equal compressive strength. The higher rates of carbonation (depth penetration per time) were attributed to microcracks and to smaller contents of hydrated CaO. In ordinary portland cement concrete, hydrated CaO reacts with incoming CO_2 and fills cracks with $CaCO_3$ (54).

CHAPTER 3

MATERIALS AND PROCEDURES

3.1 INTRODUCTION

This chapter presents the materials and procedures used throughout this study. Materials include all those which were used in the production of concrete. Procedures Include those which were used for materials characterization, production of concrete, and testing of hardened concrete.

3.2 MATERIALS

3.2.1 PORTLAND CEMENT

Six portland cements were included in this study: two ASTM C-150 Type I cements, one ASTM Type II cement, one ASTM Type V cement, and two zero percent tricalcium aluminate cements. All cements were commercially available. Mill test reports, Including both chemical and physical information for the cements, are shown in Table 3.1. Fly ash partially replaced Type I and Type II cements in concrete. Ordinary Type V and zero percent C_3A cement concretes were included for the purpose of comparisons.

Notations for cements, are also included in Table 3.1. The Type I cements were notated "Type I-L" and "Type I-H" to Indicate relatively low and high C_3A contents, respectively. The Type I-L cement contained 9.9 percent C_3A and the Type I-H cement contained 11.2 percent C_3A. Although the total aluminum oxide contents for these cements were similar, the Type I-L cement contained a higher proportion of C_4AF, leaving less alumina for the formation of C_3A. The Type I-H cement had a slightly higher C_3S/C_2S ratio. The total sulfate and alkali contents of the Type I cements were similar.

The Type II cement contained 6.0 percent C_3A, which is on the low end of the range of permissible C_3A (5.0 to 8.0 percent).

Table 3.1 Mill Test Analyses for Ordinary Portland Cements

	ASTM C-150 Cement Type					
	Type I	Type I	Type II	Type V	0% C_3A	0% C_3A
Notation	Type I-L	Type I-H	Type II	Type V	0%L	0%H
Chemical Composition (percent by weight)						
SiO_2	20.6	20.3	21.8	22.0	21.8	21.3
Al_2O_3	5.31	5.80	4.20	3.41	2.48	2.78
Fe_2O_3	3.27	3.30	3.20	3.23	3.77	4.80
CaO	64.2	64.4	64.7	64.9	64.8	64.4
MgO	0.91	1.10	0.60	3.31	1.27	3.92
SO_3	3.47	3.00	2.97	2.52	2.26	2.96
Equiv. Na_2O	0.74	0.50	0.63	0.52	0.45	0.33
Free Lime	(1)	0.98	0.90	(1)	1.61	(1)
Loss on Ignition	0.73	0.90	0.90	0.56	1.27	0.70
Insol. Residue	0.15	0.10	0.30	0.19	0.44	0.17
C_3S	51.5	54.6	54.0	62.2	70.0	66.2
C_2S	20.1	16.9	21.8	16.2	9.60	11.3
C_3A	9.86	11.2	6.00	3.55	0.00	0.00
C_4AF	9.96	7.60	9.74	9.82	11.6*	14.6*
Blaine (cm^2/gm)	3280	3950	3350	(1)	3630	(1)
Compressive Strength (psi) **						
1 day	(1)	(1)	1970	(1)	1850	(1)
3 days	3840	4300	3550	(1)	3960	(1)
7 days	4520	5460	4450	(1)	5070	(1)
Vicat Set Time (minutes)						
Initial	(1)	95	88	(1)	140	(1)
Final	(1)	209	201	(1)	305	(1)

Note: Tests were performed in accordance with ASTM Standards.
* solid solution (C_4AF + C_2F)
** ASTM C-109 mortar cubes
(1) data not reported

The Type V cement contained 3.55 percent C_3A. Although the Type V cement contained less C_3A the the Type II cement, their C_4AF contents were similar (9.82 percent and 9.74 percent, respectively).

The zero percent tricalcium aluminate cements were designated "0%L" and "0%H" to indicate relatively low and high C_4AF contents, respectively. The 0%L cement contained 11.6 percent C_4AF and the 0%H cement contained 14.6 percent C_4AF. The C_3S/C_2S ratios of the 0%L and 0%H cements were the highest of all the cements included in this study (7.3 and 5.9, respectively).

3.2.2 CLINKER, GYPSUM, AND ANHYDRITE

Clinker, natural gypsum, and anhydrite were obtained directly from commercial cement plants, for use in the procuction of ordinary portland cements and blended fly ash cements could be produced in the laboratory. All materials were kept in sealed containers during shipment and storage.

The ordinary Type I-H and Type II cements were produced in the laboratory. The Type I-H cement clinker contained 0.7 percent SO_3 and 0.5 percent Na_2O equivalent. The Type II cement clinker contained 0.8 percent SO_3 and 0.7 percent Na_2O equivalent.

3.2.3 AGGREGATE

Both the fine and coarse aggregates were locally available materials and were known to be non-alkali reactive.

Aggregate sources and types remained constant throughout this study. Aggregate gradations, specific gravities, and absorption capacities were measured periodically and slight adjustments in concrete mixture designs were made when required. Aggregate properties did not vary significantly.

The fine aggregate was a natural river sand dredged from the Colorado River. Bulk specific gravity (saturated-surface-dry, SSD, basis) ranged from 2.57 to 2.64, absorption capacity ranged from 0.88 to 1.19 percent, and the proportion of loose solids (SSD basis) remained constant at 61.5 percent. Gradations of fine aggregate grain sizes conformed to Texas Grade #1 specifications, as shown in Table 3.2. They also conformed to ASTM C-33 grading requirements for concrete sand. Fineness moduli of the fine aggregate ranged from 2.6 to 3.0.

Table 3.2 Sieve Analyses for Fine Aggregate

Sieve Size	Cumulative Percent Retained		
	Test * #1	Test * #2	Texas Grade #1
3/8"	0.0	0.0	0
#4	0.2	0.0	0 - 5
#8	3.8	11.1	0 - 20
#16	26.5	37.3	15 - 50
#30	53.7	68.4	35 - 75
#50	77.8	89.0	65 - 90
#100	96.2	97.6	90 - 100
#200	99.6	99.6	97 - 100

Note: Fine aggregate also conformed to ASTM C-33 grading requirements for concrete sand.

* Texas Test Method Tex-401-A

The coarse aggregate was a ¾-inch nominal maximum size crushed limestone, quarried in Georgetown, Texas. Bulk specific gravity (SSD basis) ranged from 2.50 to 2.58, absorption capacity ranged from 2.0 to 3.5, and the proportion of loose solids (SSD basis) ranged from 54.7 to 57.9. Coarse aggregate gradations conformed to Texas Grade #5 specifications, as shown in Table 3.3. They also conformed to ASTM C-33 requirements for #67 coarse aggregate.

Table 3.3 Sieve Analyses for Coarse Aggregate

Sieve Size	Cumulative Percent Retained		
	Test * #1	Test * #2	Texas Grade #5
1"	0.0	0.0	0
3/4"	0.0	2.4	0 - 10
1/2"	25.1	47.5	—
3/8"	61.3	75.8	45 - 80
#4	97.6	98.9	90 - 100
#8	98.3	99.0	95 - 100

Note: Crushed limestone also conformed to ASTM C-33 grading requirements for #67 coarse aggregate.

* Texas Test Method Tex-401-A

3.2.4 WATER

Water used in concrete mixtures and in exposure solutions was obtained from municipal supplies. A chemical analysis of the mixing water is provided in Table 3.4. Chloride and sulfate contents are within the limit of 1000 ppm, as specified by Texas DOT Standard Specification 421.2. The pH is within the range of 4.5 to 8.5, which is specified by AASHTO T-26 to be an indication of acceptable water quality for use in concrete.

3.2.5 CHEMICAL ADMIXTURES

Anhydrous sodium sulfate and anhydrous sodium hydroxide were used as alkali activators in fly ash/cement mixtures. The sodium sulfate was 99^+ percent pure and the sodium hydroxide was 98^+ percent pure. The anhydrous sodium sulfate was also used in producing the sulfate exposure solutions.

Table 3.4 Chemical Analysis of Concrete Mixing Water

Chemical Composition (ppm)									pH
Na	Ca	K	Mg	Fe	Mn	Cl	SO_4	HCO_3	
40.3	18.1	3.27	19.0	0.01	0.01	69.0	51.6	57.6	8.14

3.2.6 FLY ASH

3.2.6.1 Introduction

Twenty-four fly ashes were included in this study: twelve Type A ashes and twelve Type B ashes. Fly ash notations, sources, and types are listed in Table 3.5. The Type A ashes were derived from various bituminous, subbituminous, and lignitic coals. The Type B ashes were derived primarily from Wyoming subbituminous coals. One Type B ash was derived from a North Dakota lignitic coal.

Eleven fly ashes were obtained from power plants within Texas: five Type A ashes and six Type B ashes. Four of the five Texas power plants producing Type A ash burn Texas lignitic coals. One Texas power plant producing Type A ash burns Colorado subbituminous coal. All the Texas power plants producing Type B ash burn Wyoming subbituminous coals.

3.2.6.2 Physical and Compositional Characteristics

Physical, chemical, mineralogical, and glass compositions of fly ashes included in this study are presented in Tables 3.6 through 3.9, respectively. In order to facilitate identification of prominent physical and compositional characteristics of fly ashes, selected characteristics are ranked in descending order in Appendix B. Ranks 1 through 24 correspond to the highest to lowest values for each characteristic. Ranks 1 through 12 are emphasized with shaded boxes.

Table 3.5 Descriptions of Sources of Fly Ash

Fly Ash Notation	Power Plant Location	Source Coal Location	Coal Type	Texas Type *
A-1	Chicago, IL	Illinois	Bituminous	A
A-2	Fairfield, TX	Texas	Lignite	A
A-3	Vernal, UT	Colorado	Bituminous	A
A-4	Pampa, TX	Texas	Lignite	A
A-5	Fannin, TX	Colorado	Subbituminous	A
A-6	Portage, WI	Montana	Subbituminous	A
A-7	Sask., Canada	Canada	Lignite	A
A-8	Utah	Utah	Bituminous	A
A-9	Mt. Pleasant, TX	Texas	Lignite	A
A-10	Colo. Springs, CO	Colorado	Bituminous	A
A-11	Rockdale, TX	Texas	Lignite	A
A-12	Newnan, GA	(1)	Bituminous	A
B-1	Underwood, ND	North Dakota	Lignite	B
B-2	Pueblo, CO	Wyoming	Subbituminous	B
B-3	San Antonio, TX	Wyoming	Subbituminous	B
B-4	Lagrange, TX	Wyoming	Subbituminous	B
B-5	Amarillo, TX	Wyoming	Subbituminous	B
B-6	Ft. Towson, OK	Wyoming	Subbituminous	B
B-7	Westlake, LA	Wyoming	Subbituminous	B
B-8	Omaha, NE	Wyoming	Subbituminous	B
B-9	Thompsons, TX	Wyoming	Subbituminous	B
B-10	Boyce, LA	Wyoming	Subbituminous	B
B-11	Muleshoe, TX	Wyoming	Subbituminous	B
B-12	Cason, TX	Wyoming	Subbituminous	B

* Texas Department of Transportation Materials Specification D-9-8900

(1) data not reported

Table 3.6 Physical Characteristics of Fly Ash

Fly Ash	Specific Gravity	Blaine (cm^2/gm)	Retained #325 Sieve (%)	Pozzolanic Activity Index (%)	Soundness (%)	Shrinkage (%)	Water Reqm't (%)
A-1	2.39	2010	16.5	91.0	.210	(1)	92.0
A-2	2.43	2790	23.8	90.9	-.010	.010	89.1
A-3	2.18	4030	18.2	97.2	-.019	.007	95.8
A-4	2.28	4330	16.6	103.3	-.029	.004	89.9
A-5	2.20	2460	25.8	78.3	.026	-.001	94.9
A-6	2.49	3180	10.5	105.0	.080	(1)	91.0
A-7	2.26	1790	28.2	83.0	.100	(1)	94.0
A-8	2.23	2880	46.3 *	74.1 *	.036	.009	100.0
A-9	2.32	2750	13.3	97.1	-.018	.007	89.1
A-10	2.02	2090	25.8	93.6	-.006	-.015	96.6
A-11	2.18	3070	30.7 **	89.5	.021	.001	94.1
A-12	2.43	2250	15.4	86.0	-.025	.004	90.8
B-1	2.54	3210	21.6	84.0	.060	(1)	88.0
B-2	2.62	3440	11.2	86.1	.100	.002	90.7
B-3	2.69	4250	15.1	95.6	.045	.002	90.7
B-4	2.60	3600	13.2	94.4	.005	.010	89.0
B-5	2.70	3600	18.9	91.6	.032	-.007	89.9
B-6	2.64	3440	13.1	98.5	.042	-.015	87.3
B-7	2.71	3580	17.2	91.7	.046	.006	90.8
B-8	2.47	2660	12.2	101.0	.110	(1)	89.0
B-9	2.58	3310	22.0	102.1	-.004	-.006	92.4
B-10	2.55	4370	12.3	96.9	.047	-.002	89.0
B-11	2.73	3460	15.7	105.4	.047	-.013	88.2
B-12	2.79	3480	10.4	91.5	.100	-.005	88.2

Note: Tests were performed in accordance with ASTM C-204 and C-311 procedures.
pozzolanic activity index - determined with portland cement at 28 days
soundness - autoclave expansion
shrinkage - increase in drying shrinkage of mortar bars at 28 days
* failed both ASTM C-618 and Texas D-9-8900 physical requirements
** failed Texas D-9-8900 physical requirements
(1) data not reported

Table 3.7 Bulk Chemical Compositions of Fly Ash

Fly Ash	Bulk Chemical Composition (percent by weight)										
	SiO_2	Al_2O_3	Fe_2O_3	Sum Oxides	CaO	MgO	SO_3	Na_2O equiv.	Free Lime	Moisture Content	Loss on Ignition
A-1	50.7	20.0	16.7	87.4	4.80	0.90	1.22	2.28 †	(1)	0.29	0.87
A-2	52.9	17.9	8.98	79.8	9.55	1.66	0.90	0.40	0.09	0.03	0.19
A-3	45.9	24.2	4.66	74.8	3.68	0.53	0.42	(1)	0.00	0.04	1.62
A-4	42.5	24.1	5.96	72.6	10.1	1.58	0.52	(1)	0.00	0.04	0.93
A-5	45.0	23.6	7.49	76.1	7.90	0.00	0.89	1.90 †	(1)	0.08	0.31
A-6	46.9	20.9	5.30	73.1	15.0	4.70	1.45	0.53	(1)	0.06	0.11
A-7	46.5	22.3	3.60	72.4	12.4	(1)	0.58	3.14 †	(1)	0.05	1.05
A-8	50.9	18.6	5.60	75.1	8.76	1.20	0.71	(1)	2.08	0.19	3.90 **
A-9	55.5	18.6	4.33	78.5	6.97	0.81	0.26	0.30	0.01	0.07	0.04
A-10	47.3	24.4	5.56	77.3	4.24	0.08	0.39	1.76 †	0.18	0.11	0.39
A-11	51.3	20.9	6.00	78.3	7.98	1.05	0.52	0.25	(1)	0.09	0.17
A-12	43.0	27.4	16.1	86.5	1.57	0.70	1.24	(1)	0.01	0.18	0.90
B-1	44.6	15.5	7.70	67.8	20.9	(1)	1.50	0.89	(1)	0.01	0.05
B-2	30.4	21.7	4.47	56.6	28.4	4.29	5.60 *	3.75 †	0.94	0.13	0.18
B-3	32.8	22.9	5.10	60.8	27.4	4.82	2.21	1.56 †	0.29	0.02	0.53
B-4	31.5	19.9	4.90	56.3	27.8	5.72 ‡	2.27	1.11	0.07	0.08	0.16
B-5	32.2	22.2	4.97	59.4	29.9	5.63 ‡	2.48	1.67 †	0.45	0.10	0.03
B-6	36.2	21.4	6.00	63.5	26.0	6.22 ‡	2.69	0.86	0.57	0.11	0.35
B-7	33.5	18.4	6.20	58.0	25.6	5.12 ‡	2.78	2.18 †	(1)	0.02	0.27
B-8	39.0	19.5	4.80	63.3	23.1	5.60 ‡	2.30	2.19 †	(1)	0.04	0.13
B-9	35.6	22.4	5.14	63.1	23.1	4.25	2.10	2.04 †	0.11	0.02	0.52
B-10	36.5	22.3	6.27	65.1	24.0	5.54 ‡	2.16	1.87 †	0.09	0.05	0.24
B-11	30.8	21.9	4.66	57.4	31.3	6.14 ‡	1.97	1.67 †	0.79	0.06	0.17
B-12	28.4	20.2	4.94	53.5	33.9	5.91 ‡	4.45	1.54 †	1.62	0.02	0.25

Note: Tests were performed in accordance with ASTM C-114 and C-311 procedures.
* failed both ASTM C-618 and Texas D-9-8900 chemical requirements
** failed Texas D-9-8900 chemical requirements
† failed both ASTM C-618 and Texas D-9-8900 optional chemical requirements
‡ failed Texas D-9-8900 optional chemical requirements
(1) data not reported

Table 3.8 Mineralogical Compositions of Fly Ash

Fly Ash	Mineralogical Composition (percent by weight)													
	Ah	As	C_3A	Hm	Lm	Ml	Mu	Mw	Pc	Pl	Qz	So	Sp	Total
A-1	0.7	0.0	0.0	2.3	1.5	0.0	7.3	0.0	0.0	0.0	5.6	0.0	7.8	25.2
A-2	0.0	0.0	0.0	0.9	0.0	0.0	5.7	0.0	0.0	0.0	14.3	0.0	1.5	22.4
A-3	0.0	0.0	0.0	0.0	0.3	0.0	18.2	0.0	0.4	0.0	9.1	0.0	1.4	29.4
A-4	0.2	0.0	0.0	0.0	0.0	0.0	11.5	0.0	0.0	0.0	7.5	0.0	0.9	20.1
A-5	0.5	0.0	0.0	0.0	0.0	0.0	8.9	0.0	0.0	0.0	6.7	0.0	0.8	16.9
A-6	0.9	0.0	0.0	0.0	0.6	1.1	11.0	0.0	1.4	0.0	10.3	0.0	3.2	28.5
A-7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.1	0.0	5.7	0.0	1.0	7.8
A-8	0.4	0.0	0.4	0.0	0.6	0.0	7.0	0.0	1.1	1.6	12.3	0.0	1.1	24.5
A-9	0.0	0.0	0.0	0.0	0.0	0.0	8.9	0.0	0.0	0.0	15.4	0.0	0.0	24.3
A-10	0.0	0.0	0.0	0.0	0.0	0.0	15.0	0.0	0.0	0.0	9.1	0.0	1.0	25.1
A-11	0.0	0.0	0.0	0.3	0.4	0.0	9.9	0.0	0.0	0.0	5.0	0.0	2.6	18.2
A-12	0.3	0.0	0.0	4.9	0.1	0.6	10.8	0.0	0.0	0.0	4.7	0.0	6.6	28.0
B-1	0.9	0.0	1.8	0.0	0.9	1.3	0.0	0.0	2.1	0.0	2.6	0.0	3.9	13.5
B-2	1.6	4.1	0.0	2.7	2.2	2.3	2.5	10.8	2.2	0.0	5.1	1.7	0.0	35.2
B-3	1.1	0.0	2.3	0.0	0.5	2.7	3.0	1.8	1.4	0.0	4.3	0.6	1.5	19.2
B-4	1.1	0.0	1.1	0.0	0.3	3.5	3.0	0.8	0.8	0.0	1.7	0.3	1.8	14.4
B-5	1.4	0.0	2.3	0.0	0.8	2.0	3.5	3.1	2.4	0.0	5.1	0.6	0.5	21.7
B-6	1.4	0.0	1.7	0.0	1.3	1.3	3.0	2.1	2.8	0.0	12.0	1.8	2.2	29.6
B-7	1.9	0.0	1.2	0.0	0.5	3.9	0.0	2.7	1.1	0.0	2.5	0.0	1.4	15.2
B-8	1.9	2.4	3.1	0.0	1.5	2.2	0.0	4.2	3.3	0.0	8.7	2.0	1.3	30.6
B-9	1.0	0.0	1.9	0.0	0.4	2.3	3.3	0.6	1.4	0.0	6.1	0.3	1.7	19.0
B-10	1.0	0.0	1.2	0.0	0.1	2.1	3.0	1.6	1.0	0.0	3.3	0.0	1.5	14.8
B-11	1.0	0.0	2.4	1.4	2.0	2.1	4.3	3.9	3.6	0.0	6.2	1.5	1.2	29.6
B-12	2.9	2.6	2.3	1.8	2.5	3.4	2.4	4.5	4.9	0.0	7.2	2.7	1.3	38.5

Note: Mineralogical information was supplied by North Dakota State University.
Ah = anhydrite, As = alkali sulfates, C_3A = tricalcium aluminate, Hm = hematite, Lm = lime, Ml = melilite, Mu = mullite,
Mw = merwinite, Pc = periclase, Pl = portlandite, Qz = quartz, So = sodalite structures, Sp = ferrite spinel

Table 3.9 Glass Compositions of Fly Ash

Fly Ash	Glass Composition (percent by weight)									Normalized Oxides (wt.%)		
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	eq.Na_2O	Other	Total	SiO_2	Al_2O_3	CaO
A-1	43.0	14.8	7.3	3.0	0.2	0.8	2.3	2.5	73.9	70.8	24.3	5.0
A-2	37.0	13.8	6.7	9.6	1.5	0.9	0.4	7.5	77.4	61.3	22.9	15.8
A-3	31.7	11.1	3.4	3.4	0.0	0.4	(1)	19.0	69.0	68.6	24.1	7.3
A-4	31.8	15.8	5.1	10.0	1.5	0.4	(1)	14.3	79.0	55.1	27.5	17.4
A-5	35.8	17.2	6.8	7.7	0.0	0.6	1.9	12.9	82.8	59.0	28.4	12.7
A-6	33.1	12.8	2.4	13.6	2.9	0.9	0.5	5.1	71.4	55.7	21.5	22.8
A-7	40.8	22.3	2.7	12.4	(1)	0.6	3.1	9.2	91.1	54.0	29.5	16.4
A-8	36.6	13.4	4.6	6.5	0.0	0.5	(1)	9.9	71.6	64.7	23.7	11.5
A-9	37.6	12.2	4.3	7.0	0.8	0.3	0.3	13.2	75.7	66.2	21.5	12.3
A-10	34.0	13.6	4.7	4.2	0.0	0.4	1.8	15.9	74.5	65.5	26.3	8.2
A-11	43.5	13.8	3.3	7.6	0.8	0.5	0.3	11.8	81.6	67.1	21.3	11.7
A-12	35.1	19.5	5.2	1.1	0.0	1.1	(1)	9.1	71.1	62.9	35.1	2.0
B-1	41.6	14.6	4.2	18.0	(1)	1.0	0.9	6.3	86.4	56.1	19.7	24.2
B-2	19.9	18.6	1.8	18.4	0.6	2.1	2.0	1.2	64.6	34.9	32.7	32.4
B-3	26.1	19.1	3.7	22.8	2.9	1.5	1.6	2.7	80.3	38.4	28.1	33.5
B-4	27.5	16.5	3.3	24.4	4.4	1.6	1.1	6.6	85.4	40.2	24.2	35.7
B-5	24.3	18.1	4.5	24.5	2.7	1.6	1.7	1.0	78.3	36.3	27.1	36.6
B-6	22.2	17.5	4.0	20.8	2.9	1.6	0.9	0.2	70.0	36.7	28.9	34.4
B-7	28.7	17.2	4.9	20.6	3.3	1.7	2.2	5.9	84.5	43.2	25.9	30.9
B-8	28.0	16.9	3.6	15.1	1.5	0.0	1.1	3.0	69.3	46.7	28.2	25.1
B-9	27.6	18.7	3.6	19.7	2.4	1.5	2.0	4.9	80.5	41.8	28.4	29.9
B-10	31.1	19.3	4.9	21.1	4.0	1.6	1.9	1.2	85.0	43.5	27.0	29.5
B-11	21.3	16.8	2.2	24.0	1.8	1.2	1.7	1.4	70.2	34.3	27.0	38.7
B-12	17.8	15.6	2.0	24.1	0.1	0.9	0.4	0.4	61.2	30.9	27.2	41.9

(1) oxide not reported in bulk chemical analysis

Comparisons between the physical properties of Type A fly ashes and Type B fly ashes revealed the following general trends:

1) Type A ashes had higher proportions retained on the #325 sieve and
2) Type B fly ashes had higher specific gravities.

Comparisons between the chemical compositions of Type A fly ashes and Type B fly ashes revealed the following general trends:

1) Type A ashes contained larger proportions of SiO_2 and Fe_2O_3,
2) Type A ashes contained larger proportions of unburnt carbon (larger proportions of mass lost on ignition), and
3) Type B ashes contained larger proportions of CaO, SO_3, and Na_2O equivalent.

Comparisons between the mineralogical compositions of Type A fly ashes and Type B fly ashes revealed the following general trends:

1) Type A ashes contained larger proportions of mullite (Mu), Quartz (Qz), and ferrite spinel (Sp) and
2) Type B ashes contained larger proportions of C_3A, melilite (Ml), merwinite (Mw), and sodalite structures (So).

Comparisons between the glass compositions of Type A fly ashes and Type B fly ashes revealed the following general trends:

1) glass in Type A ashes contained larger proportions of SiO_2 and Fe_2O_3 and
2) glass in Type B ashes contained larger proportions of Al_2O_3 and CaO.

E.R. Dunstan (99) compared fly ash compositions on the basis of ternary plots of bulk silica, alumina, and calcium oxide contents. The compositions of fly ashes included in this study are plotted on a similar ternary diagram in Figure 3.1. Type A and B fly ashes composition plots are clustered separately: Type A fly ash compositions plotted in the mullite and anorthite fields while the Type B fly ash compositions plotted in the anorthite and gehlenite fields. The composition of ash B-1 is unique in that it is intermediate between the Type A and Type B ash composition clusters. Fly ash B-1 was the only Type B ash in this study derived from lignitic coal; all other lignitic coal ashes in this study were classed as Type A.

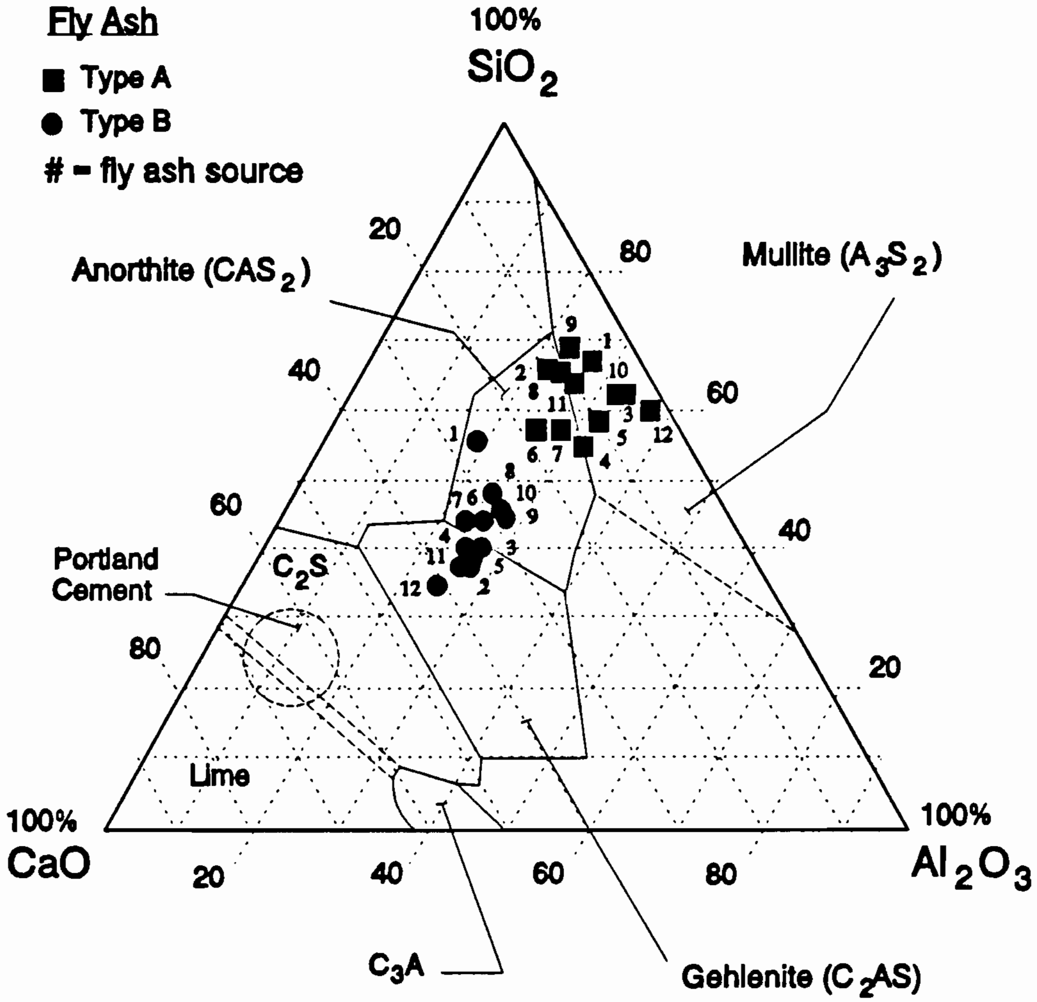


Figure 3.1 Ternary (SiO_2-CaO-Al_2O_3) Chemical Compositions of Fly Ash

Mineralogical analyses for fly ashes in this study permitted a similar ternary plot for glass compositions, as shown in Figure 3.2. Trends are similar; composition plots shifted only slightly. Glass compositions of ashes A-6 and B-8 joined that of B-1 as intermediate between clusters. Both ashes A-6 and B-8 were derived from subbituminous coal. Ash A-6 contained relatively large proportions of quartz and mullite, which reduced proportions of silica and aluminum oxides in glass. Ash B-8 contained relatively large proportions of anhydrite, tricalcium aluminate, and sodalite, which reduced the proportion of calcium oxide present as glass.

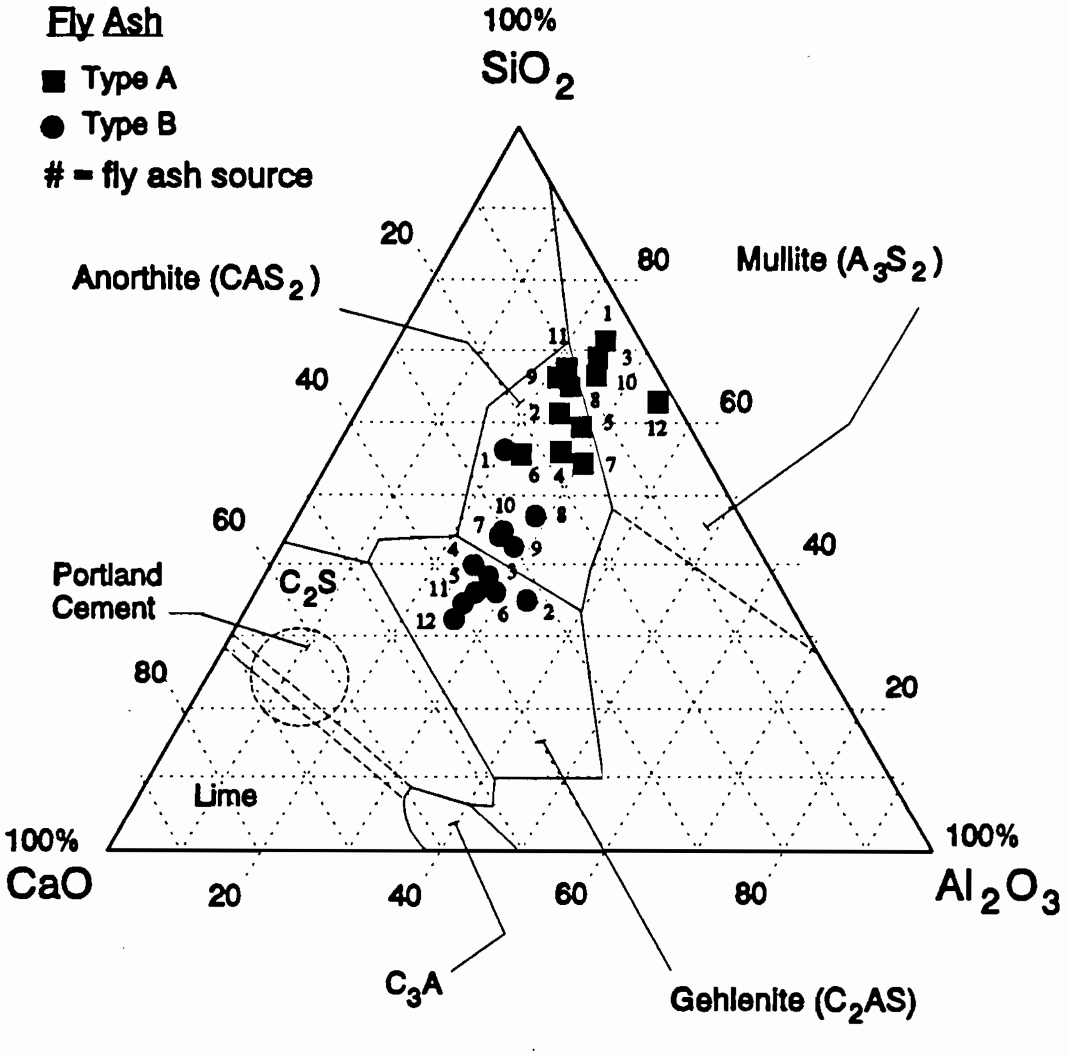


Figure 3.2 Ternary (SiO_2-CaO-Al_2O_3) Glass Compositions of Fly Ash

X-ray diffractograms permitted an additional method of characterizing fly ash glass compositions: the positions of maximum background elevations. X-ray diffraction response to the glass in fly ash is a broad elevation through a range of diffraction angles. The highest point of the background, often termed "broad diffuse maximum" or "halo", reflects the main peak of the crystalline compound that would have formed had the glass devitrified (88). Halo positions of several fly ashes included in this study are provided in Table 3.10.

Integral knowledge of fly ash composition permits predictions of the effects of fly ash on the sulfate resistance of concrete. Various models to predict these effects were discussed in the literature review in Chapter 2. Among these models were fly ash Resistance Factor, Calcium Aluminate Potential, and Calcium Sulfate Equivalent. These parameters were calculated for the fly ashes included in this study and are presented in Table 3.10.

3.3 PROCEDURES

3.3.1 FLY ASH MINERALOGICAL ANALYSES

Researchers at North Dakota State University (NDSU), Department of Chemistry, performed all the quantitative X-ray diffraction analyses. They used the Reference Intensity Ratio (RIR) method, which is based on the concept that the proportions of phases within mixtures are related to the intensities of their Bragg reflections.

Reference Intensity Ratio is defined as the ratio of Bragg reflection intensities between a single fly ash phase and the strongest peak of an internal standard (260). The Reference Intensity Ratio for each fly ash phase was derived in a 50:50 percent mixture containing the single fly ash phase and the internal standard. A known weight of the internal standard (10 percent by weight) was then interground with the fly ash and the ratio between the peak of the standard and each fly ash phase was measured. The weight percent of each fly ash crystalline phase was then calculated from the following relationship (423):

$$\text{wt.\% (crystalline phase)} = \frac{\text{wt.\% (standard)} \times \text{I (crystalline phase)}}{\text{RIR} \times \text{I (standard)}}\text{, where} \qquad (3.1)$$

I = Bragg reflection intensity and

RIR = (strongest crystalline phase peak)/(strongest standard peak) in a 1:1 mixture.

The researchers at NDSU chose rutile (TiO_2) as the internal standard because it met the following criteria: Its peak Bragg reflections did not overlap with the peaks of primary fly ash phases, it exhibited long-term stability in air and during grinding, and it was economical (255).

Table 3.10 Sulfate Resistance Parameters for Fly Ash

Fly Ash	Peak 2Θ *	Dunstan's Resistance Factor	Calcium Aluminate Potential	Calcium Sulfate Equivalent
A-1	(1)	-0.01	0.58	2.07
A-2	27.0	0.51	0.81	1.53
A-3	24.5	-0.28	0.57	0.71
A-4	28.0	0.86	0.98	0.88
A-5	25.5	0.39	0.88	1.51
A-6	(1)	1.89	0.87	2.47
A-7	(1)	2.06	0.92	0.99
A-8	25.5	0.67	0.68	1.21
A-9	25.5	0.45	0.63	0.44
A-10	25.5	-0.14	0.66	0.66
A-11	24.5	0.50	0.57	0.88
A-12	24.5	-0.21	0.74	2.11
B-1	(1)	2.06	0.93	2.55
B-2	31.0	5.23	2.03	9.52
B-3	32.0	4.39	1.85	3.76
B-4	31.0	4.65	1.66	3.86
B-5	31.5	5.01	2.05	4.22
B-6	31.0	3.50	2.05	4.57
B-7	(1)	3.32	1.53	4.73
B-8	(1)	3.77	1.44	3.91
B-9	31.5	3.52	1.60	3.57
B-10	30.5	3.03	1.50	3.67
B-11	32.0	5.64	2.19	3.35
B-12	32.0	5.85	2.61	7.57

* broad diffuse maximum (Cu radiation)

(1) crystalline compositions reported without diffractograms

Reference Intensity Ratios were derived for all of the common crystalline phases in fly ash. Crystalline phases which were not available commercially were synthesized in the laboratory.

Melilite and ferrite spinel, which are solid solution phases, required multiple RIR measurements. RIRs were determined for the end members of melilite (akermanite and gehlenite) and for a 50:50 percent solid solution of akermanite and gehlenite. RIRs were determined for the end members of ferrite spinel: magnesioferrite and magnetite. These RIRs were essentially the same, so no intermediate compositions were studied (423).

Two five-gram samples of each fly ash were analyzed by X-ray diffraction. The samples were ground for ten minutes in a micronizing mill with ethanol added as a grinding medium. The slurries were allowed to dry and were then gound manually for an additional five minutes. Mixtures of 90 percent by weight ground fly ash and 10 percent by weight rutile standard (TiO_2) were homogenized by intergrinding for ten minutes. Samples were loaded into an aluminum holder and were analyzed with an automated powder diffractometer using a Cu focus tube (λ = 1.54178 Å). Generator settings were 50 kV and 23 mÅ. Data were collected in 0.03° steps for a 2 second count time. The scan range was 10° to 55° 2Θ. Peak positions and heights were read manually using x-y cursors on a graphics terminal screen (255, 423).

Most maximum intensity peak heights of fly ash phases were easily detected and measured. However, mullite, tricalcium aluminate, merwinite, hematite, and ferrite spinel overlapped, so their relative intensities were difficult to decipher. McCarthy and Thedchanamoorthy (423) developed procedures for proportioning these overlapped intensities based on secondary, non-overlapping peaks and bulk chemical analyses of fly ash. These procedures, which were developed from a database of hundreds of fly ash samples, are quite intricate and will not be discussed in this text. Proportioning overlapped intensities for these fly ash phases may introduce errors. Therefore, this method of quantifying crystalline phases has often been labelled "semi-quantitative" XRD analysis.

3.3.2 CALCULATION OF FLY ASH GLASS COMPOSITION

Quantitative XRD data and bulk chemical composition data for fly ashes permitted estimates of the average composition of the glassy portion of fly ash (439). In this approach, average glass composition was estimated from the difference between bulk chemical contents and crystalline compositions. The proportions of fly ash which were lost on ignition were also accounted for:

$$\text{glass composition} = 100\% - \sum(\text{crystalline phases}) - \text{LOI} . \qquad (3.2)$$

Loss on ignition accounts for unburnt carbon and alkali sulfate salts in fly ash.

3.3.3 APPROXIMATING X-RAY DIFFRACTOGRAM GLASS MAXIMA

The diffractogram backgrounds were traced manually, as demonstrated in Figure 3.3. Tracing techniques were consistent and followed examples provided by Diamond (88, 89). Due to the broadness of the glass diffractions and the inaccuracies involved, estimates of maximum elevations were restricted to one-half degree 2Θ increments.

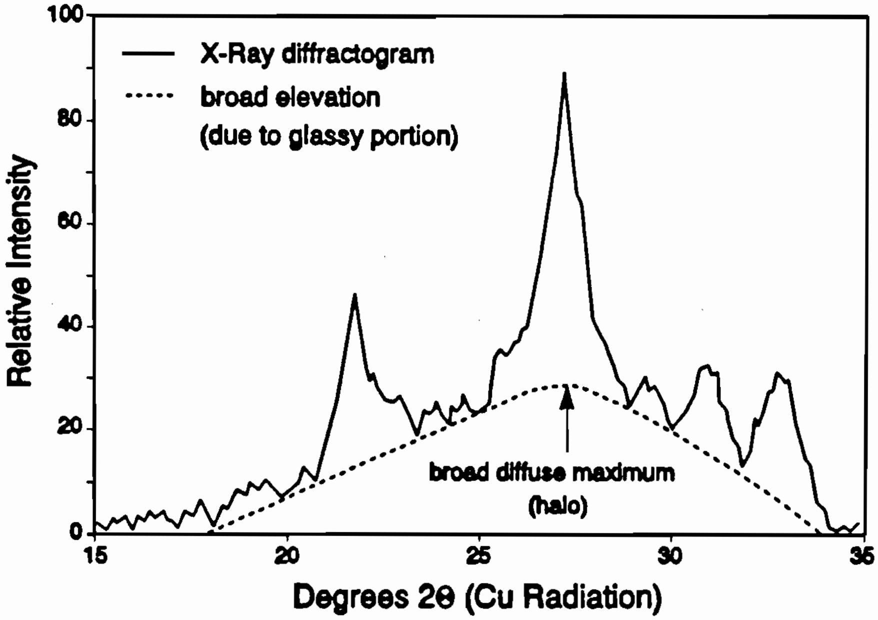


Figure 3.3 Broad Diffuse Maximum of an X-Ray Diffractogram for a Partially Amorphous Fly Ash (88)

3.3.4 INCORPORATION OF FLY ASH WITH CEMENT

3.3.4.1 Fly Ash as a Mineral Admixture

Concrete mixtures in which fly ash was added as a mineral admixture are representative of ready-mix operations in which fly ash and cement are added separately to concrete trucks. At truck loading platforms, fly ash and cement are stored in separate hoppers and therefore may be added in any desired proportions.

In the laboratory, fly ash and cement were weighed in the same container but were not hand-mixed. The fly ash and cement were then added to the rotating-drum concrete mixer simultaneously.

3.3.4.2 Interground Fly Ash

Concrete mixtures in which fly ash was interground with cement clinker and gypsum are representative of commercially available blended fly ash cements. Large-scale procedures for the production of blended cements involves adding fly ash, cement clinker, and gypsum (and anhydrite if needed) to the grinding ball mill simultaneously.

The ball mill used in the laboratory was a scaled-down version of industrial ball mills which are used for the production of cement. The 26-gallon laboratory mill had a dry-batch capacity of 88 lbs and discharged into a fully enclosed housing. The drum rotated at approximately 40 revolutions per minute and contained approximately 500 lb of steel balls with the gradation of sizes shown in Table 3.11.

Prior to blending fly ash cements, ordinary portland cements were produced to simulate those produced at the plants. Grinding times were adjusted until the Blaine Air Permeabilities of the laboratory-produced cements were similar to the plant-produced cements. Relative proportions of clinker and gypsum were adjusted until the bulk SO_3 contents of laboratory-produced cements were similar to the plant-produced cements.

In order to ensure uniformity of laboratory-produced cements and blends, all clinker and gypsum particles were crushed to 100 percent passing a ¾-inch sieve prior to charging the ball mill. Also, after grinding, all cements were sieved through a 150 μm (#100) sieve to remove any hard, unground clinker particles.

Table 3.11 Gradation of Steel Balls in the Laboratory Grinding Mill

Steel Ball Diameter	Weight (lbs)	Proportion (wt.%)
1-1/2"	112	22
1-1/4"	119	24
1"	91	18
7/8"	76	15
3/4"	106	21
Total	504	100

Adhering to the procedures of cement plants, the only source of sulfate for the Type II cement was gypsum. The Type I-H cement contained both gypsum and anhydrite. At the cement plant, the relative proportions of gypsum and anhydrite were adjusted to attain proper C_3A hydration and the desired cement paste set times. These proportions were 70 percent gypsum and 30 percent anhydrite by weight, which corresponds to anhydrite providing 35 percent of the sulfur trioxide by weight. These same relative proportions were used in the laboratory. Grinding times and constituents of the two ordinary portland cements produced in the laboratory are shown in Table 3.12.

Table 3.12 Ordinary Portland Cements Produced in the Laboratory

Cement	Grinding Time (minutes)	Blaine Fineness (cm^2/gm)	Proportions (percent by weight)			Bulk SO_3* (%)
			Clinker	Gypsum	Anhydrite	
Type II	135	3350	95.0	5.00	—	3.00
Type I-H	205	3950	95.9	2.81	1.25	2.99

* measured in accordance with procedures of ASTM Test Specification C-114

Grinding times and the relative proportions of clinker, gypsum, and anhydrite remained contant throughout all subsequent blending operations. Seventy-two fly ash/cement blends were produced in the laboratory for this study. The dry batch weights for all the blends are listed in Appendix C.

3.3.5 CONCRETE MIXTURE DESIGN

Concrete mixtures were designed in accordance with procedures of Texas DOT Method 414-A. Cement factor was specified as 5.5 sacks cement per cubic yard concrete for most mixtures. However, selected mixtures were also designed with a cement factor of 7.0. Based on aggregate gradations and trial mixtures, coarse aggregate factor ranged from 0.62 to 0.68. Depending on anticipated water requirements, water factor for the 5.5 sack mixtures ranged from 5.6 to 6.0 gallons per sack of cement. Water factor for the 7.0 sack mixtures remained constant at 4.75 gallons per sack of cement. Water was added to all mixtures until a slump of 5 to 7 inches was obtained. Air factor was assumed as 2.0 percent for all mixture designs in this study.

Bulk specific gravities (SSD basis), absorption capacities, and percent solids (absolute volume, SSD) were monitored for both fine and coarse aggregate stockpiles. Slight adjustments in mixture designs were required periodically. Moisture contents of both fine and coarse aggregates were measured prior to designing concrete mixtures. Adjustments for moisture were made and the aggregates were stored in air-tight containers until time of batching.

Fly ash replaced cement on an absolute volume basis; replacements included 25, 35, 45, and 55 percent. Specific gravities of the Type II, Type I-L, and Type I-H cements were measured to be 3.10, 3.15, and 3.15, respectively. Specific gravities of fly ashes ranged from 2.02 to 2.79.

Chemical additives were considered as part of the cement. They replaced small portions of cement on an equal mass basis. For mixture design purposes, the specific gravities of cements and blends were assumed unchanged by the presence of chemical additives.

Concrete mixture descriptions and proportions are provided in Appendix D.

3.3.6 MIXING, CASTING, AND CURING CONCRETE

Mixing sequence, vibration, and curing procedures followed the requirements of ASTM Standard C-192. Chemical additives were dissolved in a portion of the mixing water. This portion of the mixing water was used first in order to ensure that the full amount of chemical additives was added to the concrete. The remaining mixing water, which was plain tap water, was added to the concrete mixture until the desired slump was attained. Prior to batching, all concrete materials were stored in a temperature controlled environment until they reached a temperature between 70 and 85 °F. All mixing was performed in a 3 ft^3 capacity rotating-drum mixer.

Concrete specimens included 6x12-inch cylinders for 28-day compressive strengths, 4x8-inch cylinders for permeability tests, and 3x6-inch cylinders for early-age strength testing and sulfate exposure tests. All cylinder molds were plastic. The concrete in 6x12-inch cylinders was compacted with tamping rods. The concrete in smaller specimens was compacted with a vibrating table.

After finishing, all concrete specimens were covered with wet burlap and a sheet of plastic. The plastic prevented the burlap from losing moisture by evaporation.

Specimens were removed from molds 24 ±8 hours after casting and were immediately placed in a 73 ±3 °F moisture cabinet.

3.3.7 FRESH CONCRETE TESTS

Concrete slumps were measured in accordance with Texas Method 415-A and ASTM Standard C-143. Air contents of selected concrete mixtures were measured by Volumetric Air Meter, in accordance with Texas Method 416-A and ASTM Standard C-173.

3.3.8 COMPRESSIVE STRENGTH TESTS

Each compressive strength test included two replicates. Compressive strength specimens were kept moist until the time of testing. Ends of cylinders were inspected visually for deviations from perpendicular to the longitudinal axis; no cylinders which appeared to be malformed were tested. Neoprene pads were used to eliminate the effects of surface roughness. All cylinders were tested at rates of 20 to 50 psi per second, in accordance with Texas Test Method 418-A and ASTM C-39.

Strengths at various ages up to 28 days were measured with 3x6-inch concrete cylinders. Early-age strengths were required for conformance with a sulfate exposure criterion. Strengths at 28 days were measured with both 3x6-inch and 6x12-inch cylinders. The relationship between strengths, as measured with the two specimen sizes, is shown in Figure 3.4. In order to be consistent, all strength comparisons will be based on the test results of 3x6-inch cylinders. Concrete mixture descriptions and compressive strength test results are provided in Appendix D.

3.3.9 SULFATE EXPOSURE TEST

3.3.9.1 Introduction

Sulfate exposure test procedures were modified from the United States Bureau of Reclamation Standard 4908 (Method B). Concrete specimens of dimensions 3x6 inches were cast with a ¾-inch stainless steel gage stud at each end; the studs fascilitated length measurements. During casting and initial curing operations, apparatuses consisting of acrylic plates and steel bolts held the gage studs in place. The gage studs were threaded into the acrylic plates, leaving about one-half of the lengths of studs embedded within concrete.

Four replicates of sulfate exposure specimens were cast for each concrete mixture. The exposure specimens were initially cured at 73 °F in a 100 percent relative humidity moisture cabinet. All exposure specimens were immersed in sulfate solution when companion cylinders reached a compressive strength of 3500 psi. If the strength criterion was not satisfied by 28 days, the exposure specimens were immersed at that time.

3.3.9.2 Exposure Solution

The principal exposure environment, in accordance with USBR Standard 4908 (Method B), was ten percent sodium sulfate solution. Selected mixtures were also immersed in 5 percent and 2.1 percent sodium sulfate solutions in order to study the effects of exposure solution concentration. Exposure solutions were maintained at 73 ± 5 °F.

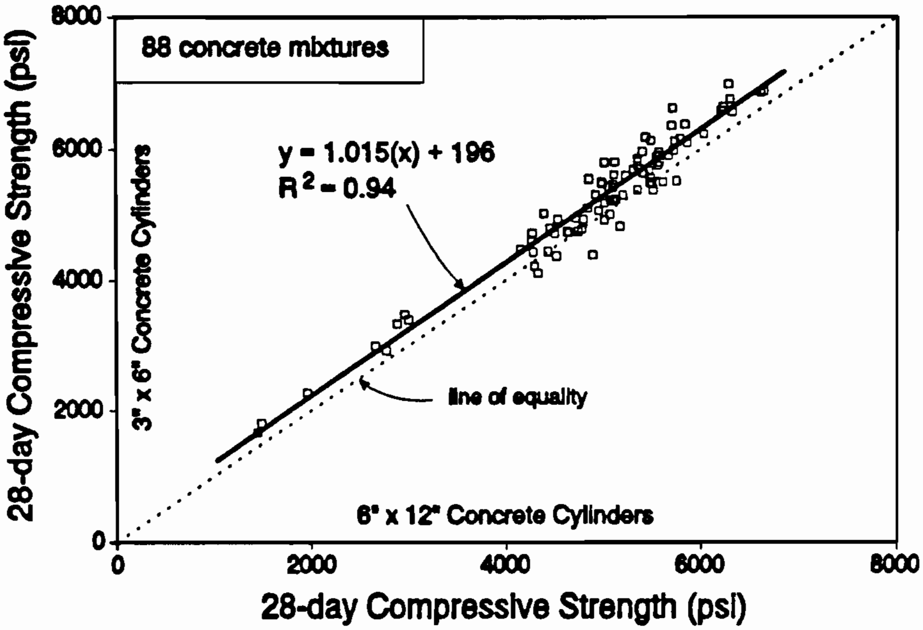


Figure 3.4 Compressive Strength of Concrete as Measured by 3x6-inch Cylinders and 6x12-inch Cylinders

Many tanks containing the exposure solutions were required to hold the large quantity of exposure specimens. Therefore, measures were taken to ensure that exposure severity was uniform:

1) (exposure solution)/specimen volume ratios were maintained at 4 ± 0.5,
2) specimens were rotated between tanks at least once every three months,
3) specimens were rotated 180 degrees vertically at least once every three months, and
4) solutions were periodically replaced.

Solution replacement was required due to its changing composition; leachable concrete constituents accumulate and sulfates are consumed. P.W. Brown (42) monitored solution composition during immersion of a Type I cement mortar in 0.2 molarity Na_2SO_4 solution. Over time, the hydroxyl ion (OH^-) concentration rose rapidly toward the value determined by the solubility product of calcium hydroxide. The sulfate ion (SO_4^{2-})

concentration was consumed at a decreasing rate. One mole of sulfate ions was consumed for each two moles of hydroxyl ions liberated, which is consistent with the chemistry of the formation of gypsum and various calcium sulfoaluminates during sulfate attack (42).

Based on these observations by Brown, solution pH was used to monitor conditions of sulfate exposure solutions in this study. Solutions were replaced when pH exceeded 10.5. Minimum and maximum time spans between solution replacements were set at two weeks and six months, respectively.

3.3.9.3 Length and Mass Measurements

Sulfate exposure specimens were measured for length and mass in their saturated-surface-dry conditions. The SSD condition was obtained by blotting the surfaces of specimens until the glossy, moist appearance faded. Lengths were measured with a length comparator, relative to the known length of an invar bar. The invar bar was 6.6250 inches long and its length was checked periodically with a micrometer. The accuracy of length measurements were to the nearest 0.0001 inches. With the exception of specimen size and shape, length measurements were performed in accordance with ASTM Standard C-490.

Mass was measured to the nearest 0.1 grams. No effort was made to remove loose fragments of specimens prior to measurement. However, mass was often lost during blotting procedures.

Initial mass and length measurements were taken after 7 days of immersion in order to eliminate the effects of initial absorption of solution. Masses and lengths were measured every month for six months and every three months thereafter.

3.3.9.4 Dynamic Tests

Dynamic modulus of elasticity and damping capacity were monitored for selected specimens. Both parameters were measured by exciting the sulfate exposure cylinders at their longitudinal resonant frequencies. The exposure cylinders were 3x6 inches and were in a saturated-surface-dry condition. The cylinders were assumed to have free ends (no strain) and were excited in the first normal mode of vibration, as shown in Figure 3.5. In order to minimize signal disturbance, the specimens were held at their centers (point of no displacement) by a knife-edge.

In first mode longitudinal resonance, the velocity of longitudingal waves (V) can be approximated as (356):

$$V = 2(f_m)L, \text{ where} \tag{3.3}$$

f_m = resonant frequency and

L = length of specimen.

In finite, rod-shaped elastic media, such as concrete cylinders at small strains, dynamic modulus (E_d) can be approximated as (356):

$$E_d = \rho V^2, \text{ where} \tag{3.4}$$

ρ = density of concrete.

Substituting equation (3.3) into equation (3.4) yields an approximate solution for dynamic modulus in terms of resonant frequency:

$$E_d = 4\,\rho(f_m)^2(L)^2. \tag{3.5}$$

The method used in this study to monitor changes in dynamic moduli of sulfate exposure specimens is similar to the technique described in ASTM C-666 for monitoring deterioration of freeze-thaw specimens. The densities and dimensions of specimens are assumed to not change significantly during exposure tests. Therefore, changes in dynamic moduli are proportional to changes in resonant frequencies squared. Deterioration is monitored as ratios of dynamic moduli:

$$RM_t = \frac{fm_t^2}{fm_o^2} \times 100\%, \text{ where} \tag{3.6}$$

RM_t = relative dynamic modulus of elasticity at time t (percent),

fm_t = longitudinal resonant frequency at time t, and

fm_o = initial longitudinal resonant frequency (after 7 days exposure).

Frequency-amplitude data also permitted the sulfate exposure specimens to be monitored for changes in damping capacity. Relative to dynamic modulus of elasticity, damping capacity is often a better indication of the soundness of a material. Small

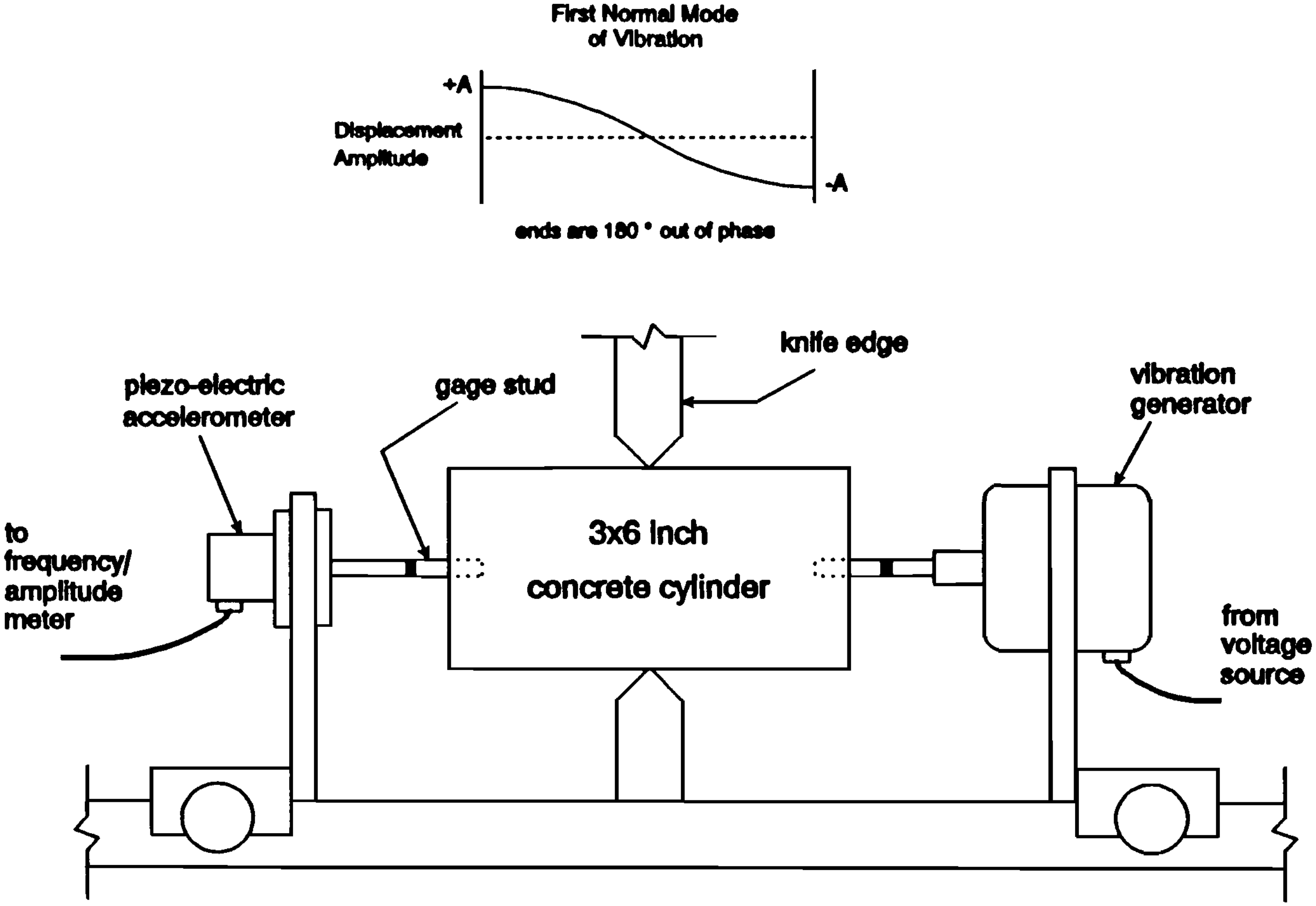


Figure 3.5 Longitudinal Vibration of Concrete Cylinders

imperfections in materials, such as microcracks produced during freezing and thawing cycles of concrete, may cause relatively large changes in damping constants (172).

The simplest mathematical element used to model energy dissipation in a freely vibrating system is the viscous damper or dashpot. The force in the dashpot is directly proportional to the velocity ($\dot{z}$) of the moving element in the system and has a value computed from the viscous damping coefficient, c (lb/in/sec):

$$. \quad \text{Force} = c(\dot{z}). \tag{3.7}$$

The force exerted by the dashpot opposes the motion of the mass.

A critically damped system, damping coefficient = c_c, allows the displacement amplitude (z) in Figure 3.6(a) to change sign only once (356). An underdamped system ($c < c_c$) exhibits gradual decay of free vibrations such as that shown in Figure 3.6(b). A property of this gradual decay is that the ratio of any two successive amplitudes is constant. The natural logarithm of any two successive amplitudes (z) of motion in the underdamped system is defined as the logarithmic decrement (δ) (356):

$$\delta = \ln \frac{z_1}{z_2} . \tag{3.8}$$

Damping ratio (D) is defined as the ratio of viscous-damping coefficient to critical damping coefficient:

$$D = \frac{c}{c_c} . \tag{3.9}$$

Damping ratio is often used to compare material damping capacities. Logarithmic decrement and damping ratio are related as follows (356):

$$\delta = \frac{2\pi D}{\sqrt{1-D^2}} . \tag{3.10}$$

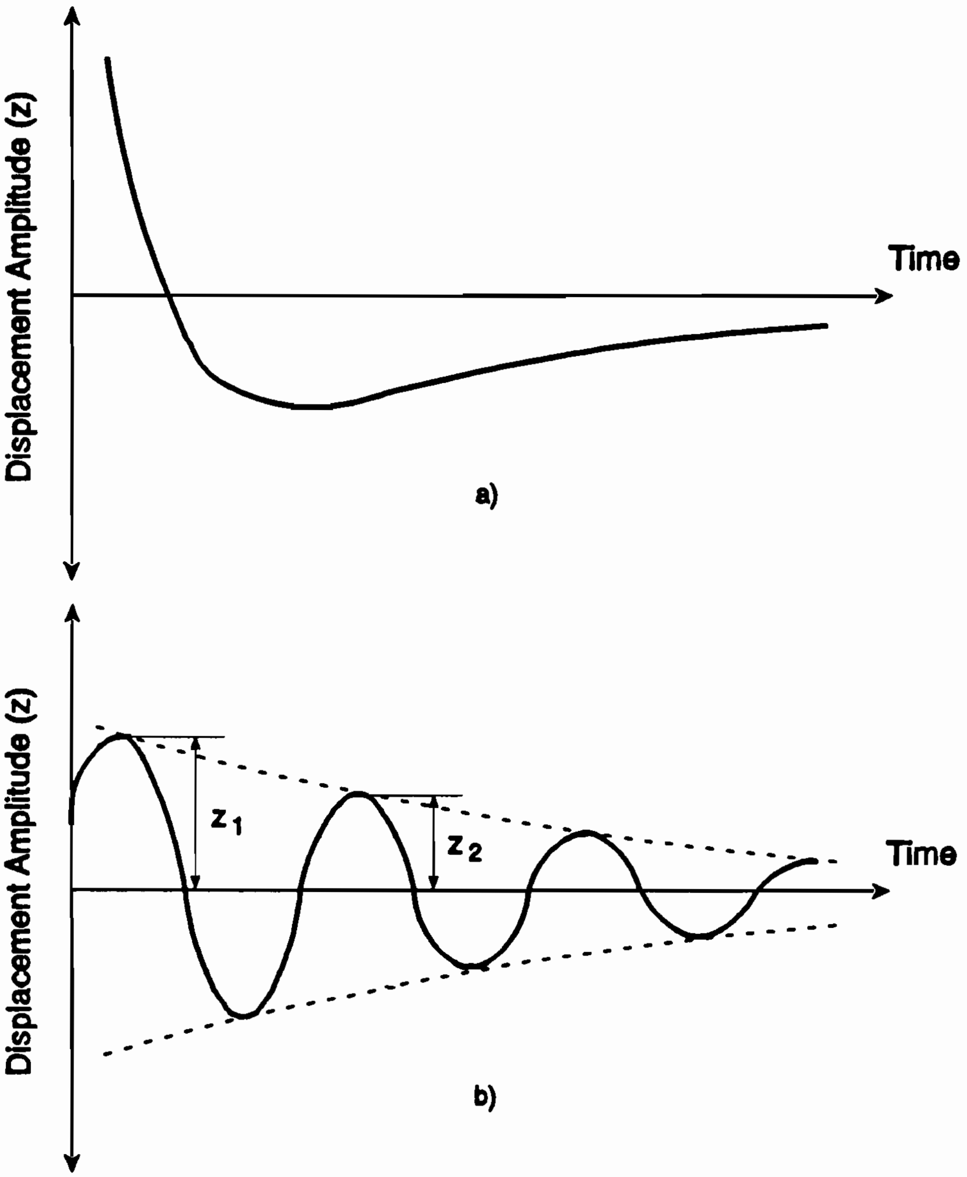


Figure 3.6 Free Vibrations of a Viscously Damped System a) Critically Damped and b) Underdamped (356)

The logarithmic decrement can be calculated from frequency-amplitude data obtained during resonant frequency tests. A typical response curve for a constant-force amplitude vibration is shown in Figure 3.7. The logarithmic decrement is calculated as follows (356):

$$\delta = \frac{\pi}{2} \frac{f_2^2-f_1^2}{f_m^2} \sqrt{\frac{A^2}{A_{max}^2-A^2}} \frac{\sqrt{1-2D^2}}{1-D^2} . \tag{3.11}$$

When D is small, the last term can be assumed equal to 1.0. If A is chosen as 70.7 percent of A_{max}, an extremely simplified expression is obtained:

$$\delta = \frac{\pi(f_2-f_1)}{f_m} . \tag{3.12}$$

In this study, damping capacities are monitored as ratios of logarithmic decrement (δ):

$$RDC_t = \frac{\delta_t}{\delta_o} \times 100\%, \text{ where} \tag{3.13}$$

RDC_t = relative damping capacity at time t,
δ_t = logarithmic decrement at time t, and
δ_o = initial logarithmic decrement (after 7 days of exposure).

3.3.10 CONCRETE PERMEABILITY TEST

Chloride ion permeabilities of selected concrete mixtures were determined in accordance with AASHTO T-277 procedures:

1) two-inch thick slices of concrete were cut from four inch diameter cylinders;
2) the circumferential surfaces of slices were coated with impervious epoxy;
3) the specimens were desiccated and were then saturated with deaerated water;
4) the specimens were secured and sealed into a testing cell, as shown in Figure 3.8;
5) each end of the concrete slice faced a copper screen and a solution reservoir which was machined into an acrylic block;

   a) the screens distributed the flow of electrical current over the cross-sections of concrete slices;
   b) one reservoir contained a source of chloride ions, NaCl solution;
   c) the other reservoir contained a source of cations, NaOH solution;
6) a power potential of 60 volts D.C. was applied across the specimens for a duration of 6 hours; and
7) voltage drop across a calibrated shunt resistor was recorded every 30 minutes;
8) electrical current was shut off if the NaCl solution reservoir exceeded 190 °F.

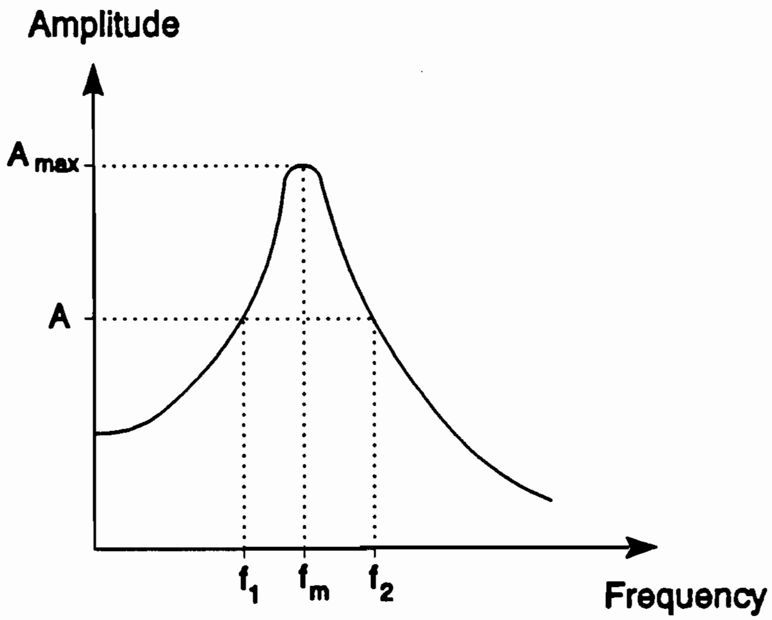


Figure 3.7 Response Curve for Constant-Force Amplitude Vibration (356)

Ohm's Law was used to calculate electrical current from voltage drop readings:

$$I = V/R, \text{ where} \tag{3.13}$$

I = electrical current (amperes),
V = voltage drop across shunt resistor (volts), and
R = shunt resistance (0.01 ohms).

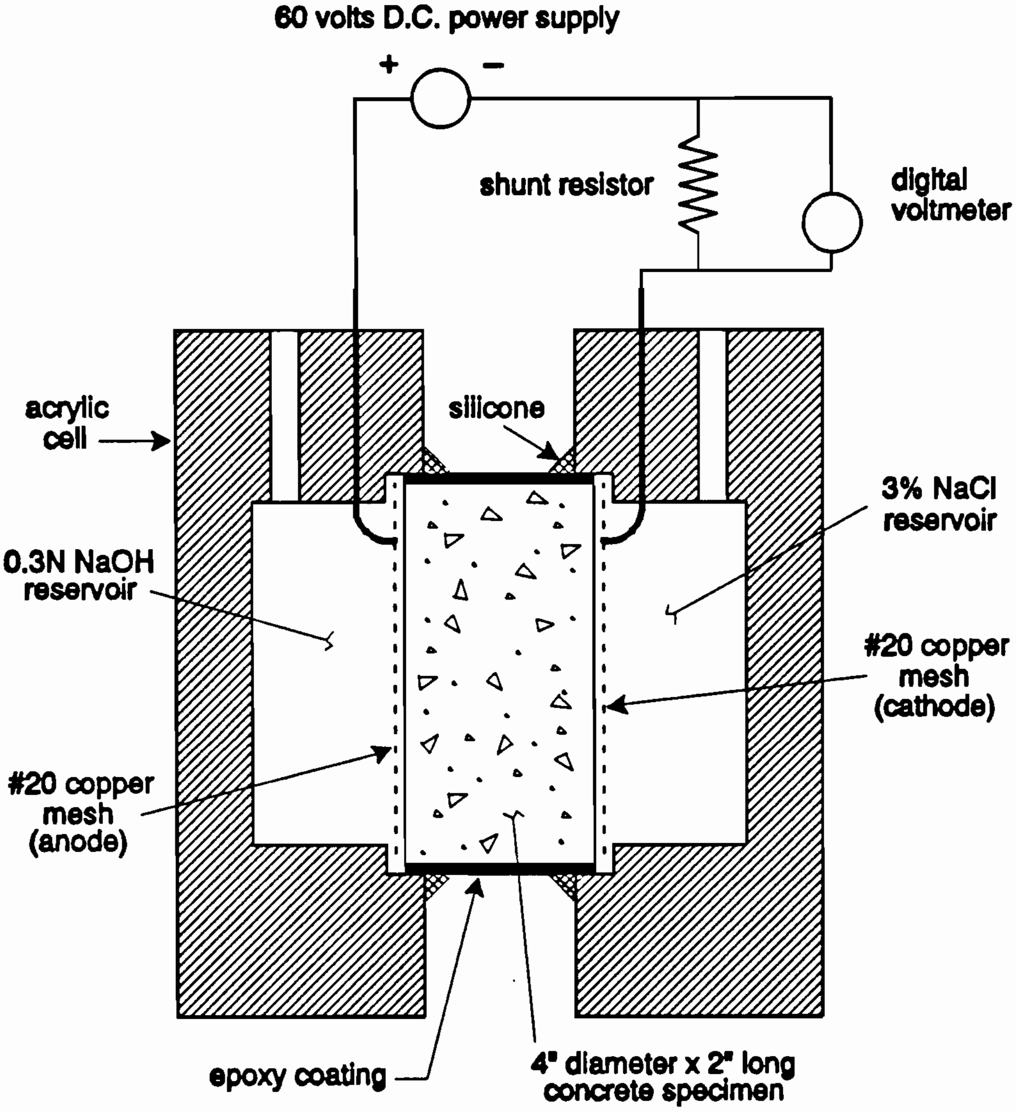


Figure 3.8 Test Cell for the Rapid Chloride Ion Permeability Test

Concrete permeabilities were compared on the basis of total electrical charge (coulombs) passed through specimens over the 6 hour test duration. Coulombs were calculated by integrating current-time plots, as shown in Figure 3.9. One coulomb is the quantity of electricity transferred by a current of one ampere sustained for one second. Total electric charge was limited to 10,000 coulombs; comparisons of charges which exceed this value are of little practical use.

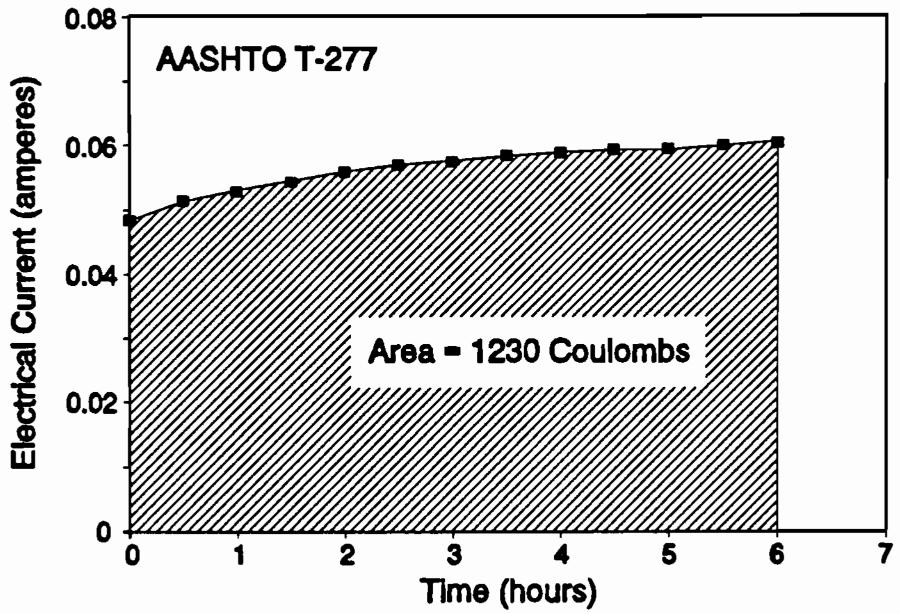


Figure 3.9 Calculation of Coulombs from a Current-Time Plot

Permeabilities were measured after 13 and 91 days of moist curing at 73 °F. A total of three replicates from two cylinders were tested for each concrete mixture. The concrete testing slices were obtained from the middle two-thirds of cylinders, thus minimizing the effects of bleed-water capillaries near the surface of cylinders and aggregate orientations near the bottom of cylinders.

A demonstration of the relationship between total electric charge passed and concrete permeabilities has been provided by David Whiting (446). During the development of AASHTO T-277 procedures, Whiting measured the permeabilities of concrete slabs representing numerous mixture designs. For each concrete slab, he compared the results of rapid chloride ion tests with the results of traditional ponding tests. Rapid chloride ion tests were performed on 3¾-inch diameter, 2-inch thick concrete slices, which were cut from slab cores. Traditional ponding tests were performed on companion slabs. Whiting used the relationships between test results on similar concrete slabs to develop a qualitative classification of concrete permeabilities based on AASHTO T-277 test results, as shown in Table 3.13.

Table 3.13 Relative Chloride Permeabilities Based on Charge Passed (446)

Charge Passed (coulombs)	Relative Chloride Permeability	Typical of
> 4000	High	conventional PCC high water/cement ratio (> 0.6)
2000 - 4000	Moderate	conventional PCC moderate water/cement ratio (0.4 to 0.5)
1000 - 2000	Low	conventional PCC low water/cement ratio (< 0.4)
100 - 1000	Very Low	latex-modified concrete internally sealed concrete
< 100	Negligible	polymer impregnated concrete polymer concrete

Note: Tests were performed on 3.75 inch diameter x 2 inch long core slices taken from laboratory prepared slabs.

CHAPTER 4

EXAMINATION OF THE SULFATE EXPOSURE TEST

4.1 INTRODUCTION

This chapter evaluates the sulfate exposure test for the following:

1) experimental error and

2) requirements for assessing the sulfate susceptibility of concrete mixtures.

All concrete mixtures were exposed to the sulfate test for at least 2 years. All sulfate exposure specimens were monitored for linear expansion and mass change. Mixtures which were produced late in the testing program were also monitored for dynamic modulus of elasticity and damping capacity.

4.2 EXPERIMENTAL ERROR

4.2.1 INTRODUCTION

Experimental error was measured by the variation of results between experimental units treated alike. The experimental error of the sulfate immersion test used in this study was measured by two types of variability of results:

1) variability between replicates of a single mixture and

2) variability between similar mixtures.

Two ordinary portland cement concrete control mixtures, which were repeatedly produced and subjected to the immersion test, provided the information for this analysis.

4.2.2 EXPERIMENTAL ERROR BETWEEN REPLICATES

Linear expansion, mass change, relative dynamic modulus of elasticity, and relative damping capacity are displayed for four replicates of each of the two control mixtures in Figures 4.1 through 4.4. In all cases, similar replicates follow similar trends.

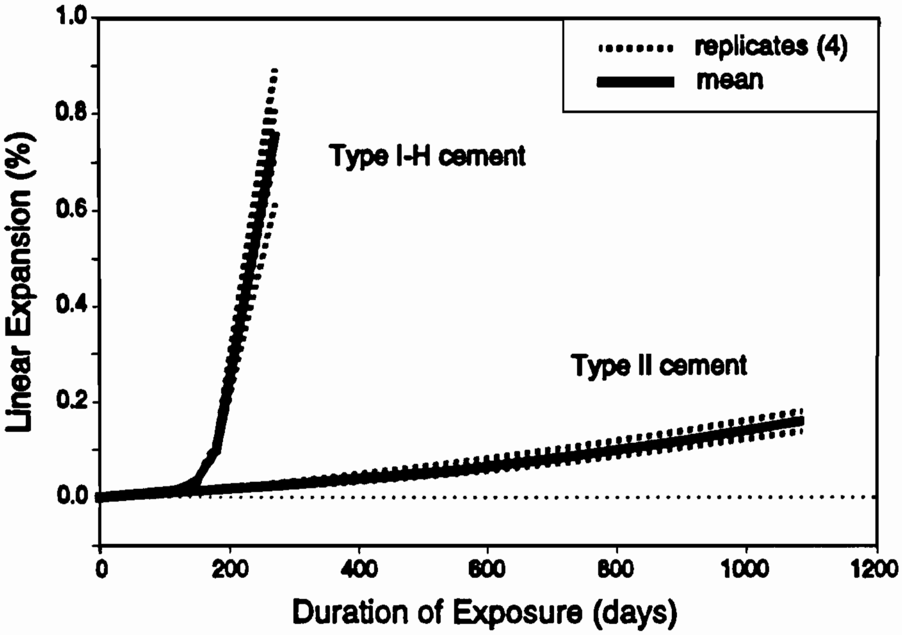


Figure 4.1 Linear Expansions of Ordinary Portland Cement Concrete (Replicates and Means)

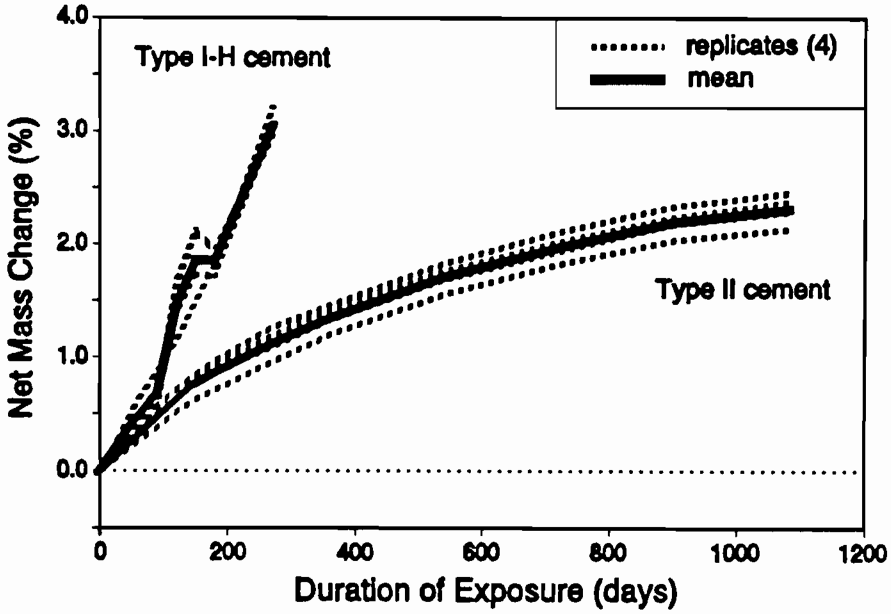


Figure 4.2 Net Mass Changes of Ordinary Portland Cement Concrete (Replicates and Means)

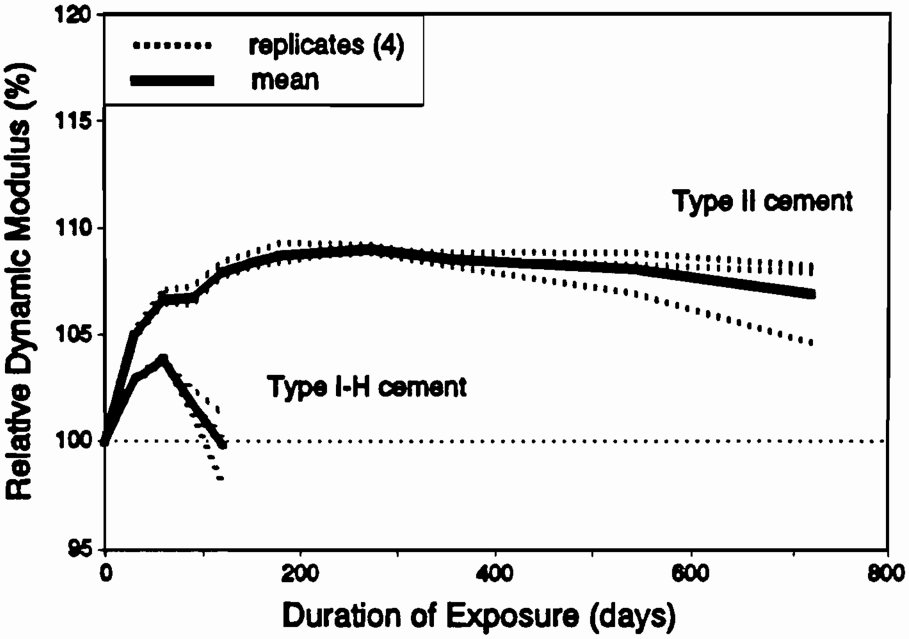


Figure 4.3 Relative Dynamic Moduli of Ordinary Portland Cement Concrete (Replicates and Means)

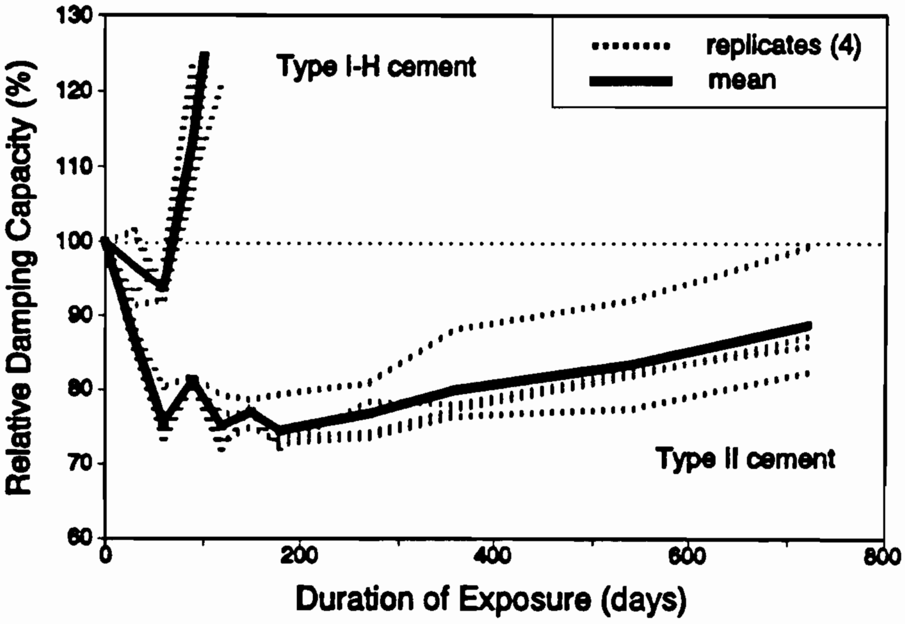


Figure 4.4 Relative Damping Capacities of Ordinary Portland Cement Concrete (Replicates and Means)

Sources of variability between replicates include inhomogeneities in concrete from the same mixture, variations in exposure solution within the same exposure tank, and inaccuracies in the methods of monitoring concrete deterioration. Coefficients of variation (COV) between replicates for each mixture at various times of immersion are shown in Table 4.1. The within-test COVs are all less than 20 percent at exposure durations greater than or equal to 180 days.

4.2.3 EXPERIMENTAL ERROR BETWEEN SIMILAR MIXTURES

The Type I-H cement concrete control mixture was produced twice and the Type II cement concrete control mixture was produced six times throughout the duration of the study. Each mixture was represented by four replicates. Trends of linear expansion and mass change for similar control mixtures are alike, as shown in Figures 4.5 and 4.6.

The Type I-H cement concrete was mixed only twice, so the coefficient of variation (COV) for the rate of deterioration of these mixtures would be of little use. Therefore, only Type II cement concrete mixtures were analyzed for variablity between similar mixtures.

The COV for expansion of the six Type II cement mixtures was high at early ages, as shown in Table 4.2. This was at least partially attributable to the low mean value for early expansion; experimental treatments with low means are susceptible to high COVs, even with relatively low standard deviations. At durations of exposure greater than or equal to 720 days, the coefficient of variation between expansions was less than 20 percent.

The COV for mass change of Type II cement concrete mixtures was less than 20 percent at durations of exposure greater than or equal to 270 days.

Variabilities between similar mixtures were larger than variabilities between replicates of the same mixtures. Similar mixtures were produced at various times during the study, so slight variations in cement composition, aggregate characteristics, and concrete mixing conditions may have contributed to the experimental error.

Table 4.1 Coefficients of Variation Between Replicates of Ordinary Portland Cement Concrete Control Mixtures

Mixture	Test Parameter	Duration of Exposure (days)							
		90	180	270	360	540	720	900	1080
		Coefficient of Variation (%)							
Type I-H Cement	Linear Exp.	9.02	12.3	15.9	(2)	—	—	—	—
	Mass Chg.	22.5	5.77	3.54	(2)	—	—	—	—
	RDM	0.51	(1)	(1)	(2)	—	—	—	—
	RDC	7.0	(1)	(1)	(2)	—	—	—	—
Type II Cement	Linear Exp.	6.54	6.84	16.3	16.8	18.3	15.5	12.4	10.9
	Mass Chg.	18.2	12.9	11.7	8.64	6.85	6.17	5.74	5.98
	RDM	0.35	0.37	0.15	0.27	0.75	1.52	—	—
	RDC	0.81	4.42	4.56	6.89	7.40	8.33	—	—

Note: Each mixture was represented by 4 replicates.
RDM = relative dynamic modulus
RDC = relative damping capacity
(1) = at least one specimen did not register a longitudinal funamental frequency
(2) = at least one specimen had fractured

4.3 METHOD FOR ASSESSING THE DETERIORATION OF SULFATE EXPOSURE SPECIMENS

4.3.1 INTRODUCTION

The following text presents:

1) requirements which were established for the sulfate exposure test and
2) the method which was developed and used for comparing the susceptibility of concrete mixtures to sulfate attack.

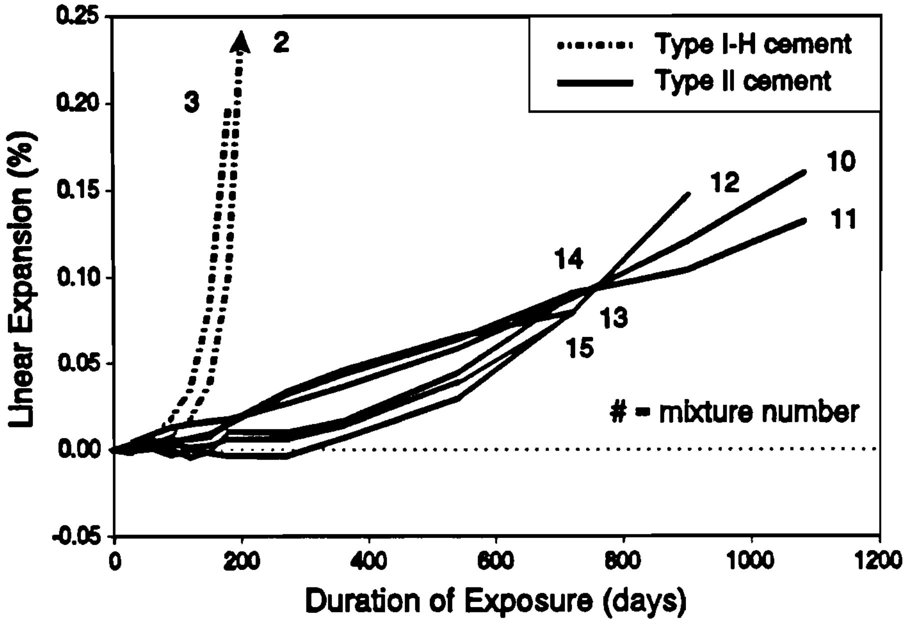


Figure 4.5 Linear Expansions of Ordinary Portland Cement Concrete (Multiple Similar Mixtures)

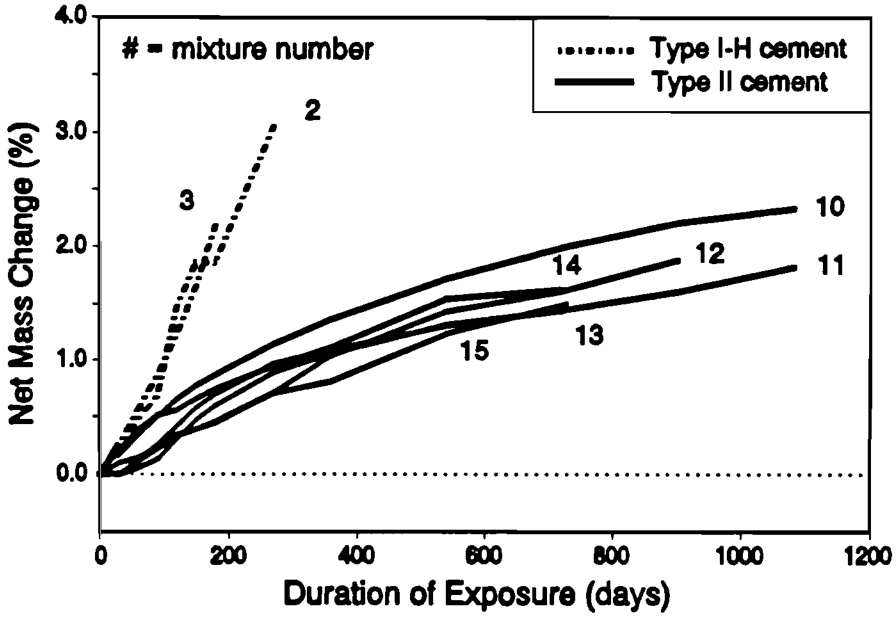


Figure 4.6 Net Mass Changes of Ordinary Portland Cement Concrete (Multiple Similar Mixtures)

Table 4.2 Coefficients of Variation Between Similar Ordinary Portland Cement Concrete Control Mixtures

Mixture	Test Parameter	Duration of Exposure (days)							
		90	180	270	360	540	720	900	1080
		Coefficient of Variation (%)							
Type II Cement	Replicates	6	6	6	6	6	5	3	3
	Linear Exp.	133	77.3	88.8	61.7	29.3	6.39	17.5	13.1
	Mass Chg.	51.4	26.3	18.1	16.1	12.6	12.7	15.7	17.0

4.3.2 EVIDENCE OF DETERIORATION

All sulfate exposure specimens were monitored for linear expansion and mass loss. Deterioration of these specimens may be classified into five groups, as shown in Table 4.3. Mixtures which were immune to sulfate attack suffered no expansion and no mass loss (no deterioration). Mixtures which were susceptible to sulfate attack suffered one of four patterns of deterioration: expansion only, expansion with delayed mass loss, mass loss with delayed expansion, and concurrent mass loss and expansion.

During sulfate exposure testing, mass loss was the result of spalling and/or surface-scaling. Spalling occured near the ends of cylinders and was preceded by visible cracks. Surface-scaling occured over the entire surface area of cylinders and was preceded by a "softening" of the outer layer of cement paste. During the "softening" stage, cylinder surfaces became mushy and non-cohesive.

Cracking and spalling are often attributed to the formation of ettringite, due to its potential for large increases in volume of solids. Surface-scaling is often attributed to an acidic-type corrosion, which is caused by the formation of gypsum from calcium hydroxide and sulfates.

Cylindrical specimens which lost mass by spalling typically also experienced measurable linear expansions. Cylindrical specimens which lost mass by surface-scaling often did not experience concurrent linear expansions. While expansions were delayed by low concrete permeabilities, the surface of cylinders were still susceptible to the acidic-type corrosion of gypsum formation.

Table 4.3 Classification of Patterns of Deterioration

Class of Deterioration	Example (mixture no.)	Linear Expansion	Mass Loss
immune	30	No	No
expansion only	10	Yes	No
expansion predominant	110	Yes	delayed
mass loss predominant	201	delayed	Yes
expansion and mass loss	258	Yes	Yes

Mixtures exemplifying each class of deterioration are identified in Table 4.3. Linear expansion and net mass change for these mixtures are shown in Figures 4.7 and 4.8, respectively. Mixtures 258 and 201 demonstrate the different patterns for mass loss. Mixture 258 lost mass by spalling and suffered significant early expansion. Mixture 201 lost a significant percentage of mass by surface-scaling but expansion was delayed by its low permeability.

It is evident that in order to properly compare the deterioration of concrete mixtures in the sulfate exposure test, both linear expansion and mass loss must be considered.

4.3.3 TEST DURATION REQUIREMENTS

Approximately sixty mixtures, representing a variety of cement types, fly ash types, and fly ash replacement percentages, were subjected to the sulfate exposure test for at least three years. These long-term test results were used to determine a minimum acceptable test duration.

Comparisons between fly ash cement concrete and Type II cement concrete without fly ash were a primary objective of this study. Therefore, the minimum acceptable test

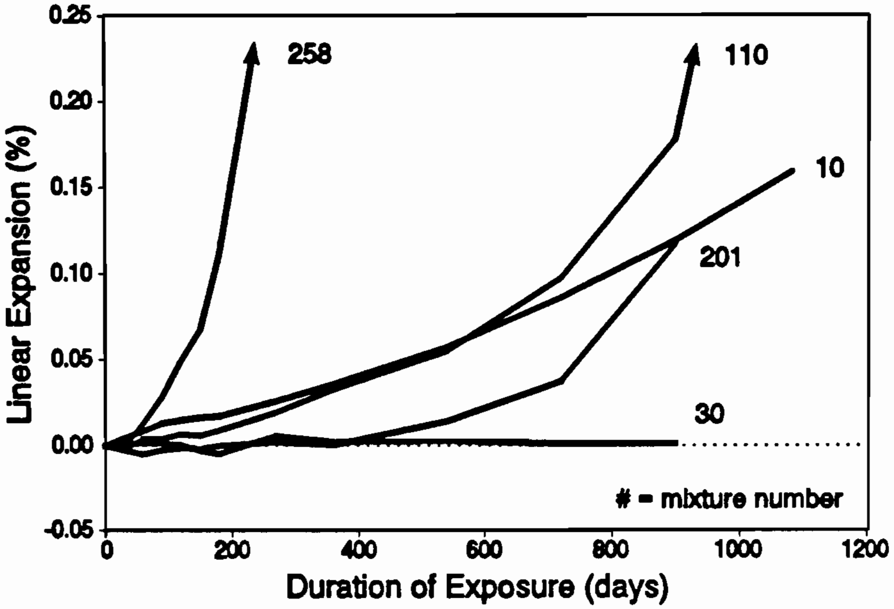


Figure 4.7 Linear Expansions of Mixtures Exemplifying Patterns of Deterioration

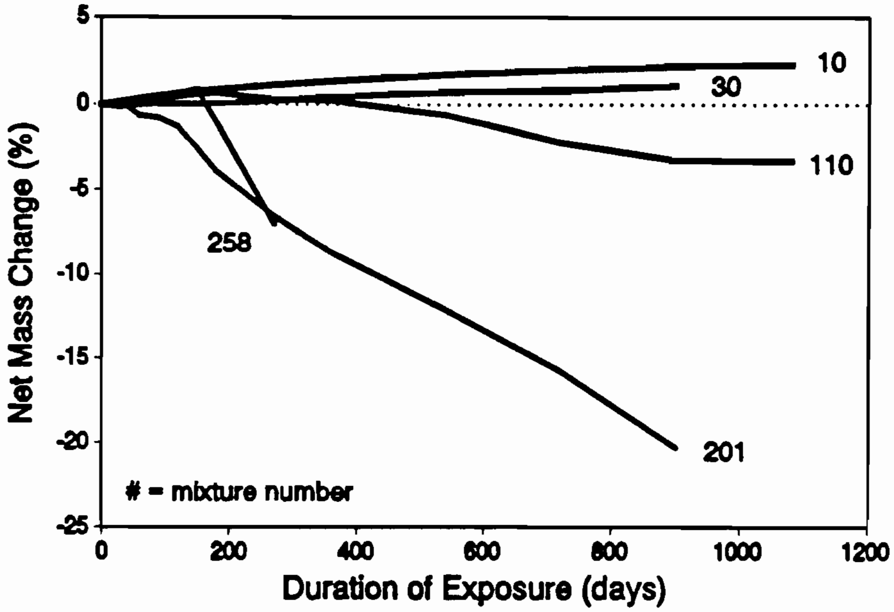


Figure 4.8 Net Mass Changes of Mixtures Exemplifying Patterns of Deterioration

duration was required to detect all mixtures which were less resistant to sulfate attack than Type II cement concrete without fly ash. Mixtures were known to be less resistant to sulfate attack than Type II cement concrete when their linear expansion or mass loss was in excess of that which the Type II cement concrete mixture experienced.

Various concrete mixtures were compared to the control Type II cement concrete at ages of 1, 2, 3, and 4 years, depending on the available data. Student's t-test was used to determine which mixtures exhibited significantly lower or higher linear expansions than Type II cement concrete; a five percent level of significance was used for all t-tests. Since Type II cement concrete suffered no mass loss during its four years of exposure, any mixtures which lost mass were identified as having experienced more deterioration of this type.

Mixtures containing ordinary portland cements and no fly ash were compared to the Type II cement concrete, as shown in Table 4.4. Mixtures containing Type I-L cement partially replaced by fly ash were compared to Type II cement concrete, as shown in Table 4.5. Mixtures containing Type II cement partially replaced by Type A and Type B fly ash were compared to ordinary Type II cement concrete, as shown in Tables 4.6 and 4.7, respectively. Durations of exposure at which mixtures exhibited higher degrees of deterioration (expansion or mass loss) than Type II cement concrete are emphasized in the table cells by shading.

Observations concerning test duration requirements include:

1) ordinary portland cement concrete mixtures which were less resistant to sulfate attack than Type II cement concrete, were identified within one year,
2) mixtures which contained 25 percent fly ash and which were less resistant to sulfate attack than Type II cement concrete, were identified within two years, and
3) mixtures which contained 35 and 45 percent fly ash and which were less resistant to sulfate attack than Type II cement concrete, were identified within one year.

Therefore, a test duration of two years was sufficient for detecting all concrete mixtures which were less resistant to sulfate attack than ordinary Type II cement concrete. Mixtures containing high proportions of sulfate-susceptible fly ash deteriorated more rapidly than mixtures with smaller proportions of the same fly ash. Consequently, a sulfate exposure test duration of one year was sufficient for assessing the sulfate resistance of fly ash cement concrete which contained fly ash at levels of 35 percent or 45 percent by volume.

Table 4.4 Comparison Between the Deterioration of Type II Cement Concrete and the Deterioration of Concrete Containing Other Types of Ordinary Portland Cement

Cement	Time of Exposure (years)			
	1	2	3	4
I-L	>	>	>	fracture
I-H	fracture	fracture	fracture	fracture
0%L	=	<	<	<
0%H	>	=	=	<
V	=	<	<	<

Note: No control mixtures without fly ash lost mass.

< expansion less than the mixture containing Type II cement
= expansion not significantly different than the mixture containing Type II cement
> expansion greater than the mixture containing Type II cement

fracture - at least one specimen suffered through-cracking

The observed proposed test duration requirements were based on sulfate exposure data of mixtures designed with a cement factor of 5½ sacks, 25 percent to 45 percent fly ash, and a concrete slump of 6 to 7 inches. No additional efforts were made to decrease the permeability of concrete exposure specimens (chemical additives, intergrinding fly ash, etc.). If measures are taken to decrease concrete permeability, the exposure test duration should specified as at least two years in order to be conservative.

Table 4.5 Comparison Between the Deterioration of Type II Cement Concrete and the Determination of Concrete in Which Type I-L Cement was Partially Replaced by Fly Ash

Fly Ash	Volume Percent	Time of Exposure (years)		
		1	2	3
A-2	25	<	<	<
A-5	25	<	=	=
A-9	25	<	<	<
A-9	35	<	<	<
A-10	25	<	<	<
A-11	25	<	<	<
A-11	35	=	=	<
B-3	25	= *	> *	fracture
B-5	25	< *	= *	fracture
B-5	35	fracture	fracture	fracture
B-6	25	<	< *	< *
B-9	25	<	< *	< *
B-9	35	> *	fracture	fracture
B-10	25	<	<	<
B-10	35	= *	fracture	fracture

< expansion less than the mixture containing Type II cement
= expansion not significantly different than the mixture containing Type II cement
> expansion greater than the mixture containing Type II cement
* mass loss

fracture - at least one specimen suffered through-cracking

Table 4.6 Comparison of Between the Deterioration of Type II Cement Concrete and the Deterioration of Concrete in Which Type II Cement was Partially Replaced by Type A Fly Ash

Fly Ash	Volume Percent	Time of Exposure (years)			
		1	2	3	4
A-2	25	=	=	<	<
A-2	35	=	<	<	<
A-2	45	=	<	<	<
A-3	25	=	<	<	<
A-3	45	=	<	<	<
A-4	25	>	>	>	>
A-4	45	=	<	<	<
A-5	35	<	<	<	<
A-8	25	=	=	=	=
A-8	45	=	<	<	<
A-9	25	=	<	<	<
A-9	35	=	<	<	<
A-9	45	=	<	<	<
A-10	35	<	<	<	<
A-11	35	<	<	<	<
A-12	35	=	=	<	<

< expansion less than the mixture containing Type II cement
= expansion not significantly different than the mixture containing Type II cement
> expansion greater than the mixture containing Type II cement

fracture - at least one specimen suffered through-cracking

Table 4.7 Comparison Between the Deterioration of Type II Cement Concrete and the Deterioration of Concrete in Which Type II Cement was Partially Replaced by Type B Fly Ash

Fly Ash	Volume Percent	Time of Exposure (years)			
		1	2	3	4
B-2	35	<	<	<	<
B-3	25	=	= *	> *	fracture
B-3	35	= *	> *	fracture	fracture
B-3	45	> *	fracture	fracture	fracture
B-5	25	>	fracture	fracture	fracture
B-5	35	fracture	fracture	fracture	fracture
B-5	45	> *	fracture	fracture	fracture
B-6	25	>	>	>	fracture
B-6	35	> *	> *	fracture	fracture
B-6	45	> *	fracture	fracture	fracture
B-9	25	>	>	fracture	fracture
B-9	35	> *	fracture	fracture	fracture
B-9	45	= *	fracture	fracture	fracture
B-10	25	=	<	<	<
B-10	35	=	=	=	=
B-10	45	<	<	<	<
B-11	25	>	fracture	fracture	fracture
B-11	35	> *	fracture	fracture	fracture
B-11	45	fracture	fracture	fracture	fracture
B-12	25	fracture	fracture	fracture	fracture
B-12	35	fracture	fracture	fracture	fracture
B-12	45	fracture	fracture	fracture	fracture

< expansion less than the mixture containing Type II cement
= expansion not significantly different than the mixture containing Type II cement
> expansion greater than the mixture containing Type II cement
* mass loss

fracture - at least one specimen suffered through-cracking

4.3.4 QUANTIFYING THE RESISTANCE OF CONCRETE TO SULFATE ATTACK

4.3.4.1 Introduction

The method for quantifying the resistance of concrete mixtures to sulfate attack had to meet three criteria:

1) the method needed to fascilitate comparisons of deterioration of all mixtures with the deterioration of a control mixture: Type II cement concrete without fly ash,
2) the method needed to account for concrete deterioration in the forms of both linear expansion and mass loss, and
3) the method needed to include a technique for quantifying the sulfate susceptibilities of concrete whose specimens fractured and became unmeasurable during the exposure test.

Fracture, or through-cracking, of exposure specimens occured over a wide range of linear expansions. The minimum expansion measured just before fracture was approximately 0.15 percent. Therefore, 0.15 percent was established as an expansion limit. All concete specimens which exceeded this expansion were regarded to be on the verge of fracture.

Once mixtures lost mass due to spalling or surface-scaling, they continued to lose mass. In most cases, these mixtures swelled and fractured. Therefore, any mass loss was taken to be an early indication of continued concrete deterioration. In order to fascilitate early detection of concrete which was susceptible to sulfate attack, the limit for mass loss was established as zero percent.

4.3.4.2 Sulfate Susceptibility Rating

A parameter termed Sulfate Susceptibility Rating (SSR) was defined in order to fascilitate comparison of concrete deterioration after 720 days of exposure. The Sulfate Susceptibility Rating for mixtures which had not exceeded the expansion limit of 0.15 percent or the mass loss limit of zero percent was defined as:

$$SSR_i = \frac{\text{linear expansion (\%) of mixture i}}{\text{linear expansion (\%) of control Type II cement concrete}} \quad . \qquad (4.1)$$

The linear expansion of Type II cement concrete at 720 days was 0.086 percent. By definition, the Sulfate Susceptibility Rating of Type II cement concrete without fly ash was unity.

For mixtures which exceeded the expansion or mass loss limit, Sulfate Susceptibility Rating was defined as 3.0. This value was chosen simply because it was sufficiently high to identify these mixtures as much more susceptible to sulfate attack than Type II cement concrete without fly ash.

Examples of the use of Sulfate Susceptibility Ratings are provided by the mixtures exemplifying the five classes of deterioration. Linear expansion and mass loss of these mixtures were shown in Figures 4.7 and 4.8, respectively. Sulfate Susceptibility Ratings are shown in Table 4.8. Mixture 10, Type II cement concrete, had a Sulfate Susceptibility Rating equal to unity. Mixture 30 suffered no mass loss through 720 days, so its SSR was calculated as the ratio of its expansion to that of Type II cement concrete. Mixtures 110, 201, and 258 exceeded the expansion limit and/or the mass loss limit within 720 days. These three mixtures were assigned Sulfate Susceptibility Ratings of 3.0.

Table 4.8 Sulfate Susceptibility Ratings of Mixtures Exemplifying Patterns of Deterioration

Mixture Number	Days Exposure at Onset of Mass Loss *	Linear Expansion (%) at 720 days	SSR at 720 days
10 **	no mass loss	.086	(.086/.086) = 1.0
30	no mass loss	.001	(.001/.086) = 0.012
110	270	fracture	3.0
201	60	fracture	3.0
258	180	fracture	3.0

* accompanied by visual deterioration on at least two of four replicates
** Type II cement control mixture

4.3.4.3 Dynamic Testing

Sulfate exposure specimens which were produced late in the test program were monitored for dynamic modulus of elasticity and damping capacity in addition to linear expansion and mass loss. Deterioration of concrete, as revealed by dynamic characteristics, may be classified into three groups:

1) immune,
2) increasing damping capacity, and
3) increasing damping capacity and decreasing dynamic modulus of elasticity.

No cases were observed in which dynamic modulus of elasticity decreased without a corresponding increase in damping capacity.

The dynamic characteristics of mixtures 214, 168, and 167 provide examples of the three classes of deterioration, as shown in Figures 4.9 and 4.10. Mixture 214 was immune to sulfate attack. Mixture 168 suffered an increase in Relative Damping Capacity (RDC) without a corresponding decrease in Relative Dynamic Modulus (RDM). Mixture 167 suffered both an increase in RDC and a decrease in RDM.

Type II cement concrete, which is also shown in Figures 4.9 and 4.10, did not suffer a net loss in dynamic modulus or a net increase in damping capacity. However, both dynamic characteristics were beginning to show signs of concrete deterioration.

Relative Dynamic Modulus (RDM) and Relative Damping Capacity (RDC) measurements were compared for the efficiency with which they detected concrete deterioration, as shown in Table 4.9. Concrete which registered RDM below 100 percent or RDC above 100 percent were known to be less resistant to sulfate attack than Type II cement concrete. Mixtures which were determined to be less resistant to sulfates than Type II cement concrete are emphasized in Table 4.9 with shaded boxes.

Concrete deterioration was detected at earlier ages and in more cases by Relative Damping Capacity measurements, as compared to Relative Dynamic Modulus measurements. This observation is emphasized by the total quantity of shaded boxes (deteriorating concrete), which are listed for various durations of exposure in the last row of the table. At each duration of exposure, RDC detected more than twice the quantity of deteriorating concrete mixtures, as compared to RDM.

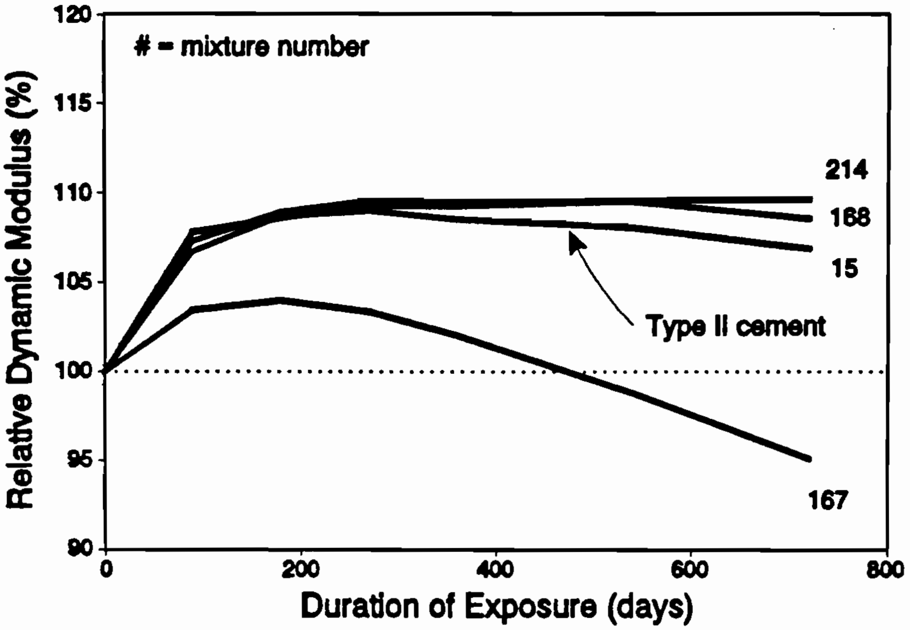


Figure 4.9 Relative Dynamic Moduli of Mixtures Exemplifying Patterns of Deterioration

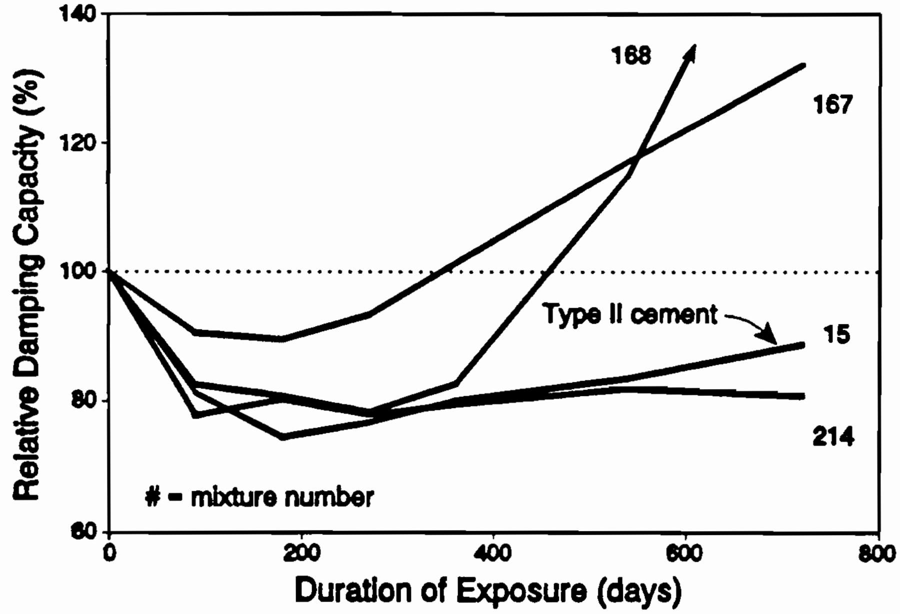


Figure 4.10 Relative Damping Capacities of Mixtures Exemplifying Patterns of Deterioration

Table 4.9 Comparison of Deterioration as Measured by Relative Dynamic Modulus of Elasticity and Relative Damping Capacity

Mixture Number	Relative Dynamic Modulus			Relative Damping Capacity (%)		
	360 days	540 days	720 days	360 days	540 days	720 days
3	fracture	fracture	fracture	fracture	fracture	fracture
15	108.6	108.1	106.9	80.0	83.4	88.7
115	106.8	106.6	106.0	88.8	105.2	115.6
117	103.2	103.0	102.3	111.8	124.4	128.9
119	104.3	103.7	102.9	94.4	112.0	117.4
120	109.3	109.5	109.6	76.9	84.3	101.7
122	103.7	103.6	103.7	92.3	100.2	100.8
124	104.2	103.7	102.8	90.3	91.1	95.9
133	fracture	fracture	fracture	fracture	fracture	fracture
134	fracture	fracture	fracture	fracture	fracture	fracture
138	no rdg.	no rdg.	no rdg.	no rdg.	no rdg.	no rdg.
140	105.8	105.7	105.3	86.4	93.1	95.4
142	104.7	103.8	102.6	90.5	97.1	101.0
143	110.3	109.5	109.5	145.0	173.4	168.4
145	105.4	105.1	104.9	87.8	95.1	99.0
147	104.0	103.6	102.7	85.5	91.0	90.1
163	107.5	107.1	107.0	82.8	93.3	211.8
165	106.8	106.4	106.2	80.0	85.9	84.1
167	102.1	98.8	95.1	101.4	117.2	132.2
168	109.6	109.6	108.6	82.6	115.1	167.9
170	104.7	104.5	104.7	83.4	90.7	94.4
172	104.8	104.5	103.6	87.6	91.0	90.3
207	114.4	114.1	no rdg.	178.0	241.6	no rdg.
208	121.5	122.6	123.0	61.4	60.7	85.0
209	108.8	108.5	108.4	81.2	87.8	89.7
211	104.8	103.9	103.1	98.5	101.7	238.9

Table 4.9 (continued)

Mixture Number	Relative Dynamic Modulus			Relative Damping Capacity (%)		
	360 days	540 days	720 days	360 days	540 days	720 days
213	104.4	102.9	101.2	86.7	98.2	104.0
214	109.3	109.6	109.7	79.5	81.9	80.8
216	104.7	104.5	104.7	82.1	83.3	85.5
218	104.3	103.9	102.9	83.1	84.6	86.9
226	111.6	111.4	111.3	85.1	115.8	208.8
229	111.1	111.0	110.7	65.5	68.9	70.9
233	107.8	107.5	107.5	85.6	81.7	79.1
237	106.8	no rdg.	no rdg.	227.9	no rdg.	no rdg.
238	106.0	no rdg.	fracture	321.1	no rdg.	fracture
262	114.9	no rdg.	no rdg.	288.7	no rdg.	no rdg.
263	119.4	118.3	117.6	142.5	131.1	162.2
264	no rdg.	no rdg.	no rdg.	no rdg.	no rdg.	no rdg.
266	104.8	103.6	101.9	119.4	134.0	180.8
268	103.6	101.7	no rdg.	103.5	106.4	no rdg.
269	109.0	108.4	107.2	82.7	107.4	159.1
271	106.1	106.3	106.4	81.2	82.7	85.9
273	103.9	102.9	101.7	94.0	94.5	94.8
281	no rdg.	no rdg.	no rdg.	no rdg.	no rdg.	no rdg.
284	109.7	107.7	105.0	81.9	96.7	103.7
288	108.4	106.6	105.2	78.8	83.3	80.7
292	107.5	no rdg.	no rdg.	252.3	no rdg.	no rdg.
293	no rdg.	no rdg.	no rdg.	no rdg.	no rdg.	no rdg.
Total Shaded Boxes	7	11	14	18	25	30

no rdg. - at least one specimen did not register a longitudinal funamental frequency
fracture - at least one specimen suffered through-cracking

The inefficiency of RDM measurements may be attributed to the mismatch between the location of concrete deterioration and the path followed by stress waves. External sulfate attack starts at the surface of concrete. However, the velocity of longitudinal stress waves in concrete cylinders is affected primarily by the core of the specimens. Deterioration may have to be well advanced before RDM measurements are affected.

However, Relative Damping Capacity is a function of the integrity of the entire concrete specimen. Relative Damping Capacity measurements are affected by deterioration near the surface of specimens, such as that which occurs in the initial stages of sulfate attack.

Relative Damping Capacity measurements were also compared to linear expansion and mass loss for efficiency in detecting concrete deterioration, as shown in Table 4.10. Concrete mixtures were known to be less resistant to sulfate attack than Type II cement concrete if linear expansion was greater or if mass was lost. Mixtures determined to be less resistant to sulfates than the Type II cement mixture are emphasized in Table 4.10 with shaded boxes.

Relative Damping Capacity measurements detected deterioration in several mixtures in which no deterioration was detected by linear expansion or mass loss. This observation is emphasized by the larger total quantities of shaded boxes (deteriorating concrete) for RDC, as listed in the last row of Table 4.10.

However, there were also two cases (mixtures 273 and 288) in which concrete expansions were larger than the control Type II cement mixture, while RDC detected no deterioration. These two mixtures both contained abnormally high sulfate contents, which may have induced internal sulfate attack. Since sulfates were readily available, the specimens were not damaged during the ingress of sulfates. The 720-day expansions may not have been sufficient to cause internal cracking (expansions did not exceed 0.125 percent).

Relative Damping Capacity seemed to be the dynamic test parameter which detected deterioration most efficiently. When dynamic test data was available, the Relative Damping Capacities of concrete specimens were compared qualitatively.

Table 4.10 Comparison of Deterioration as Measured by Linear Expansion and Mass Loss and Relative Damping Capacity

Mixture Number	Linear Expansion and Mass Loss			Relative Damping Capacity (%)		
	360 days	540 days	720 days	360 days	540 days	720 days
3	fracture	fracture	fracture	fracture	fracture	fracture
15	<	=	=	80.0	83.4	88.7
115	<	<	<	88.8	105.2	115.6
117	<	<	<	111.8	124.4	128.9
119	=	=	=	94.4	112.0	117.4
120	<	<	<	76.9	84.3	101.7
122	<	<	<	92.3	100.2	100.8
124	=	=	=	90.3	91.1	95.9
133	fracture	fracture	fracture	fracture	fracture	fracture
134	fracture	fracture	fracture	fracture	fracture	fracture
138	<	< *	< *	no rdg.	no rdg.	no rdg.
140	<	<	<	86.4	93.1	95.4
142	=	=	=	90.5	97.1	101.0
143	< *	< *	< *	145.0	173.4	168.4
145	<	<	<	87.8	95.1	99.0
147	=	=	=	85.5	91.0	90.1
163	<	<	<	82.8	93.3	211.8
165	<	<	<	80.0	85.9	84.1
167	>	>	>	101.4	117.2	132.2
168	<	<	<	82.6	115.1	167.9
170	<	<	<	83.4	90.7	94.4
172	=	=	=	87.6	91.0	90.3
207	< *	< *	< *	178.0	241.6	no rdg.
208	<	<	<	61.4	60.7	85.0
209	<	<	<	81.2	87.8	89.7
211	<	<	<	98.5	101.7	238.9
213	>	=	=	86.7	98.2	104.0
214	<	<	<	79.5	81.9	80.8

Table 4.10 (continued)

Mixture Number	Linear Expansion and Mass Loss			Relative Damping Capacity (%)		
	360 days	540 days	720 days	360 days	540 days	720 days
216	<	<	<	82.1	83.3	85.5
218	=	<	<	83.1	84.6	86.9
226	<	<	<	85.1	115.8	208.8
229	<	<	<	65.5	68.9	70.9
233	<	<	<	85.6	81.7	79.1
237	< *	< *	< *	227.9	no rdg.	no rdg.
238	< *	= *	fracture	321.1	no rdg.	fracture
262	< *	< *	= *	288.7	no rdg.	no rdg.
263	= *	= *	= *	142.5	131.1	162.2
264	<	< *	= *	no rdg.	no rdg.	no rdg.
266	<	<	<	119.4	134.0	180.8
268	>	>	>	103.5	106.4	no rdg.
269	< *	< *	< *	82.7	107.4	159.1
271	<	<	<	81.2	82.7	85.9
273	>	>	>	94.0	94.5	94.8
281	< *	= *	> *	no rdg.	no rdg.	no rdg.
284	=	<	=	81.9	96.7	103.7
288	>	>	>	78.8	83.3	80.7
292	< *	< *	= *	252.3	no rdg.	no rdg.
293	<	=	>	no rdg.	no rdg.	no rdg.
Total Shaded Boxes	16	18	19	18	25	30

< expansion less than the mixture containing Type II cement
= expansion not significantly different than the mixture containing Type II cement
> expansion greater than the mixture containing Type II cement
* mass loss

no rdg. - at least one specimen did not register a longitudinal fundamental frequency
fracture - at least one specimen suffered through-cracking

Since, the Relative Damping Capacity of Type II cement concrete was 88.7 percent at 720 days, it did not suffer a net increase in damping capacity. Other mixtures which exhibited RDCs less than 100 percent after 720 days of exposure, had not suffered significantly greater deterioration than the control Type II cement mixture. However, mixtures which exhibited RDC's greater than 100 percent or which became unreadable within the 720 day test period did suffer net increases in damping capacity. Therefore, they were known to be less resistant to sulfate attack than the control Type II cement concrete.

The durability of mixtures with RDCs less than 100 percent were not compared in terms of dynamic test data. These comparisons would not have been accurate: damping capacities decrease as mixtures hydrate, independent of their resistance to exposure conditions. Therefore, mixtures which continued to gain strength after the initiation of exposure would tend to have lower final damping capacities than weaker mixtures with similar resistance to sulfates.

4.3.5 CONTROL CEMENT MIXTURES

Six ordinary portland cement (OPC) concrete mixtures were included in this study. The performances of these mixtures in the sulfate exposure test provided standards to which other mixtures could be compared. Linear expansion and mass change of these control mixtures are shown in Figures 4.11 and 4.12, respectively.

None of the ordinary portland cement concretes lost mass, but both the Type I-H cement concrete and the Type I-L cement concrete exceeded the expansion limit. The relative sulfate resistance of cement Types I-H, I-L, II and V coincide with their relative tricalcium aluminate contents. The 0% C_3A cements, however, did not exhibit significantly greater resistance to sulfates than the Type II cement or the Type V cement. The 720-day Sulfate Susceptibility Ratings for all these OPC concretes are shown in Table 4.11.

After three years of exposure, the sulfate resistance of the 0% C_3A cement concretes were still comparable with the Type II cement concrete and the Type V cement concrete, as shown in Figures 4.11 and 4.12. High C_4AF contents and high C_3S/C_2S ratios for the 0% C_3A cements may have been responsible for their inability to provide greater resistance to sulfate attack than the other cements. Tetracalcium aluminoferrite contents in excess of

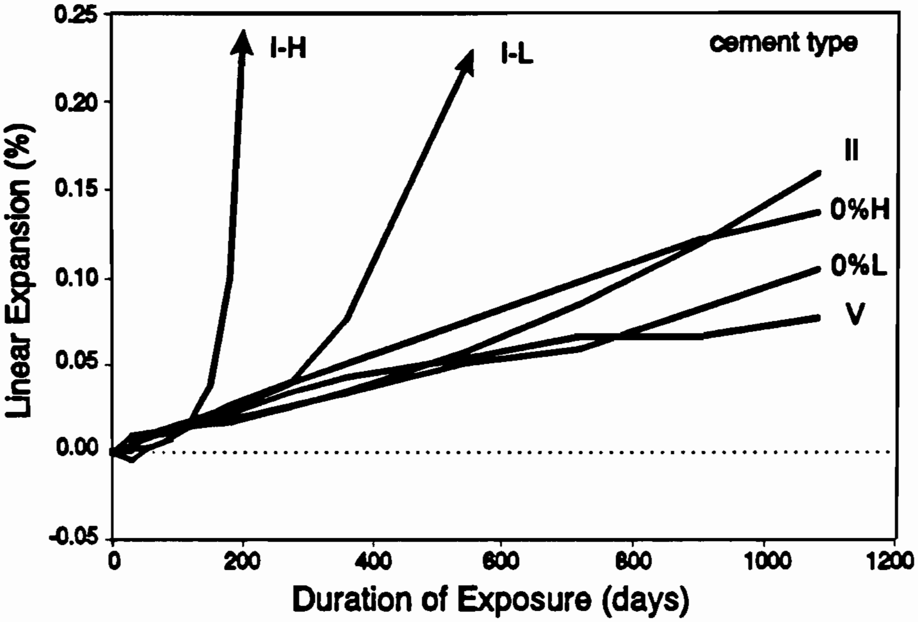


Figure 4.11 Linear Expansions of Ordinary Portland Cement Concrete Control Mixtures

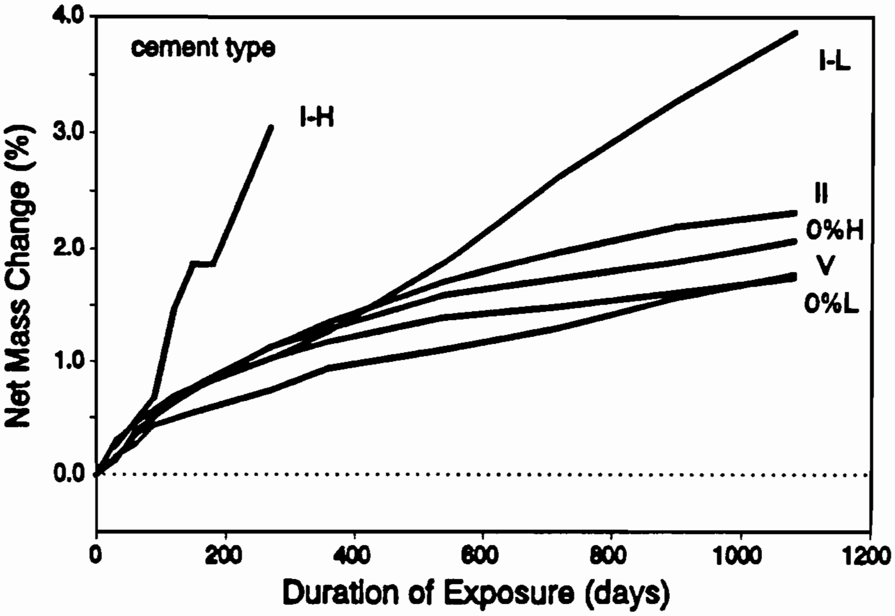


Figure 4.12 Net Mass Changes of Ordinary Portland Cement Concrete Control Mixtures

10 percent have been shown to increase the susceptibility of cements to sulfate attack (37). High proportions of C_3S result in the formation of high proportions of calcium hydroxide. Calcium hydroxide may increase the susceptibility of concrete to sulfate-induced damage by reacting with sulfates to form gypsum.

Table 4.11 Sulfate Susceptibility Ratings of Ordinary Portland Cement Concrete Control Mixtures

Control Cement Type	C_3A (%)	C_4AF (%)	SSR at 720 days
I-H	11.2	7.60	3.0
I-L	9.86	9.96	3.0
II	6.00	9.74	1.00
V	3.55	9.82	(.066/.086) = 0.77
0%H	0	14.6	(.100/.086) = 1.16
0%L	0	11.6	(.060/.086) = 0.70

4.4 SUMMARY

The sulfate exposure environment used in this study and the methods used to monitor deterioration provided a uniform and repeatable sulfate susceptibility test for hardened concrete mixtures.

A parameter titled Sulfate Susceptibility Rating was developed for comparing the susceptibilities of mixtures to sulfate attack. The method required that the concrete exposure specimens be monitored for both linear expansion and mass loss.

A test duration of two years was shown to be sufficient for detecting mixtures which were more susceptible to sulfate attack than Type II cement concrete without fly ash. These mixtures were designed for 5½ sacks of cement, 0 percent to 45 volume percent fly ash replacement by volume, and a concrete slump of 5 to 7 inches. A test duration of only one year seems to be sufficient if fly ash replacement is limited to proportions greater than or equal to 35 percent by volume.

Mixtures which were produced late in the test program were monitored for dynamic modulus of elasticity and damping capacity in addition to linear expansion and mass loss. The susceptibility of these mixtures to sulfate attack were assessed by both their Sulfate Susceptibility Rating and Relative Damping Capacity.

Damping capacity measurements detected external sulfate attack more efficiently than dynamic modulus of elasticity or linear expansion and mass loss: deterioration was detected in more mixtures and at earlier ages of exposure. Linear expansion detected the early stages of internal sulfate attack most efficiently. Test duration requirements would be minimized by monitoring exposure specimens for both Relative Damping Capacity and linear expansion.

CHAPTER 5

ASTM TYPE II CEMENT CONCRETE WITH FLY ASH ADDED AS A MINERAL ADMIXTURE

5.1 INTRODUCTION

The objective of this portion of the study was to investigate the effects of fly ash on the sulfate resistance of Type II cement concrete. Twelve Type A fly ashes and twelve Type B fly ashes replaced cement at levels of 25, 35, and 45 percent by volume and were added as mineral admixtures at the time of batching concrete. Mixtures were designed with 5½ sacks cement per cubic yard concrete and a concrete slump of 5 to 7 inches.

Results for concrete mixtures are presented in the following order:

1) mixing water requirements,
2) compressive strengths, and
3) sulfate resistance.

Various techniques for predicting the effects of fly ash are compared with the performances of fly ash concrete in the sulfate exposure test. These predictions, which are based on fly ash chemical and mineralogical characteristics, include:

1) bulk calcium oxide content,
2) Dunstan Resistance Factor, and
3) Calcium Aluminate Potential.

5.2 MIXING WATER REQUIREMENT

Water was added to concrete mixtures until the desired slump was attained. Therefore, water/(cement + pozzolan) ratios were variable. The average water/cement ratio, by weight, of the six control Type II cement mixtures was 0.55.

Partial replacement of Type II cement with Type A fly ash had variable effects on water demand, as shown in Figure 5.1. Water demand was dependent on fly ash source and on the percentage of cement replacement. Water demand was generally highest at a fly ash content of 45 percent by volume. High water demands were partially attributable to the relatively low specific gravities of the Type A fly ashes. Replacement of cement on an equal volume basis resulted in cement/fly ash mixtures with decreased solid mass for the same volume of fine particles. Less solid mass resulted in increased water/(solid mass) ratios.

Mixtures containing fly ashes A-3, A-8, and A-11 required particularly large proportions of water. Fly ashes A-3 and A-8 lost 1.6 percent and 3.9 percent mass on ignition, respectively. Loss on ignition is an indication of unburnt carbon content. Unburnt carbon particles are porous and absorptive. Fly ashes A-8 and A-11 contained 46.3 percent and 30.7 percent particles larger than 45 μm, respectively. Coarse fly ash particles are typically bulky agglomerates or unburnt carbon (estimated by loss on ignition). Similar to unburnt carbon, agglomerates of particles absorb water and increase water demand.

Mixtures containing fly ashes A-6 and A-9 required relatively small proportions of water. Relative to other Type A fly ashes, these ashes had high specific gravities, 2.49 and 2.32, respectively. They also had small proportions of particles larger than 45 μm, 10.5 percent and 13.3 percent, respectively. Fine fly ash particles are typically smooth, solid glassy spheres. Glassy surfaces are hygroscopic, so the small spheres become lubricated and decrease water demand by a "ball bearing" effect.

Partial replacement of Type II cement with Type B fly ash had variable effects on water demand, as shown in Figure 5.2. However, contrary to the Type A fly ash mixtures, there were no Type B fly ash mixtures which required excessive quantities of mixing water ($w/(c+p)$ greater than 0.60). The absence of large water demands for mixtures containing Type B fly ash, relative to Type A fly ash, may be partially attributed to higher specific gravities. Also, the proportion of Type B ashes retained on #325 sieve and the proportion lost on ignition did not exceed 22.0 percent and 0.53 percent, respectively.

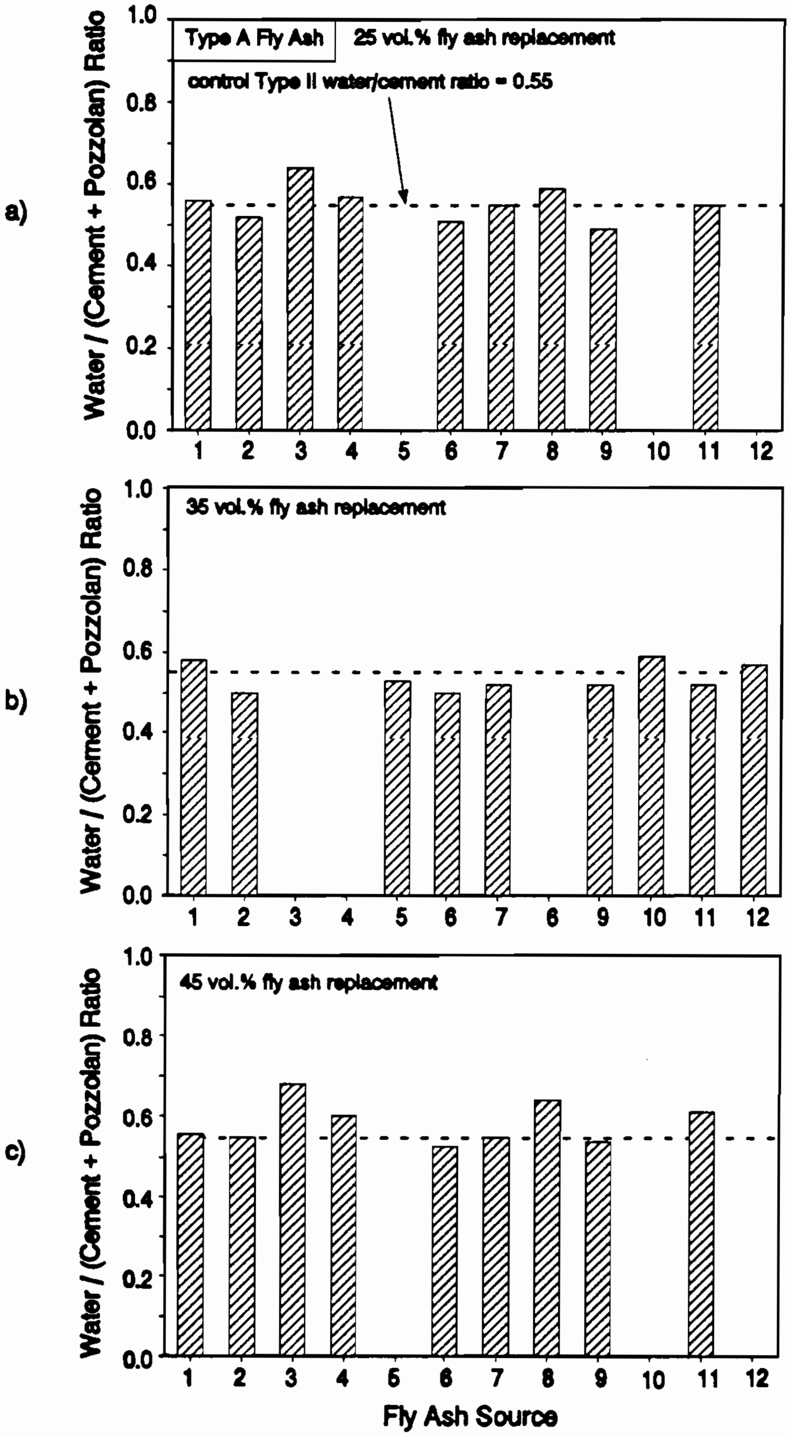


Figure 5.1 Mixing Water Requirements for Type A Fly Ash/Type II Cement Mixtures

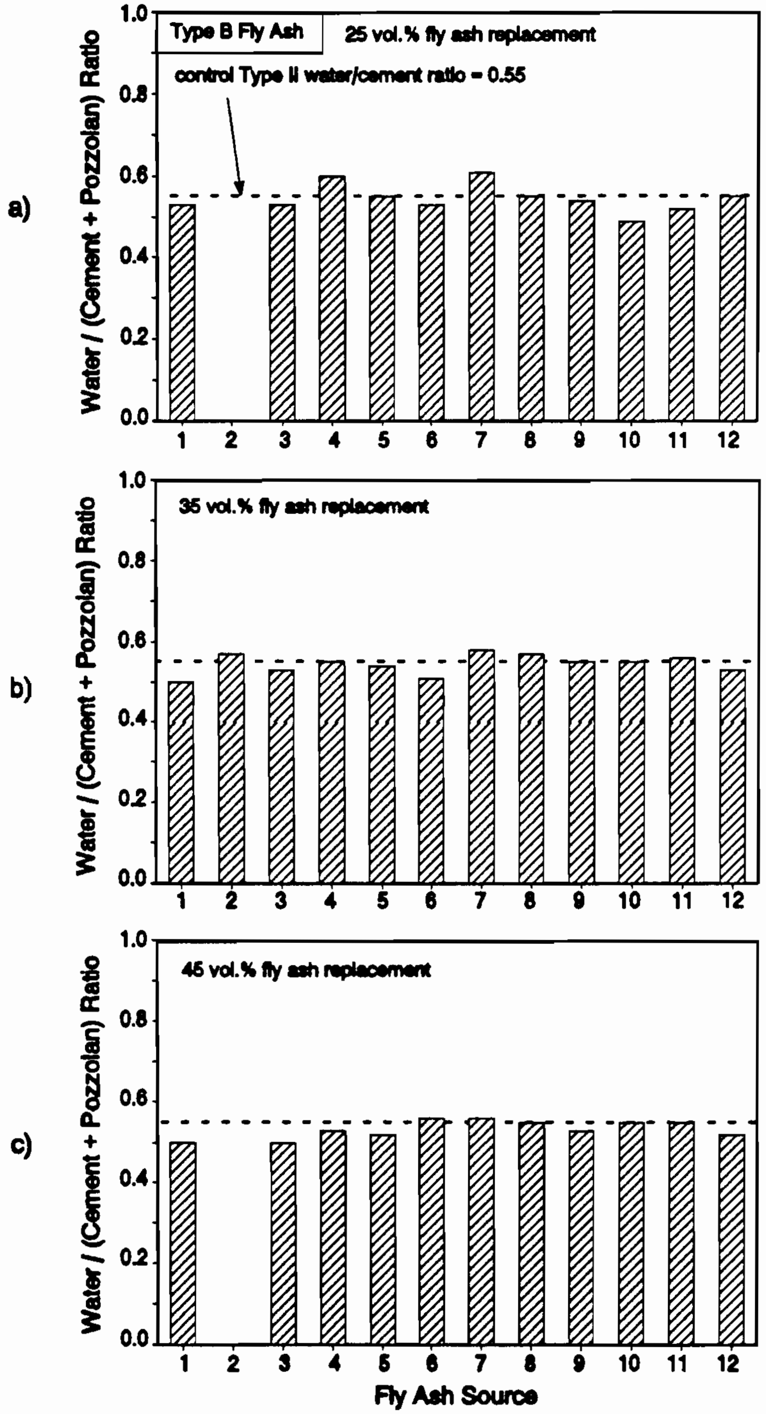


Figure 5.2 Mixing Water Requirements for Type B Fly Ash/Type II Cement Mixtures

5.3 COMPRESSIVE STRENGTH

The 28-day compressive strengths of mixtures containing Type A fly ash were generally lower than the control Type II cement mixture and generally decreased with increases in fly ash content, as shown in Figure 5.3. The effect of Type A fly ash on compressive strength of concrete was dependent on fly ash reactivity and calcium content. Fly ashes A-3, A-8, A-10, and A-12 had the most adverse effects on strengths. Fly ash A-8 failed ASTM C-618 limits on percent retained on #325 sieve and pozzolanic activity index, both of which are indicators of reactivity. Fly ashes A-3, A-10, and A-12 had the lowest calcium contents of all the fly ashes included in this study, 3.68 percent, 4.24 percent, and 1.57 percent, respectively. Fly ash A-6, which had the least detrimental effect on strength of all the Type A fly ashes, had the highest calcium oxide content (15.0 percent).

Partial replacement of Type II cement with Type B fly ash had variable effects on 28-day compressive strength, as shown in Figure 5.4. Effects were dependent on both fly ash fineness and crystallinity. Fly ashes B-3, B-4, and B-10 had the most desirable effects on concrete strengths. These fly ashes all had less than 16 percent retained on the #325 sieve and were all at least 80 percent glass. Fly ashes B-2 and B-12, which had the most undesirable effects on concrete strength, contained more than 35 percent crystalline material. These were the most crystalline ashes included in this study.

5.4 SULFATE SUSCEPTIBILITY

5.4.1 LINEAR EXPANSION AND MASS LOSS

Partial replacement of Type II cement with Type A fly ash had variable effects on linear expansion due to sulfate attack, as shown in Figure 5.5. Expansion of fly ash cement mixtures generally decreased with increases in the volume percentage of Type A fly ash.

Type A fly ash cement mixtures generally did not lose mass as a result of sulfate attack, as shown in Figure 5.5. However, one mixture containing Type A fly ash lost mass within the 720 day exposure period: 45 percent by volume fly ash A-6.

All the Type A fly ash/Type II cement mixtures which expanded more than the control Type II cement mixture or which lost mass contained fly ashes A-4, A-6, A-7, and A-8. Fly

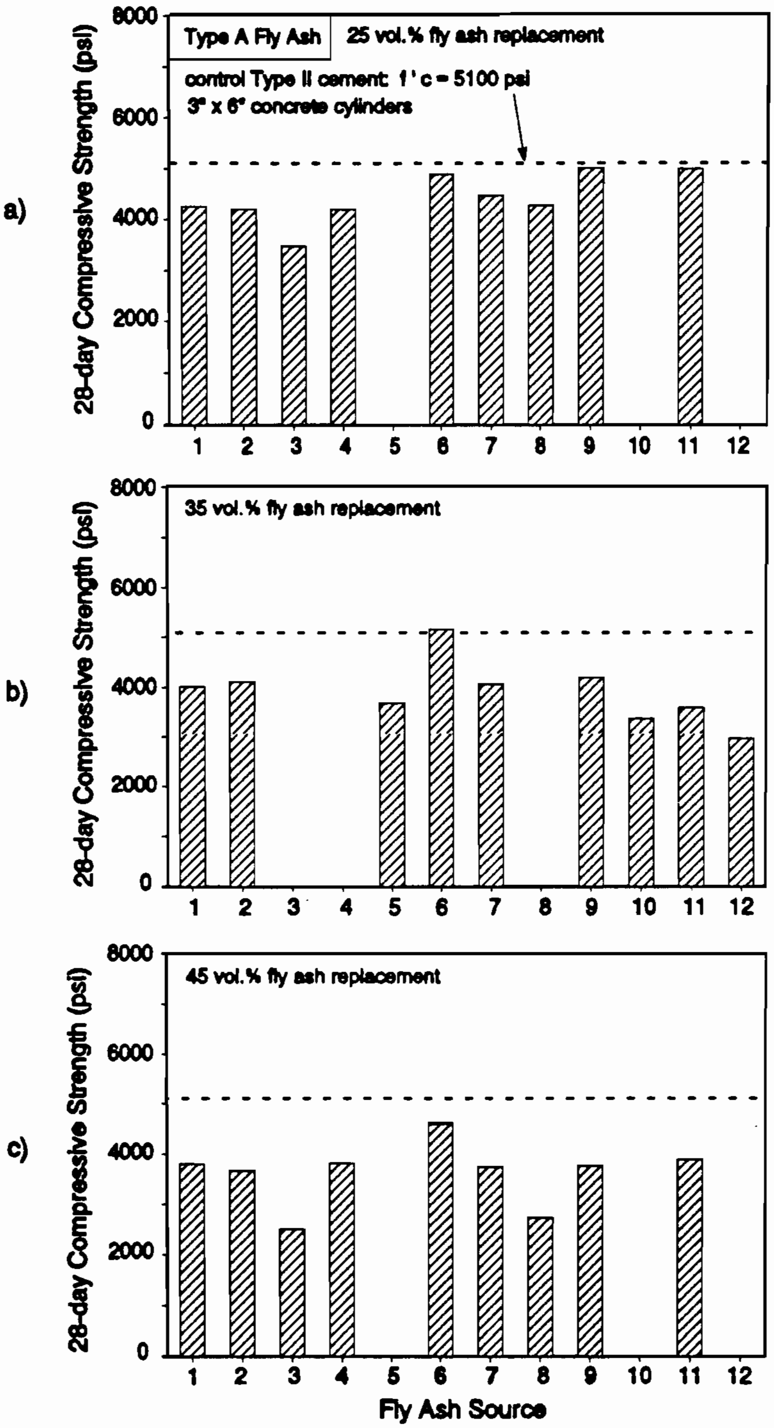


Figure 5.3 Compressive Strengths at 28 Days for Type A Fly Ash/Type II Cement Mixtures

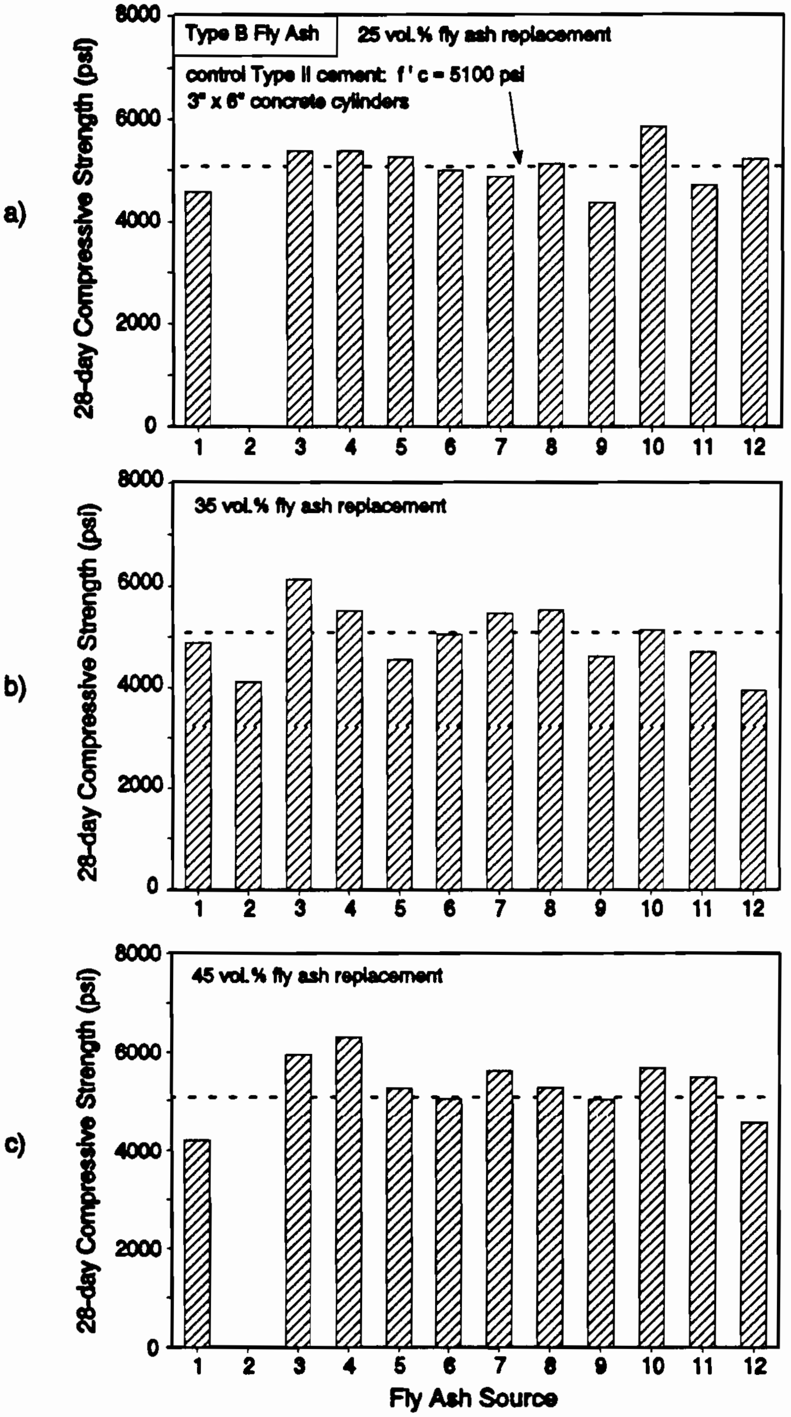


Figure 5.4 Compressive Strengths at 28 Days for Type B Fly Ash/Type II Cement Mixtures

ashes A-4, A-6, and A-7 contained high bulk calcium oxide contents relative to the other Type A fly ashes, 10.1, 15.0, and 12.4 percent, respectively. Fly ash A-8 failed both ASTM C-618 and Texas D-9-8900 physical requirements for fineness and pozzolanic activity.

Most of the mixtures containing Type B fly ash exceeded the limit for expansion and/or suffered mass loss within the 720 day testing period, as shown in Figure 5.6. As the volume percentage of Type B fly ash increased, the proportion of mixtures which lost mass increased and the duration of exposure at which mass loss began generally decreased.

The only Type B fly ash/Type II cement mixtures which expanded less than the control Type II cement mixture contained fly ashes B-1, B-2, and B-10. Fly ashes B-1 and B-10 contained low proportions of bulk calcium oxide content, 20.9 percent and 24.0 percent, respectively, relative to other Type B fly ashes. Fly ash B-2 contained a relatively high calcium oxide content, 28.4 percent. However, it also contained high proportions of sulfur trioxide and equivalent alkalies, 5.6 percent and 3.75 percent, respectively. The sulfur trioxide content was higher than allowed by ASTM C-618 and Texas D-9-8900 chemical requirements. The alkali content, Na_2O equivalent exceeded the optional chemical requirements of ASTM and Texas fly ash specifications. These unique chemical properties of fly ash B-2 may have influenced its effects on the sulfate resistance of concrete. The alkalies may have fascilitated early dissolution and reactivity of the fly ash. The high concentration of sulfur trioxide may have promoted the formation of ettringite during early hydration reactions, leaving a smaller proportion of calcium aluminates available for expansive reactions after the concrete had hardened.

5.4.2 SULFATE SUSCEPTIBILITY RATING

5.4.2.1 Introduction

The Sulfate Susceptibility Rating, as defined in Chapter 4, is a single-value parameter which depicts the rate of deterioration of concrete. This parameter includes deterioration in the forms of expansion and mass loss. It permits comparisons between the sulfate susceptibilities of all mixtures.

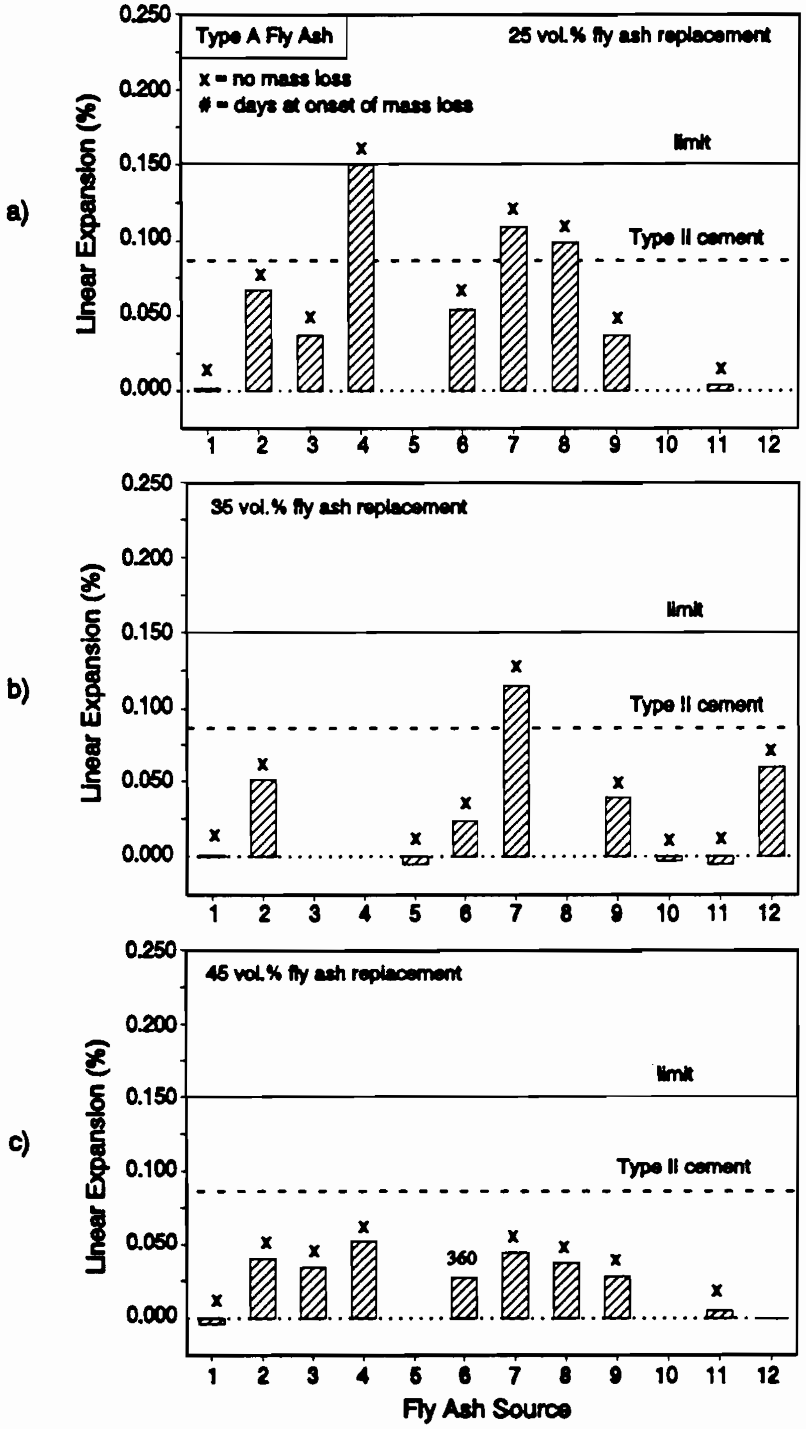


Figure 5.5 Linear Expansion and Mass Loss for Type A Fly Ash/Type II Cement Mixtures

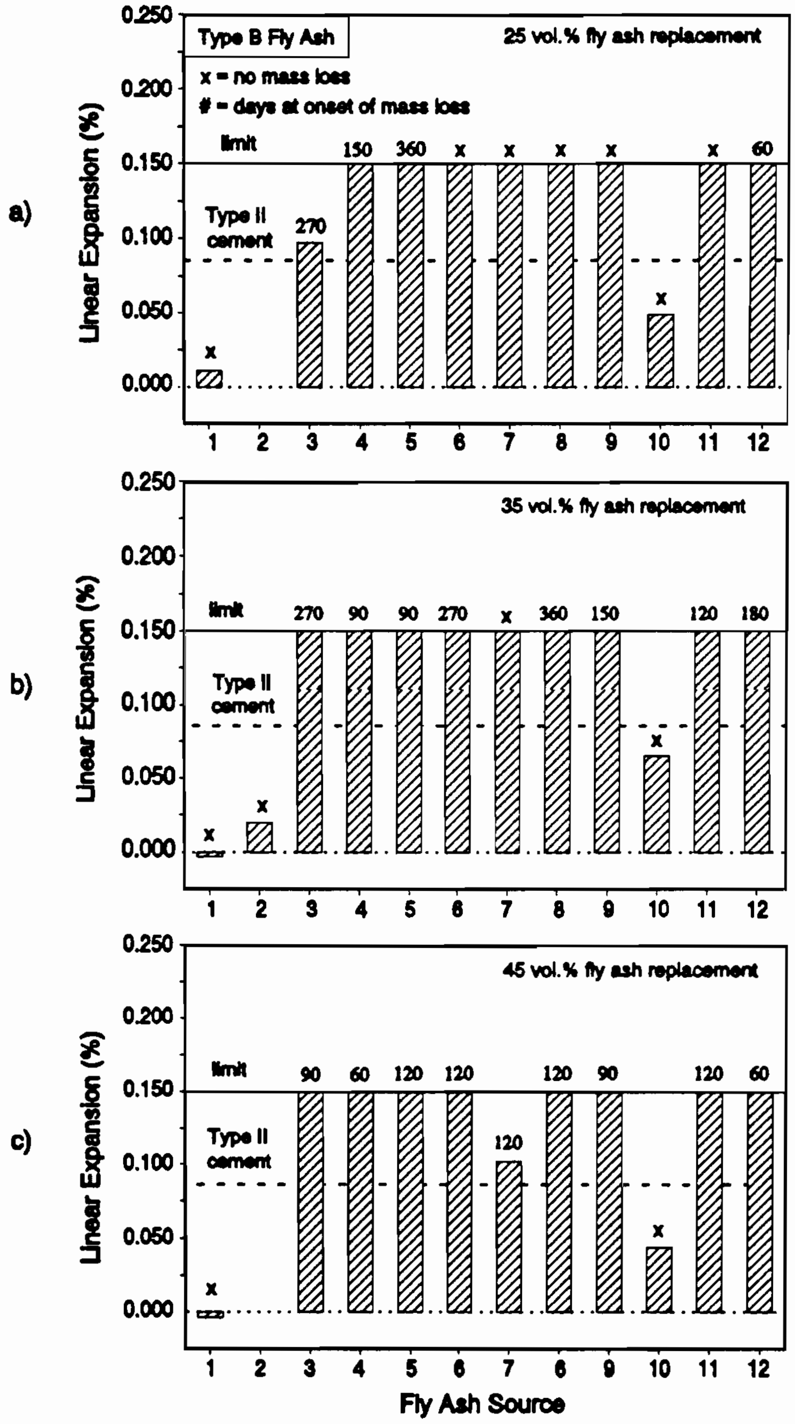


Figure 5.6 Linear Expansion and Mass Loss for Type B Fly Ash/Type II Cement Mixtures

5.4.2.2 Fly Ash Type and Percent Replacement

The sulfate susceptibilities of mixtures containing either Type A fly ash or Type B fly ash ranged from more resistant than Type II cement concrete to less resistant than Type II cement concrete, as shown in Figures 5.7 and 5.8. Relative to the Type B ashes, a larger proportion of the Type A ashes were beneficial in terms of sulfate resistance.

The sulfate susceptibilities of Type A fly ash/Type II cement mixtures generally decreased as the amount of fly ash increased, however, the trend was not absolute. The sulfate susceptibilities of Type B fly ash/Type II cement mixtures generally increased as the amount of fly ash increased. However, the trend was also not absolute. In order to investigate further the effects of the amount of fly ash, fly ashes were classified into three groups:

1) fly ashes which decreased the sulfate susceptibility of Type II cement concrete at all three volume percent replacements,
2) fly ashes which increased the sulfate susceptibility of Type II cement concrete at all three volume percent replacements, and
3) fly ashes which increased or decreased the sulfate susceptibility of Type II cement concrete, depending on the volume percent replacement.

The sulfate susceptibilities of mixtures containing fly ash from the first group were lowest at cement replacements of 35 and 45 percent by volume, as shown in Figure 5.9. This group included 5 Type A ashes and 1 Type B ash; the Type A ashes contained 9.55 percent calcium oxide or less and the Type B ash contained 20.9 percent calcium oxide.

Mixtures containing fly ash from the second group were highly susceptible to sulfate attack at all three percentages of fly ash, as shown in Figure 5.9. This group included 9 Type B ashes with calcium oxide contents greater than or equal to 23.1 percent.

The sulfate susceptibility of mixtures containing fly ash from the third group either increased or decreased as the volume percentage of fly ash increased, as shown in Figure 5.9. This group included four Type A ashes, A-4, A-6, A-7, and A-8. It also included and 1 Type B ash, B-10. Fly ashes A-4, A-6, and A-7 contained the highest proportions of calcium oxide relative to all other Type A ashes included in this study, 10.1 percent, 15.0 percent, and 12.4 percent, respectively. Fly ash A-8 failed the ASTM C-618 and Texas

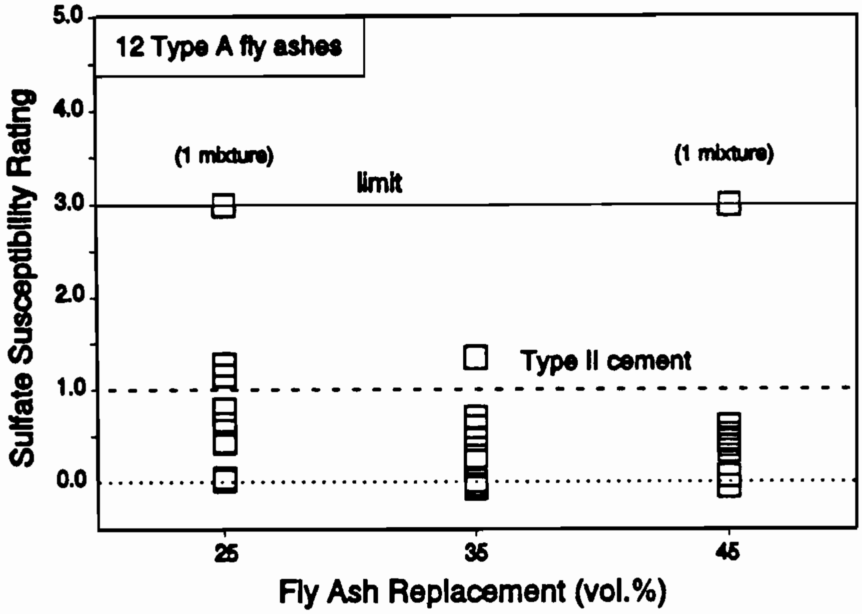


Figure 5.7 Sulfate Susceptibility Ratings for Type A Fly Ash/Type II Cement Mixtures

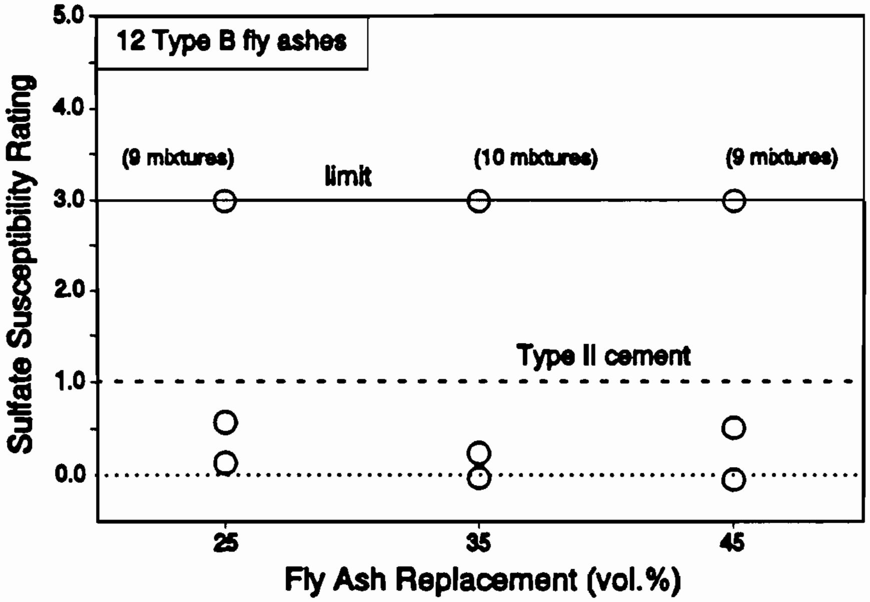


Figure 5.8 Sulfate Susceptibility Ratings for Type B Fly Ash/Type II Cement Mixtures

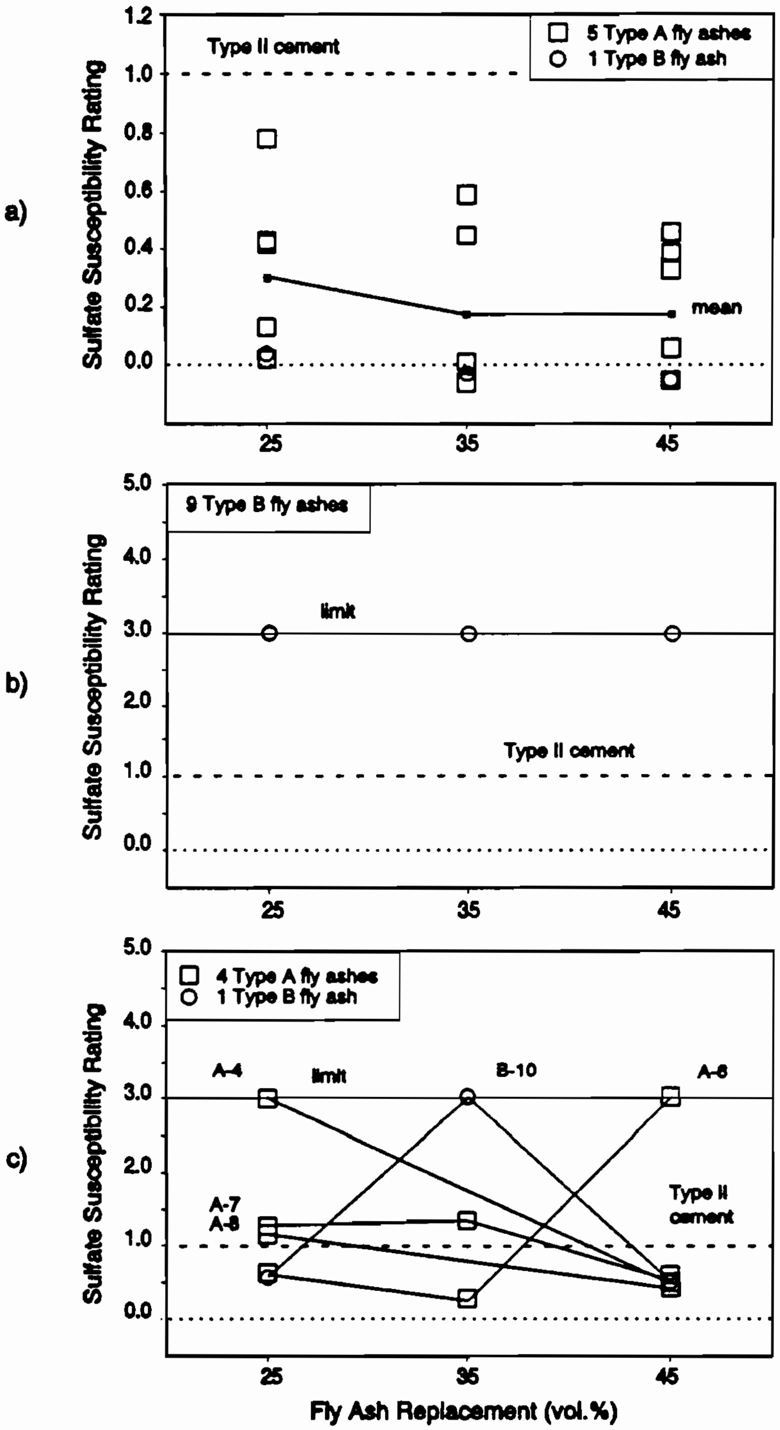


Figure 5.9 Sulfate Susceptibility Ratings of Fly Ash/Type II Cement Mixtures for a) Sulfate Resistant Fly Ashes, b) Non-Sulfate Resistant Fly Ashes, and c) Fly Ashes with Variable Effects

D-9-8900 requirements for fineness (percent retained on #325 sieve) and pozzolanic activity index. The calcium oxide content of the Type B ash was low relative to most other Type B ashes, 24.0 percent.

5.4.2.3 Fly Ash Bulk Calcium Oxide Content

Fly ashes with bulk calcium oxide contents less than or equal to approximately 8 percent improved the sulfate resistance of Type II cement concrete, as shown in Figure 5.10. Fly ashes with bulk calcium oxide contents greater than approximately 25 percent decreased the sulfate resistance of Type II cement concrete. Fly ashes with bulk calcium oxide contents between 8 percent and 25 percent had variable effects on the sulfate resistance of Type II cement concrete.

Bulk calcium oxide content may be used conservatively to decide whether a fly ash has the potential to decrease the sulfate resistance of Type II cement concrete. However, consideration of calcium content alone will not permit recognition of high-calcium fly ashes which are resistant to sulfate attack. For example, fly ash B-1 contained a relatively high bulk calcium content, but its resistance to sulfates is typical of low-calcium fly ashes.

Also, consideration of calcium oxide content alone will not differentiate between the low-calcium fly ashes which are very effective in improving the sulfate resistance of Type II cement concrete and those which are only moderately effective. For example, fly ash A-12 contained the lowest proportion of calcium oxide but its effects on sulfate resistance were not the most desireable.

5.4.2.4 Dunstan Resistance Factor

Dunstan's Resistance Factor (R-factor), which was discussed in Chapter 2, includes the beneficial influence of fly ash ferric oxide content in its predictions of the effects of fly ash on the sulfate resistance of concrete:

$$\text{Dunstan Resistance Factor} = \frac{\text{bulk CaO\%} - 5}{\text{bulk Fe}_2\text{O}_3\text{\%}} \; . \qquad (5.1)$$

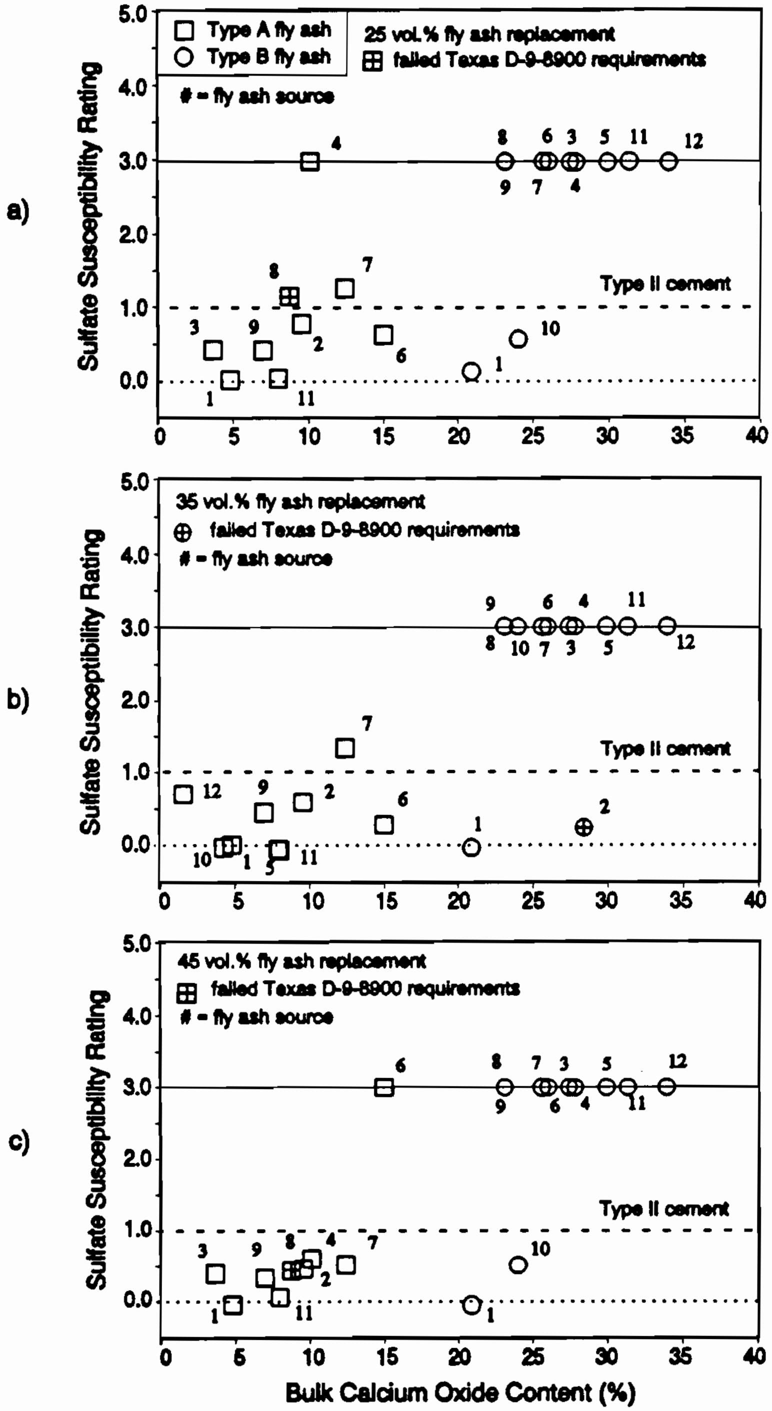


Figure 5.10 Sulfate Susceptibility Ratings of Fly Ash/Type II Cement Mixtures Versus Bulk Calcium Oxide Content of Fly Ash

Fly ashes with Resistance Factors less than or equal to approximately 0.5 all improved the sulfate resistance of Type II cement concrete, as shown in Figure 5.11. Fly ashes with Resistance Factors greater than approximately 3.5 decreased the sulfate resistance of Type II cement concrete. Fly ashes with Resistance Factors between 0.5 and 3.5 had variable effects on the sulfate resistance of Type II cement concrete.

Predictions of the effects of fly ashes A-2, A-7, and B-1 on the sulfate susceptibility of Type II cement concrete were fascilitated by the consideration of ferric oxide contents. Fly ashes A-2 and B-1 were relatively resistant to sulfates and they contained high proportions of ferric oxide, 8.98 percent and 7.70 percent, respectively. Fly ash A-7 was susceptible to sulfates, relative to other Type A ashes, and it contained the lowest proportion of ferric oxide (3.60 percent).

The Resistance Factor of fly ash A-12 was misleading. Due to its low proportion of calcium oxide and high proportion of ferric oxide, the R-factor of fly ash A-12 was lower than the R-factors of most other Type A ashes included in this study. However, the Type II cement concrete containing fly ash A-12 was not the most sulfate resistant concrete. This inaccuracy in predictions by the Resistance Factor may be attributed to the absence of consideration for fly ash alumina content; fly ash A-12 contained the highest proportion of aluminum oxide, relative to all other ashes included in this study.

5.4.2.5 Fly Ash Calcium Aluminate Potential

Calcium Aluminate Potential (CAP), which was discussed in Chapter 2, uses fly ash mineralogical characteristics to differentiate between reactive and nonreactive phases in its predictions of the effects of fly ash on the sulfate resistance of fly ash concrete:

$$\text{Calcium Aluminate Potential} = \frac{CaO^{**} + Al_2O_3^{*} + Fe_2O_3^{*}}{SiO_2^{*}} \text{, where} \qquad (5.2)$$

oxide* = proportion of bulk oxide in reactive components and

CaO** = calcium oxide in reactive components, less CaO in immediately reactive components (lime, anhydrite, portlandite).

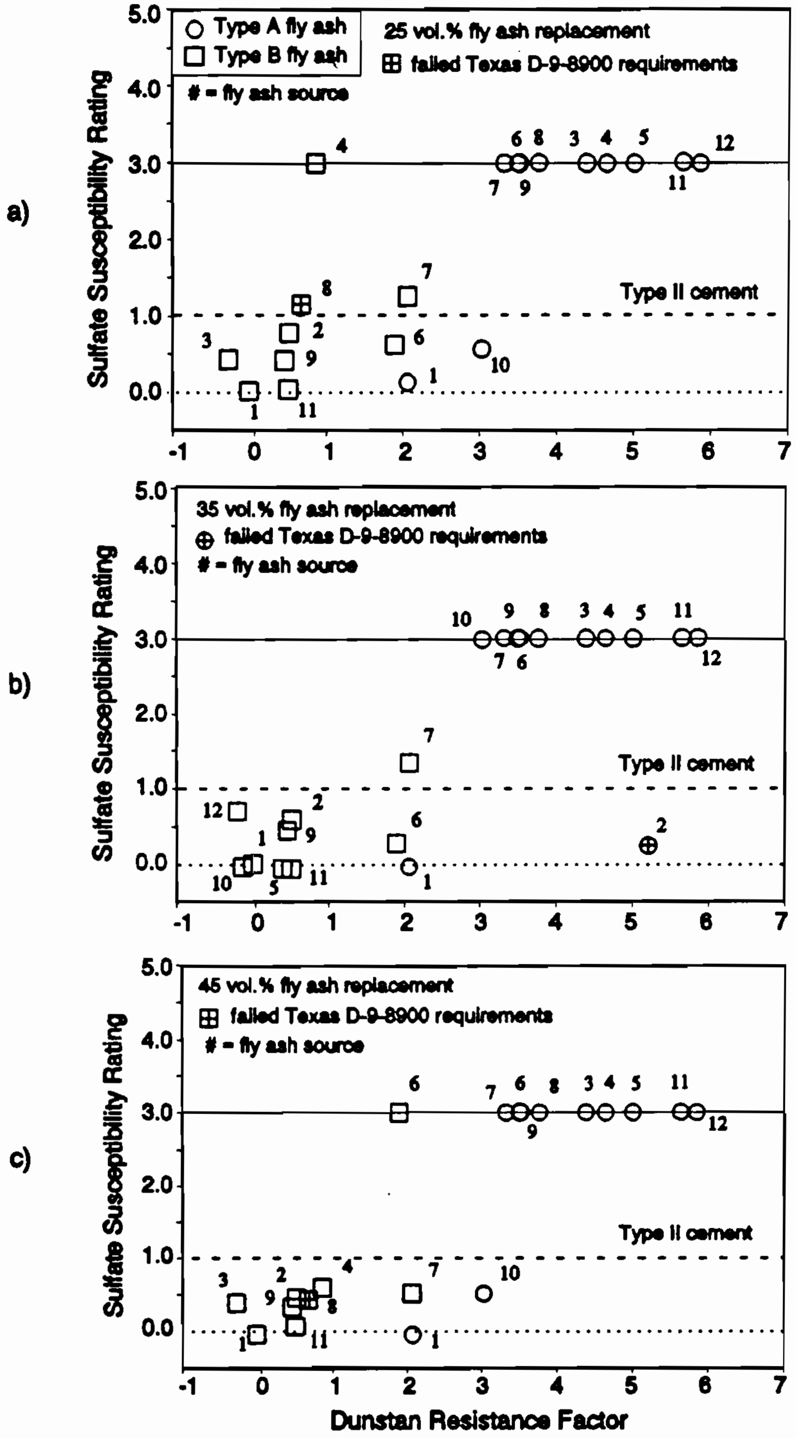


Figure 5.11 Sulfate Susceptibility Ratings of Fly Ash/Type II Cement Mixtures Versus Dunstan Resistance Factor of Fly Ash

Fly ash with CAPs less than or equal to approximately 0.7 all improved the sulfate resistance of Type II cement concrete, as shown in Figure 5.12. Fly ashes with CAPs greater than approximately 1.75 all decreased the sulfate resistance of Type II cement concrete. Fly ashes with CAPs between 0.7 and 1.75 had variable effects on the sulfate resistance of Type II cement concrete.

Calcium Aluminate Potential includes the detrimental effects of reactive alumina. Therefore, the prediction of the performance of fly ash A-12, which contained a high proportion of alumina, was improved relative to the prediction by Dunstan's Resistance Factor.

Calcium Aluminate Potential includes the beneficial effects of reactive silica, which resists the formation of calcium-aluminate glass. Calcium-aluminate glass is the glass type which contributes to the formation of sulfate susceptible compounds. This aspect of Calcium Aluminate Potential contributed to the improved prediction of the sulfate susceptibility of mixtures containing fly ash A-4. Fly ash A-4 contained the lowest proportion of silica of all Type A ashes and it contained a moderate proportion of quartz. Due to its small proportion of reactive silica and its moderate calcium content, ash A-4 had the highest calculated CAP of all Type A fly ashes.

All reactive ferric oxide is considered undesirable in calculations of Calcium Aluminate Potential, which is contrary to the assumption made by E.R. Dunstan. The undesirable effects of ferric oxide had been observed in mixtures containing a fly ash with a very high proportion of ferric oxide, 39.0 percent (276). The assumption of undesirable effects of ferric oxide, however, hindered the predictions of the performances of fly ashes A-6 and A-7 included in this study. The bulk ferric oxide contents of fly ashes A-6 and A-7 were both relatively low, 5.30 percent and 3.60 percent, respectively. Due to the containment of portions of these oxides in ferrite spinel, the resulting proportions of ferric oxide in glass were the lowest of all Type A ashes included in this study, 2.4 percent and 2.7 percent, respectively. The low proportions of reactive ferric oxide decreased their calculated CAPs relative to other Type A fly ashes, even though these ashes were observed to increase the sulfate susceptibility of Type II cement concrete.

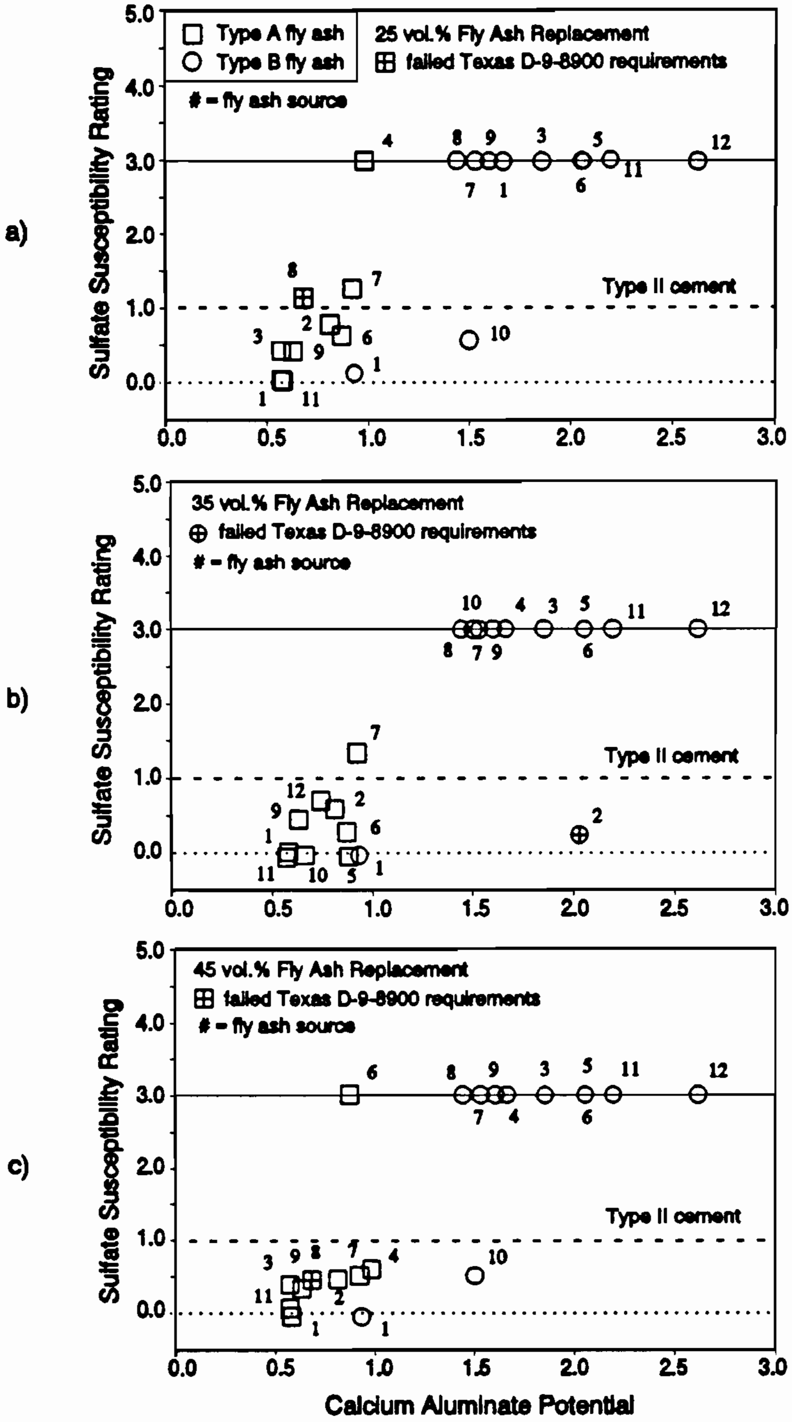


Figure 5.12 Sulfate Susceptibility Ratings of Fly Ash/Type II Cement Mixtures Versus Calcium Aluminate Potential of Fly Ash

5.4.2.6 Modified Calcium Aluminate Potential

An improved model for predicting the effects of fly ash, incorporating advantages of the previously discussed models, seems justified. The following aspects of previously discussed models appear to contribute to prediction accuracy:

1) reactive alumina, in addition to reactive calcium, contributes to the formation of compounds which are susceptible to attack by sulfates,
2) reactive silica resists the formation of calcium-aluminate glass, the glass type which contributes to the formation of sulfate susceptible compounds, and
3) although excessive ferric oxide contents may promote the formation of Fe-substituted monosulfoaluminate, moderate ferric oxide contents are advantageous due to the formation of less expansive, iron-rich ettringite.

These desirable prediction model characteristics indicate that a slight modification to the Calcium Aluminate Potential model may improve its accuracy:

$$\text{Modified CAP} = \frac{CaO^{**} + Al_2O_3^{*}}{SiO_2^{*} + Fe_2O_3^{*}}, \text{ where} \tag{5.3}$$

oxide* = proportion of bulk oxide in reactive components and

CaO** = calcium oxide in reactive components, less CaO in reactive components which do not participate in sulfate-related reactions (lime, anhydrite, portlandite, C_2S, and C_3S).

Modified Calcium Aluminate Potentials for all the fly ashes included in this study are listed in Table 5.1.

Fly ashes with Modified CAPs less than or equal to approximately 0.60 all improved the sulfate resistance of Type II cement concrete, as shown in Figure 5.13. Fly ashes with Modified CAPs greater than approximately 1.25 all decreased the sulfate resistance of Type II cement concrete. Fly ashes with Modified CAPs between 0.60 and 1.25 had variable effects on the sulfate resistance of Type II cement concrete.

Similar to Dunstan's Resistance Factor, this model predicted fly ashes A-6 and A-7 to be potentially susceptible to sulfates by recognizing their high ratios of reactive calcium to reactive ferric oxide. Similar to the Calcium Aluminate Potential, this model predicted fly ash A-4 to be potentially susceptible to sulfates by recognizing its low reactive silica content.

Table 5.1 Modified Calcium Aluminate Potentials of Fly Ash

Fly Ash	Modified CAP
A-1	0.35
A-2	0.53
A-3	0.41
A-4	0.70
A-5	0.59
A-6	0.74
A-7	0.80
A-8	0.49
A-9	0.46
A-10	0.46
A-11	0.46
A-12	0.51

Fly Ash	Modified CAP
B-1	0.75
B-2	1.78
B-3	1.50
B-4	1.37
B-5	1.58
B-6	1.59
B-7	1.16
B-8	1.16
B-9	1.30
B-10	1.16
B-11	1.90
B-12	2.25

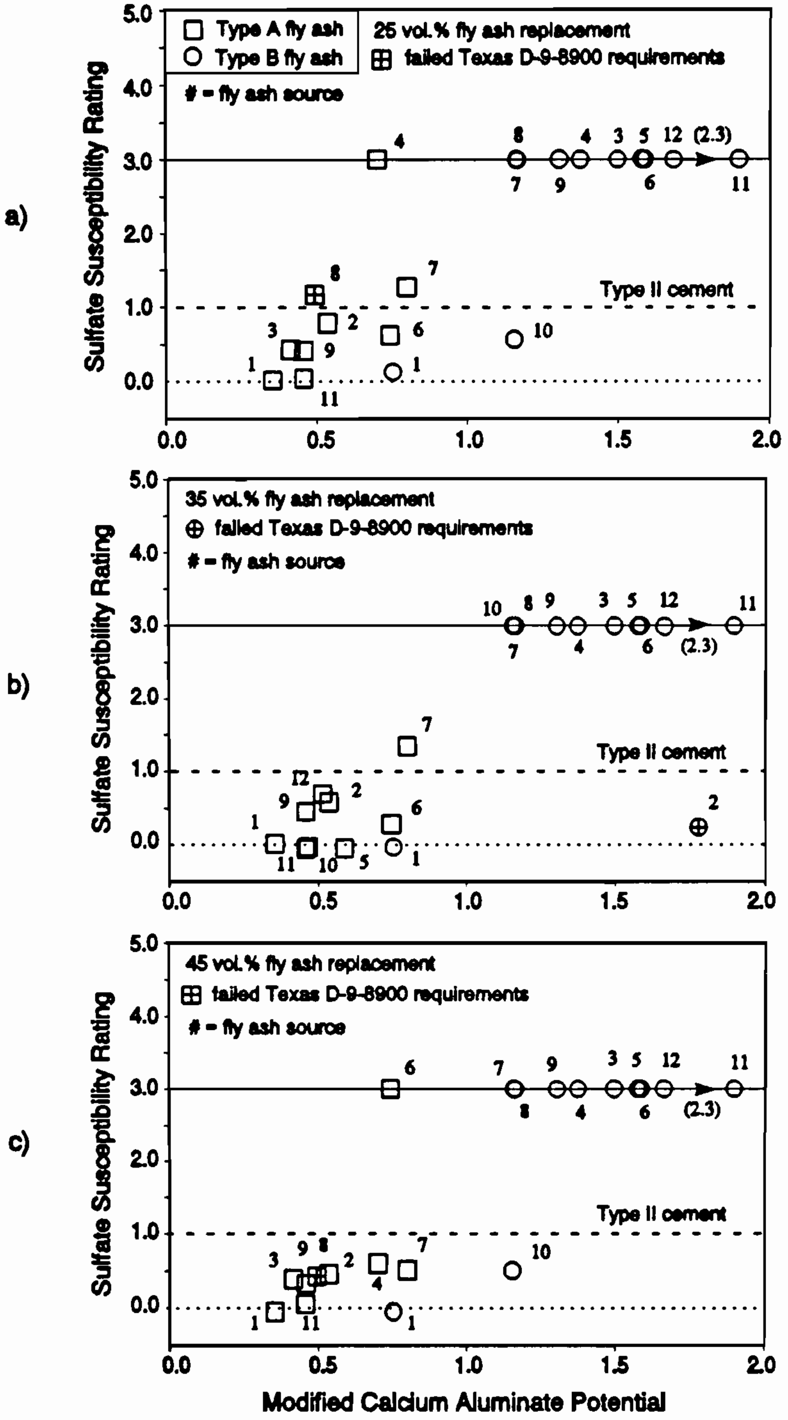


Figure 5.13 Sulfate Susceptibility Ratings of Fly Ash/Type II Cement Mixtures Versus Modified Calcium Aluminate Potential of Fly Ash

5.4.2.7 Modified Calcium Aluminate Potential (Chemical Basis)

Since an accurate calcium aluminate potential model has been established with the available sulfate exposure data, it is of interest to examine the accuracy of a similar model which uses only bulk chemical analyses:

$$\text{Bulk Chemical Modified CAP} = \frac{CaO + Al_2O_3}{SiO_2 + Fe_2O_3}\text{, where} \tag{5.4}$$

oxide = weight percentage from bulk chemical analysis.

Bulk Chemical Modified CAPs for all the fly ashes included in this study are listed in Table 5.2. If this model is as accurate as the Modified Calcium Aluminate Potential model, it would provide a simpler and less expensive alternative because no mineralogical analyses would be required.

Fly ashes with Bulk Chemical Modified CAPs less than or equal to approximately 0.60 improved the sulfate resistance of Type II cement concrete, as shown in Figure 5.14. Fly ashes with Bulk Chemical Modified CAPs greater than approximately 1.25 all decreased the sulfate resistance of Type II cement concrete. Fly ashes with Bulk Chemical Modified CAPs between 0.60 and 1.25 had variable effects on the sulfate resistance of Type II cement concrete. These limits are the same as those for the mineralogy-based Modified Calcium Aluminate Potential.

Similar to the mineralogy-based Modified CAP, the Bulk Chemical Modified CAP recognized the sulfate-susceptibilities of fly ashes A-4, A-6, and A-7. The Bulk Chemical Modified CAP also recognized the unique characteristics of fly ash B-1, relative to the other Type B fly ashes included in this study.

The Bulk Chemical Modified CAP model provided accuracy comparable with that of the mineralogy-based Modified CAP model.

5.4.2.8 Significance of Considering Fly Ash Mineralogy

Studying the relationships between mineralogy-based Modified CAPs and the Bulk Chemical Modified CAPs of fly ashes, along with the Sulfate Susceptibility Ratings of fly ash concrete, provides insight into the potential advantages of considering fly ash mineralogy when predicting the sulfate resistance of fly ash. Direct comparisons between these two prediction models is useful due to the similar means and ranges of the values calculated for the fly ashes included in this study.

Table 5.2 Bulk Chemical Modified Calcium Aluminate Potentials of Fly Ash

Fly Ash	Bulk Chemical Modified CAP
A-1	0.37
A-2	0.44
A-3	0.55
A-4	0.71
A-5	0.60
A-6	0.69
A-7	0.69
A-8	0.48
A-9	0.43
A-10	0.54
A-11	0.50
A-12	0.49

Fly Ash	Bulk Chemical Modified CAP
B-1	0.70
B-2	1.44
B-3	1.33
B-4	1.31
B-5	1.40
B-6	1.12
B-7	1.11
B-8	0.97
B-9	1.12
B-10	1.08
B-11	1.50
B-12	1.62

Differences between the mineralogy-based Modified CAPs and the Bulk Chemical Modified CAPs are compared with Sulfate Susceptibility Ratings in Figure 5.15. For negative differences between CAPs, Modified CAP is less than Bulk Chemical Modified CAP. In these cases, consideration of fly ash mineralogy would predict increased sulfate resistance for fly ash, relative to the prediction based on chemical analyses alone. For positive differences

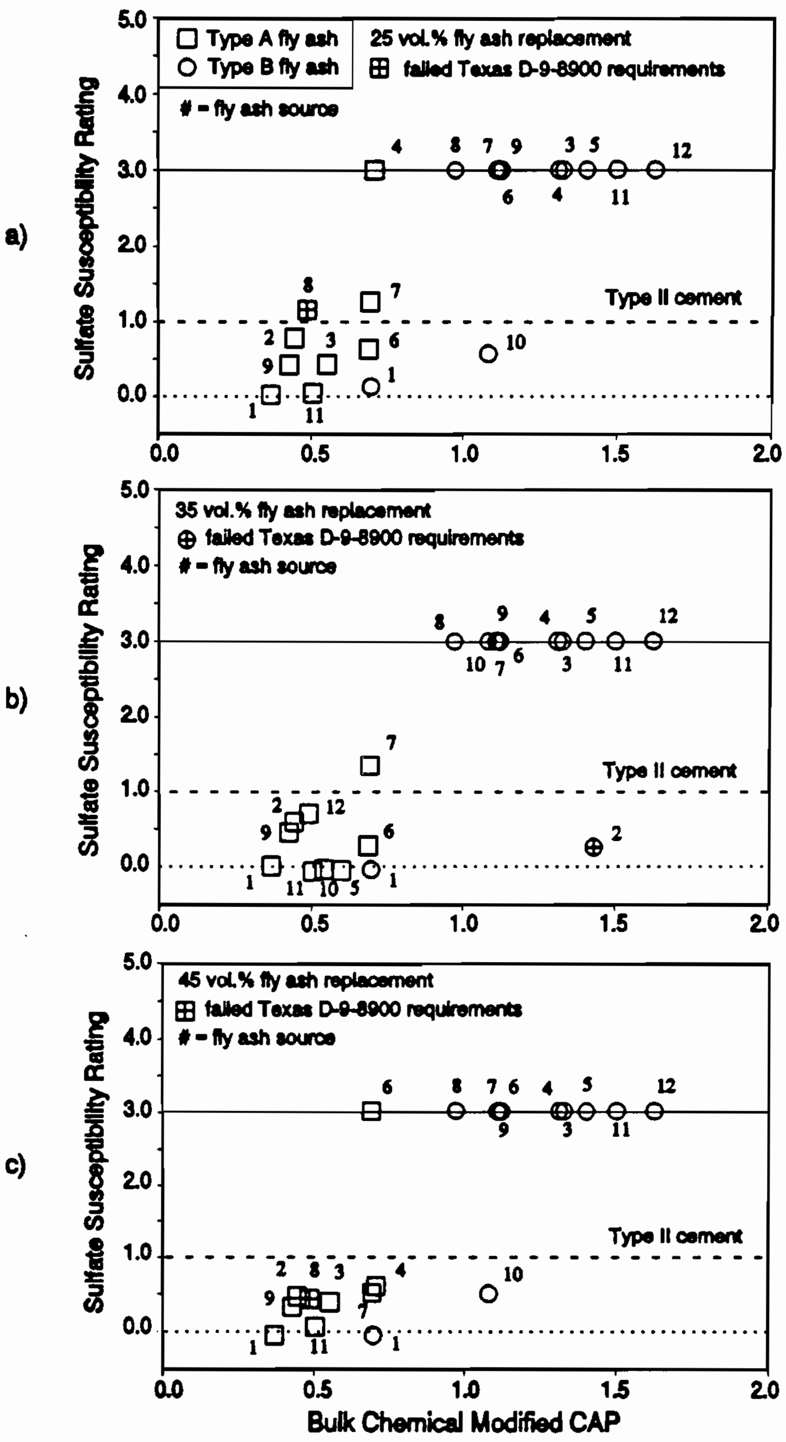


Figure 5.14 Sulfate Susceptibility Ratings of Fly Ash/Type II Cement Mixtures Versus Bulk Chemical Calcium Aluminate Potential of Fly Ash

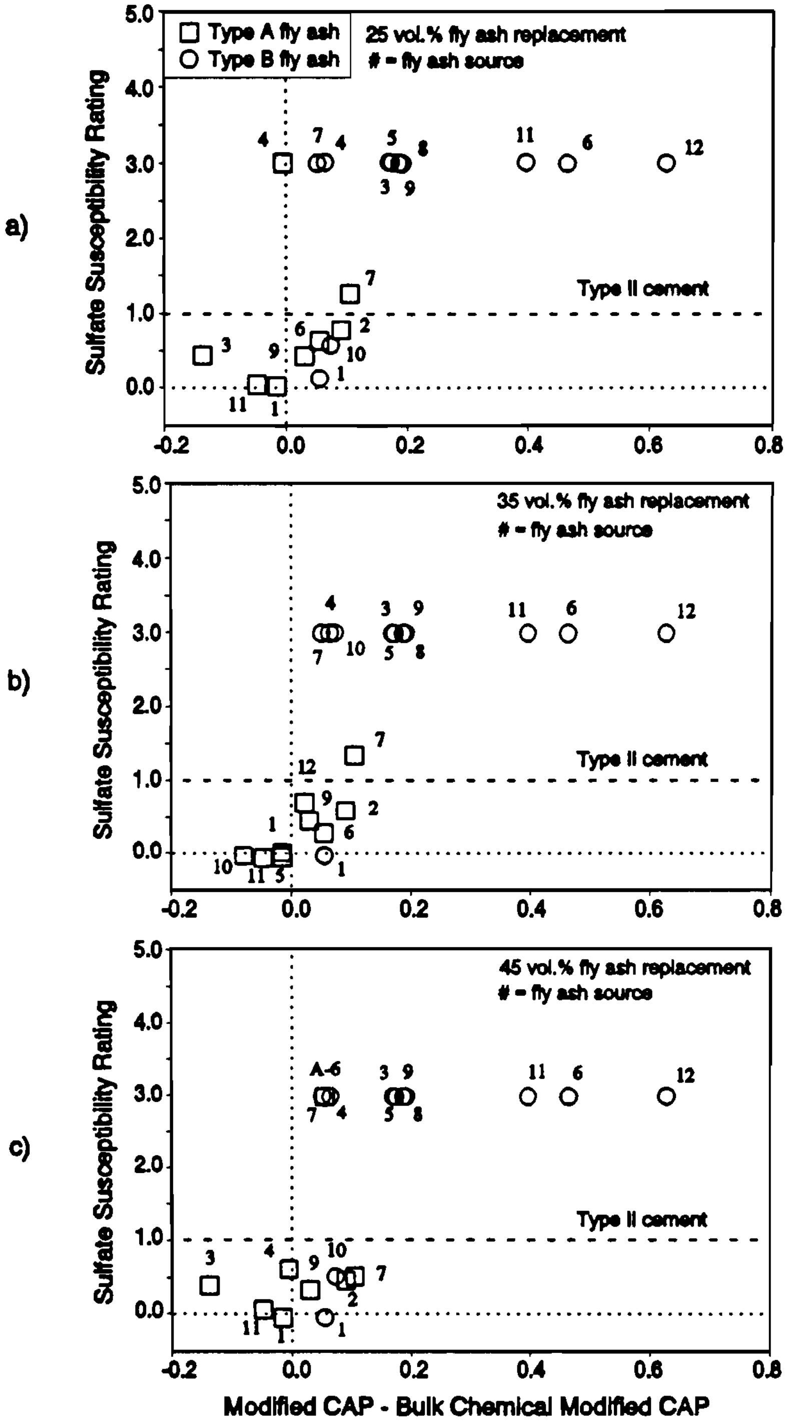


Figure 5.15 Sulfate Susceptibility Ratings of Fly Ash/Type II Cement Mixtures Versus the Difference Between Modified CAP and Bulk Chemical Modified CAP

between CAPs, Modified CAP is greater than Bulk Chemical Modified CAP. In these cases, consideration of fly ash mineralogy would predict decreased sulfate resistance for fly ash, relative to the prediction based on chemical analyses alone.

Large negative differences occured only for fly ashes which decreased the linear expansion of Type II cement concrete mixtures by approximately 50 percent or more (SSR less than or equal to 0.5). Large positive differences occured only for fly ashes which significantly increased the deterioration of Type II cement concrete (SSR greater than or equal to 2.0). Consideration of fly ash mineralogy, therefore, improved these predictions of the effects of fly ash on the sulfate resistance of Type II cement concrete. The following discussion of several fly ashes with unique characteristics illustrates the advantages of considering mineralogy when predicting the effects of fly ash on the sulfate resistance of concrete.

For fly ash A-3, the difference between the mineralogy-based Modified CAP and the Bulk Chemical Modified CAP was the highest negative value of all fly ashes included in this study. Consideration of the mineralogy of fly ash A-3, therefore, provided an improved prediction of its high resistance to sulfates. Fly ash A-3 contained a high proportion of mullite and relatively low proportions of quartz and ferrite spinel. Therefore, a large proportion of detrimental alumina was contained in a nonreactive phase, while only small proportions of beneficial silica and ferric oxide were confined in nonreactive phases.

For fly ash A-7, the difference between the mineralogy-based Modified CAP and the Bulk Chemical Modified CAP was the highest positive value of all Type A fly ashes included in this study. Consideration of the mineralogy of fly ash A-7, therefore, provided an improved prediction of its susceptibility to sulfate attack. Fly ash A-7 contained only a small proportion of crystallinity (7.8 percent), most of which was quartz. Therefore, the proportion of reactive silica was reduced while the proportions of deleterious reactive oxides were not.

All Type B fly ashes had positive differences between the mineralogy-based Modified CAP and the Bulk Chemical Modified CAP. The sum of proportions of silica and ferric oxides confined in nonreactive phases were consistently larger than the sum of the proportions of deleterious alumina and calcium oxides confined in nonreactive phases.

Consideration of mineralogy did not improve the prediction of the effects of fly ash B-1, which was the Type B ash most resistant to sulfates. The resistance of this high-calcium ash to sulfate attack may have been influenced by characteristics which are not included in either Modified CAP model. These characteristics include fineness, alkali content, sulfate content, and effects on water/(cement+pozzolan) ratio of concrete.

Fly ash B-12 had the largest positive difference between the mineralogy-based Modified CAP and the Bulk Chemical CAP of all fly ashes included in this study. Consideration of the mineralogy of fly ash B-12, therefore, provided an improved prediction of its high susceptibility to sulfate attack. Ash B-12 contained a high proportion of crystalline material, including tricalcium aluminate, quartz, ferrite spinel, and hematite. Consequently, it contained very small proportions of reactive silica and reactive ferric oxide, both of which are beneficial in terms of sulfate resistance.

5.5 SUMMARY

The primary objective of this portion of the study was to investigate the effects of fly ash on the sulfate resistance of Type II cement concrete. The effects of fly ash on the mixing water requirement and compressive strength of Type II cement concrete were also presented. Twelve Type A fly ashes and twelve Type B fly ashes replaced cement at levels of 25, 35, and 45 percent by volume. Fly ash was added as a mineral admixture at the time of batching concrete. Mixtures were designed with 5½ sacks of cement per cubic yard of concrete. Mixing water was added until a concrete slump of 5 to 7 inches was attained.

Fly ash had variable effects on the water requirement of ASTM Type II cement concrete. Water requirements were particularly high for mixtures containing fly ash with large proportions of coarse particles and large proportions of unburnt carbon (high loss on ignition). Water requirements were particularly low for mixtures containing fly ash with low proportions of coarse particles and high specific gravities.

Texas Type A fly ash generally decreased the 28-day compressive strength of ASTM Type II cement concrete. Decreases in strength were most significant for mixtures containing large proportions of low-calcium fly ash.

Texas Type B fly ash had variable effects on the 28-day compressive strength of ASTM Type II cement concrete. Inclusion of fine, high-calcium fly ash increased compressive strength.

The Texas classification of fly ash, Types A and B, was not the most accurate criterion for selecting fly ash to be used in concrete exposed to sulfates. Contrary to expectations, some Texas Type A fly ashes decreased the sulfate resistance of ASTM Type II cement concrete. Also, some Texas Type B fly ashes improved the sulfate resistance of ASTM Type II cement concrete.

A model termed Modified Calcium Aluminate Potential was presented as an improved method for selecting fly ash for concrete to be exposed to sulfates. The Modified CAP model utilized fly ash chemistry and mineralogy to estimate the potential for fly ash to contain reactive calcium aluminate-type phases:

1) fly ash with Modified CAPs less than or equal to 0.6 improved the sulfate resistance of Type II cement concrete,
2) fly ash with Modified CAPs greater than 1.25 decreased the sulfate resistance of Type II cement concrete,
3) fly ash with Modified CAPs between 0.6 and 1.25 had variable effects on the sulfate resistance of Type II cement concrete.

A Modified CAP model based only on chemical analyses was also presented as an alternative for predicting the effects of fly ash on the sulfate resistance of Type II cement concrete. The accuracy of the Bulk Chemical Modified CAP was comparable with its mineralogy-based counterpart. However, some information was sacrificed when the effects of fly ash mineralogy were ignored. Relative to all prediction models which did not require mineralogical analyses, the Bulk Chemical Modified CAP was the most accurate. The limits for fly ash composition that were defined for Modified CAP also apply to Bulk Chemical Modified CAP.

If used conservatively, bulk calcium oxide content may also serve as a criterion for selecting fly ash to be used in concrete exposed to sulfates. Fly ash with calcium oxide contents less than or equal to approximately 8 percent improved the sulfate resistance of ASTM Type II cement concrete.

The sulfate resistance of ASTM Type II cement concrete containing low-calcium fly ash (less than 8 percent CaO) increased as the proportion of fly ash increased from 25 percent to 45 percent by volume. The sulfate resistance of ASTM Type II cement concrete containing high-calcium fly ash (greater than 25 percent CaO) decreased as the proportion of fly ash increased from 25 percent to 45 percent by volume. Increases in the proportion of intermediate-calcium fly ash had variable effects on the sulfate resistance of ASTM Type II cement concrete.

CHAPTER 6

ASTM TYPE I CEMENT CONCRETE WITH FLY ASH ADDED AS A MINERAL ADMIXTURE

6.1 INTRODUCTION

The objective of this portion of the study was to investigate the effects of fly ash on the sulfate resistance of Type I cement concrete. The performance of fly ash/Type I cement concrete mixtures were compared with that of Type II cement concrete without fly ash.

Results are presented for mixtures containing cements designated Type I-L and Type I-H with fly ash added as a mineral admixture. Relative to typical Type I cements, Type I-L cement contained a low proportion of tricalcium aluminate, 9.86 percent. Type I-H cement contained a high proportion of tricalcium aluminate, 11.2 percent.

Results for concrete mixtures are presented in the following order:

1) mixing water requirements,
2) compressive strengths, and
3) sulfate resistance.

Three models are presented for predicting the effects of fly ash on the sulfate resistance of concrete:

1) bulk calcium oxide content,
2) Dunstan Resistance Factor, and
3) Modified Calcium Aluminate Potential.

These models are the simplest, the most well-known, and the most accurate models, respectively.

6.2 TYPE I-L CEMENT PARTIALLY REPLACED BY FLY ASH

6.2.1 INTRODUCTION

Five Type A fly ashes and five Type B fly ashes partially replaced the Type I-L cement at levels including 25 and 35 percent by volume. These mixtures were designed with 5½ sacks of cement per cubic yard of concrete prior to fly ash replacement. Mixing water was added until a concrete slump of 5 to 7 inches was attained. Fly ash was added simultaneously with cement at the time of batching concrete.

6.2.2 MIXING WATER REQUIREMENT

Water was added to concrete mixtures until the desired slump was attained. Therefore, water/(cement+pozzolan) ratios were variable. Type I-L cement concrete required a water/cement ratio, by mass, of 0.52. Inclusion of 25 percent fly ash by volume generally increased water demand, as shown in Figure 6.1. Inclusion of 35 percent fly ash by volume generally had no significant effect, as shown in Figure 6.2.

At 25 percent replacement, fly ashes A-2, B-3, and B-10 were least detrimental to water demand. Relative to other Type A fly ashes, ash A-2 had the highest specific gravity (2.43). Therefore, for the same volume of fine particles, ash A-2 contributed the most mass. Relative to other Type B fly ashes, ashes B-3 and B-9 were both fine (less than 16 percent retained on 45 μm sieve) and had high glass contents (greater than 80 percent).

6.2.3 COMPRESSIVE STRENGTH

Inclusion of 25 volume percent Type A fly ash did not effect significantly the 28-day compressive strength of Type I-L cement concrete, as shown in Figure 6.3. Inclusion of 35 volume percent Type A fly ash decreased significantly the 28-day compressive strength of Type I-L cement concrete, as shown in Figure 6.4.

Inclusion of Type B fly ash generally increased or had no significant effect on the compressive strength of Type I-L cement concrete, as shown in Figures 6.3 and 6.4. Large increases in compressive strength resulted from the inclusion of 25 volume percent Type B fly ash.

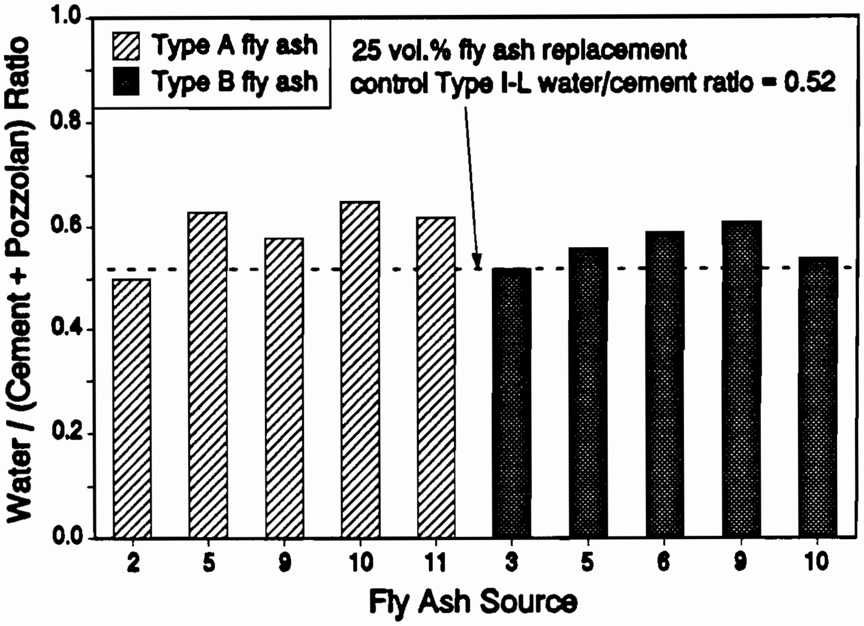


Figure 6.1 Mixing Water Requirements for Type I-L Cement Mixtures Containing 25 Volume Percent Fly Ash

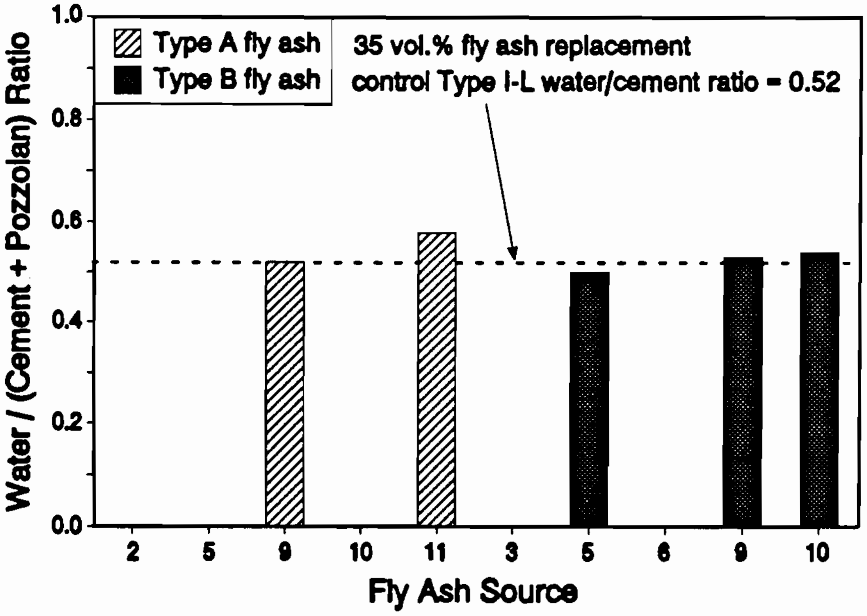


Figure 6.2 Mixing Water Requirements for Type I-L Cement Mixtures Containing 35 Volume Percent Fly Ash

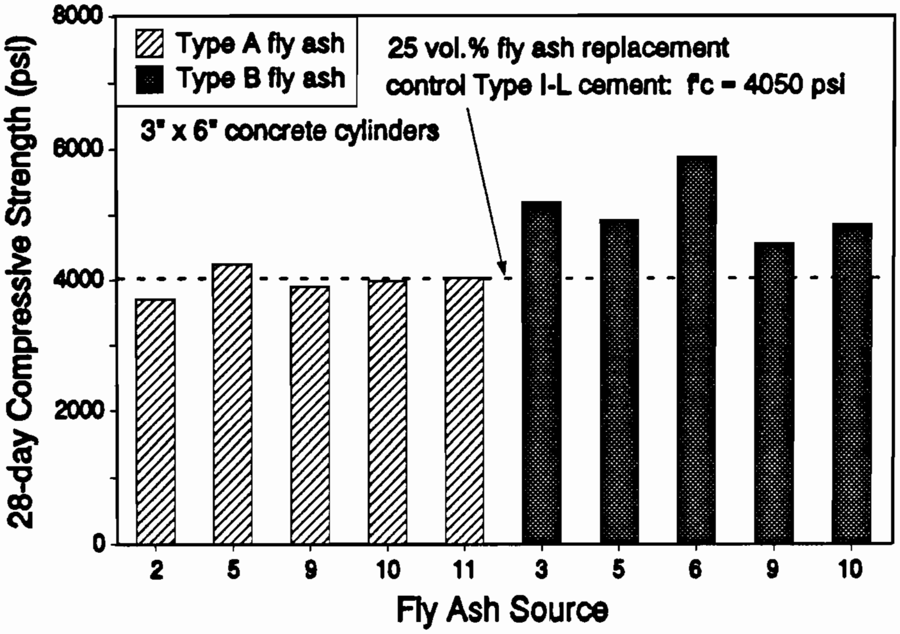


Figure 6.3 Compressive Strengths at 28 Days for Type I-L Cement Concrete Containing 25 Volume Percent Fly Ash

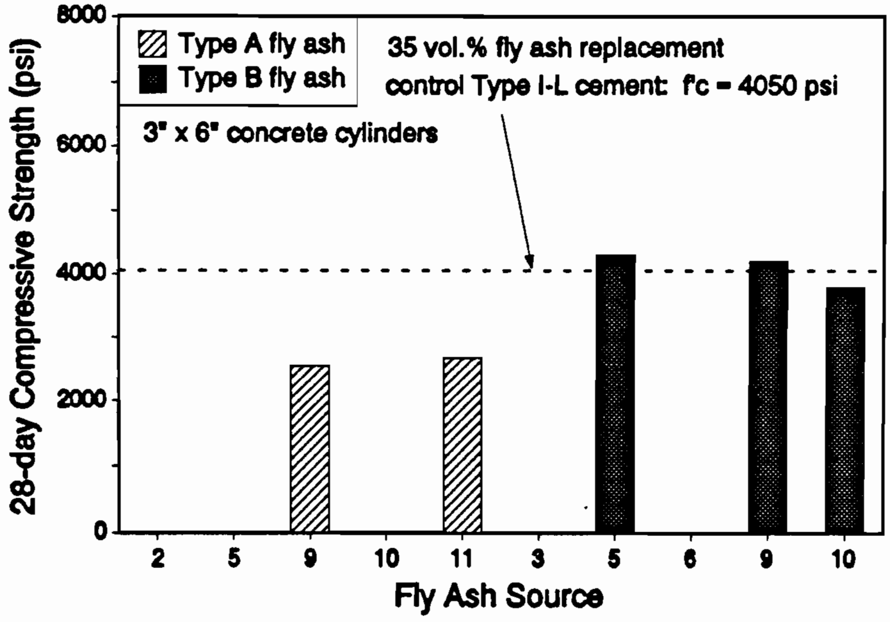


Figure 6.4 Compressive Strengths at 28 Days for Type I-L Cement Mixtures Containing 35 Volume Percent Fly Ash

Effects on strength did not correlate with effects on water requirement. For example, relative to all mixtures containing 25 percent by volume fly ash, the mixture containing fly ash A-2 required the least amount of water and had the lowest 28-day strength.

6.2.4 SULFATE SUSCEPTIBILITY

6.2.4.1 Linear Expansion and Mass Loss

All Type I-L cement mixtures containing Type A fly ash expanded less than the control Type II cement mixture and suffered no mass loss, as shown in Figures 6.5 and 6.6.

Type I-L cement mixtures containing 25 volume percent of several Type B fly ashes expanded less than the control Type II cement mixture, as shown in Figure 6.5. However, almost all mixtures containing 25 volume percent Type B fly ash lost mass as a result of sulfate attack. The only Type B fly ash/Type I-L cement mixture which suffered minimal expansions and did not lose mass contained ash B-10. Relative to the other Type B ashes, B-10 was characterized as having the lowest Modified Calcium Aluminate Potential and a low proportion of particles larger than 45 μm.

Increasing the proportion of Type B fly ash from 25 volume percent replacement to 35 volume percent replacement increased expansion in all cases and decreased the time at which mass loss was initiated, as shown in Figure 6.6.

6.2.4.2 Sulfate Susceptibility Rating

The Sulfate Susceptibility Rating, as defined in Chapter 4, is a single-value parameter which represents the rate of deterioration of concrete. This parameter includes deterioration in the forms of expansion and mass loss. It permits comparisons between the sulfate susceptibilities of all mixtures.

Sulfate Susceptibility Ratings for all Type I-L cement mixtures containing Type A fly ash and Type B fly ash are shown in Figures 6.7 and 6.8. All Type I-L cement mixtures containing Type A fly ash were more resistant to sulfates than Type II cement concrete without fly ash. With exception for 25 volume percent fly ash B-10, all the Type I-L cement mixtures containing Type B fly ash were less resistant than Type II cement concrete without fly ash. Sulfate resistance decreased with increases in the proportion of Type B fly ash.

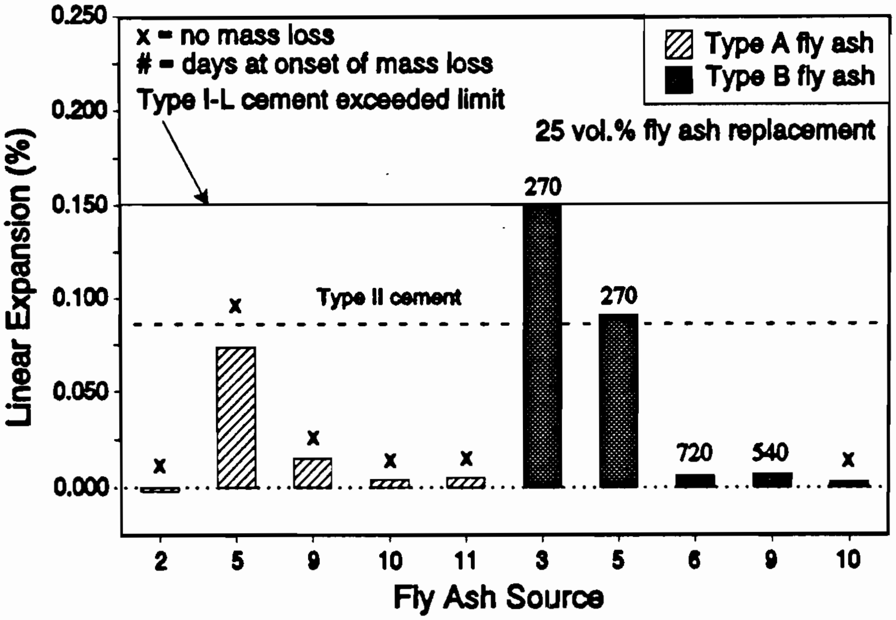


Figure 6.5 Linear Expansions and Mass Loss for Type I-L Cement Mixtures Containing 25 Volume Percent Fly Ash

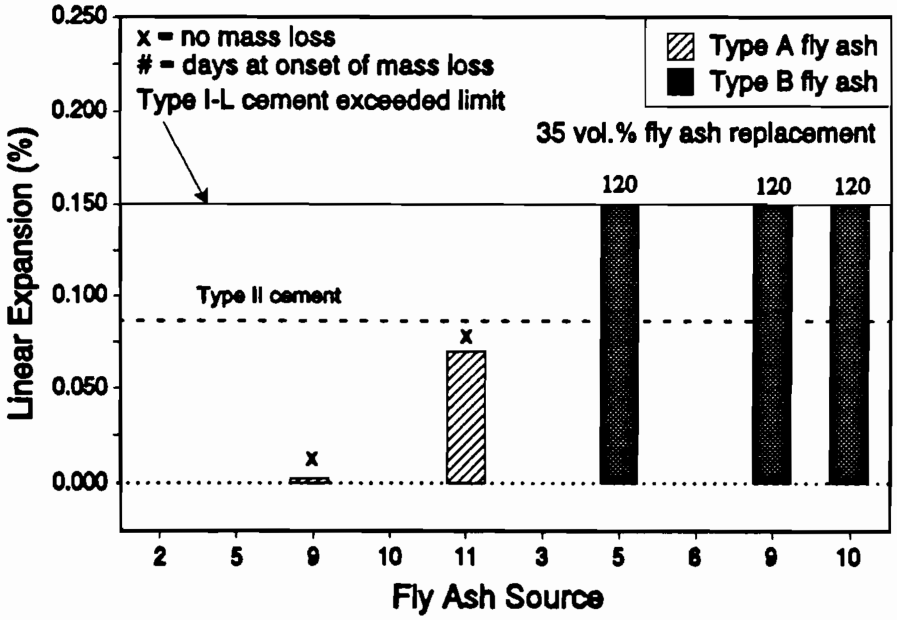


Figure 6.6 Linear Expansions and Mass Loss for Type I-L Cement Mixtures Containing 35 Volume Percent Fly Ash

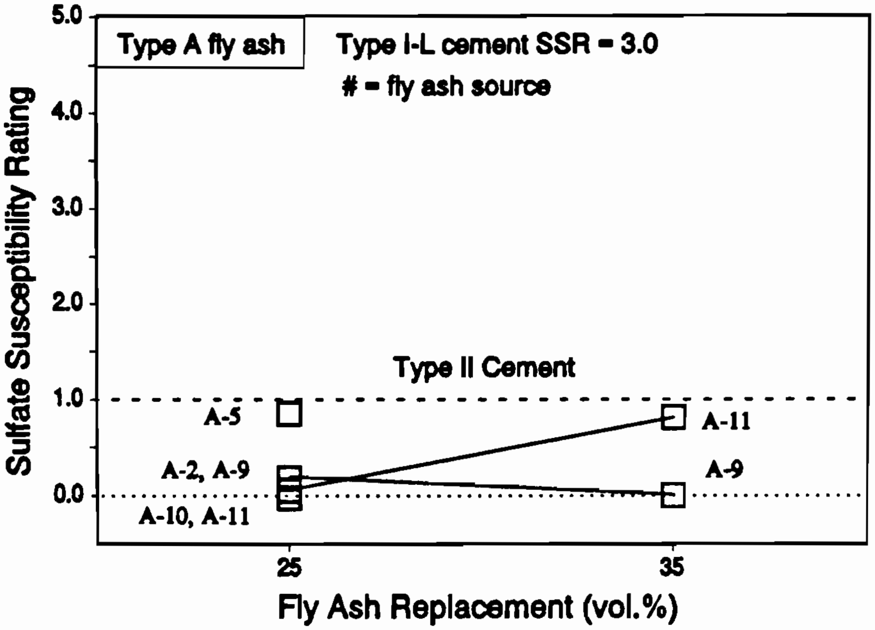


Figure 6.7 Sulfate Susceptibility Ratings of Type A Fly Ash/Type I-L Cement Concrete

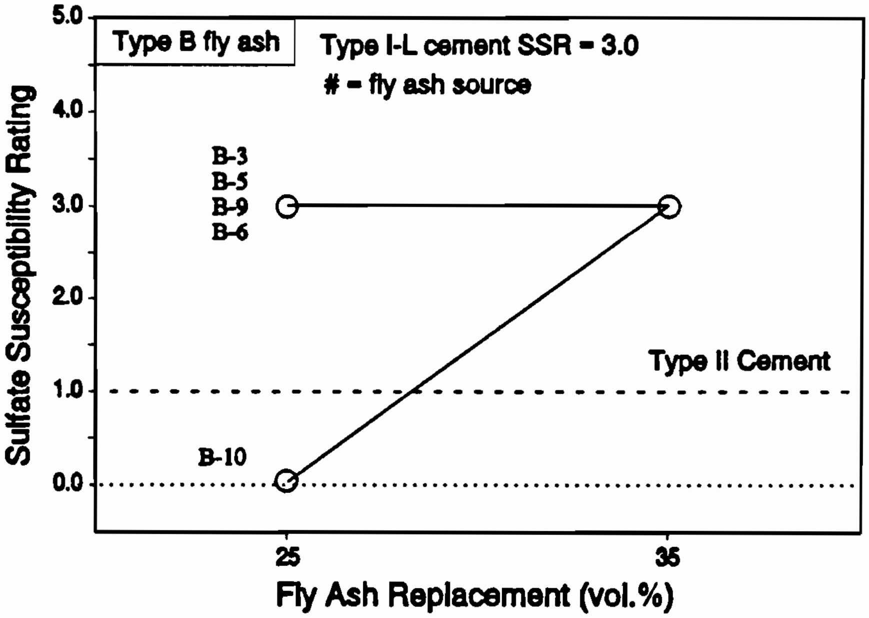


Figure 6.8 Sulfate Susceptibility Ratings for Type B Fly Ash/Type I-L Cement Concrete

6.2.4.3 Sulfate Susceptibility Prediction Models

The following text compares the Sulfate Susceptibility Ratings of fly ash/Type I-L cement mixtures with models which may be used to predict the effects of fly ash on sulfate susceptibility. Prediction model limits, which were developed with Type II cement mixtures, are analyzed for their appropriateness for Type I-L cement mixtures. As previously defined, fly ashes which improved the sulfate resistance of Type II cement concrete include:

1) those which contain 8 percent calcium oxide or less,
2) those which are characterized with Dunstan Resistance Factors of 0.5 or less, and
3) those which are characterized with Modified Calcium Aluminate Potentials of 0.6 or less.

Type I-L cement mixtures containing fly ash with bulk calcium oxide contents less than or equal to approximately 8 percent were more resistant to sulfates than Type II cement without fly ash, as shown in Figures 6.9 and 6.10. Type I-L cement mixtures containing fly ash with bulk calcium oxide contents greater than approximately 25 percent were less resistant to sulfates than Type II cement without fly ash. Due to the limited fly ashes included in this portion of the study, conclusions could not be drawn for intermediate bulk calcium oxide contents.

Type I-L cement mixtures containing fly ash with Dunstan Resistance Factors less than or equal to approximately 0.5 were more resistant to sulfates than Type II cement without fly ash, as shown in Figures 6.11 and 6.12. Type I-L cement mixtures containing fly ash with Dunstan Resistance Factors greater than approximately 3.5 were less resistant to sulfates than Type II cement without fly ash. Due to the limited fly ashes included in this portion of the study, conclusions could not be drawn for intermediate Resistance Factors.

Type I-L cement mixtures containing fly ash with Modified Calcium Aluminate Potentials less than or equal to approximately 0.6 were more resistant to sulfates than Type II cement without fly ash, as shown in Figures 6.13 and 6.14. Type I-L cement mixtures containing fly ash with Modified Calcium Aluminate Potentials greater than approximately 1.25 were less resistant to sulfates than Type II cement without fly ash. Due to the limited fly ashes included in this portion of the study, conclusions could not be drawn for intermediate Modified Calcium Aluminate Potentials.

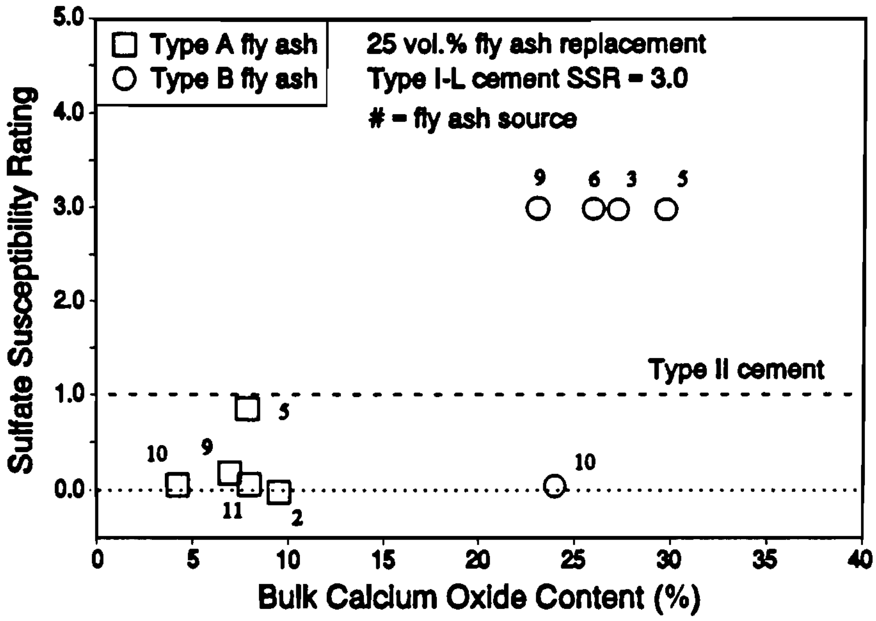


Figure 6.9 Sulfate Susceptibility Ratings of Type I-L Cement Concrete Containing 25 Volume Percent Fly Ash Versus Bulk Calcium Oxide Content of Fly Ash

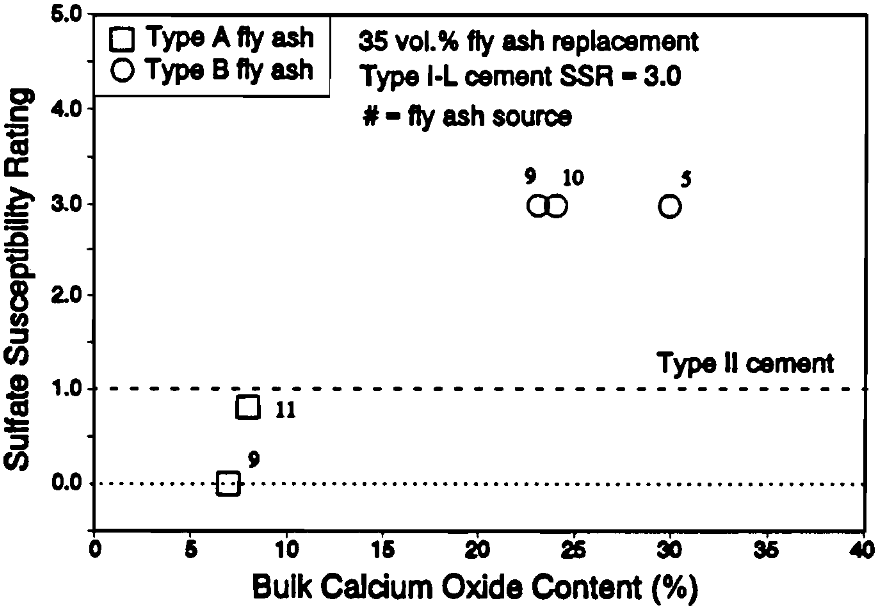


Figure 6.10 Sulfate Susceptibility Ratings of Type I-L Cement Concrete Containing 35 Volume Percent Fly Ash Versus Bulk Calcium Oxide Content

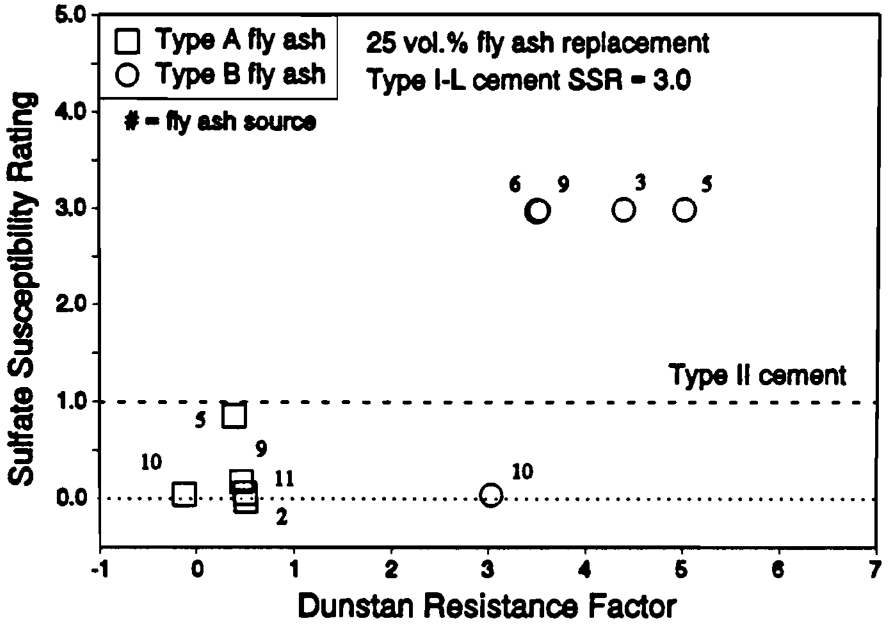


Figure 6.11 Sulfate Susceptibility Ratings of Type I-L Cement Concrete Containing 25 Volume Percent Fly Ash Versus Dunstan Resistance Factor of Fly Ash

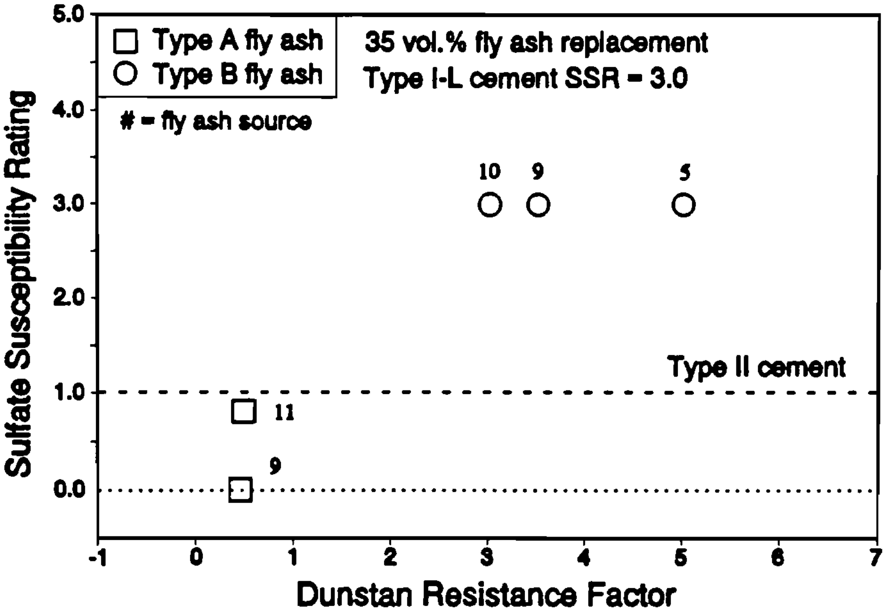


Figure 6.12 Sulfate Susceptibility Ratings of Type I-L Cement Concrete Containing 35 Volume Percent Fly Ash Versus Dunstan Resistance Factor of Fly Ash

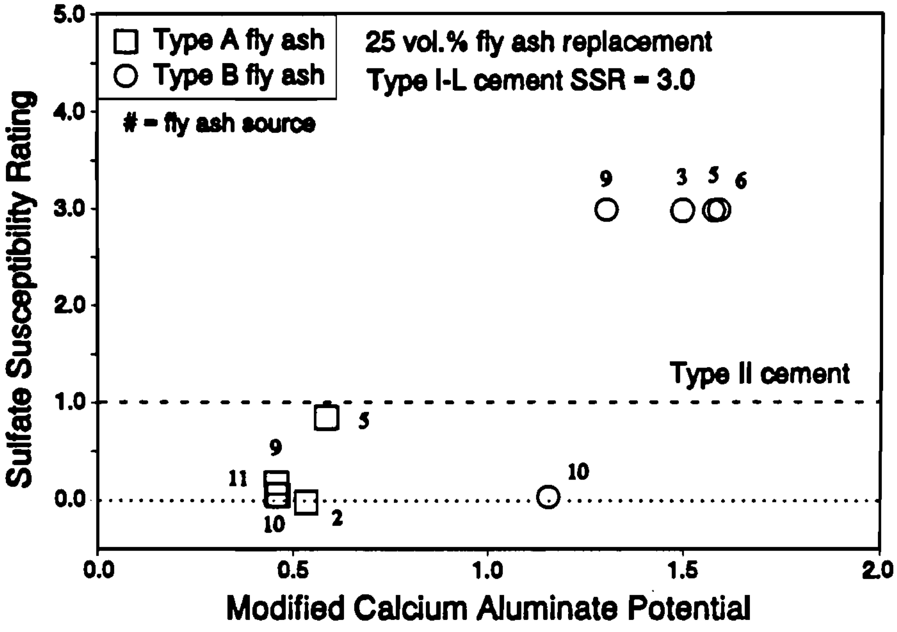


Figure 6.13 Sulfate Susceptibility Ratings of Type I-L Cement Concrete Containing 25 Volume Percent Fly Ash Versus Modified Calcium Aluminate Potential of Fly Ash

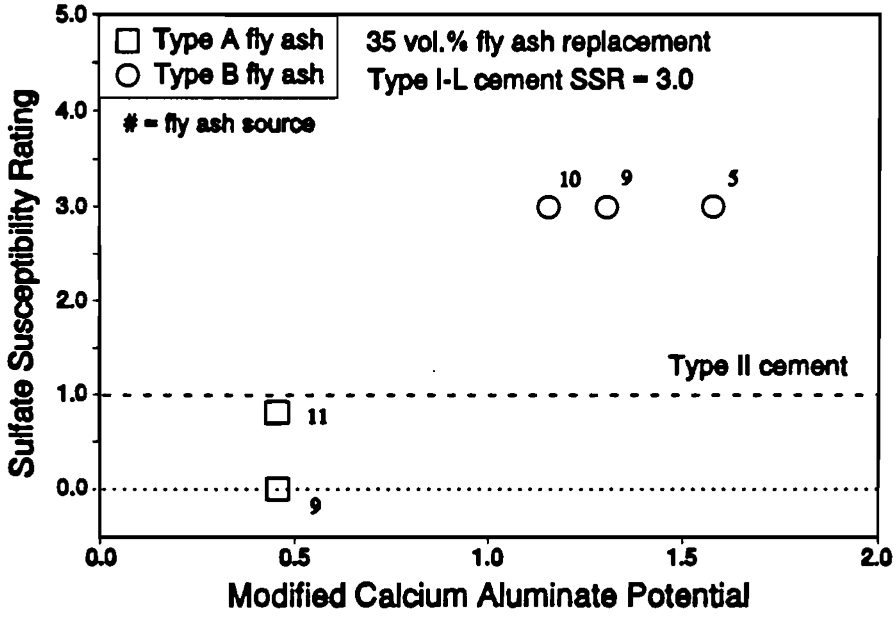


Figure 6.14 Sulfate Susceptibility Ratings of Type I-L Cement Concrete Containing 35 Volume Percent Fly Ash Versus Modified Calcium Aluminate Potential of Fly Ash

In general, the same sulfate susceptibility prediction model limits were applicable to the Type I-L cement mixtures as well as the Type II cement mixtures.

6.3 TYPE I-H CEMENT PARTIALLY REPLACED BY FLY ASH

6.3.1 INTRODUCTION

Six Type A fly ashes and seven Type B fly ashes partially replaced the Type I-H cement at levels of 25 and 35 percent by volume. Design of these mixtures included 5½ sacks of cement per cubic yard of concrete prior to fly ash replacement. Mixing water was added until a concrete slump of 5 to 7 inches was attained. Fly ash for these mixtures was added as a mineral admixture at the time of batching concrete.

6.3.2 MIXING WATER REQUIREMENT

Water was added to concrete mixtures until a slump of 5 to 7 inches was attained. Therefore, water/(cement + pozzolan) ratios were variable. The two control Type I-H cement mixtures required an average water/cement ratio, by mass, of 0.54.

Type A fly ash generally increased or had no significant effect on water demand, as shown in Figures 6.15 and 6.16. Relative to all Type A fly ash mixtures, the mixture containing fly ash A-6 required the least amount of water. Fly ash A-6 contained a relatively small proportion of particles larger than 45 μm (10.5 percent).

Type B fly ash generally decreased or had no significant effect on water demand, as shown in Figures 6.15 and 6.16. Relative to the Type A ashes, the Type B ashes were generally finer and had higher specific gravities. Higher specific gravities permitted more mass for the same volume of fly ash particles.

Water demand of Type I-H cement mixtures generally decreased with increases in the percent replacement of both types of fly ash. Relative to Type I-H cement without fly ash, inclusion of 35 volume percent Type B fly ash reduced water/(cement + pozzolan) ratios by up to approximately 15 percent.

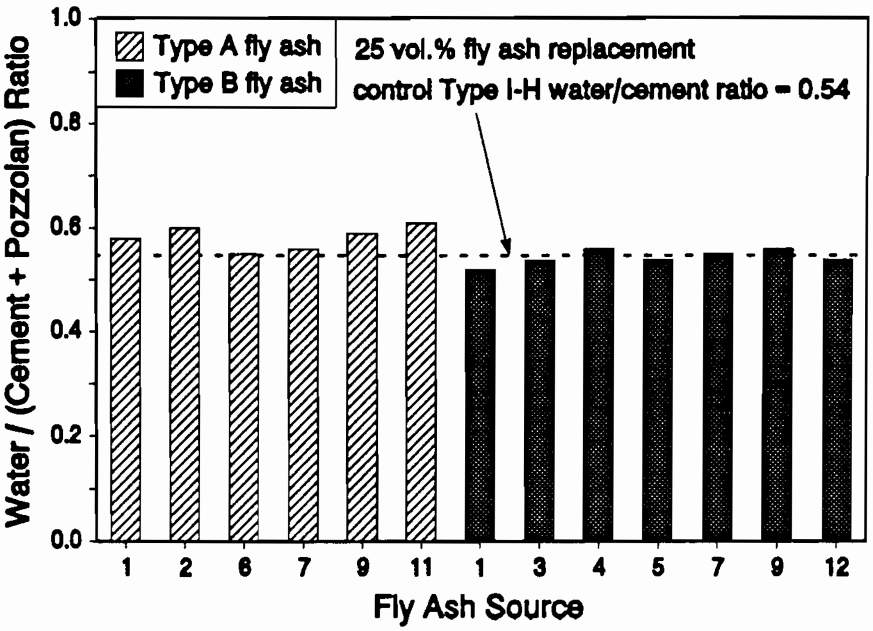


Figure 6.15 Mixing Water Requirements for Type I-H Cement Concrete Containing 25 Volume Percent Fly Ash

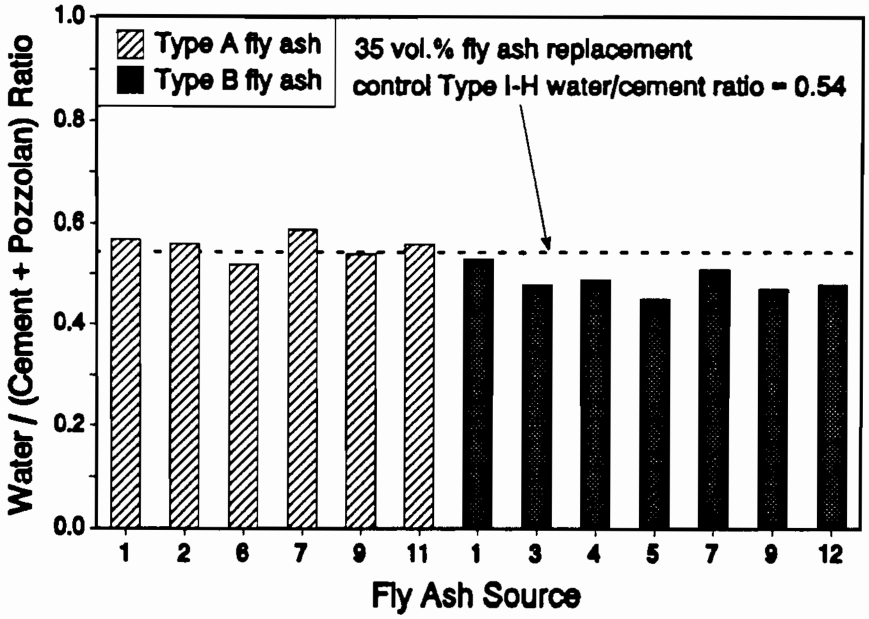


Figure 6.16 Mixing Water Requirements for Type I-H Cement Concrete Containing 35 Volume Percent Fly Ash

6.3.3 COMPRESSIVE STRENGTH

Inclusion of Type A fly ash generally decreased 28-day compressive strength, as shown in Figures 6.17 and 6.18. Fly ash A-6 was the only Type A ash which increased the compressive strength of Type I-H cement concrete. Relative to the other Type A fly ashes included in this portion of the study, ash A-6 contained the largest proportion of calcium oxide.

Inclusion of Type B fly ash in Type I-H cement concrete mixtures generally increased the 28-day compressive strength. Inclusion of fly ashes B-3 and B-4 resulted in the largest increases in compressive strength. These ashes contained relatively large proportions of calcium oxide and large proportions of glass.

6.3.4 SULFATE SUSCEPTIBILITY

6.3.4.1 Linear Expansion and Mass Loss

Linear expansion and days at onset of mass loss for Type I-H cement mixtures containing Type A fly ash and Type B fly ash are presented in Figures 6.19 and 6.20. With exception for the mixture containing 35 volume percent fly ash A-1, all mixtures exceeded limits of expansion and/or mass loss. Increases in the volume percentage of Type A ash and Type B ash decreased expansions in several cases, but did not substantially delay the onset of mass loss.

6.3.4.2 Sulfate Susceptibility Rating

The Sulfate Susceptibility Rating, as defined in Chapter 4, is a single-value parameter which represents the rate of deterioration of concrete. This parameter includes deterioration in the forms of expansion and mass loss. It permits comparisons between the sulfate susceptibilities of all mixtures.

With exception for one mixture, fly ash/Type I-H cement concretes were not as resistant to sulfates as Type II cement concrete, as shown in Figures 6.21 and 6.22. The only fly ash/Type I-H cement mixture which performed well contained 35 volume percent fly ash A-1. Relative to all fly ashes included in this portion of the study, fly ash A-1

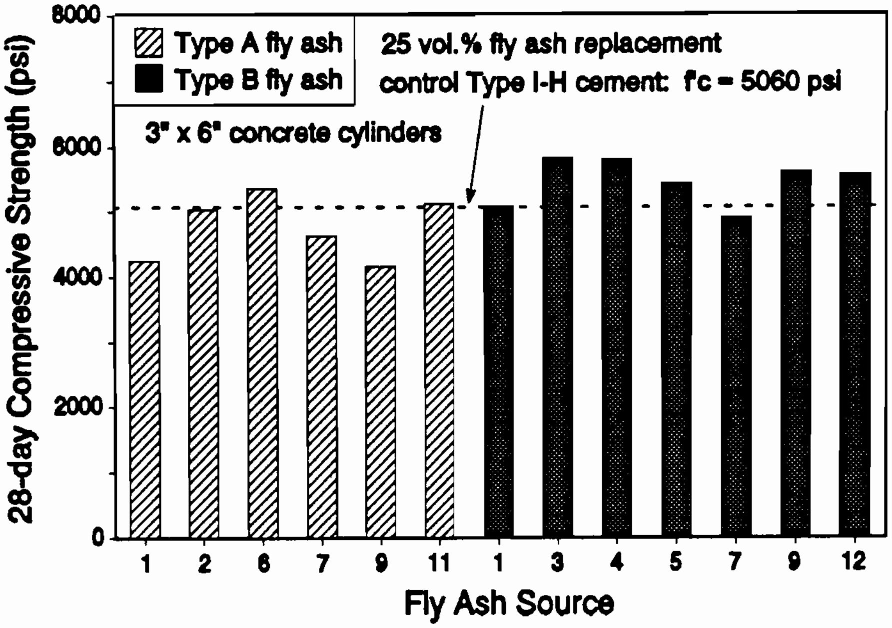


Figure 6.17 Compressive Strengths at 28 Days for Type I-H Cement Concrete Containing 25 Volume Percent Fly Ash

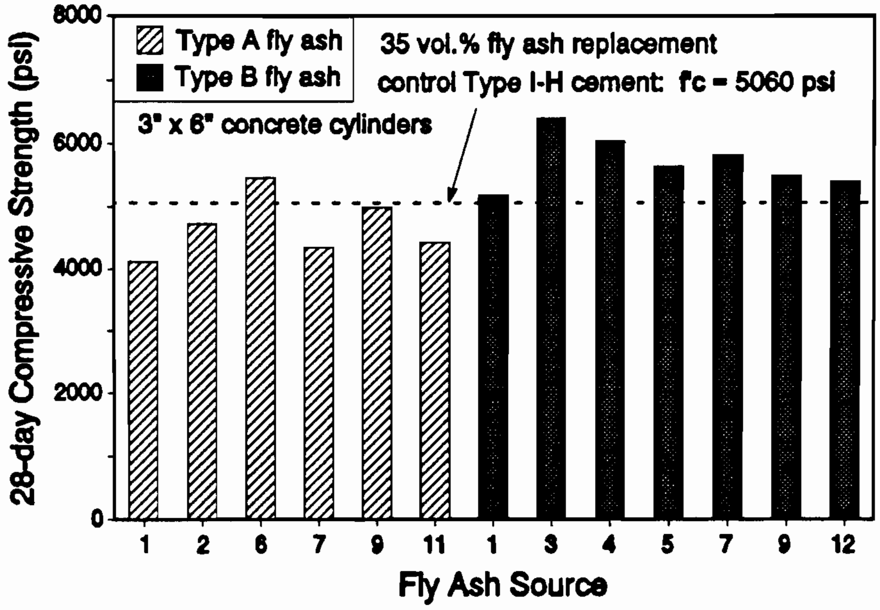


Figure 6.18 Compressive Strengths at 28 Days for Type I-H Cement Concrete Containing 35 Volume Percent Fly Ash

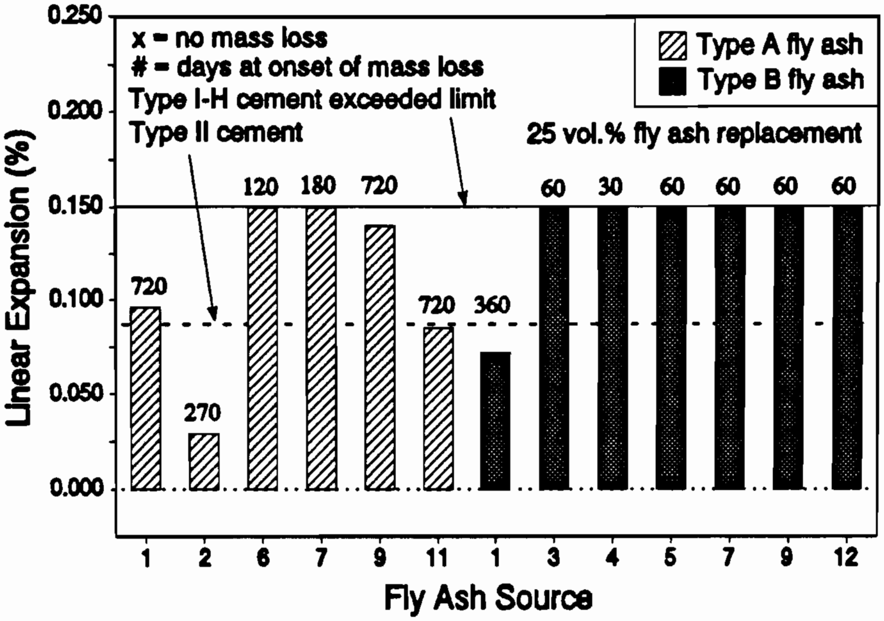


Figure 6.19 Linear Expansions and Mass Loss of Type I-H Cement Concrete Containing 25 Volume Percent Fly Ash

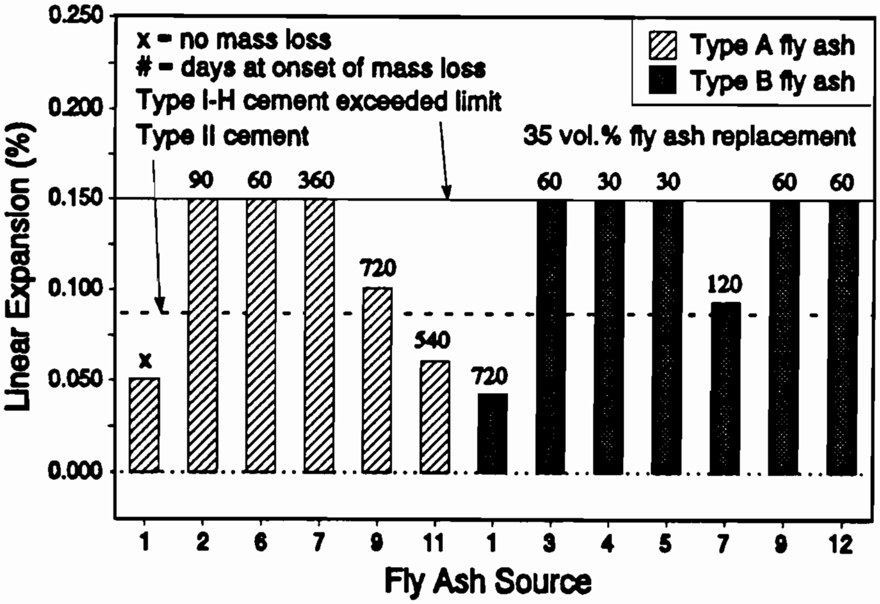


Figure 6.20 Linear Expansions and Mass Loss of Type I-H Cement Concrete Containing 35 Volume Percent Fly Ash

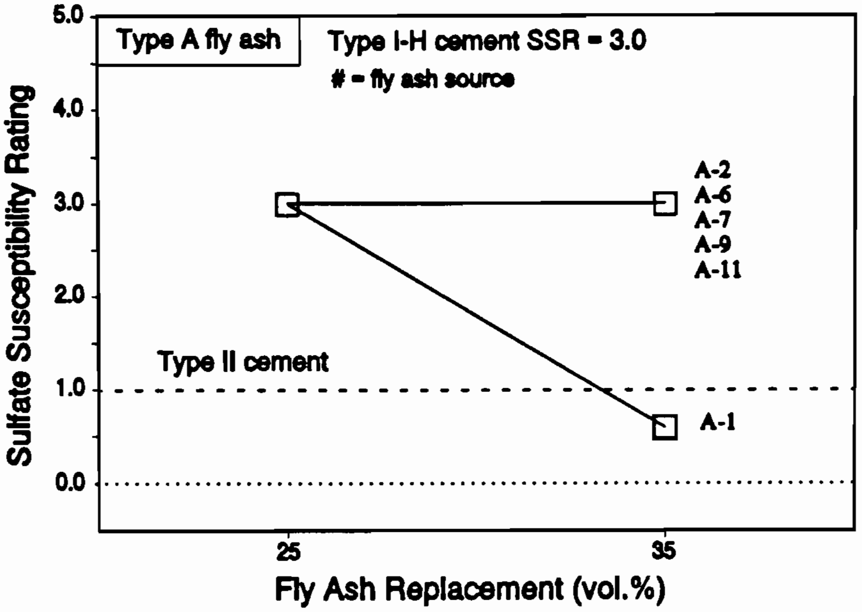


Figure 6.21 Sulfate Susceptibility Ratings of Type A Fly Ash/Type I-H Cement Concrete

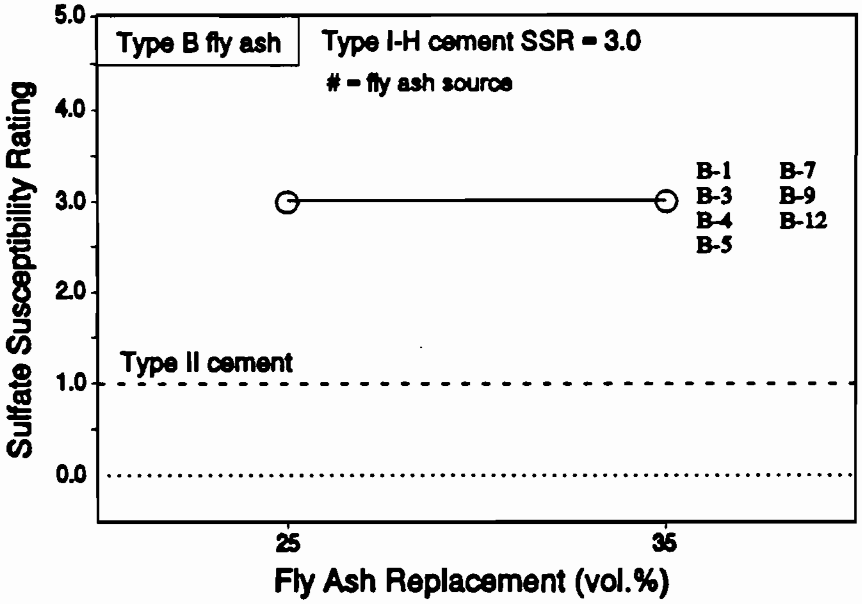


Figure 6.22 Sulfate Susceptibility Ratings of Type B Fly Ash/Type I-H Cement Concrete

contained the lowest proportion of calcium oxide, 4.80 percent. It was also characterized as having the lowest Dunstan Resistance Factor, -0.01, and the lowest Modified Calcium Aluminate Potential, 0.35.

6.4 SUMMARY

The primary objective of this portion of the study was to investigate the effects of fly ash on the sulfate resistance of Type I cement concrete. The performance of fly ash/Type I cement concrete mixtures were compared with that of Type II cement concrete without fly ash. The effects of fly ash on the mixing water requirements and compressive strengths of Type I cement concrete were also presented.

Results were presented for mixtures containing cements designated Type I-L and Type I-H with fly ash added as a mineral admixture. Relative to typical Type I cements, Type I-L cement contained a low proportion of tricalcium aluminate and Type I-H cement contained a high proportion of tricalcium aluminate.

The Type I-L cement was replaced by five Type A fly ashes and five Type B fly ashes at levels of 25 and 35 percent by volume. The Type I-H cement was replaced by six Type A fly ashes and seven Type B fly ashes at levels of 25 and 35 percent by volume. These mixtures were designed for 5½ sacks of cement per cubic yard of concrete. Mixing water was added until a concrete slump of 5 to 7 inches was attained.

Inclusion of Type A fly ash or 25 volume percent Type B fly ash in Type I cement concrete generally increased mixing water requirements or had no significant effect. Inclusion of 35 volume percent Type B fly ash generally decreased mixing water requirements or had no significant effect.

Inclusion of Type A fly ash in Type I cement concrete generally decreased 28-day compressive strength or had no significant effect. Inclusion of Type B fly ash generally increased 28-day strength or had no significant effect.

Relative to the Type II cement concrete, the two Type I cement concretes were significantly less resistant to sulfate attack. With respect to improvements in sulfate resistance, these two Type I cements responded differently to the inclusion of fly ash. The cement with the lower tricalcium aluminate content (Type I-L) exhibited more impovements as a result of the use of fly ash. Inclusion of Type A fly ash at levels of 25 percent and 35 percent by volume improved the sulfate resistance of Type I-L cement concrete to a level comparable to or better than Type II cement concrete without fly ash. These Type A fly ashes had bulk calcium oxide contents less than 10 percent, Dunstan Resistance Factors less than 0.75, and Modified Calcium Aluminate Potentials less than 0.6.

Only one fly ash/Type I-H cement concrete was more resistant to sulfates than Type II cement concrete without fly ash. The mixture included fly ash A-1 at a level of 35 percent by volume. Fly ash A-1 contained the lowest calcium oxide content (4.80 percent) of all ashes included in this portion of the study. It was also characterized as having the lowest Dunstan Resistance Factor (-0.01) and the lowest Modified Calcium Aluminate Potential (0.35).

The Type I-H cement concrete without fly ash and most mixtures containing Type I-H cement and Type B fly ash deteriorated rapidly in the 10 percent sodium sulfate solution. The accelerated nature of these failures did not permit an evaluation of the effect of the different ashes when used with Type I-H cement concrete. Therefore, selected mixtures were subjected to milder exposure solutions, 5 percent and 2.1 percent sodium sulfate. Deterioration in mild solutions did not occur as rapidly, so comparisons between the sulfate resistance of Type I-H cement concrete mixtures were possible. The results of these mild-solution exposure tests are discussed in Chapter 8.

CHAPTER 7

FLY ASH CEMENT CONCRETE WITH A HIGH CEMENT FACTOR

7.1 INTRODUCTION

The objective of this portion of the study was to investigate the effects of high cement contents on the sulfate resistance of fly ash concrete. Several Type B fly ash/Type II cement mixtures were produced with cement contents of 7 sacks per cubic yard of concrete. These fly ash/cement mixtures were previously shown to be susceptible to sulfate attack when designed with 5½ sacks cement per cubic yard concrete. Increased concrete strength and impermeability were anticipated to increase sulfate resistance.

Six Type B fly ashes replaced Type II cement at levels of 25, 35, and 45 percent by volume. Fly ashes were added as mineral admixtures at the time of batching concrete. Mixing water was added until a concrete slump of 5 to 7 inches was attained.

The effects of fly ash and cement contents on the following concrete properties are presented and discussed:

1) mixing water requirements,
2) compressive strengths, and
3) sulfate resistance.

The discussion on sulfate resistance includes comparisons between sulfate susceptibility ratings of fly ash concrete and models which utilize fly ash composition to predict their effects on sulfate susceptibility.

7.2 MIXING WATER REQUIREMENT

Relative to the 7-sack mixture without fly ash, inclusion of Type B ash either decreased water demand or had no significant effect, as shown in Figure 7.1. Some of the same

Type B fly ashes increased water demand in mixtures which were designed for 5½ sacks of cement per cubic yard concrete.

Increases in water/(cement+pozzolan) ratios, by weight, are partially attributable to the lower specific gravity of fly ash. For the same volume of fine particles, fly ash/cement mixtures have less mass than portland cement mixtures without fly ash. Decreases in water/(cement+pozzolan) ratios are partially attributable to the spherical, hygroscopic nature of fly ash particles. In high cement content mixtures, the effects which decrease water demand may be more prominent than the effects which increase water demand.

7.3 COMPRESSIVE STRENGTH

Relative to the 7-sack mixture without fly ash, inclusion of all Type B fly ashes increased 28-day compressive strengths, as shown in Figure 7.2. Contrarily, a few of the same Type B fly ashes decreased 28-day strengths in 5½-sack mixtures. These different effects are in accord with the different effects on water/(cement+pozzolan) ratios.

Inclusion of fly ash B-4 in the 7-sack mixtures resulted in the highest compressive strengths. Fly ash B-4 was a moderately high-calcium fly ash with a low proportion of coarse particles (13.2 percent retained on #325 sieve) and a low proportion of crystalline material (14.4 percent).

7.4 SULFATE SUSCEPTIBILITY

7.4.1 LINEAR EXPANSION AND MASS LOSS

Increasing the cement content from 5½ sacks to 7 sacks caused large decreases in linear expansion due to sulfate attack, as shown in Figure 7.3. Decreased concrete permeability limited the depth to which sulfates could penetrate.

However, increasing the mixture design cement content was not effective in eliminating sulfate-related mass loss. Although the depth of penetration of sulfates was limited, expansions near the surface of cylinders caused cracking and subsequent spalling. As fly ash content increased, duration of exposure prior to the initiation of mass loss decreased.

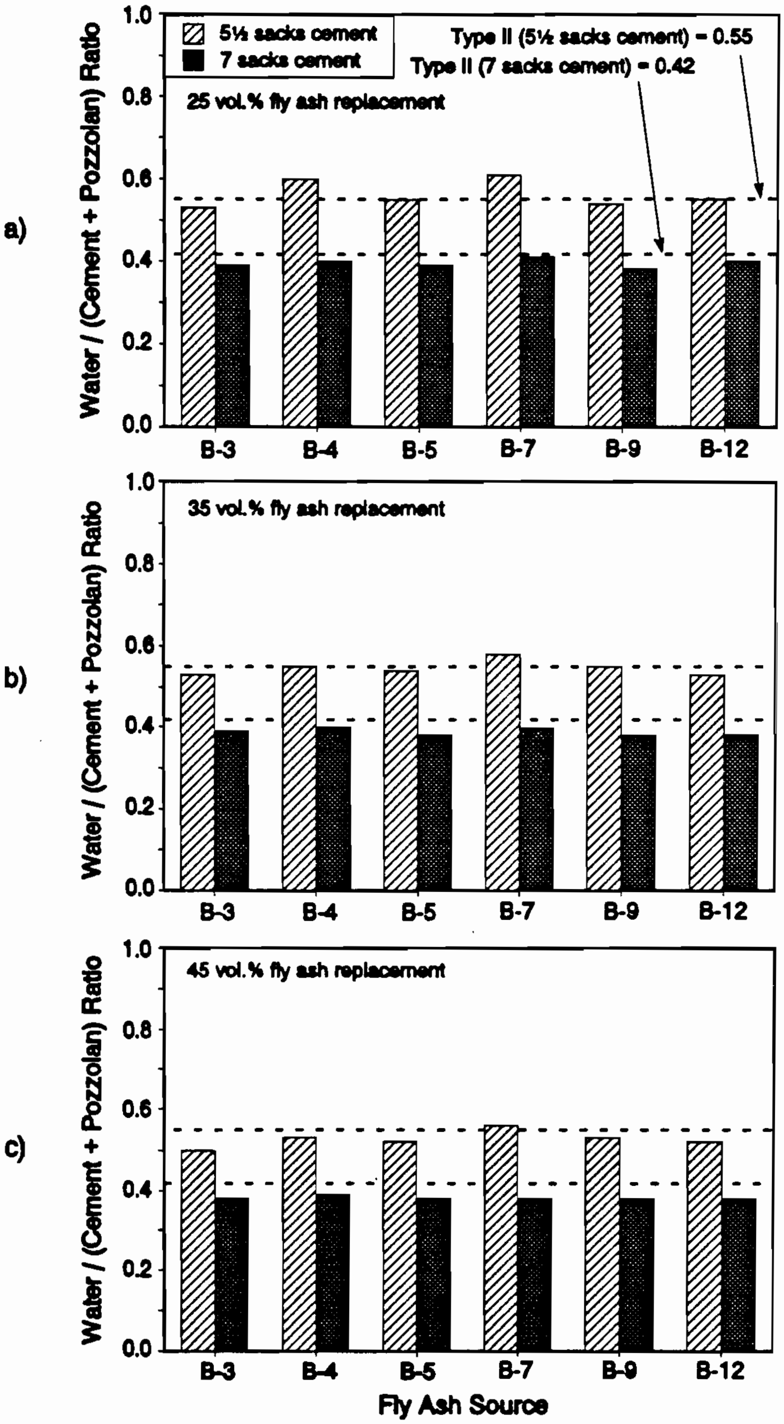


Figure 7.1 Mixing Water Requirements for 7-Sack Fly Ash/Type II Cement Concrete for a) 25%, b) 35%, and c) 45% Replacement by Volume

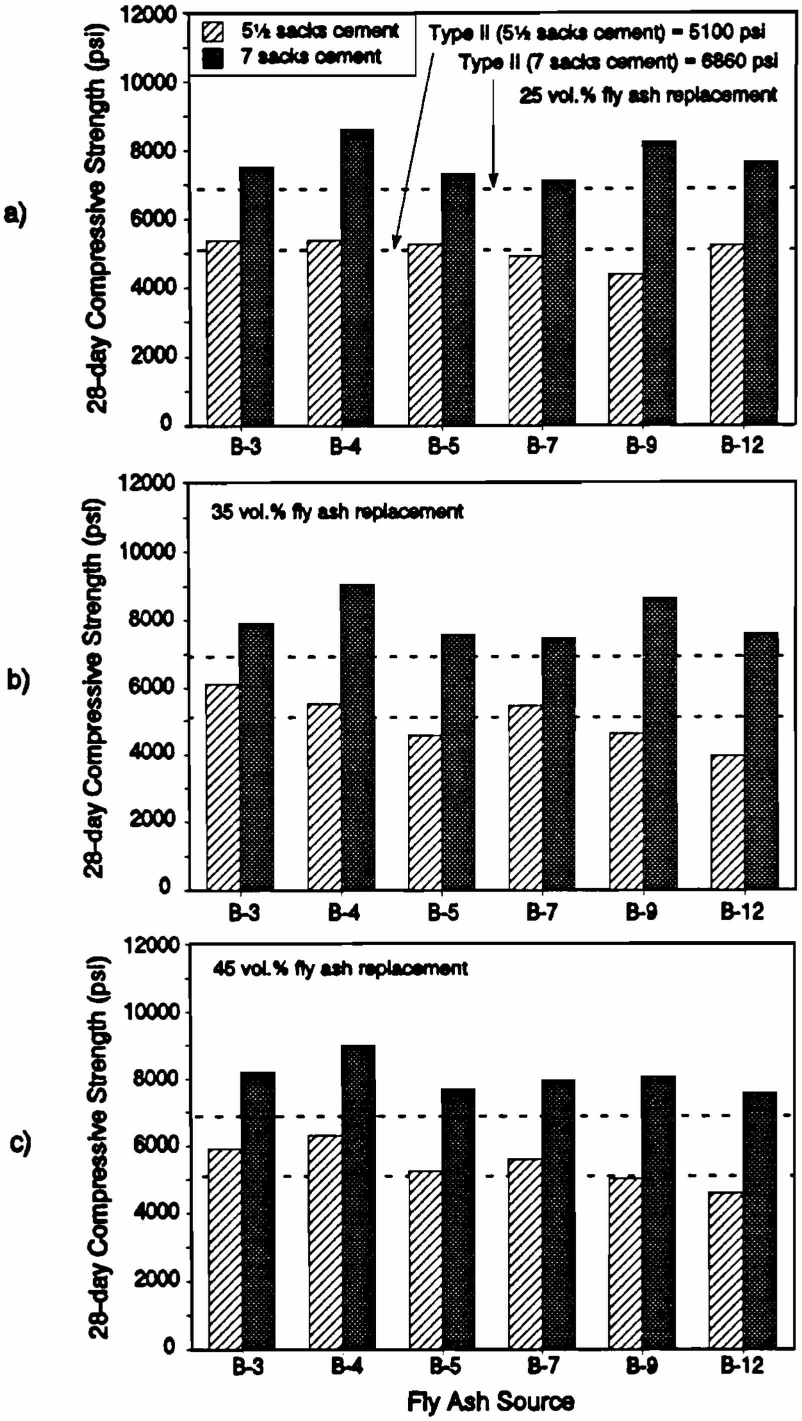


Figure 7.2 Compressive Strengths at 28 Days for 7-Sack Fly Ash/Type II Cement Concrete for a) 25%, b) 35%, and c) 45% Replacement by Volume

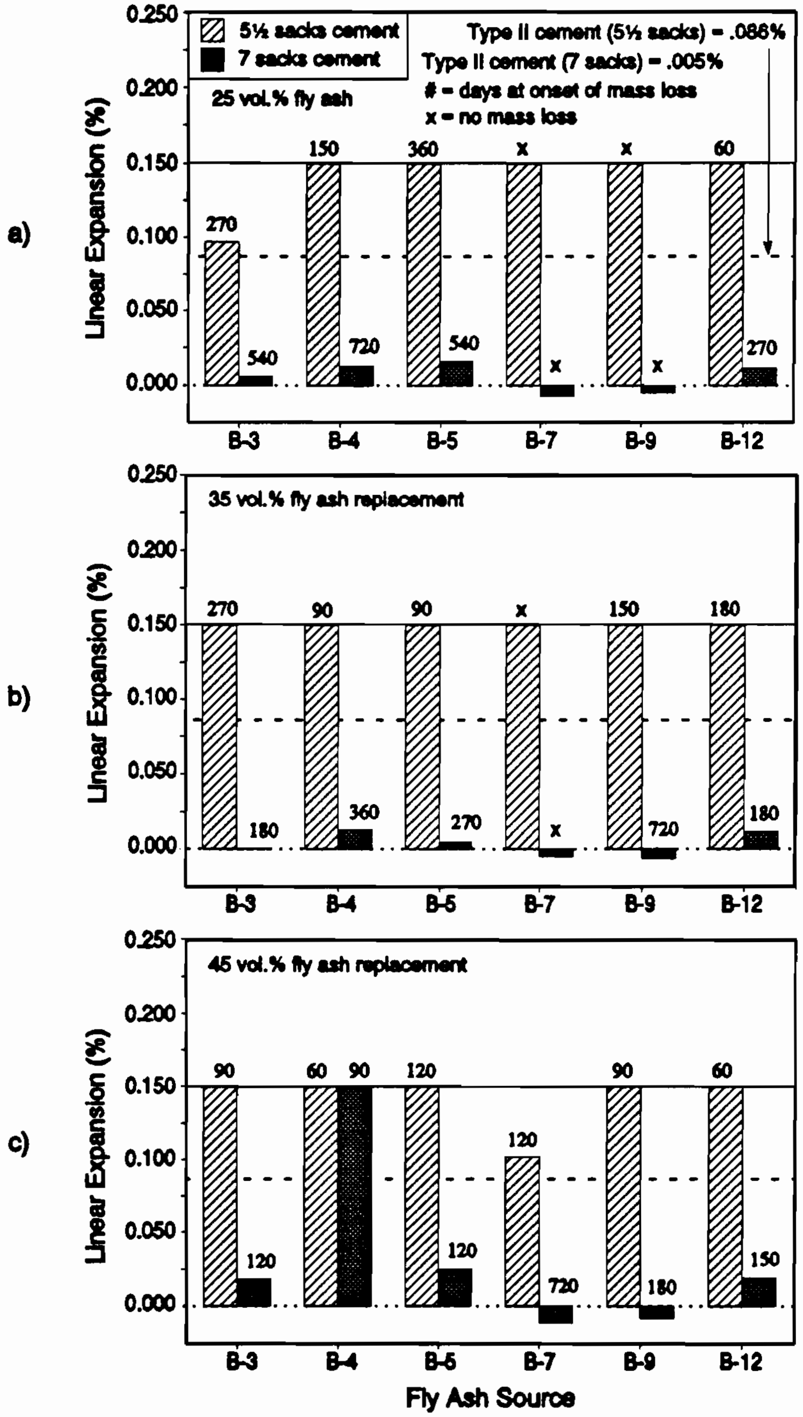


Figure 7.3 Linear Expansions (%) for 7-Sack Fly Ash/Type II Cement Concrete for a) 25%, b) 35%, and c) 45% Replacement by Volume

The only 7-sack mixtures which did not suffer expansion or mass loss contained low proportions of fly ashes B-7 and B-9. Of the Type B fly ashes included in this portion of the study, these ashes contained the lowest bulk calcium oxide contents (25.6 percent and 23.1 percent, respectively).

7.4.2 SULFATE SUSCEPTIBILITY RATING

The Sulfate Susceptibility Rating, as defined in Chapter 4, is a single-value parameter which depicts the rate of deterioration of concrete. This parameter includes deterioration in the forms of expansion and mass loss. It permits comparisons between the sulfate susceptibilities of all mixtures.

Sulfate Susceptibility Ratings of 7-sack mixtures are compared with those of similar 5½-sack mixtures in Figure 7.4. Increased mixture design cement content either decreased sulfate susceptibility or had no significant effect. High cement content mixtures containing 25 volume percent fly ashes B-7 and B-9 were as resistant to sulfates as the 7-sack Type II cement mixture without fly ash. The high cement content mixture containing 35 volume percent fly ash B-7 was also resistant to sulfate attack.

7.4.3 SULFATE SUSCEPTIBILITY PREDICTION MODELS

Sulfate Susceptibility Ratings for 7-sack mixtures containing 25, 35, and 45 percent fly ash by volume are compared with fly ash bulk calcium oxide content, Dunstan Resistance Factor, and Modified Calcium Aluminate Potential in Figures 7.5 through 7.7, respectively. Fly ashes B-7 and B-9, which were least susceptible to sulfates, contained the lowest proportions of calcium oxide. They were also characterized as having the lowest Dunstan Resistance Factors and the lowest Modified Calcium Aluminate Potentials.

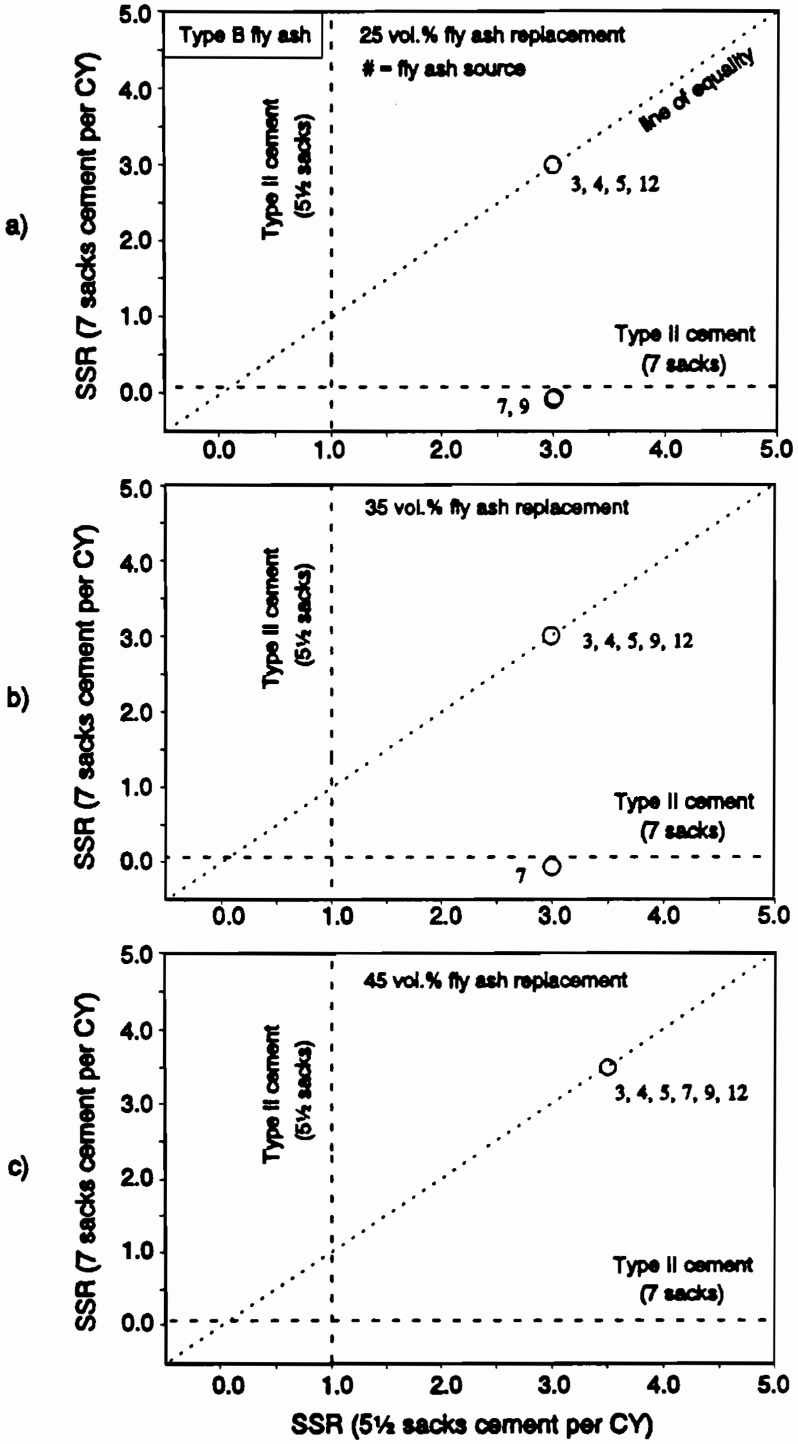


Figure 7.4 Sulfate Susceptibility Ratings of 7-Sack Fly Ash/Type II Cement Concrete for a) 25%, b) 35%, and c) 45% Replacement by Volume

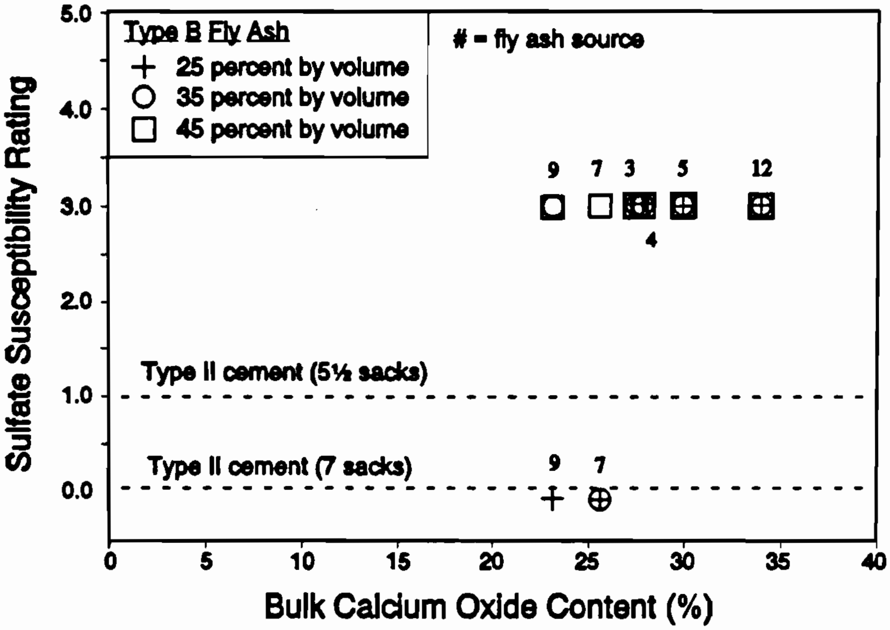


Figure 7.5 Sulfate Susceptibility Ratings of 7-Sack Fly Ash/Type II Cement Concrete Versus Bulk Calcium Oxide Content of Fly Ash

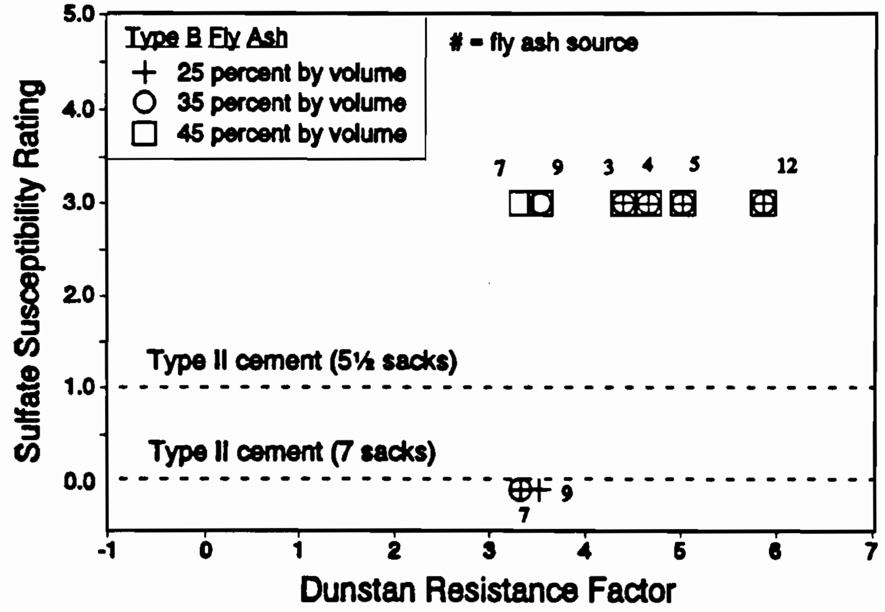


Figure 7.6 Sulfate Susceptibility Ratings of 7-Sack Fly Ash/Type II Cement Concrete Versus Dunstan Resistance Factor of Fly Ash

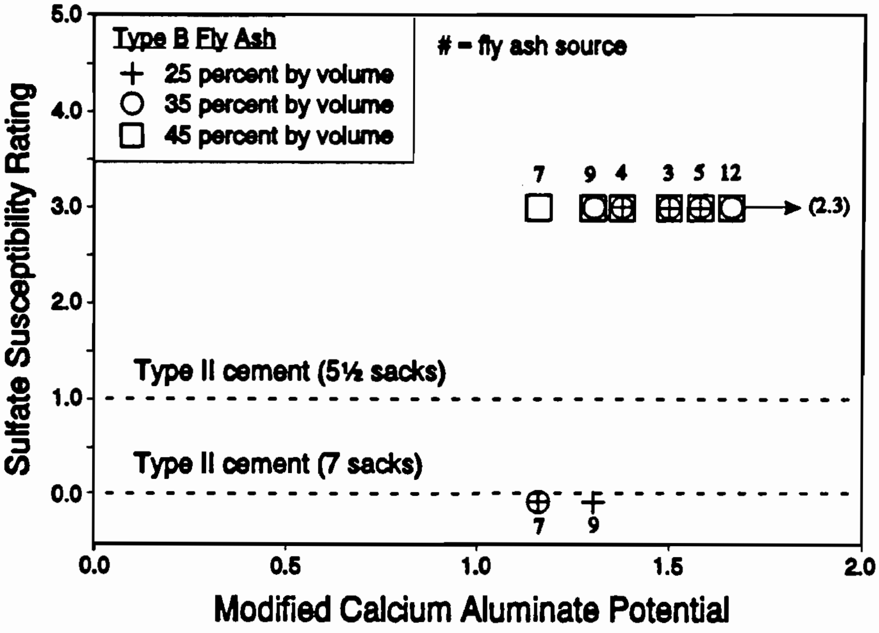


Figure 7.7 Sulfate Susceptibility Ratings of 7-Sack Fly Ash/Type II Cement Concrete Versus Modified Calcium Aluminate Potential of Fly Ash

7.5 SUMMARY

The primary objective of this portion of the study was to investigate the effects of high cement content on the sulfate resistance of fly ash concrete. Several Type B fly ash/Type II cement concrete mixtures were produced with cement contents of 7 sacks per cubic yard. These fly ash concrete mixtures were previously shown to be susceptible to sulfate attack when designed with 5½ sacks cement per cubic yard. Increased concrete strength and impermeability were anticipated to increase the sulfate resistance of concrete.

In addition to sulfate resistance, mixing water requirement and compressive strength were discussed.

Six Type B fly ashes replaced Type II cement at levels of 25, 35, and 45 percent by volume. Fly ashes were added as mineral admixtures at the time of batching concrete. Mixing water was added until a concrete slump of 5 to 7 inches was attained.

In the high cement content mixtures, partial replacement of Type II cement with Type B fly ash reduced the mixing water requirements and increased 28-day compressive strengths in all cases.

The sulfate resistance of Type II cement concrete without fly ash was improved significantly by increasing the mixture design cement content. The linear expansion in 10 percent sodium sulfate solution was reduced by 94 percent.

The Type B fly ash/Type II cement concretes with a cement content of 5½ sacks per cubic yard had a sulfate resistance which was in all cases considerably worse than Type II cement concrete without fly ash. The sulfate resistance of these fly ash concretes was in most cases not significantly improved by increasing the cement content to 7 sacks per cubic yard. The permeability characteristics of these concretes were improved, which minimized intrusion of sulfate ions. However, the exposed surface of the concrete was attacked by sulfates, as demonstrated by the losses in mass.

A few of the 7-sack Type B fly ash/Type II cement mixtures were able to withstand the exposure environment without any expansion or mass loss. These fly ashes contained the lowest proportions of bulk calcium oxide (less than 26 percent) and were characterized as having the lowest Dunstan Resistance Factors (less than 3.5) and the lowest Modified Calcium Aluminate Potentials (less than 1.25). These fly ash cement concretes were only resistant to sulfates when the proportion of fly ash was low (generally 25 percent replacement by volume).

CHAPTER 8
BLENDED FLY ASH CEMENT CONCRETE

8.1 INTRODUCTION

The objective of this portion of the study was to investigate the effects of intergrinding fly ash on the physical properties of fly ash cement and on the mechanical properties of fly ash concrete, particularly sulfate resistance. Mixtures in which fly ash was interground with cement clinker and gypsum are compared with mixtures in which fly ash was added as a mineral admixture. Results are presented for mixtures in which Type II and Type I cements were partially replaced by Type A and Type B fly ashes. The Type I cement used in this portion of the study was designated Type I-H for its high C_3A content (11.2 percent). The Type II cement contained 6.0 percent tricalcium aluminate.

Results are presented in the following order:

1) method of production of blended cements,
2) effects of intergrinding fly ash on the physical properties of fly ash cement,
3) fly ash/Type II cement concrete mixtures, and
4) fly ash/Type I-H cement concrete mixtures.

8.2 PRODUCTION OF BLENDED CEMENT

8.2.1 METHOD

Ordinary Type I-H and Type II portland cements were produced in the laboratory prior to producing blended fly ash cements. Grinding times in the laboratory were determined as those which produced laboratory cements with Blaine fineness similar to plant-produced cements, as shown in Table 8.1. Relative proportions of gypsum and cement clinker were determined as those which produced cements with sulfur trioxide contents similar to the plant-produced cements. Specific gravities and percent retained on #325 sieve were also similar between laboratory-produced cements and plant-produced cements, as shown in

Table 8.1. The grinding times and relative proportions of gypsum and cement clinker remained constant throughout the production of blended fly ash cements.

The similarity between cements produced in the laboratory and cements produced at commercial plants was ensured by comparing their resistance to sulfates. Rates of linear expansion and mass gain were similar between similar types of cement, as shown in Figures 8.1 and 8.2, respectively.

Table 8.1 Characteristics of Cements Produced at Cement Plants and in the Laboratory

Cement	Production	Grinding Time (minutes)	Blaine Air Permeability (cm^2/gm)	Retained #325 Sieve (%)	Specific Gravity	SO_3 (%)
Type II	Plant	—	3350	7.5	3.10	2.97
	Lab.	135	3340	11.3	3.06	3.00
Type I-H	Plant	—	3950	11.7	3.15	3.00
	Lab.	205	3900	14.8	3.12	2.99

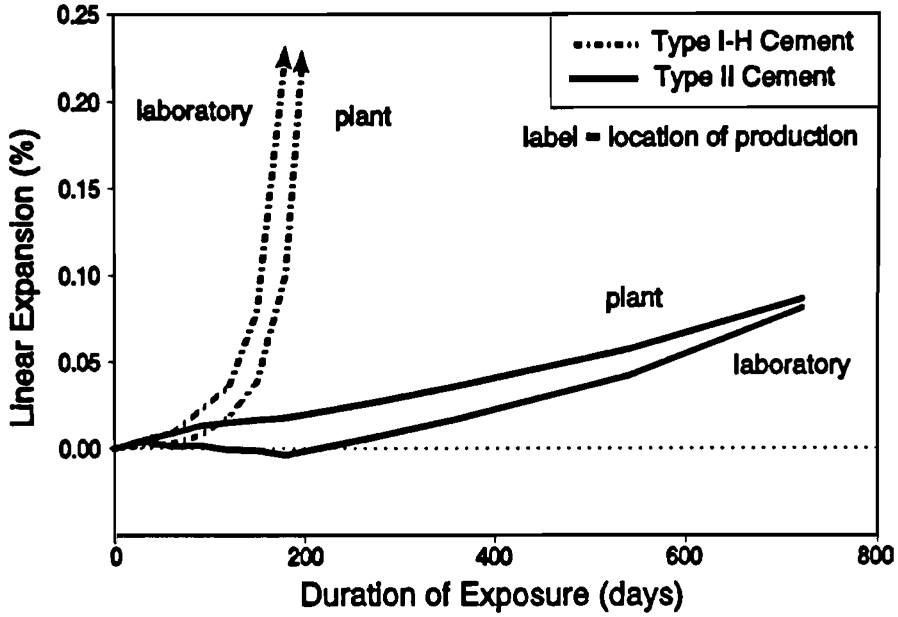


Figure 8.1 Linear Expansions of Cements Produced at Cement Plants and in the Laboratory

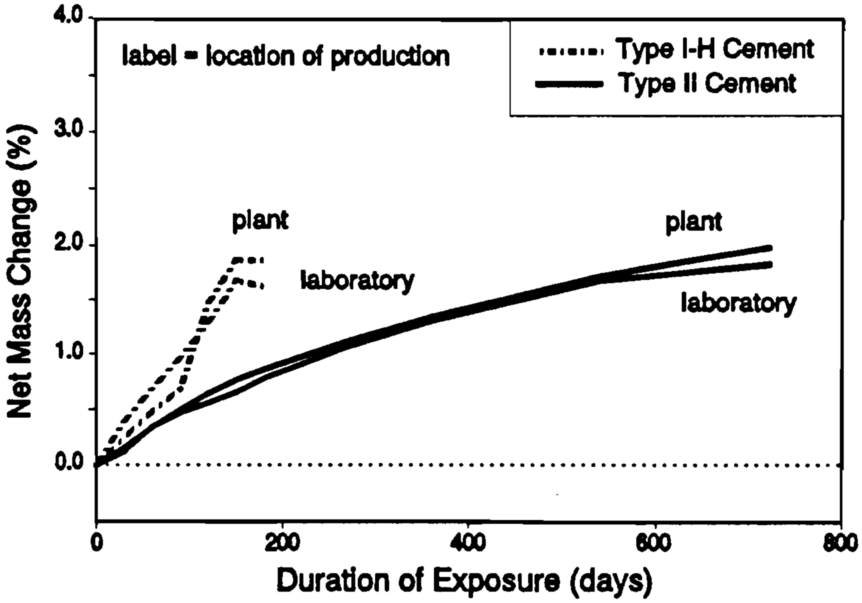


Figure 8.2 Net Mass Changes of Cements Produced at Cement Plants and in the Laboratory

8.2.2 EFFECTS ON THE PHYSICAL PROPERTIES OF FLY ASH CEMENT

Specific gravity and percent retained on #325 sieve were measured for several blended fly ash cements. These physical properties were also calculated for similar mixtures in which fly ash was not interground. The method for calculating the specific gravity of non-interground fly ash cements was the same as that which is recommended for aggregate blends in ASTM C-127:

$$SG = \frac{W_1 + W_2}{V_1 + V_2} = \frac{100}{\frac{P_1}{G_1} + \frac{P_2}{G_2}} \text{ , where} \qquad (8.1)$$

SG = average specific gravity,

W_i = weight in grams for solids 1 and 2,

V_i = volume in milliliters for solids 1 and 2,

P_i = weight percentage of solids 1 and 2, and

G_i = specific gravity of solids 1 and 2.

The steps missing in the derivation of this formula are lengthy, so they are not included in this text. However, the complete derivation is illustrated in ASTM C-127.

A simple weighted average was used for calculating the percent retained on #325 sieve for non-interground fly ash cements:

$$\text{Total Percent Retained} = P_1\,(R_1) + P_2\,(R_2) \text{ , where} \qquad (8.2)$$

P_i = weight percentage of solids 1 and 2 and

R_i = percent retained on #325 sieve for solids 1 and 2.

Intergrinding fly ash increased the specific gravities of blended cements containing Type II and Type I-H cements, as shown in Figures 8.3 through 8.6. Increases in specific gravity were largest for the blended cements containing fly ash with relatively low specific gravities; specific gravities of Type A fly ashes were lower than those of Type B fly ashes. Increases in specific gravity were also largest for blended cements containing high proportions of fly ash (35 volume percent).

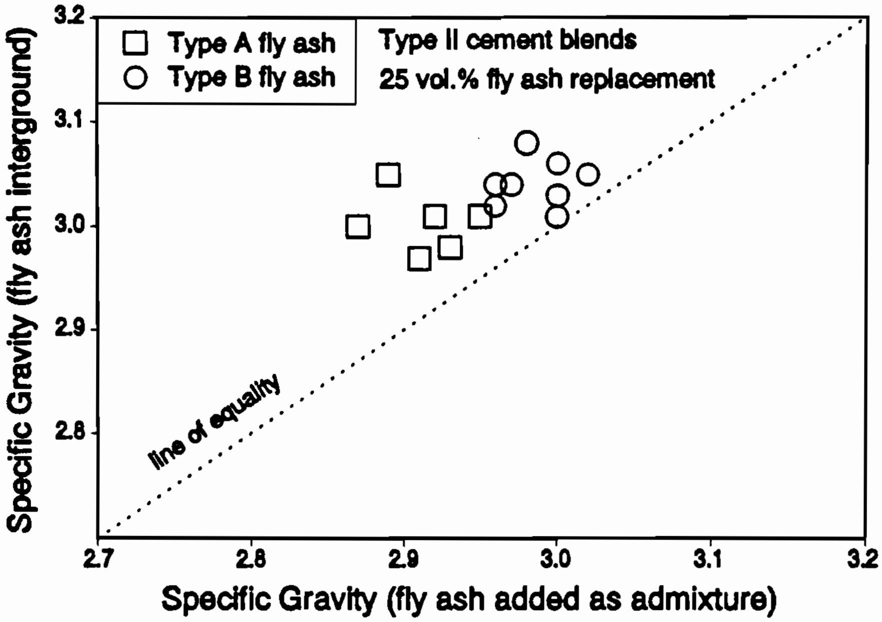


Figure 8.3 Specific Gravities of Type II Cements Containing 25 Percent Fly Ash by Volume

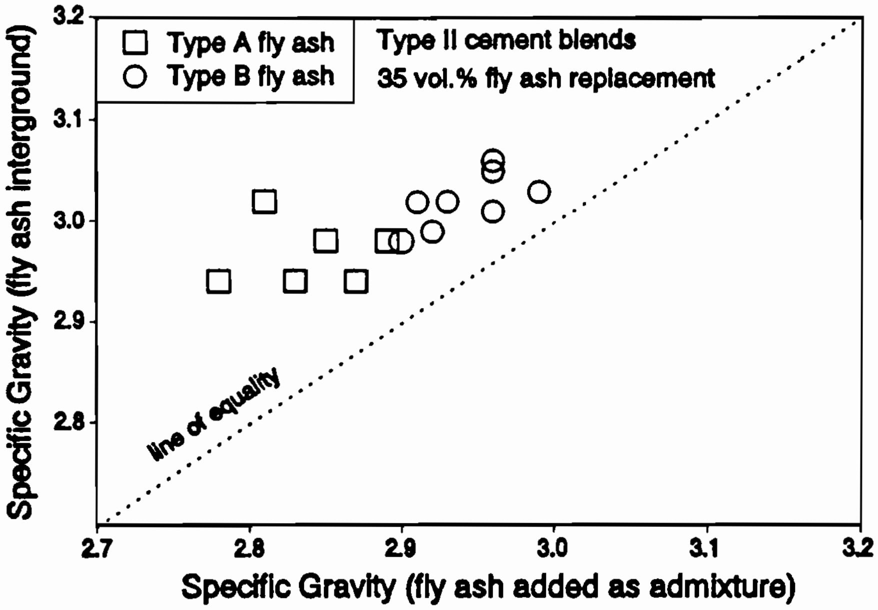


Figure 8.4 Specific Gravities of Type II Cements Containing 35 Percent Fly Ash by Volume

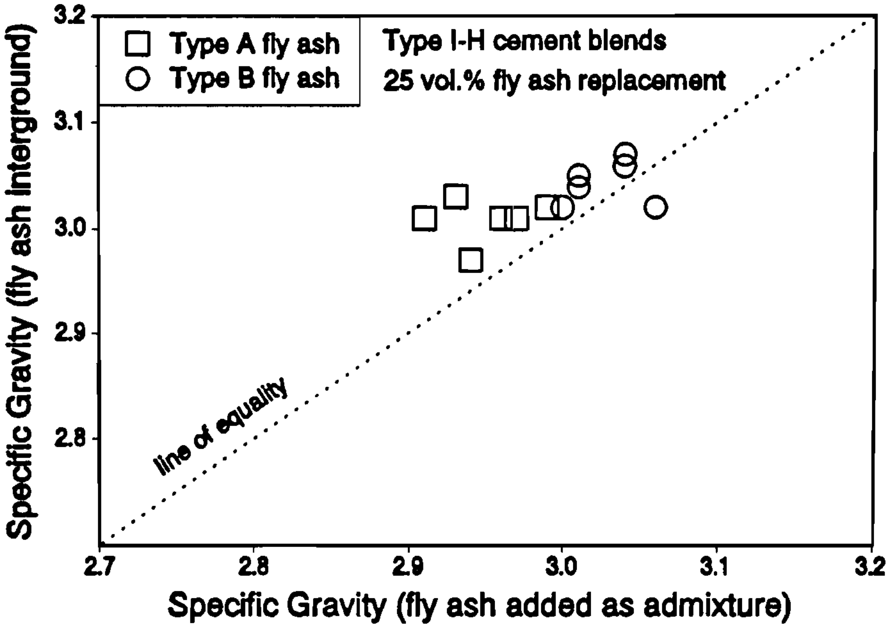


Figure 8.5 Specific Gravities of Type I-H Cements Containing 25 Percent Fly Ash by Volume

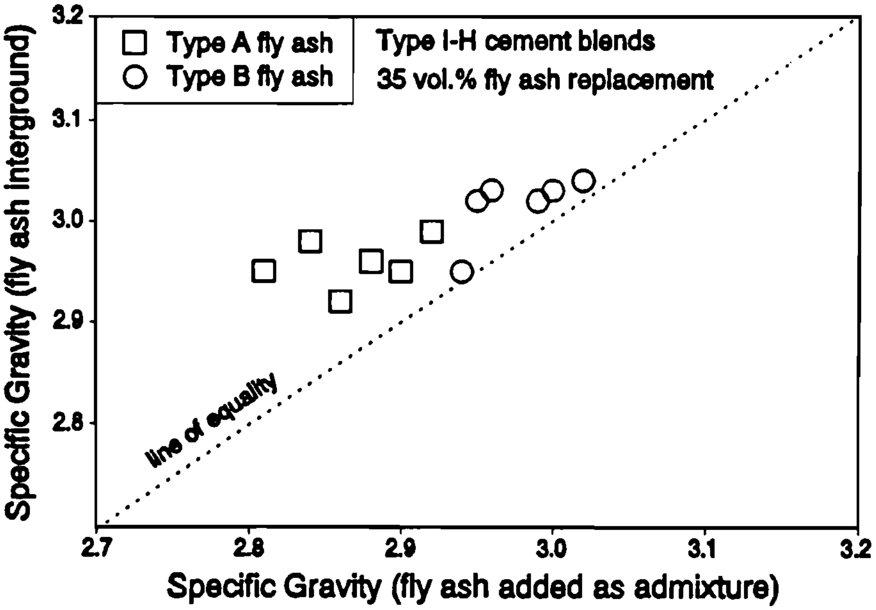


Figure 8.6 Specific Gravities of Type I-H Cements Containing 35 Percent Fly Ash by Volume

The range of specific gravities of fly ash cements was reduced by intergrinding fly ash. For example, the range of specific gravities of mixtures containing Type II cement and 35 volume percent fly ash as admixture was approximately 2.78 to 2.99 (0.21 difference). Intergrinding fly ash in these same mixtures reduced the range of specific gravities to approximately 2.94 to 3.06 (0.12 difference).

Intergrinding 35 volume percent fly ash in Type II cement mixtures reduced the percentage of particles retained on #325 sieve in all cases, as shown in Figure 8.7. These decreases were largest for mixtures containing fly ash with relatively high proportions of large particles. The range of the percentages of particles retained on #325 sieve was also reduced by intergrinding fly ash. When fly ash was added as a mineral admixture, the range of coarse particles was approximately 8 percent to 14 percent (6 percent difference). When fly ash was interground, the range of coarse particles was approximately 6 percent to 10 percent (4 percent difference).

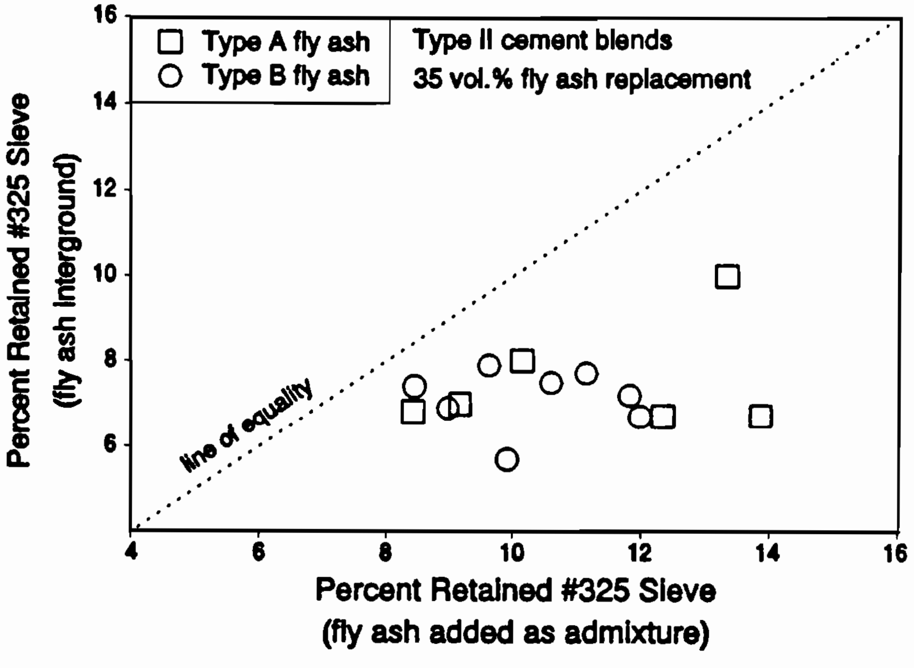


Figure 8.7 Fineness of Type II Cements Containing 35 Percent Fly Ash by Volume

These changes in the physical properties of fly ash cement, which are caused by intergrinding, are attributed to the crushing of hollow and porous particles and to the dispersion of agglomerates of particles. Increases in specific gravity and decreases in the proportion of coarse particles in fly ash cements contribute to improvements in the mechanical properties of blended cement concrete.

Fluctuations in fly ash specific gravity and fineness, which even exist for fly ash from a single source, affect the quality of blended cements. Reducing the ranges of these physical properties, as a result of intergrinding, contributes to increased consistency in the quality of fly ash cements.

8.3 TYPE II CEMENT PARTIALLY REPLACED BY FLY ASH

8.3.1 INTRODUCTION

Type II cement was partially replaced by six Type A fly ashes and eight Type B fly ashes at levels including 25 and 35 percent by volume. These mixtures were designed with 5½ sacks of cement per cubic yard of concrete prior to fly ash replacement. Mixing water was added until a fresh concrete slump of 5 to 7 inches was attained.

Mixtures are compared for mixing water requirements, compressive strengths, and susceptibilities to sulfate attack.

8.3.2 MIXING WATER REQUIREMENT

Water was added to concrete mixtures until the desired slump was attained. Therefore, water/(cement+pozzolan) ratios were variable. The average water/cement ratio, by weight, of the six control Type II cement mixtures was 0.55.

Intergrinding fly ash generally decreased the water requirement or had no significant effect, as shown in Figures 8.8 and 8.9. Decreases in water/(cement+pozzolan) ratio, by weight, were as large as approximately 18 percent. All blended Type A fly ash mixtures required less water than the control Type II cement mixture. At 25 volume percent replacement, the only Type A fly ash which did not exhibit decreased water requirement as a result of intergrinding was ash A-6. Ash A-6 was the Type A fly ash with the lowest proportion of particles larger than 45 μm and therefore had the least to gain by intergrinding.

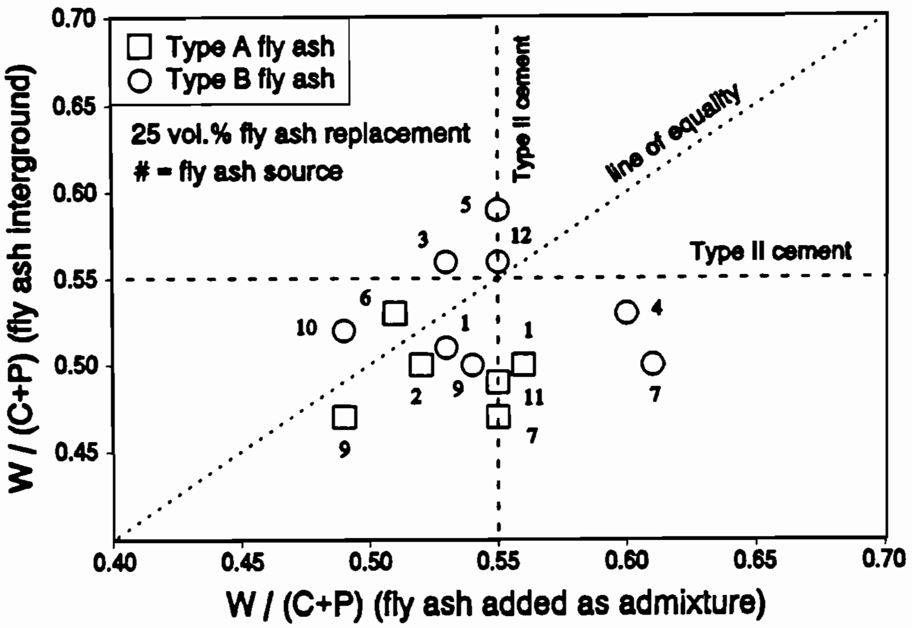


Figure 8.8 Mixing Water Requirements for Type II Cement Concrete Containing 25 Percent Fly Ash by Volume

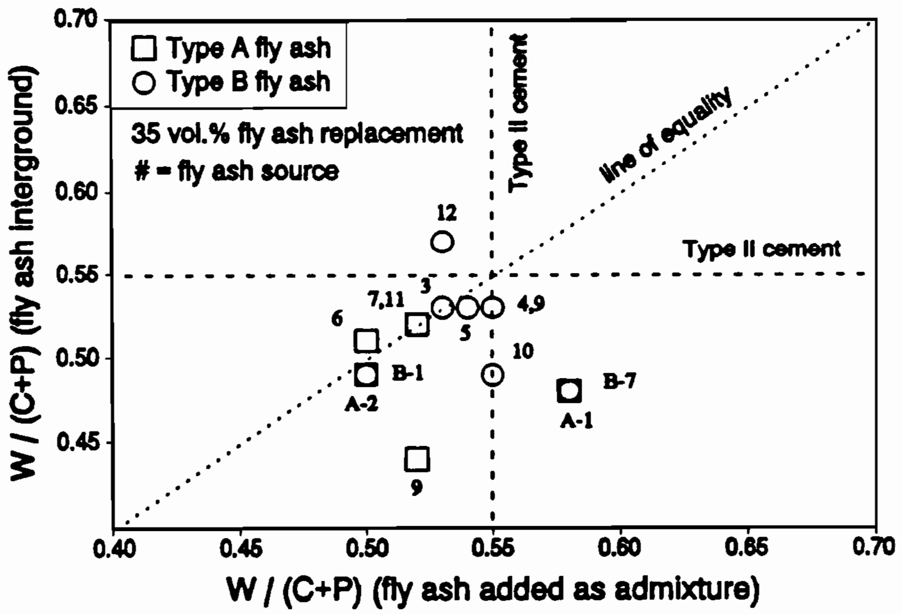


Figure 8.9 Mixing Water Requirements for Type II Cement Concrete Containing 35 Percent Fly Ash by Volume

The effects of intergrinding Type B fly ash mixtures were more variable. The water requirements of several Type B fly ash mixtures were not decreased by intergrinding and some of the interground Type B fly ash cement mixtures required more mixing water than the control Type II cement mixture. The variability in the effects of intergrinding Type B fly ash was not a function of the proportion of particles retained on the #325 sieve. Studies of fly ash particle size distributions and extents of agglomeration may be required to obtain a better understanding of these variable effects.

8.3.3 COMPRESSIVE STRENGTH

Intergrinding fly ash generally increased the 28-day compressive strength of fly ash/ Type II cement concrete, as shown in Figures 8.10 and 8.11. Increases in strength were largest for mixtures containing 35 volume percent fly ash and were as high as approximately 45 percent.

Relative to the control Type II cement concrete, all blended fly ash cement mixtures had equal or higher 28-day compressive strengths. When fly ash was added as a mineral admixture, the only mixtures with strengths significantly higher than the control Type II cement mixture contained Type B fly ash.

8.3.4 SULFATE SUSCEPTIBILITY

8.3.4.1 Linear Expansion and Mass Loss

Intergrinding Type A fly ash generally decreased expansion due to sulfate attack, as shown in Figures 8.12 and 8.13. Expansions of all the blended Type A fly ash cement mixtures were either non-existent or very small. Expansion in all cases was less than the control Type II cement mixture without fly ash. None of the Type A fly ash/Type II cement mixtures lost mass, whether the fly ash was interground or added as an admixture.

Intergrinding was generally less effective in improving the performance of mixtures containing Type B fly ash. In many cases expansion was not reduced by intergrinding and in no cases was mass loss eliminated by intergrinding, shown in Figures 8.14 and 8.15.

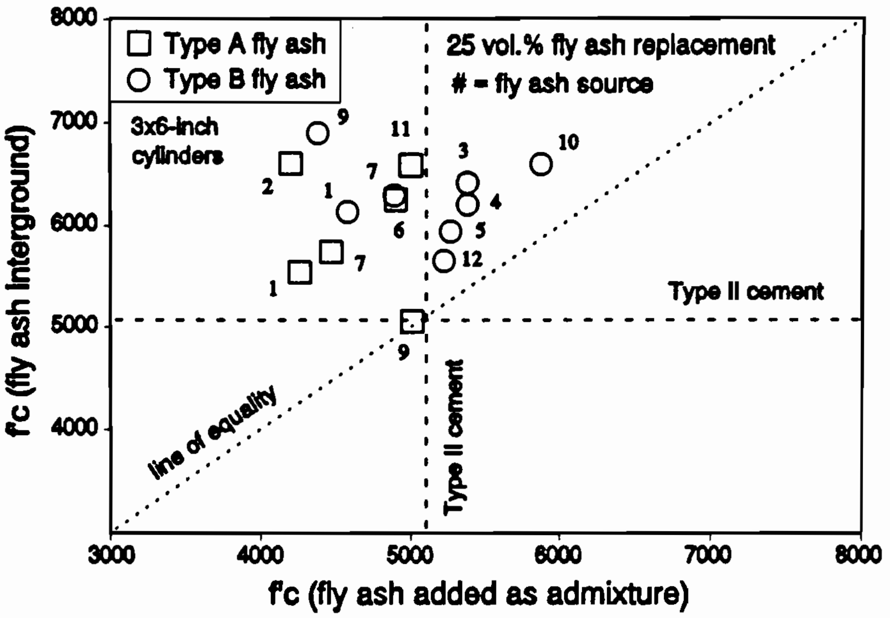


Figure 8.10 Compressive Strengths at 28 Days for Type II Cement Concrete Containing 25 Percent Fly Ash by Volume

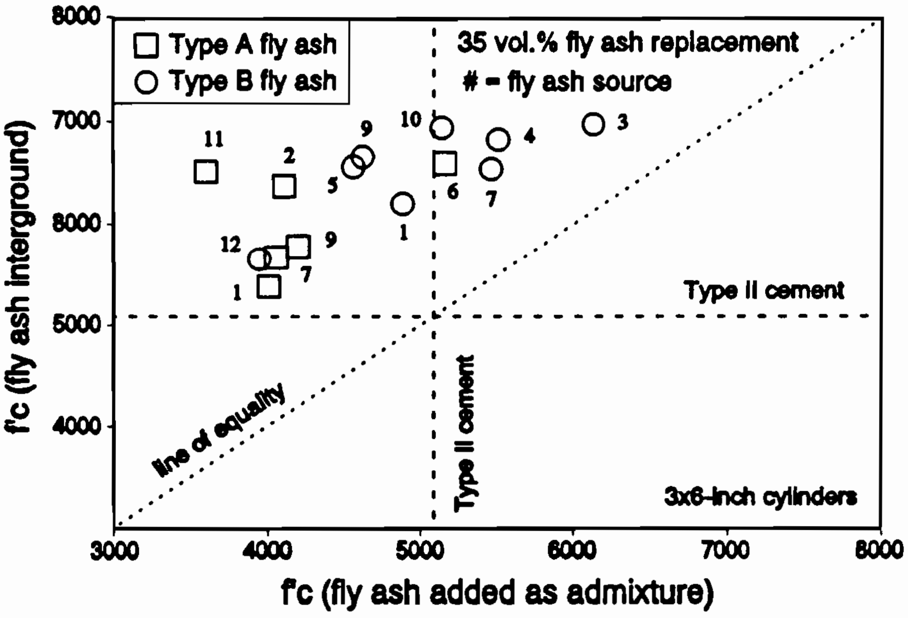


Figure 8.11 Compressive Strengths at 28 Days for Type II Cement Concrete Containing 35 Percent Fly Ash by Volume

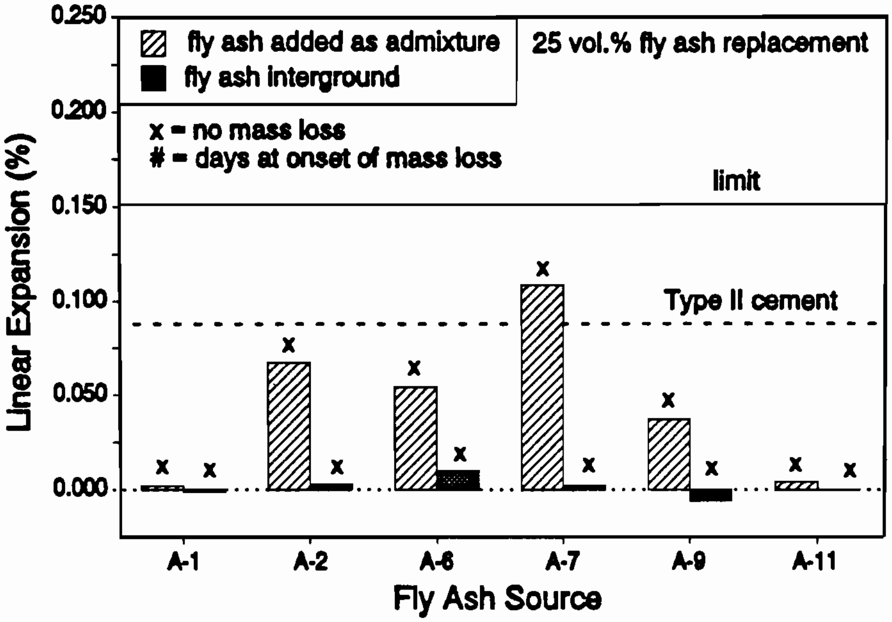


Figure 8.12 Linear Expansions and Mass Loss for Type II Cement Concrete Containing 25 Volume Percent Type A Fly Ash

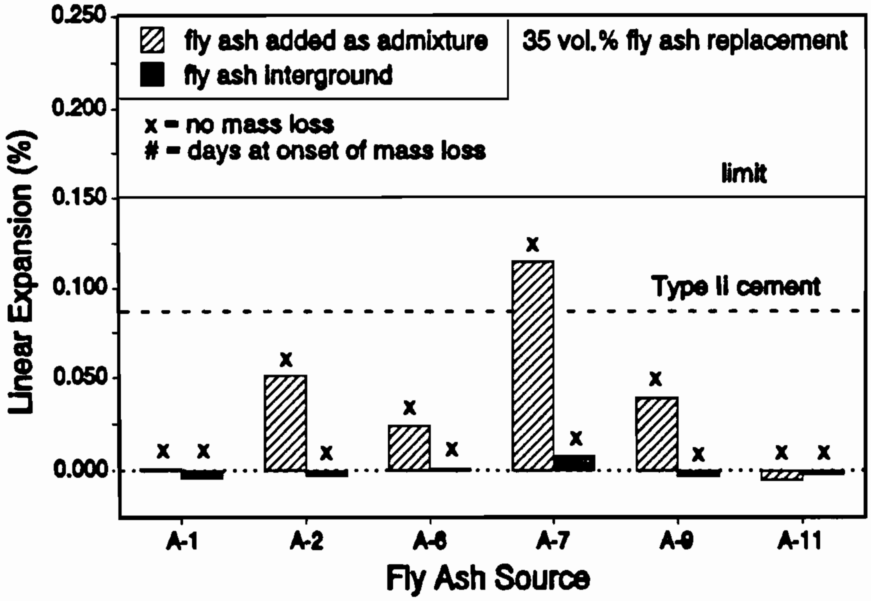


Figure 8.13 Linear Expansions and Mass Loss for Type II Cement Concrete Containing 35 Volume Percent Type A Fly Ash

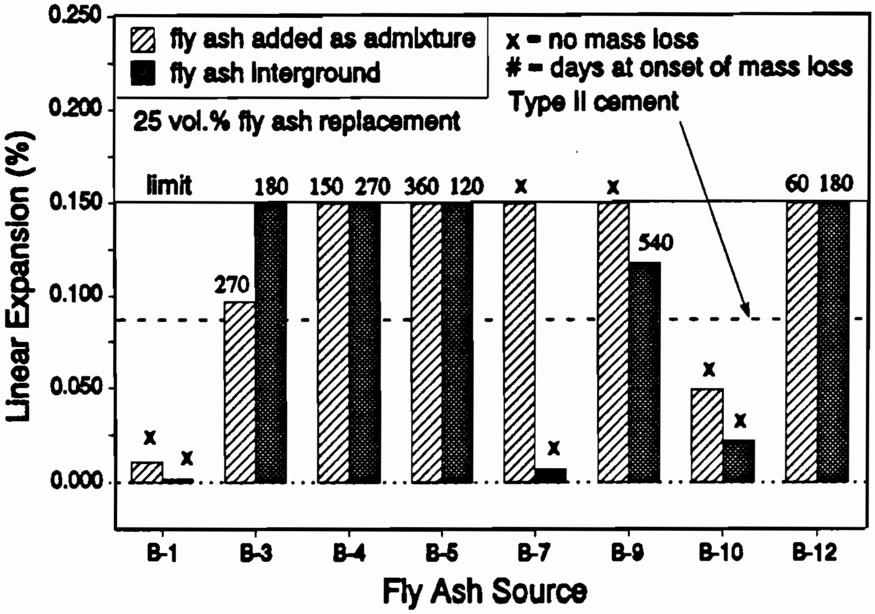


Figure 8.14 Linear Expansions and Mass Loss for Type II Cement Concrete Containing 25 Volume Percent Type B Fly Ash

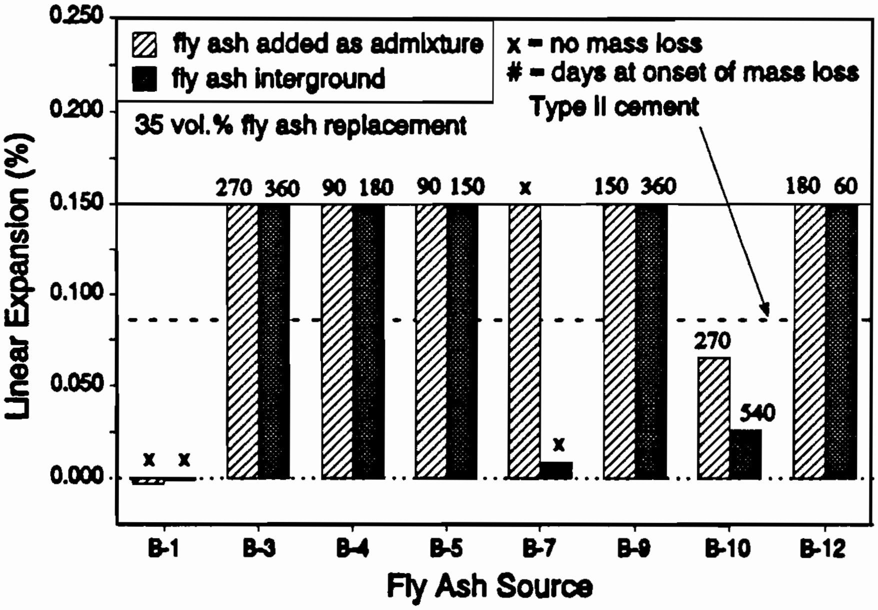


Figure 8.15 Linear Expansions and Mass Loss for Type II Cement Concrete Containing 35 Volume Percent Type B Fly Ash

However, expansions were reduced for mixtures containing three Type B fly ashes. These mixtures included 25 volume percent of ashes B-1, B-7, and B-10 and 35 volume percent of ashes B-1 and B-7. Exposure specimens for these mixtures did not lose mass whether the fly ash was added as an admixture or interground. Fly ash B-1 contained the lowest calcium oxide content of all Type B ashes (20.9 percent). Fly ashes B-7 and B-10 contained calcium oxide contents of 25.6 percent and 24.0 percent, respectively. All three fly ashes were characterized with Modified Calcium Aluminate Potentials of 1.16 or less and contained approximately 85 percent glass.

8.3.4.2 Sulfate Susceptibility Rating

The Sulfate Susceptibility Rating, as defined in Chapter 4, is a single-value parameter which represents the rate of deterioration of concrete. This parameter includes deterioration in the forms of expansion and mass loss. It permits comparisons between the sulfate susceptibilities of all mixtures.

Intergrinding fly ash either decreased sulfate susceptibility or had no significant effect for all fly ash/Type II cement mixtures, as shown in Figures 8.16 and 8.17. All mixtures containing 25 percent or 35 percent by volume interground Type A fly ash were more resistant to sulfates than Type II cement concrete without fly ash.

Mixtures containing fly ash A-7 were less resistant than the control Type II cement mixture when the fly ash was added as an admixture, but were more resistant than the Type II cement when the fly ash was interground. Relative to other Type A ashes, A-7 had a high calcium content (12.4 percent) and a high proportion of coarse particles (28.2 percent retained on 45 μm sieve). It was also characterized as having the highest Modified Calcium Aluminate Potential (0.80).

The only blended fly ash cement mixtures containing Type B fly ash which were more resistant to sulfates than the Type II cement without fly ash were those containing ashes B-1, B-7, and B-10. In addition to containing low calcium oxide contents relative to the other Type B fly ashes, ashes B-1, B-7, and B-10 had the lowest Modified Calcium Aluminate Potentials (0.75, 1.16, and 1.16, respectively). All other Type B fly ashes included in this portion of the study had Modified CAPs of greater than or equal to 1.30.

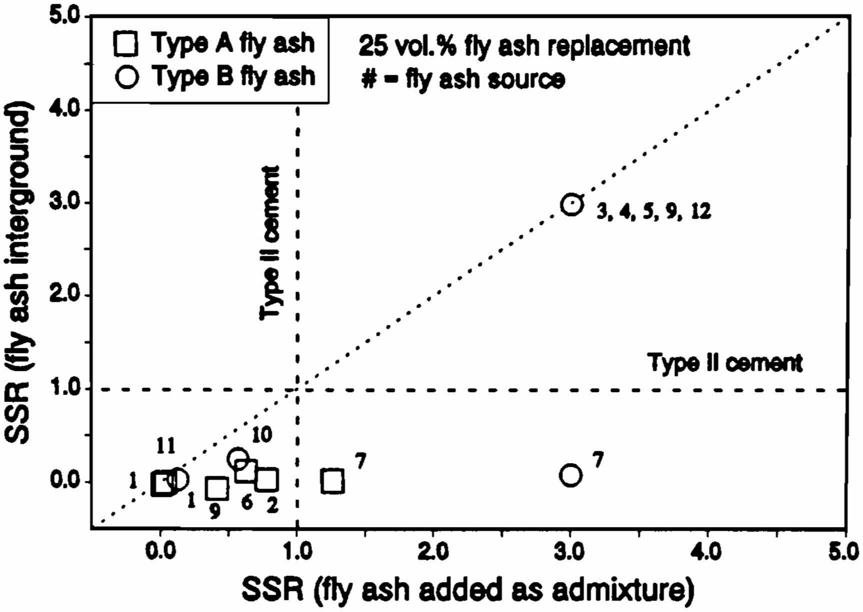


Figure 8.16 Sulfate Susceptibility Ratings of Type II Cement Concrete Containing 25 Percent Fly Ash by Volume

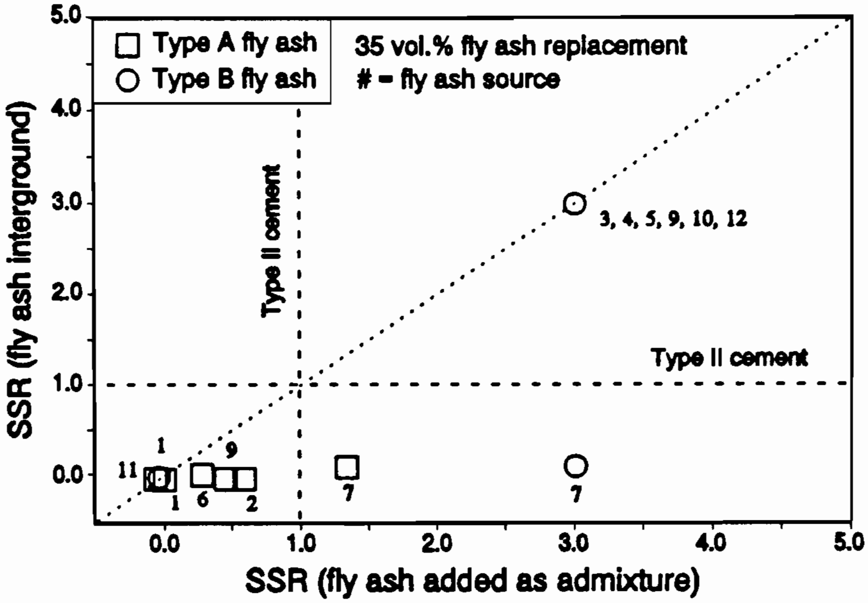


Figure 8.17 Sulfate Susceptibility Ratings of Type II Cement Concrete Containing 35 Percent Fly Ash by Volume

Mixtures containing fly ash B-7 were less resistant to the control Type II cement mixture when the fly ash was added as an admixture, but were more resistant than Type II cement when the fly ash was interground. Relative to other Type B ashes, B-7 had moderately high contents of calcium (25.6 percent), sulfates (2.78 percent), and coarse particles (17.2 percent retained on 45 μm sieve). Mixtures containing fly ash B-7 also experienced the largest decreases in water/(cement+pozzolan) ratio as a result of intergrinding the fly ash.

8.4 TYPE I CEMENT PARTIALLY REPLACED BY FLY ASH

8.4.1 INTRODUCTION

The Type I cement included in this portion of the study was designated as Type I-H for its relatively high tricalcium aluminate content (11.2 percent). Six Type A fly ashes and seven Type B fly ashes partially replaced the cement at levels of 25 and 35 percent by volume. These mixtures were designed with 5½ sacks of cement per cubic yard of concrete prior to fly ash replacement. Mixing water was added until a fresh concrete slump of 5 to 7 inches was attained.

Mixtures are compared for mixing water requirements, compressive strengths, and sulfate susceptibilities.

8.4.2 MIXING WATER REQUIREMENT

Water requirements of all Type A fly ash/ Type I-H cement mixtures were decreased by intergrinding the fly ash, as shown in Figures 8.18 and 8.19. Mixtures containing fly ashes A-2, A-7, and A-11 experienced the largest decreases in water/(cement+pozzolan) ratios, by weight, as a result of intergrinding fly ash. These decreases were as large as 20 percent. These fly ashes all contained at least 23 percent particles larger than 45 μm. Fly ashes with large proportions of coarse particles may benefit more by the effects of intergrinding.

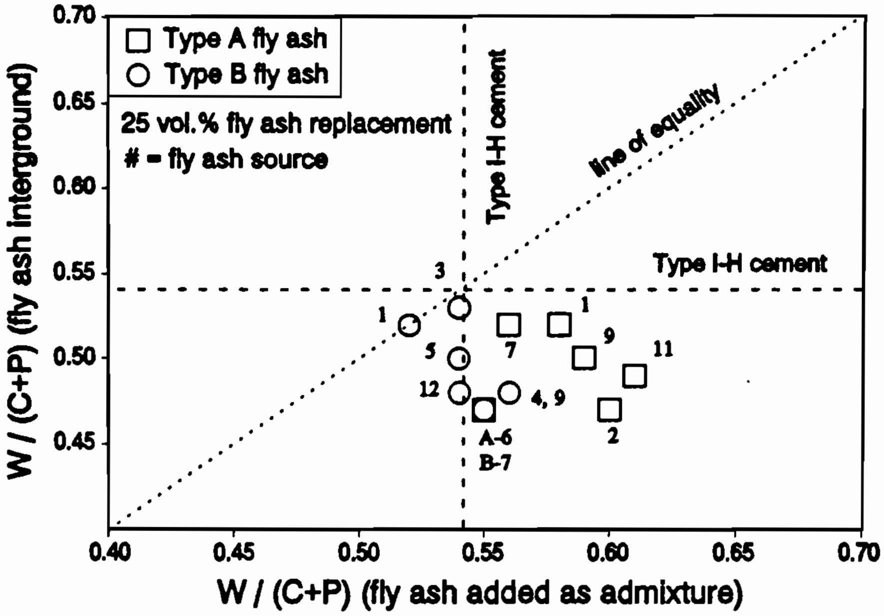


Figure 8.18 Mixing Water Requirements for Type I-H Cement Concrete Containing 25 Percent Fly Ash by Volume

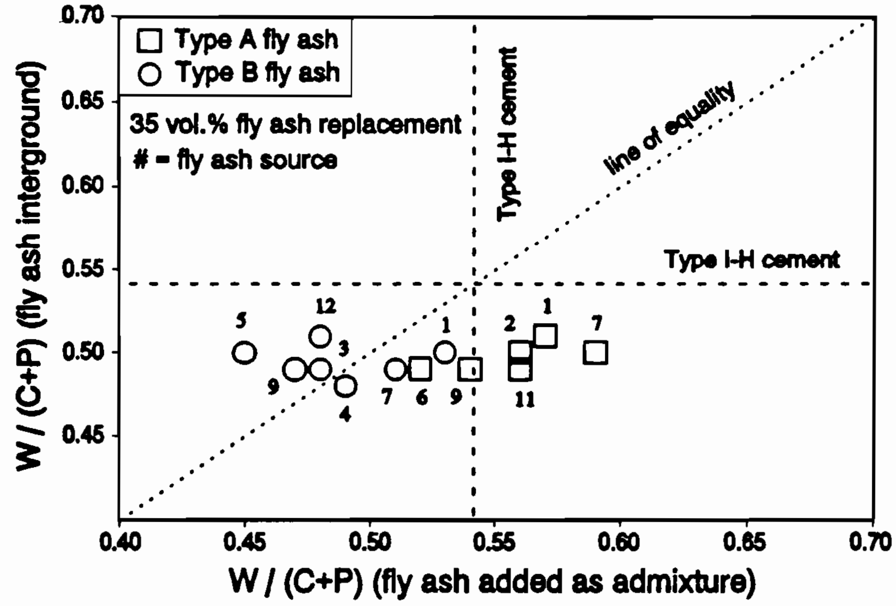


Figure 8.19 Mixing Water Requirements for Type I-H Cement Concrete Containing 35 Percent Fly Ash by Volume

Intergrinding Type B fly ash generally decreased water requirements when the fly ash replaced 25 percent cement by volume, as shown in Figure 8.18. However, intergrinding Type B fly ash had variable effects on water requirement when fly ash replaced 35 percent cement by volume. Specific gravities of Type B fly ashes were generally larger than the specific gravities of Type A fly ashes. In addition to containing heavier minerals, the Type B fly ashes may have contained fewer hollow and porous particles. Therefore, they would have had less to gain from the process of intergrinding.

All mixtures in which fly ash was interground had lower water/(cement+pozzolan) ratios, by weight, than the control Type I-H cement mixture. When fly ash was added as an admixture, all mixtures containing 25 volume percent Type A fly ash and most mixtures containing 35 volume percent Type A fly ash had higher water/(cement+pozzolan) ratios than the control Type I-H cement mixture.

8.4.3 COMPRESSIVE STRENGTH

Intergrinding fly ash increased the 28-day compressive strengths of all fly ash/ Type I-H cement mixtures, as shown in Figures 8.20 and 8.21. Strengths were increased by as much as 30 percent. All concrete containing blended fly ash cements had higher 28-day strengths than the Type I-H cement concrete without fly ash.

Even when Type B fly ash was added as a mineral admixture to Type I-H cement concrete, compressive strength generally increased. When Type A fly ash was added as a mineral admixture, the compressive strength of Type I-H cement concrete was in many cases reduced.

8.4.4 SULFATE SUSCEPTIBILITY

8.4.4.1 Linear Expansion and Mass Loss

The linear expansion of all Type A fly ash/Type I-H cement mixtures was either extremely small or non-existent, as shown in Figures 8.22 and 8.23. These expansions were all less than that experienced by the control Type II cement mixture. However, most of these Type A fly ash/Type I-H cement mixtures lost mass.

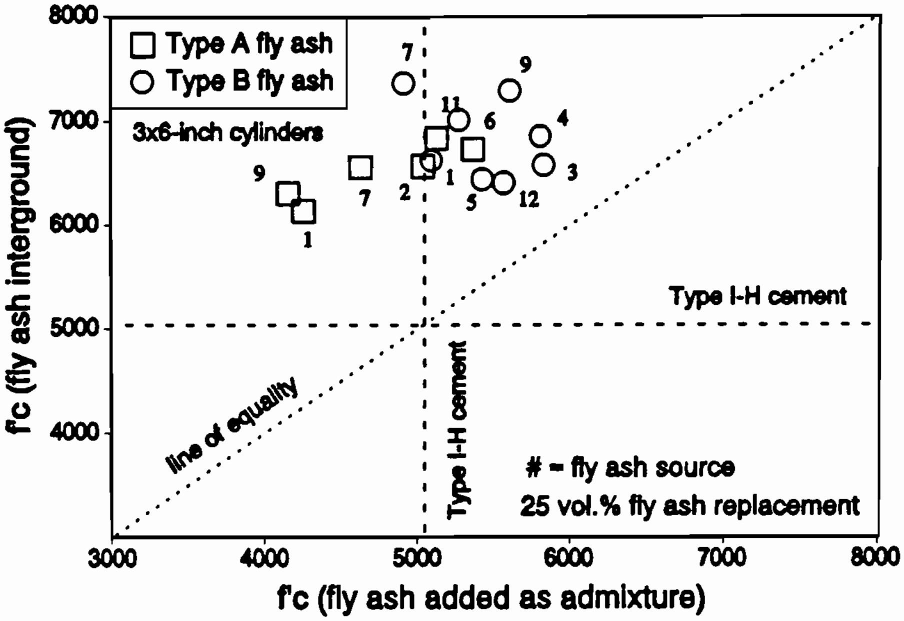


Figure 8.20 Compressive Strength at 28 Days for Type I-H Cement Concrete Containing 25 Percent Fly Ash by Volume

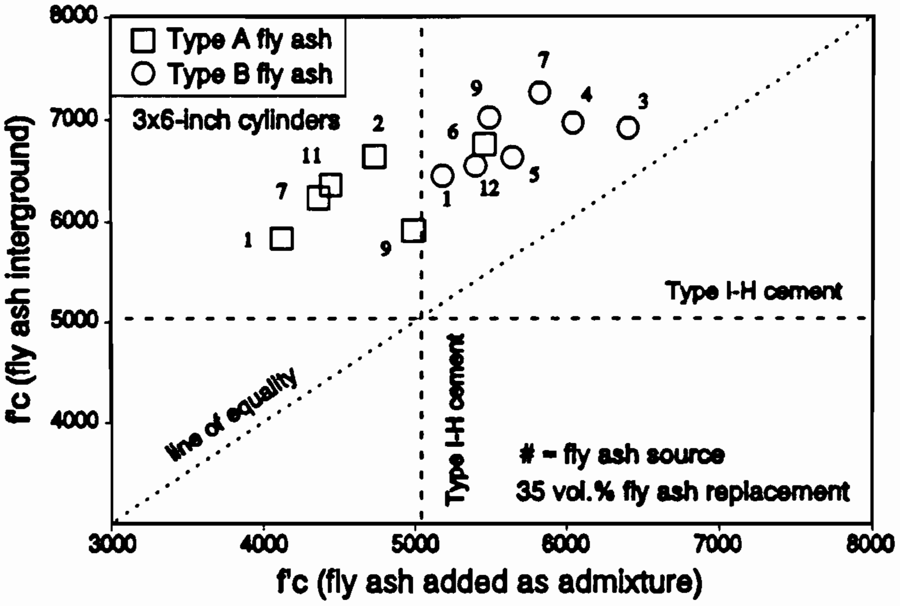


Figure 8.21 Compressive Strength at 28 Days for Type I-H Cement Concrete Containing 35 Percent Fly Ash by Volume

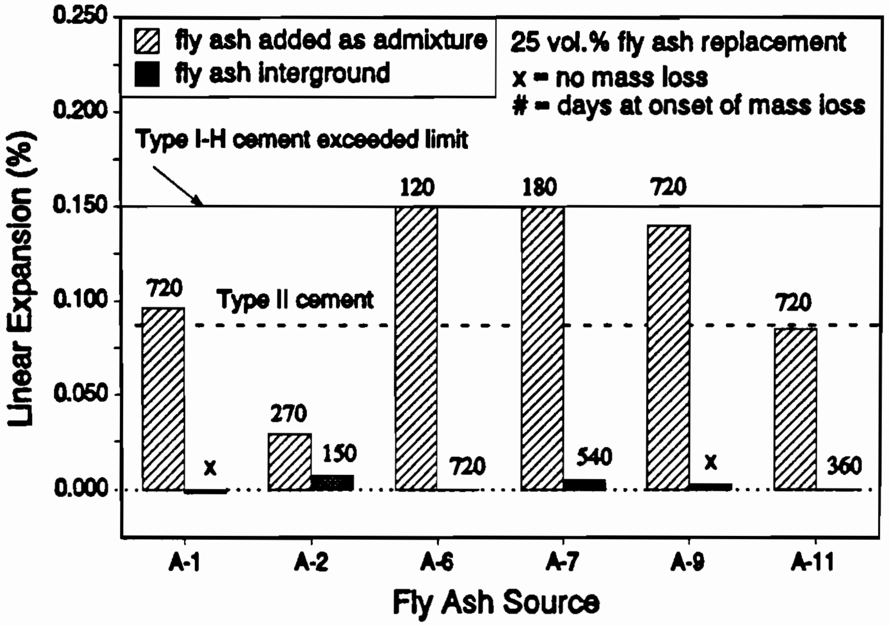


Figure 8.22 Linear Expansions and Mass Loss for Type I-H Cement Concrete Containing 25 Volume Percent Type A Fly Ash

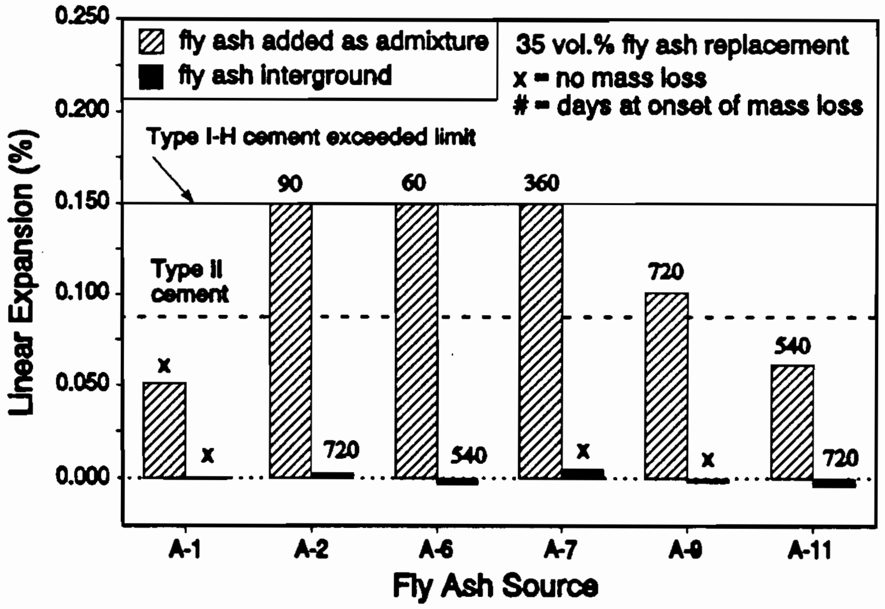


Figure 8.23 Linear Expansions and Mass Loss for Type I-H Cement Concrete Containing 35 Volume Percent Type A Fly Ash

Intergrinding Type B fly ash with Type I-H cement was in most cases not effective in decreasing sulfate-induced expansions or eliminating mass loss, as shown in Figures 8.24 and 8.25. The only mixture containing Type B fly ash which did not lose mass was the mixture containing 35 volume percent fly ash B-1 (interground). Of all Type B fly ashes, B-1 contained the lowest calcium oxide content (20.9 percent) and was characterized as having the lowest Modified Calcium Aluminate Potential (0.75).

8.4.4.2 Sulfate Susceptibility Rating

The Sulfate Susceptibility Rating, as defined in Chapter 4, is a single-value parameter which represents the rate of deterioration of concrete. This parameter includes deterioration in the forms of expansion and mass loss. It permits comparisons between the sulfate susceptibilities of all mixtures.

Several blended cements containing Type A fly ash and Type I-H cement were more resistant to sulfates than Type II cement without fly ash, as shown in Figures 8.26 and 8.27. Only one mixture containing Type A fly ash as a mineral admixture was more resistant to sulfates than the Type II cement mixture.

The effects of fly ash were related to calcium oxide content and Modified Calcium Aluminate Potential. Fly ash A-1 was the most effective fly ash in improving sulfate resistance when added as a mineral admixture; it contained the lowest calcium oxide content (4.80 percent) and the lowest Modified Calcium Aluminate Potential (0.35) of all ashes included in this portion of the study. Fly ash A-9 was effective in improving sulfate resistance when it was interground at percentages of both 25 and 35 volume percent. Fly ash A-9 contained the second lowest calcium oxide content (6.97 percent) and the second lowest Modified Calcium Aluminate Potential (0.46) of all ashes included in this portion of the study.

With the exception of one mixture containing fly ash B-1, intergrinding did not significantly improve the performance of Type B fly ash/Type I-H cement mixtures. Deterioration of most of these mixtures was very rapid, which made comparisons difficult.

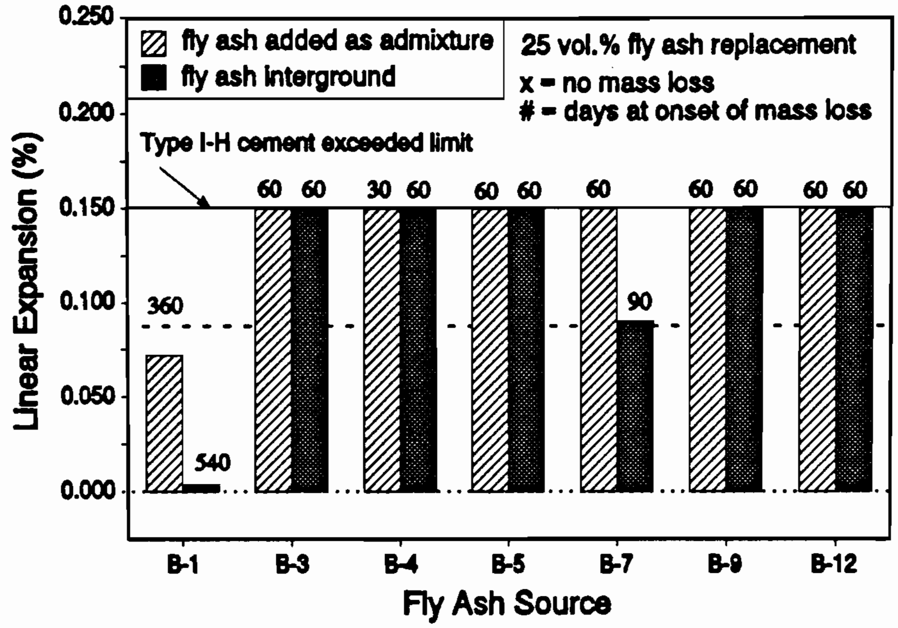


Figure 8.24 Linear Expansions and Mass Loss for Type I-H Cement Concrete Containing 25 Volume Percent Type B Fly Ash

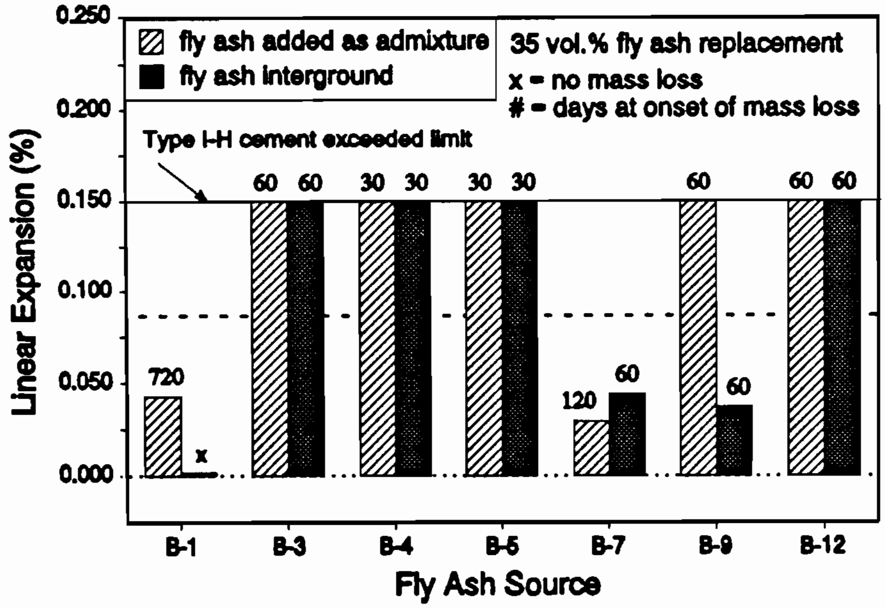


Figure 8.25 Linear Expansions and Mass Loss for Type I-H Cement Concrete Containing 35 Volume Percent Type B Fly Ash

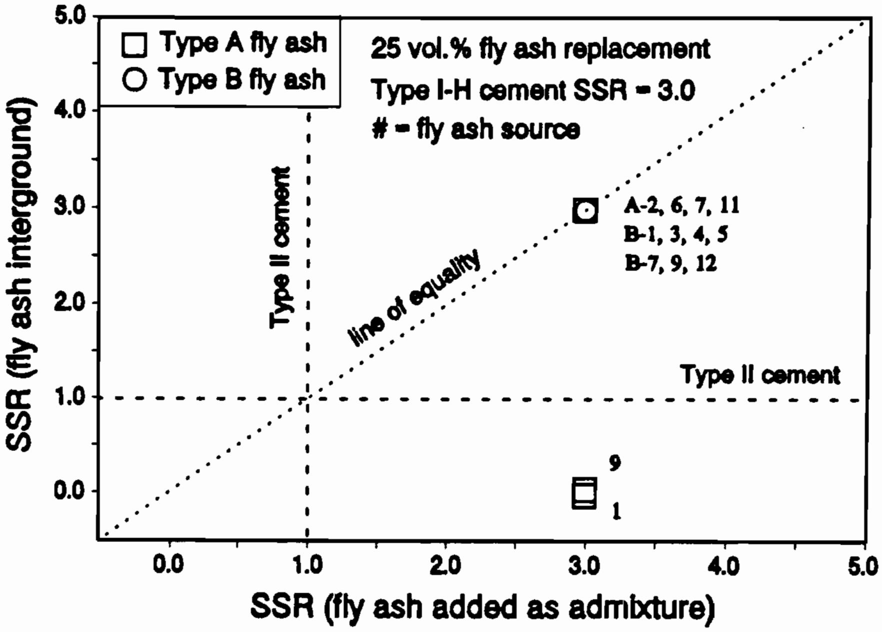


Figure 8.26 Sulfate Susceptibility Ratios of Type I-H Cement Concrete Containing 25 Percent Fly Ash by Volume

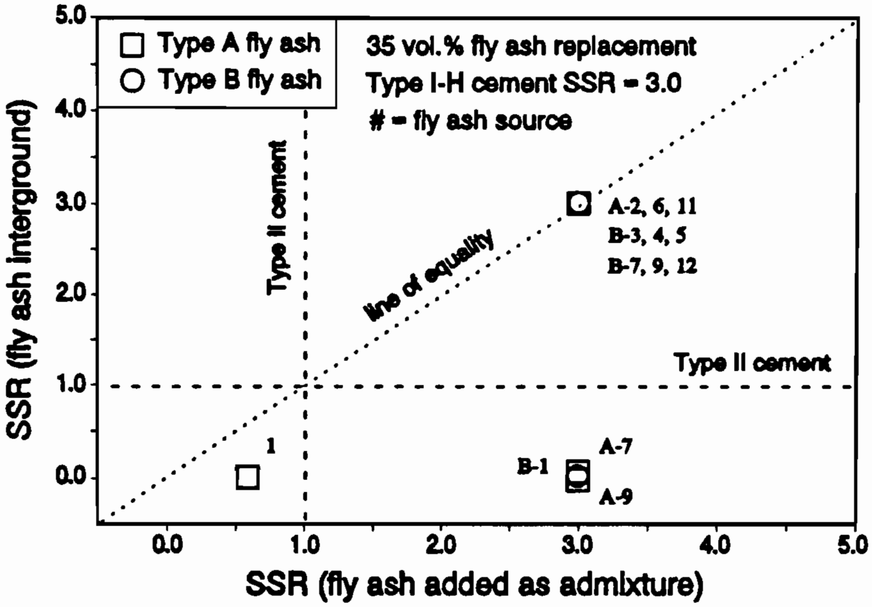


Figure 8.27 Sulfate Susceptibility Ratios of Type I-H Cement Concrete Containing 35 Percent Fly Ash by Volume

In order to fascilitate comparisons, the rates of deterioration of these mixtures needed to be reduced. This was accomplished by immersing companion concrete cylinders in milder sulfate exposure solutions.

8.4.5 LOW SULFATE CONCENTRATION EXPOSURE SOLUTION

8.4.5.1 Introduction

Some of the fly ash/Type I-H cement mixtures deteriorated very rapidly in the 10 percent sodium sulfate solution, so comparisons between these rates of deterioration were difficult. In order to obtain comparisons which were easier to interpret, several of these mixtures were exposed to milder sodium sulfate solutions. The milder exposure solutions contained 5 percent and 2.1 percent sodium sulfate by weight.

Sulfate exposure test standard ASTM C-1012 includes 5 percent sodium sulfate as a recommended exposure solution concentration. Sulfate exposure test standard USBR 4908 includes 2.1 percent sodium sulfate as a recommeded exposure solution concentration. Groundwater which contains 2.1 percent sodium sulfate consists of approximately 14,200 ppm SO_4. This concentration of SO_4 is classified by USBR as very severe in terms of potential for sulfate attack on concrete (435). Therefore, a 2.1 percent sodium sulfate exposure solution could be considered as a realistically severe exposure environment. Five percent and 10 percent sodium sulfate solutions should be considered as unrealistic concentrated exposure solutions which accelerate sulfate attack on concrete.

The primary objective of this portion of the study was to continue the investigaton on the effects of fly ash on the sulfate susceptibility of Type I-H cement concrete. In particular, some high-calcium fly ashes were included to determine whether they could increase the susceptibility Type I-H cement concrete to sulfate attack. A second objective was to determine whether the trends and conclusions drawn from the various exposure solution severities were in aggreement. This check for concurrence permitted an evaluation of whether the concentrated exposure solutions yielded conservative results. A third objective was to study the effects of sulfate exposure severity on the rate of concrete deterioration.

In order to study the tendency for Type B fly ashes to decrease the sulfate resistance of Type I-H cement concrete, three Type B fly ashes replaced cement at a level of

35 percent by volume. In order to study the tendency for Type B fly ashes to improve the sulfate resistance of Type I-H cement concrete, two Type A fly ashes replaced cement at a level of 25 percent by volume. Mixture designs included 5½ sacks cement prior to fly ash replacement and a fresh concrete slump of 5 to 7 inches.

Mixtures included in this portion of the study were immersed in each of the three sulfate solutions for 720 days. Comparisons of the susceptibility of mixtures to sulfate attack were based on linear expansion, mass loss, and Relative Damping Capacities.

8.4.5.2 Sulfate Susceptibility

The Type I-H cement concrete without fly ash exceeded the expansion limit of 0.15 percent in both 10 percent and 5 percent sodium sulfate solutions, as shown in Figure 8.28. However, the Type I-H cement concrete in 2.1 percent sodium sulfate solution expanded only slightly. None of these mixtures suffered deterioration in the form of mass loss.

Most Type I-H cement mixtures containing Type A fly ash expanded at least slightly or lost mass in the 10 percent sodium sulfate solution, as shown in Figure 8.28. Most of these mixtures suffered no expansions or mass loss in the lower sulfate concentration immersion tests.

Type I-H cement mixtures containing Type B fly ash generally suffered large expansions and early mass loss in the 10 percent sodium sulfate solution, as shown in Figure 8.29. In the 5 percent exposure solution, expansions were generally reduced and mass loss was delayed. In the 2.1 percent solution, expansions were very small and no mass loss occured.

Based on expansion and mass loss data only, comparisons of mixtures in the 10 percent sodium sulfate solution were difficult because almost all the mixtures had suffered some form of significant deterioration. Comparisons of mixtures in the 2.1 percent sodium sulfate solution were not useful because expansions for all mixtures were very small and no mixtures suffered loss of mass. Therefore, mixtures in the 5 percent sodium sulfate solution provided the most useful data for comparing susceptibilities to sulfate attack.

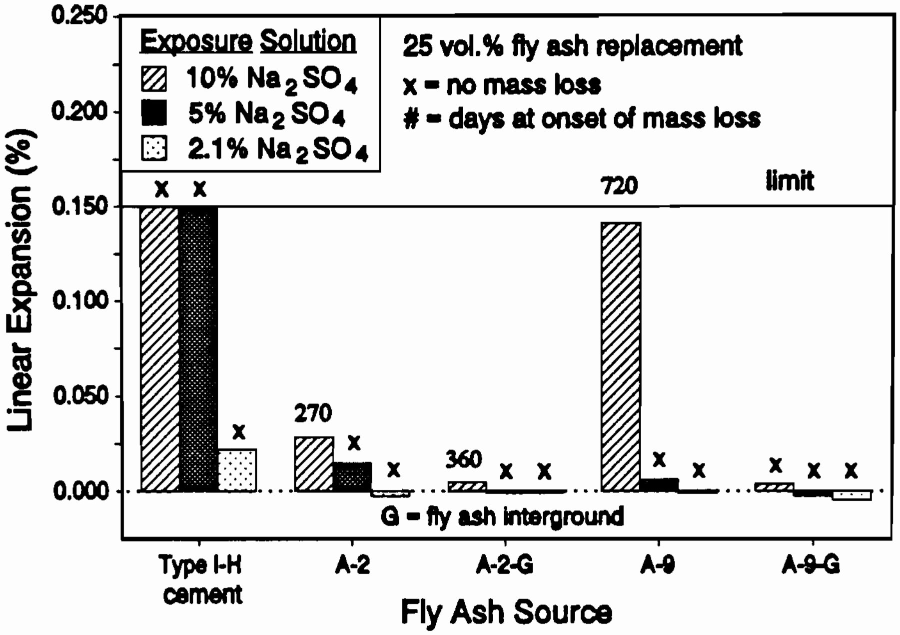


Figure 8.28 Linear Expansions and Mass Loss for the Control Type I-H Cement Mixture and Type A Fly Ash/Type I-H Cement Mixtures in Various Exposure Severities

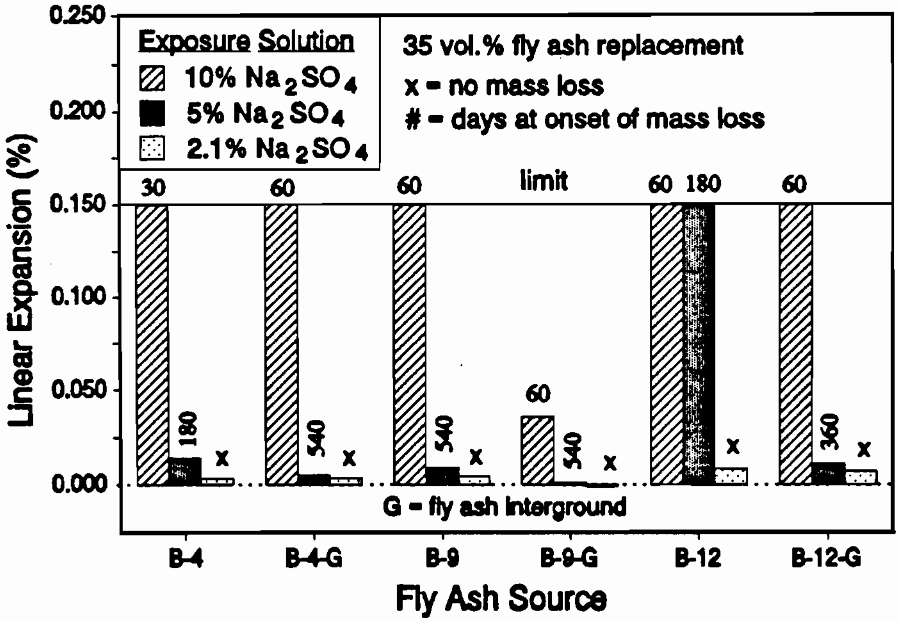


Figure 8.29 Linear Expansions and Mass Loss for Type B Fly Ash/Type I-H Cement Mixtures in Various Exposure Severities

Considering results from immersion in the 5 percent sodium sulfate solution, all mixtures containing Type A fly ash were less susceptible to sulfate attack than Type I-H cement concrete without fly ash. All mixtures containing Type B fly ash were as susceptible to sulfate attack as Type I-H cement concrete without fly ash.

Relative Damping Capacity measurements were obtained for mixtures in the 5 percent and the 2.1 percent sodium sulfate solutions. These measurements were used to confirm and further refine the conclusions drawn on the basis of linear expansion and mass loss data.

The Relative Damping Capacity (RDC) of Type I-H cement concrete exceeded 100 percent at 540 days and 720 days in the 5 percent and 2.1 percent solutions, respectively. None of the mixtures containing Type A fly ash experienced a net increase in RDC, as shown in Table 8.2. Each of the mixtures containing Type B fly ash experienced a net increase in RDC. These observations confirm the conclusions that were drawn from linear expansion and mass loss data:

1) Type A fly ash improved the sulfate resistance of Type I-H cement concrete in all cases and
2) Type B fly ash did not improve the sulfate resistance of Type I-H cement concrete in all cases.

Relative Damping Capacity measurements permitted an additional conclusion to be drawn concerning the effects of Type B fly ash. In some cases, inclusion of Type B fly ash in Type I-H cement concrete decreased the duration of immersion at which RDC exceeded 100 percent. Therefore, in some cases, the inclusion of Type B fly increased the susceptibility of Type I-H cement concrete to sulfate attack. Fly ashes B-4 and B-12, both of which contained more than 27 percent calcium oxide, were most detrimental.

8.4.5.3 Comparison Among Exposure Solutions

Comparisons between the sulfate susceptibilities of fly ash/Type I-H cement concrete mixtures and the sulfate susceptibility of Type I-H cement concrete without fly ash are summarized in Table 8.3. Cases in which conclusions drawn from different exposure solutions aggree are emphasized by shaded boxes.

Table 8.2 Relative Damping Capacities for the Control Type I-H Cement Mixture and Fly Ash/Type I-H Cement Mixtures in Various Exposure Severities

Fly Ash *	Relative Damping Capacity (days at which RDC ≥ 100%)		
	Exposure Solution (% Na_2SO_4)		
	10%	5%	2.1%
Type I-H Cement (no fly ash)	90	540	720
A-2	N	T	T
A-2-G	N	T	T
A-9	N	T	T
A-9-G	N	T	T
B-4	N	180	540
B-4-G	N	270	720
B-9	N	360	720
B-9-G	N	540	720
B-12	N	270	360
B-12-G	N	270	720

* G = fly ash was interground with cement clinker and gypsum

N = data not available
T = intact (RDC < 100% at 720 days of exposure)

Unfortunately, the available data did not permit a comparison between all three solutions. However, there were cases of aggreement between the 10 percent and 5 percent solutions and there were cases of aggreement between the 5 percent and 2.1 percent solutions.

In each of the cases where conclusions drawn from different exposure solutions did not aggree, the more concentrated solution predicted a worse performance for fly ash cement mixtures, relative to Type I-H cement concrete without fly ash. Therefore, the

10 percent solution provided a conservative evaluation of the effects of fly ash on sulfate resistance of Type I-H cement concrete.

Table 8.3 Comparisons Between Sulfate-Related Deterioration of Fly Ash/Type I-H Cement Concrete and Type I-H Cement Concrete Without Fly Ash

Fly Ash *	Linear Expansion and Mass Loss			Relative Damping Capacity		
	Exposure Sol'n (% Na_2SO_4)			Exposure Sol'n (% Na_2SO_4)		
	10%	5%	2.1%	10%	5%	2.1%
A-2	=	<	D	N	<	<
A-2-G	=	<	D	N	<	<
A-9	=	<	D	N	<	<
A-9-G	<	<	D	N	<	<
B-4	=	=	D	N	>	>
B-4-G	=	=	D	N	>	=
B-9	=	=	D	N	>	=
B-9-G	=	=	D	N	=	=
B-12	=	=	D	N	>	>
B-12-G	=	=	D	N	>	=

Note: Boxes are shaded for cases in which similar conclusions were deduced in different exposure solutions.

* G = fly ash was interground with cement clinker and gypsum

D = 720-day test duration was not sufficient to draw conclusions
N = data not available
< : less susceptible than Type I-H cement concrete without fly ash
= : susceptibility not significantly different
> : more susceptible than Type I-H cement concrete without fly ash

8.4.5.4 Rate of Deterioration

Type I-H cement concrete without fly ash was monitored for linear expansion and Relative Damping Capacity (RDC) in all three exposure solutions. Therefore, it provided complete data for studying the effects of sulfate exposure severity on rate of deterioration.

Rate of deterioration decreased as the concentration of sulfates in the exposure solution decreased, as shown in Figures 8.30 and 8.31. Relative to the 10 percent solution, time to reach the expansion limit of 0.15 percent was approximately 3.5 times longer in the 5 percent solution. A longer test duration would be required for comparisons involving the rate of linear expansion in the 2.1 percent sodium sulfate solution.

Relative to the 10 percent solution, time to exhibit a net increase in Relative Damping Capacity was approximately five times longer in the 5 percent solution and approximately eight times longer in the 2.1 percent solution.

Therefore, the rate of deterioration of Type I-H cement concrete in 5 percent solution was approximately twice the rate of deterioration in 2.1 percent solution. The rate of deterioration in 10 percent solution was approximately 8 times the rate of deterioration in 2.1 percent solution.

8.5 SUMMARY

The primary objective of this portion of the study was to investigate the effects of intergrinding fly ash on the physical properties of fly ash cement and on the mechanical properties of fly ash concrete, particularly sulfate resistance. Mixtures in which fly ash was interground with cement clinker and gypsum were compared with mixtures in which fly ash was added as a mineral admixture. Results were presented for mixtures in which Type II and Type I cements were partially replaced by Type A and Type B fly ashes. The Type I cement used in this portion of the study was designated Type I-H for its relatively high C_3A content (11.2 percent). The Type II cement contained 6.0 percent tricalcium aluminate.

Cement replacement included six Type A fly ashes and eight Type B fly ashes at levels of 25 and 35 percent by volume. Concrete mixtures were designed with 5½ sacks of cement per cubic yard of concrete prior to fly ash replacement. Mixing water was added until a fresh concrete slump of 5 to 7 inches was attained.

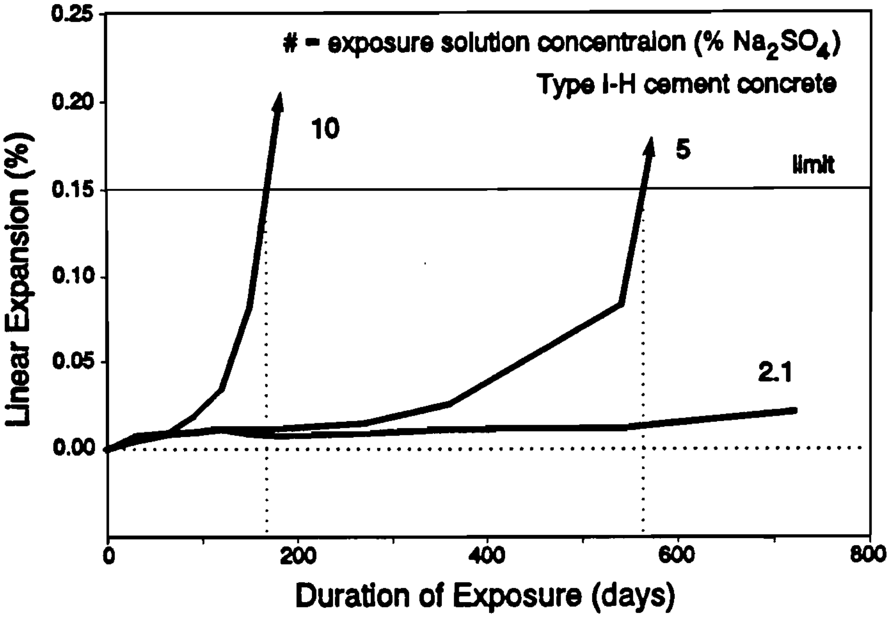


Figure 8.30 Linear Expansions for Type I-H Cement Concrete Without Fly Ash in Various Exposure Severities

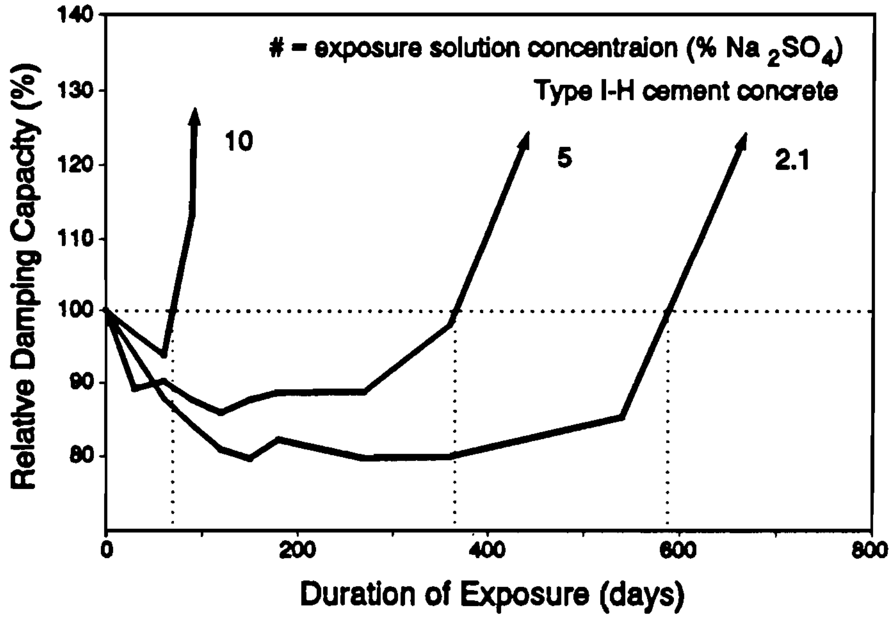


Figure 8.31 Relative Damping Capacities for Type I-H Cement Concrete Without Fly Ash in Various Exposure Severities

Relative to adding fly ash as a mineral admixture at the time of batching concrete, intergrinding fly ash with cement clinker and gypsum increased the specific gravity and fineness of fly ash cements. These effects were most significant at the higher fly ash content (35 percent by volume). These effects were also most significant for fly ash which initially contained relatively large proportions of coarse particles.

The changes in the physical properties of fly ash cement, along with increased cement homogeneity, resulted in improvements for the physical and mechanical properties of fly ash cement concrete. Intergrinding fly ash generally reduced the mixing water requirements and increased the 28-day compressive strengths. In several cases, compressive strength was increased while mixing water requirement remained unchanged. Therefore, the effects of intergrinding fly ash on the strength of fly ash concrete could not simply be attributed to the effects on water/(cement+pozzolan) ratio.

The sulfate resistance of Type A fly ash/Type II cement concrete was improved by intergrinding the fly ash with cement clinker and gypsum. All interground Type A fly ash/Type II cement mixtures were more resistant to sulfate attack than Type II cement concrete without fly ash. Improvements in sulfate resistance, as a result of intergrinding, were most noticeable for mixtures containing a Type A fly ash with a relatively high calcium content (12.4 percent).

The sulfate resistance of Type B fly ash/Type II cement concrete was generally not improved by intergrinding the fly ash with cement clinker and gypsum. Blended cements containing only three of the Type B fly ashes were as resistant to sulfate attack than Type II cement concrete without fly ash. Relative to the other Type B fly ashes, these sulfate resistant Type B fly ashes were characterized as having low Modified Calcium Aluminate Potentials (less than or equal to 1.16).

The sulfate resistance of Type A fly ash/Type I-H cement concrete was generally not improved by intergrinding the fly ash with cement clinker and gypsum. The only mixtures which were significantly improved by intergrinding contained fly ash with low calcium oxide contents (< 8 percent) and low Modified Calcium Aluminate Potentials (less than 0.5). A slight increase in strength and a slight decrease in permeability were sufficient improvements to cause these mixtures to be resistant to sulfate attack.

The sulfate resistance of Type B fly ash/Type I-H cement concrete was generally not improved by intergrinding the fly ash with cement clinker and gypsum. Only one blended cement containing 35 volume percent of a Type B fly ash was more resistant to sulfate attack than Type II cement concrete without fly ash. Relative to the other Type B fly ashes, this sulfate resistant Type B fly ash was characterized as having the lowest Modified Calcium Aluminate Potential (0.75).

Several fly ash/Type I-H cement mixtures were exposed to sodium sulfate solutions which were milder than the standard 10 percent test solution. These milder solutions, 5 percent and 2.1 percent sodium sulfate, fascilitated comparisons between mixtures which were very susceptible to sulfate attack. The milder exposure tests revealed that Type B fly ash, whether interground or added as a mineral admixture, may increase the susceptibility of Type I-H cement concrete to sulfate attack. These Type B ashes contained more than 25 percent calcium oxide and had Modified Calcium Aluminate Potentials greater than 1.25.

The mild exposure solutions also revealed that the sulfate resistance of Type I-H cement concrete may be at least slightly improved by including Type A fly ash.

Some conclusion drawn from different exposure solutions did not aggree. However, in all cases of disaggreement, the more concentrated exposure solution yielded the most conservative evaluation of the effects of fly ash on the sulfate resistance of Type I-H cement concrete.

The durations of exposure for Type I-H cement concrete to suffer a net increase in damping capacity were compared for the different solution concentrations. Relative to specimens in the 2.1 percent solution, specimens in the 5 percent solution experienced a net increase in damping capacity in approximately one-half the time. Also, relative to specimens in the 2.1 percent solution, specimens in the 10 percent solution experienced a net increase in damping capacity in approximately one-eighth the time.

CHAPTER 9

FLY ASH CEMENT CONCRETE WITH HIGH SULFATE AND/OR HIGH ALKALI CONTENTS

9.1 INTRODUCTION

The objective of this portion of the study was to investigate the effects of high sulfate and/or high alkali contents on the sulfate resistance of fly ash cement concrete. The concrete mixtures included in this portion of the study were previously determined to be highly susceptible to sulfate attack when no adjustments were made in their sulfate and alkali contents. Mixtures consisted of Type II cement with partial replacement by five Type B fly ashes. The replacement level of fly ash for cement remained constant at 35 percent by volume. Concrete was designed for 5½ sacks of cement per cubic yard of concrete. Mixing water was added until a fresh concrete slump of 5 to 7 inches was attained.

Cement sulfate and alkali contents were increased concurrently by adding sodium sulfate as a chemical admixture. Cement sulfate contents were increased individually by intergrinding additional gypsum. Cement alkali contents were increased individually by adding sodium hydroxide as a chemical admixture.

This chapter begins with a brief review of pertinent research by Van Aardt and Visser (438). Results for this study are then presented in the following order:

1) Type B fly ash/Type II cement concrete with sodium sulfate as a chemical additive and
2) Type B fly ash/Type II cement concrete with additional gypsum interground and sodium hydroxide as a chemical additive.

9.2 VAN AARDT AND VISSER LIMITS

9.2.1 INTRODUCTION

Van Aardt and Visser (438) studied the effects of alkali and sulfate contents of cement on the sulfate resistance of Type I cement concrete. The study was presented in detail in Chapter 2, but a brief review is provided in the following text.

Sulfate and alkali contents of the cement were adjusted with additions of gypsum, sodium hydroxide, and sodium sulfate. Resistance to sulfate attack was assessed by immersing mortar bars in sodium sulfate solution and monitoring them for changes in length. The sulfate resistance of the Type I cement concrete was improved with concurrent additions of sulfates and alkalies. Van Aardt and Visser considered additives as cement constituents and formulated two requirements for the composition of sulfate resistant cement (438):

$$\frac{C_3A\%}{SO_3\% + Na_2O\ eq.\%} < 3 \quad \text{and} \tag{9.1}$$

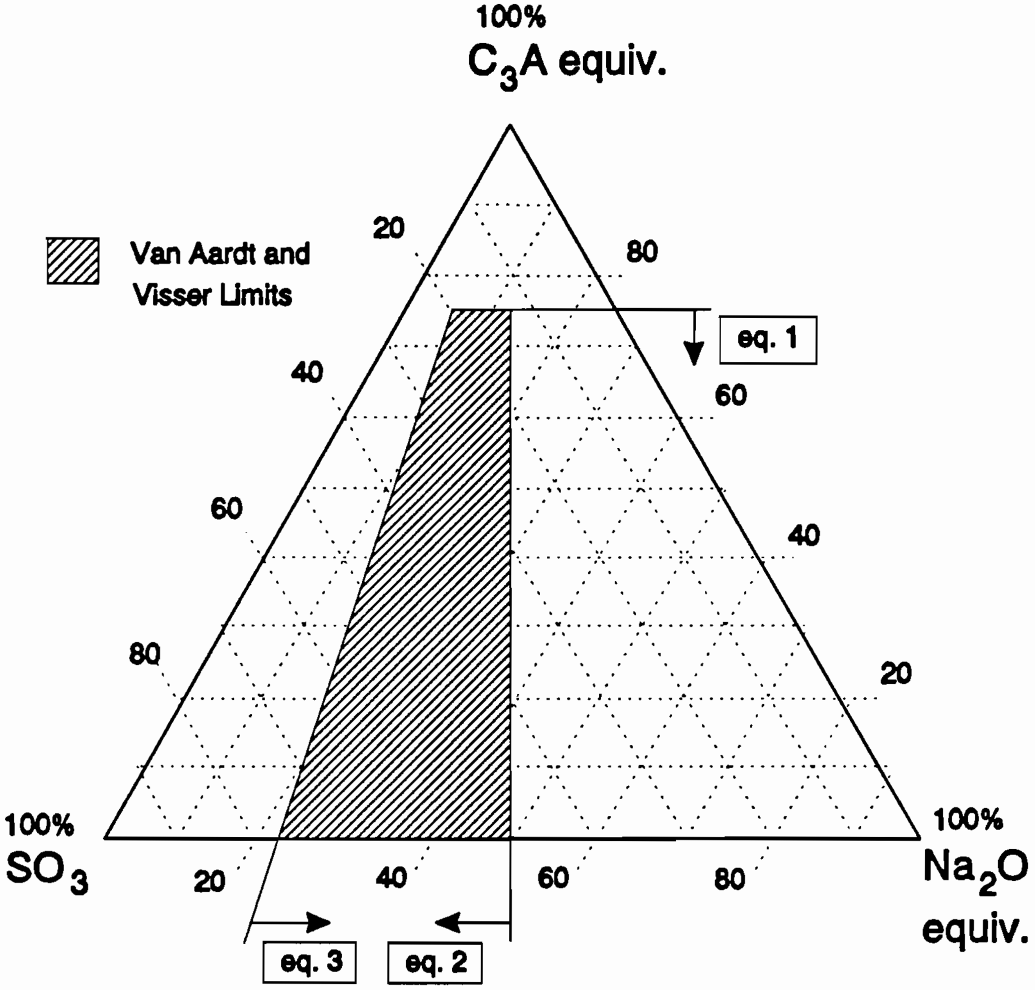
$$1 < \frac{SO_3\%}{Na_2O\ eq.\%} < 3.5\ . \tag{9.2}$$

These limits are displayed on a ternary plot of C_3A, SO_3, and equivalent Na_2O in Figure 9.1.

9.2.2 EQUIVALENT TRICALCIUM ALUMINATE CONTENTS

In order to compare fly ash cement compositions to the Van Aardt and Visser (438) cement composition criteria, all the reactive calcium aluminates in fly ash had to be represented as an equivalent tricalcium aluminate content.

Sulfate susceptible calcium aluminates in fly ash are not concentrated as tricalcium aluminate as they are in portland cement. The majority of calcium aluminates in fly ash are present as glassy phases. Calcium and aluminum oxides may exist in glass in various proportions and therefore the total quantity of sulfate susceptible calcium aluminate-like structures is difficult to quantify. Reactive crystalline forms of calcium aluminates in fly ash include tricalcium aluminate and sodalite structures.



eq. 1 $C_3A < 3\,(SO_3 + Na_2O)$

eq. 2 $SO_3 > Na_2O$

eq. 3 $SO_3 < 3.5\,(Na_2O)$

Figure 9.1 Van Aardt and Visser Limits for Cement Composition (438)

The proportions of tricalcium aluminate and sodalite structures were determined by semi-quantitative X-ray diffraction. The quantities of oxides in glass were determined from differences between bulk chemical oxide contents and the oxide compositions of crystalline compounds. The quantities of calcium aluminates present as glass were controlled by the quantities of calcium oxide present as glass. In other words, relative to alumina, higher proportions of calcium are required for the formation of typical calcium aluminate hydration products (e.g. ettringite). Also, calcium modifiers increase the reactivity of alumino-siliceous glass.

The glassy calcium aluminate contents of fly ashes were estimated assuming a calcium/alumina ratio similar to ettringite. Although tricalcium aluminate-like proportions of calcium and alumina in glass may react with gypsum to form ettringite, a higher proportion of calcium is required from the fly ash if the source of sulfate is not gypsum. If gypsum is not present, a CaO/Al_2O_3 ratio similar to ettringite may react.

The CaO/Al_2O_3 ratio similar to ettringite was considered a useful estimate of calcium aluminates in glass for two reasons. First of all, in addition to gypsum, sources of sulfate include the fly ash itself and sodium sulfate additive. Secondly, the objective of estimating equivalent tricalcium aluminate contents of fly ash was to obtain an idea of the potential for the formation of ettringite during early stages of hydration. Since some reactive calcium aluminate glass may be confined by less reactive crystalline phases, hydration of all calcium aluminates is improbable and a lower bound estimate of reactive calcium aluminates was appropriate.

The proportions of bulk chemical alumina present as reactive calcium aluminates, were calculated for the twelve Type B fly ashes included in this study. Tricalcium aluminate and sodalite structures contain alumina at levels of 37.7 percent and 16.7 percent by weight, respectively. Aluminum oxide in glass, present as reactive calcium aluminates, was estimated using a glassy calcium oxide/aluminum oxide ratio equal to 6.0 (similar to ettringite). The average proportion of fly ash alumina, which was present as reactive calcium aluminates, was 35.1 percent (Table 9.1).

Table 9.1 Estimates of Proportions of Reactive Calcium Aluminates in Fly Ash

Fly Ash	Fly Ash Characteristics					Calculations		
	Total Al_2O_3 (%)	C_3A (%)	So (%)	Glassy CaO (%)	Total Glassy Al_2O_3 (%)	Glassy Al_2O_3 (C/A=6) (%) a	Al_2O_3 as C-A (%) b	Proportion of Al_2O_3 as C-A (%) c
B-1	15.5	1.8	0.0	18.0	14.6	5.45	6.13	39.6
B-2	21.7	0.0	1.7	18.4	18.6	5.58	5.87	27.0
B-3	22.9	2.3	0.6	22.8	19.1	6.91	7.89	34.4
B-4	19.9	1.1	0.3	24.4	16.5	7.39	7.86	39.5
B-5	22.2	2.3	0.6	24.5	18.1	7.42	8.40	37.8
B-6	21.4	1.7	1.8	20.8	17.5	6.30	7.25	33.9
B-7	18.4	1.2	0.0	20.6	17.2	6.24	6.70	36.4
B-8	19.5	3.1	2.0	15.1	16.9	4.58	6.10	31.2
B-9	22.4	1.9	0.3	19.7	18.7	5.97	6.74	30.1
B-10	22.3	1.2	0.0	21.1	19.3	6.39	6.85	30.7
B-11	21.9	2.4	1.5	24.0	16.8	7.27	8.44	38.5
B-12	20.2	2.3	2.7	24.1	15.6	7.30	8.63	42.7
avg.								35.1

So = sodalite structure ($C_4A_3\bar{S}$)

a: glassy Al_2O_3 available for the formation of ettringite-like phases:
(glassy CaO)/ 3.30, where 3.30 = molar mass ratio $6(CaO)/Al_2O_3$

b: alumina present as reactive, sulfate susceptible calcium aluminates, including C_3A, $C_4A_3\bar{S}$, and glassy Al_2O_3:
$0.38(C_3A) + 0.17(So) +$ glassy Al_2O_3 (C/A = 6)

c: [Al_2O_3 as C-A (%)] / (total Al_2O_3)

In summary, one-third of the bulk chemical alumina content of fly ash was chosen as a rough estimate of the proportion of alumina existing as reactive calcium aluminate phases. These proportions of reactive alumina were converted to equivalent tricalcium aluminate contents by multiplying reactive alumina by 2.65, which is the molar mass ratio C_3A/Al_2O_3. Equivalent tricalcium aluminate contents of all Type B fly ashes are shown in Table 9.2.

Table 9.2 Equivalent Tricalcium Aluminate Contents of Fly Ash

Fly Ash	Total Al_2O_3 (%)	Al_2O_3 as Reactive C-A (%) a	Equivalent C_3A (%) b
B-1	15.5	5.17	13.7
B-2	21.7	7.23	19.2
B-3	22.9	7.63	20.2
B-4	19.9	6.63	17.6
B-5	22.2	7.40	19.6
B-6	21.4	7.13	18.9
B-7	18.4	6.13	16.2
B-8	19.5	6.50	17.2
B-9	22.4	7.47	19.8
B-10	22.3	7.43	19.7
B-11	21.9	7.30	19.3
B-12	20.2	6.73	17.8

a Total Al_2O_3 / 3

b 2.65 * (Al_2O_3 as reactive C-A), where
2.65 = molar mass ratio, C_3A / Al_2O_3

9.3 SODIUM SULFATE AS A CHEMICAL ADDITIVE

9.3.1 INTRODUCTION

Sodium sulfate was dissolved in the mixing water for several Type B fly ash/Type II cement concrete mixtures, which were previously determined to be susceptible to sulfate attack. These mixtures included partial replacement of cement by five Type B ashes at a level of 35 percent by volume. Fly ash was incorporated by two methods: added as a mineral admixture at the time of batching concrete and interground as in the production of blended cement.

9.3.2 PROPORTIONS OF SODIUM SULFATE ADDITIVE

Proportions of equivalent tricalcium aluminate, sulfur trioxide, and equivalent alkalies of fly ash cements were calculated from the known compositions of cement and fly ash, as shown in Table 9.3. These compositions of fly ash cements were valid for both mixtures in which fly ash was added as a mineral admixture and in which fly ash was interground.

Sodium sulfate is comprised of 56.3 percent SO_3 and 43.7 percent Na_2O. Therefore, additions of sodium sulfate to fly ash cement results in slightly greater increases for SO_3 content than for equivalent Na_2O content. As sodium sulfate is added to fly ash cements, the changes in composition are within the Van Aardt and Visser composition criteria, as shown in Figure 9.2.

Six proportions of sodium sulfate were added to the Type B fly ash/Type II cement mixtures. Compositions of fly ash cements, including additives, were controlled and compared based on the vertical positions of mixtures on the ternary diagram. These positions were represented as the percentage of $[SO_3 + Na_2O \text{ equiv.}]^*$:

$$[SO_3 + Na_2O \text{ eq.}]^* = \frac{SO_3 + Na_2O \text{ eq.}}{C_3A \text{ eq.} + SO_3 + Na_2O \text{ eq.}} . \qquad (9.3)$$

Table 9.3 Equivalent Tricalcium Aluminate Contents, Sulfate Contents, and Alkali Contents of Type II Cement Concrete Containing 35 Percent Type B Fly Ash by Volume

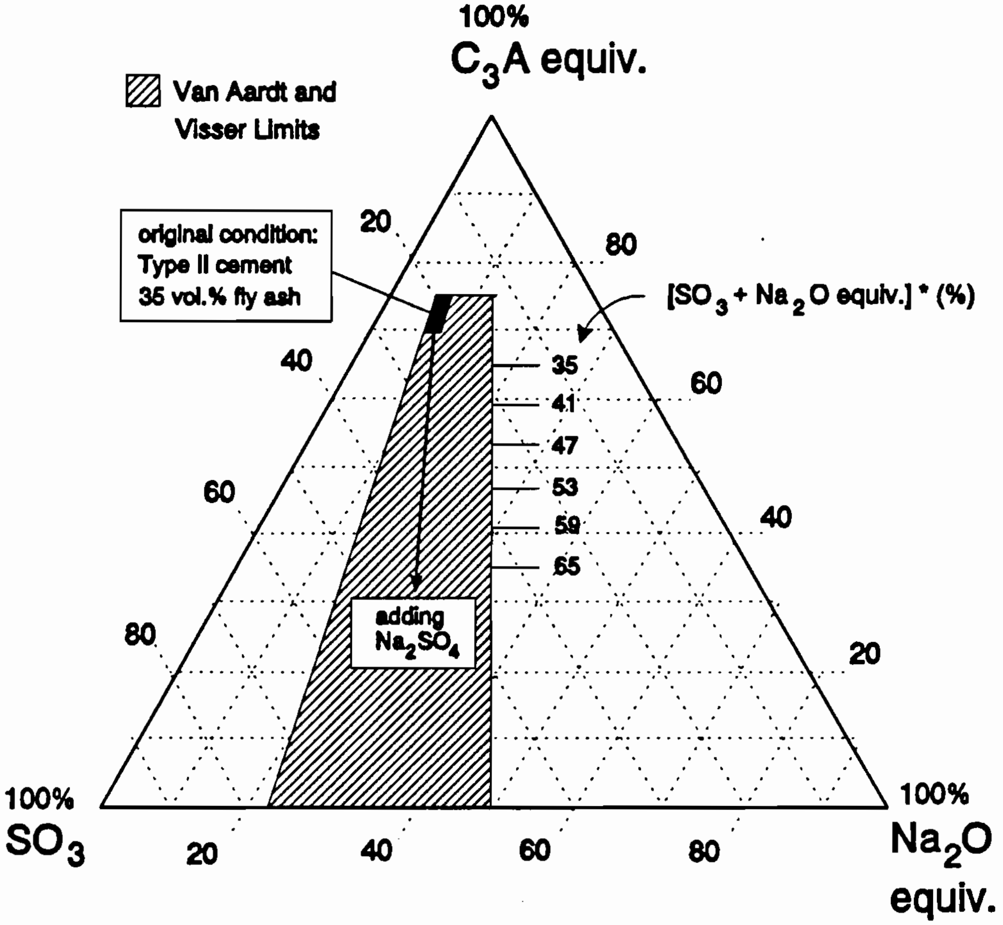
Fly Ash	Sp.Gr.	Equiv. Wt.% a	Fly Ash Cement (wt.%) b			Ternary (wt.%) c			$\frac{SO_3}{C_3A\ eq.}$
			C_3A equiv.	SO_3	Na_2O equiv.	C_3A equiv.	SO_3	Na_2O equiv.	
B-3	2.69	31.9	10.4	2.7	0.9	74.3	19.3	6.4	0.26
B-4	2.60	31.1	9.6	2.7	0.8	73.3	20.6	6.1	0.28
B-5	2.70	31.9	10.3	2.8	1.0	73.1	19.9	7.1	0.27
B-9	2.58	30.9	10.3	2.7	1.0	73.6	19.3	7.1	0.26
B-12	2.79	32.6	9.8	3.4	0.9	69.5	24.1	6.4	0.35

a based on a cement replacement of 35 percent by volume
b Type II cement partially replaced by Type B fly ash
c C_3A equiv. + SO_3 + Na_2O equiv. = 100%

The final fly ash cement compositions correspond to six [SO_3 + Na_2O equiv.]* percentages, as shown in Figure 9.2. For example, "s(35)" refers to a mixture which contained sodium sulfate as a chemical admixture and an [SO_3 + Na_2O equiv.]* content of 35 percent:

$$\frac{SO_3 + Na_2O\ \text{equiv.}}{C_3A\ \text{equiv.} + SO_3 + Na_2O\ \text{equiv.}} \times 100\% = 35\% .$$

The proportions of sodium sulfate added to the Type B fly ash/Type II cement mixtures and their final SO_3 and equivalent Na_2O contents are provided in Appendix C. Additions of sodium sulfate ranged from 0.8 percent to 13.8 percent by weight of fly ash cement. Total sulfur trioxide contents ranged from 2.7 percent to 10.1 percent. Total equivalent Na_2O contents ranged from 0.8 percent to 6.8 percent. Final [SO_3 + Na_2O equiv.]* contents for all fly ash cements corresponded to 35, 41, 47, 53, 59, and 65 percent.



$$[SO_3 + Na_2O\ \mathrm{equiv.}]^* = \frac{SO_3 + Na_2O\ \mathrm{equiv.}}{C_3A\ \mathrm{equiv.} + SO_3 + Na_2O\ \mathrm{equiv.}} \times 100\%$$

Figure 9.2 Ternary (C_3A eq.-SO_3-Na_2O eq.) Compositions of Fly Ash Cement Mixtures Containing Sodium Sulfate Additive

The mass ratio $SO_3/(C_3A$ equiv.) was increased for each fly ash cement mixture to a level beyond that which C_3A is stoichiometrically consumed by sulfates; a mass ratio of 0.9 corresponds to enough SO_3 present to react with all C_3A during the formation of ettringite. For each fly ash cement mixture type, saturation of C_3A equivalent with SO_3 occured at [SO_3 + Na_2O equiv.]* contents of approximately 59 percent.

9.3.3 MIXING WATER REQUIREMENT

Additions of sodium sulfate generally decreased water/(cement+pozzolan) ratios, by weight, as shown in Figures 9.3 and 9.4. Water requirements were in most cases less than the Type II cement mixture without fly ash.

Relative to adding fly ash as an admixture, intergrinding fly ash reduced the range of water requirements. The effects of fly ash on water requirements is largely dependent on the proportion of coarse particles and the extent of particle agglomeration. During intergrinding, some large fly ash particles are crushed and some agglomerates are dispersed.

9.3.4 COMPRESSIVE STRENGTH DEVELOPMENT

Compressive strengths for representative mixtures containing fly ashes B-3, B-4, B-5, B-9, and B-12 are shown in Figures 9.5 through 9.14. Additions of sodium sulfate increased strengths at early ages in all cases and had variable effects on strengths at 28 days. For mixtures in which fly ash was added as an admixture, additions of sodium sulfate increased or had no significant effect on the 28-day strengths. For mixtures in which fly ash was interground, additions of sodium sulfate generally decreased or had no significant effect on the 28-day strengths. Of the three proportions of sodium sulfate for which strengths are shown, the highest dosage of 59 percent [SO_3+Na_2O eq.]*, generally resulted in the highest strengths.

Intergrinding fly ash generally increased strengths at all ages. Increases in strengths, caused by intergrinding fly ash, were most significant for mixtures which did not contain sodium sulfate additive.

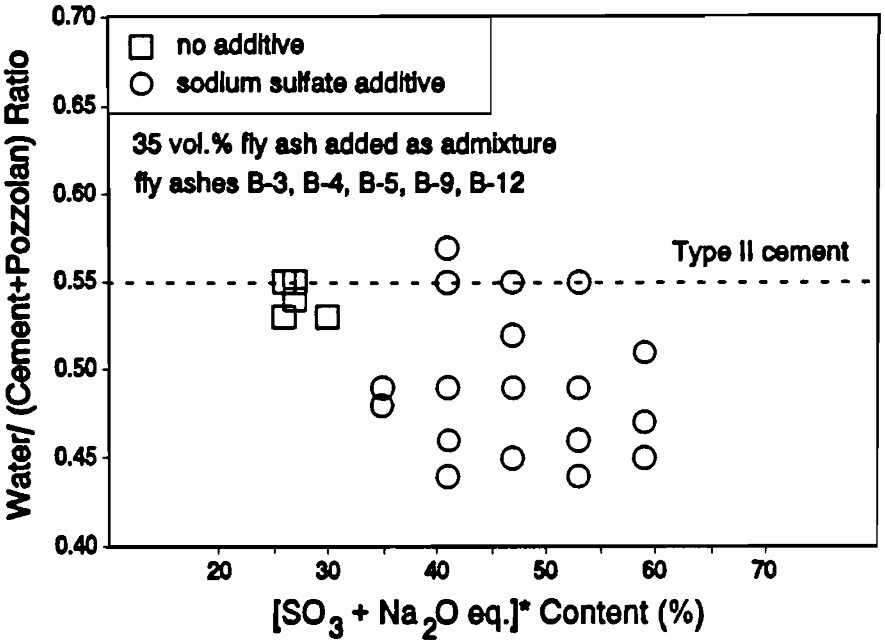


Figure 9.3 Mixing Water Requirements for Type II Cement Concrete Containing Type B Fly Ash as an Admixture and Various Proportions of Sodium Sulfate Additive

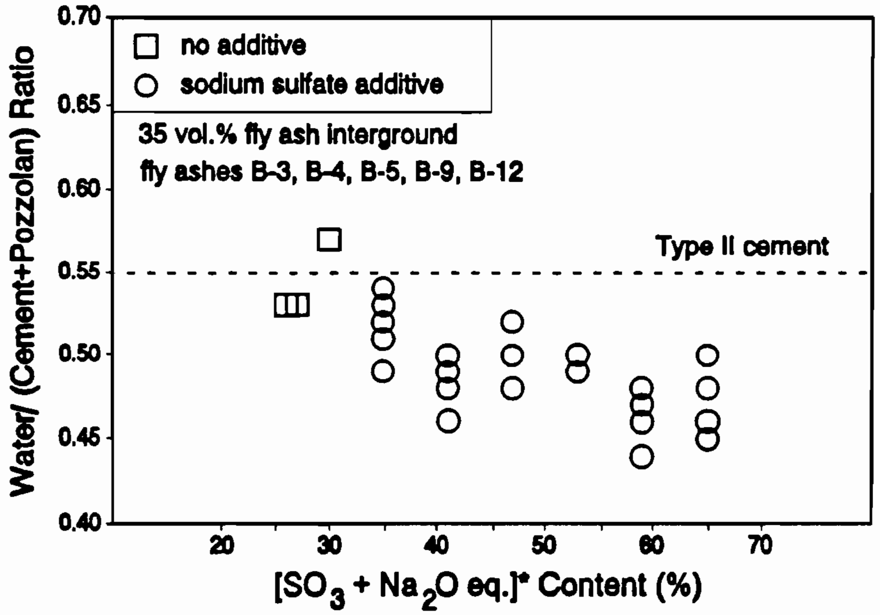


Figure 9.4 Mixing Water Requirements for Type II Cement Concrete Containing Interground Type B Fly Ash and Various Proportions of Sodium Sulfate Additive

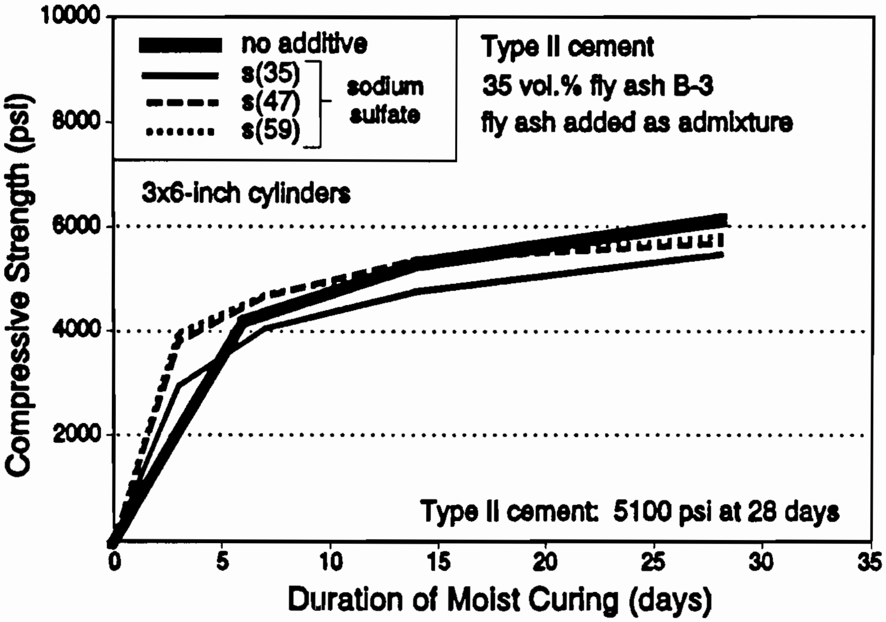


Figure 9.5 Strength Developments for Type II Cement Concrete Containing Fly Ash B-3 Added as an Admixture and Various Proportions of Sodium Sulfate Additive

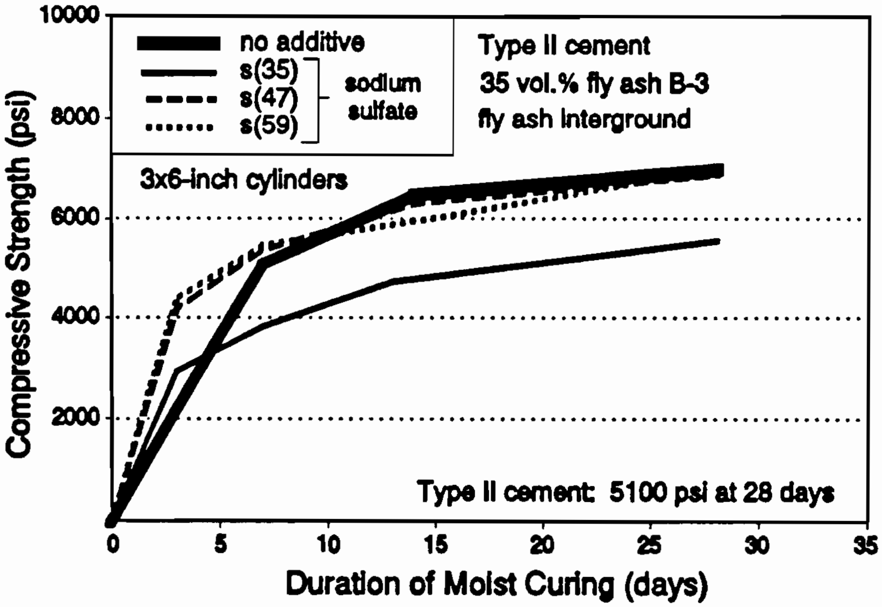


Figure 9.6 Strength Developments for Type II Cement Concrete Containing Interground Fly Ash B-3 and Various Proportions of Sodium Sulfate Additive

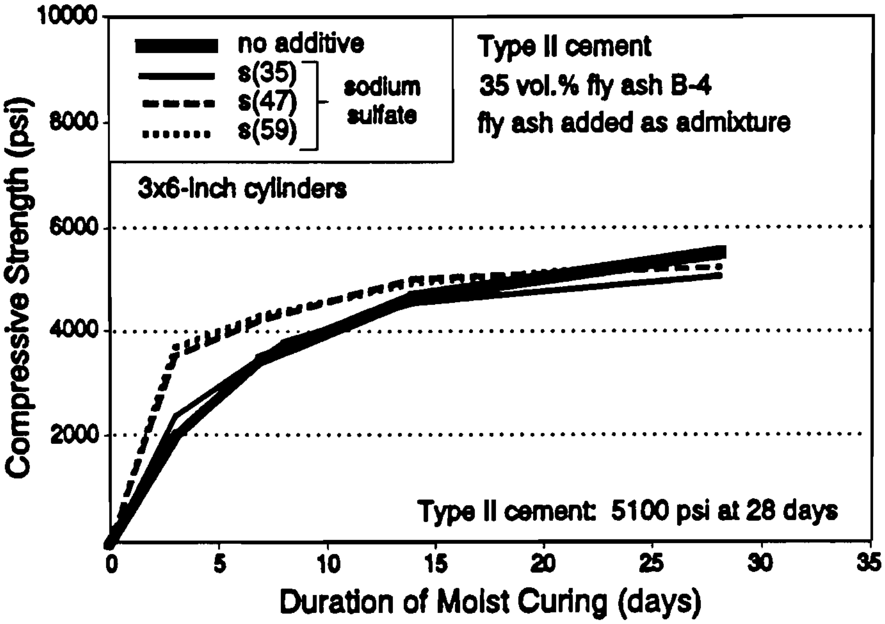


Figure 9.7 Strength Developments for Type II Cement Concrete Containing Fly Ash B-4 Added as an Admixture and Various Proportions of Sodium Sulfate Additive

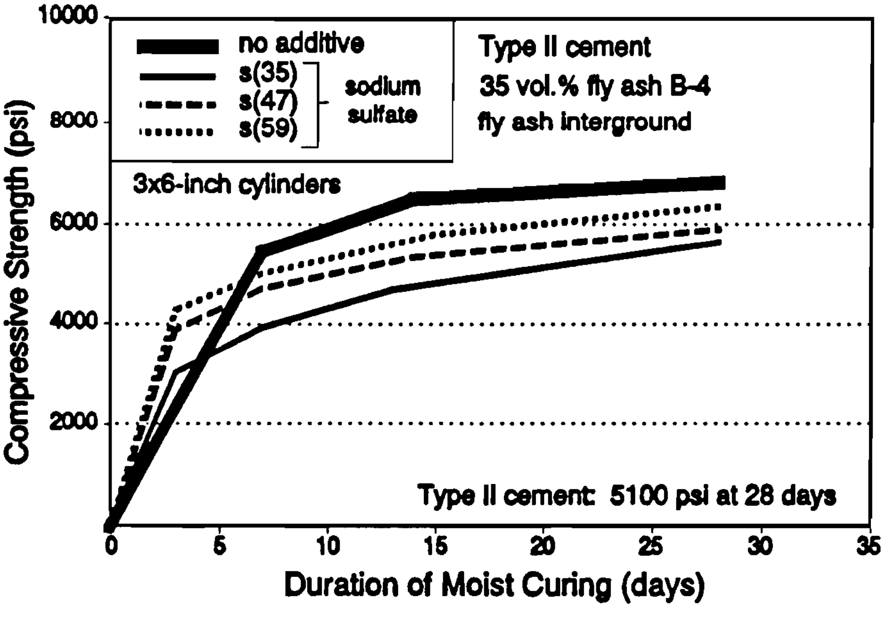


Figure 9.8 Strength Developments for Type II Cement Concrete Containing Interground Fly Ash B-4 and Various Proportions of Sodium Sulfate Additive

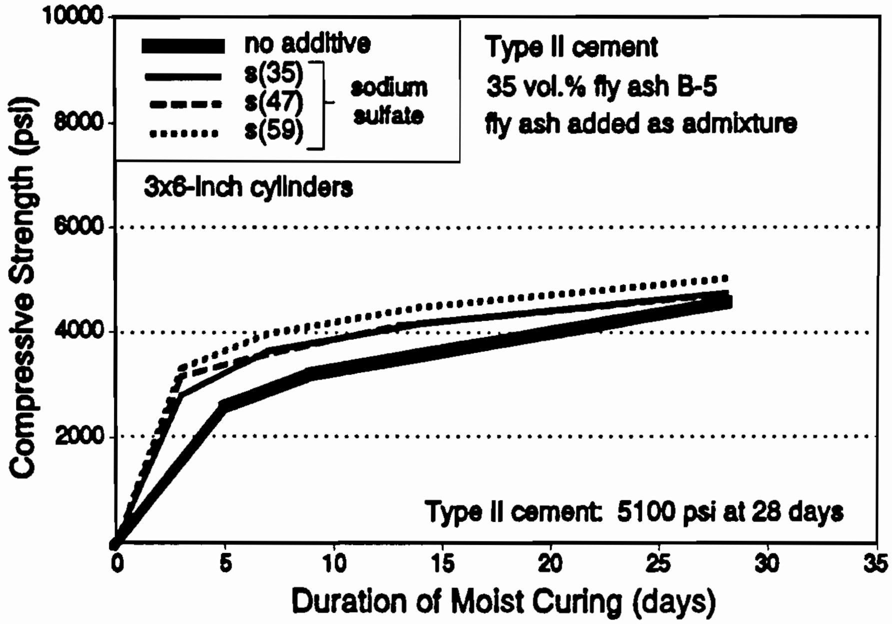


Figure 9.9 Strength Developments for Type II Cement Concrete Containing Fly Ash B-5 Added as an Admixture and Various Proportions of Sodium Sulfate Additive

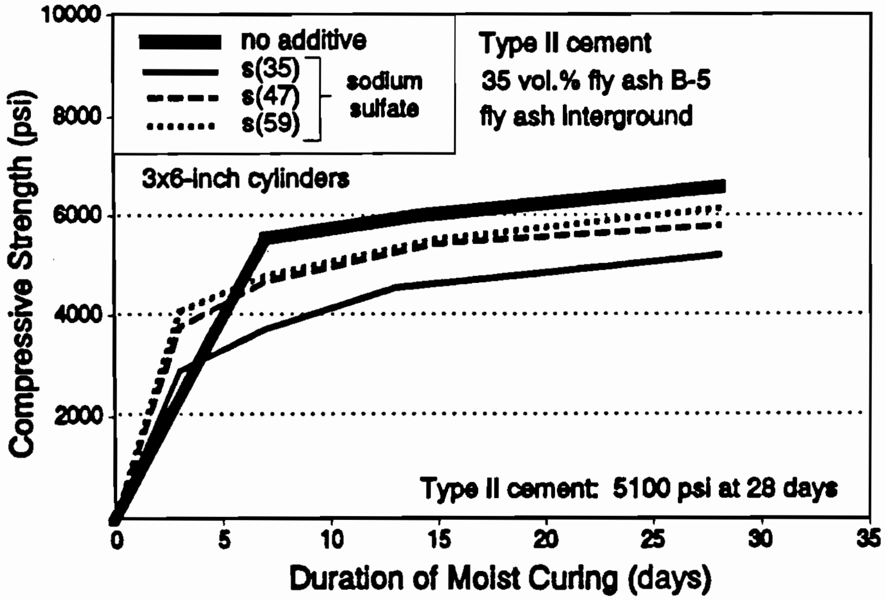


Figure 9.10 Strength Developments for Type II Cement Concrete Containing Interground Fly Ash B-5 and Various Proportions of Sodium Sulfate Additive

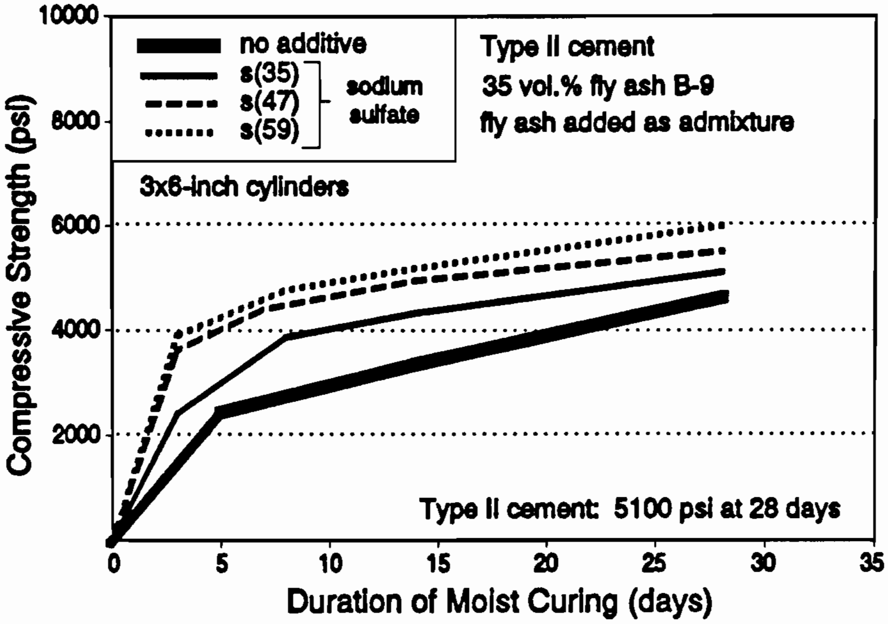


Figure 9.11 Strength Developments for Type II Cement Concrete Containing Fly Ash B-9 Added as an Admixture and Various Proportions of Sodium Sulfate Additive

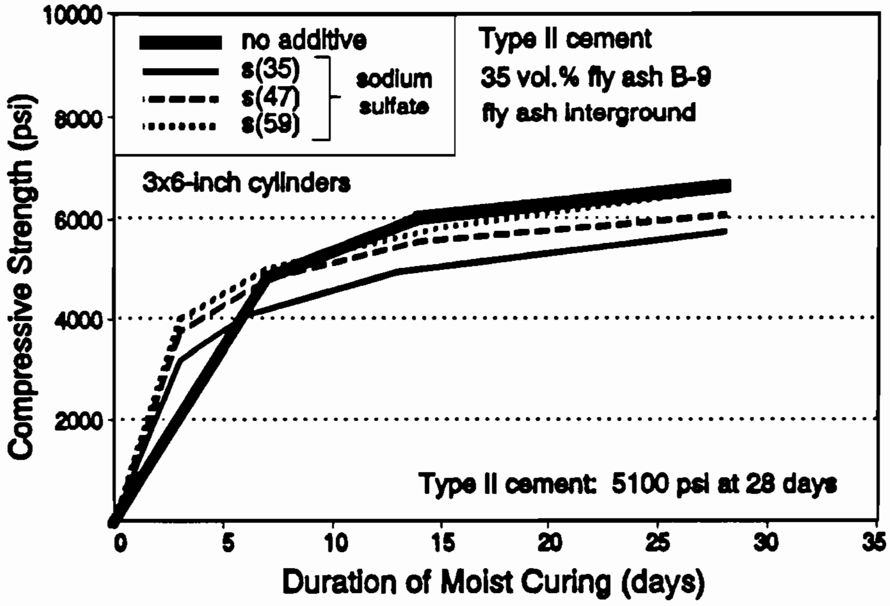


Figure 9.12 Strength Developments for Type II Cement Concrete Containing Interground Fly Ash B-9 and Various Proportions of Sodium Sulfate Additive

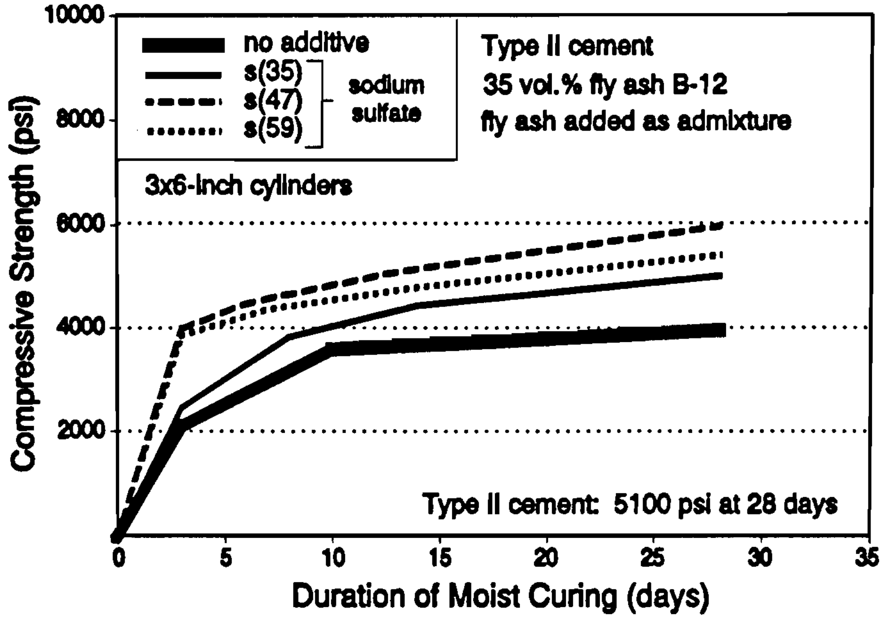


Figure 9.13 Strength Developments for Type II Cement Concrete Containing Fly Ash B-12 Added as an Admixture and Various Proportions of Sodium Sulfate Additive

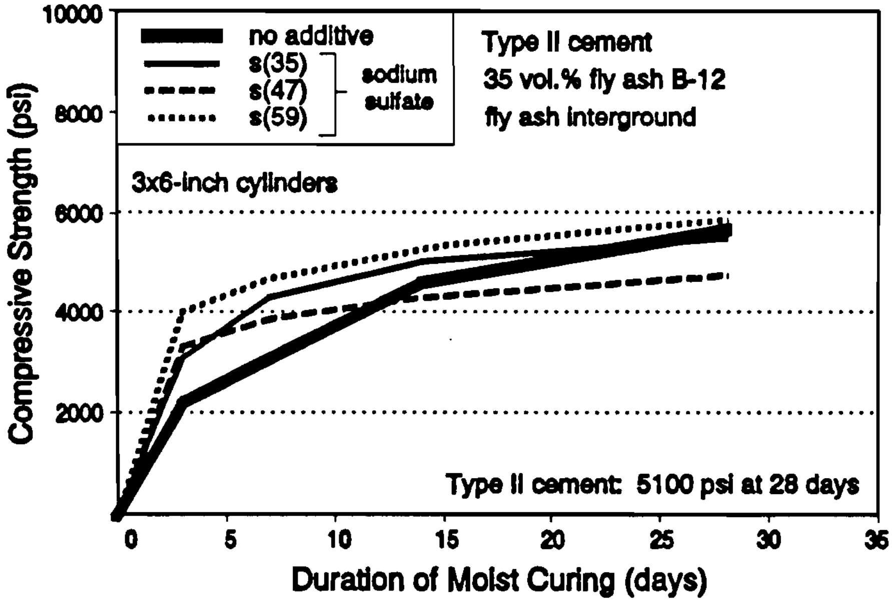


Figure 9.14 Strength Developments for Type II Cement Concrete Containing Interground Fly Ash B-12 and Various Proportions of Sodium Sulfate Additive

9.3.5 SULFATE SUSCEPTIBILITY

9.3.5.1 Linear Expansion and Mass Loss

Sulfate exposure specimens which contained sodium sulfate additive generally did not suffer mass loss, as shown in Figures 9.15 through 9.19. The only exceptions were mixtures containing fly ashes B-4 and B-12 and the lowest dosage of sodium sulfate.

Relatively low proportions of sodium sulfate were optimum in terms of reducing expansions. Expansions for mixtures containing the highest dosage of sodium sulfate were comparable to the expansions for mixtures with no sodium sulfate additive. Saturation of C_3A with SO_3 for the formation of ettringite occured at $[SO_3+Na_2O$ eq.$]^*$ contents of approximately 59 percent. Since expansions at this dosage of sodium sulfate were higher than the expansions for mixtures containing less sodium sulfate, all C_3A-like material must not have reacted while the concrete was plastic. Consequently, available sulfates within the hardened concrete caused internal sulfate attack.

9.3.5.2 Sulfate Susceptibility Rating

The Sulfate Susceptibility Rating, as defined in Chapter 4, is a single-value parameter which depicts the rate of deterioration of concrete. This parameter includes deterioration in the forms of expansion and mass loss. It permits comparisons between the sulfate susceptibilities of all mixtures.

Sulfate Susceptibility Ratings for all fly ash cement mixtures without sodium sulfate additive were 3.0 (maximum value). Sulfate Susceptibility Ratings for fly ash cement mixtures which contained $[SO_3+Na_2O$ eq.$]^*$ contents of 41 percent and 47 percent were consistently lower than the control Type II cement mixture, as shown in Figures 9.20 through 9.24. These mixtures correspond to additions of sodium sulfate of 2.1 to 5.3 percent by weight of cement.

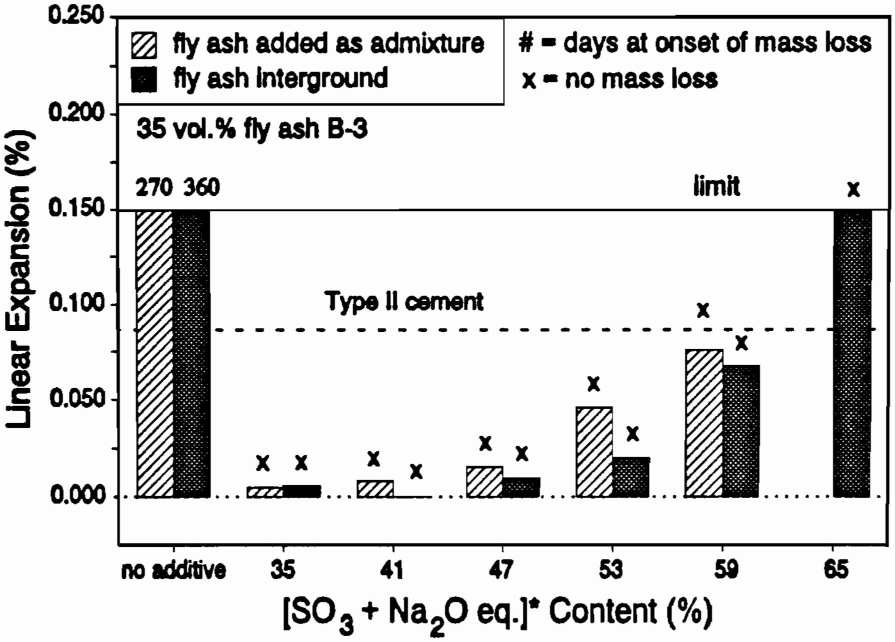


Figure 9.15 Linear Expansions of Type II Cement Concrete Containing Fly Ash B-3 and Various Proportions of Sodium Sulfate Additive

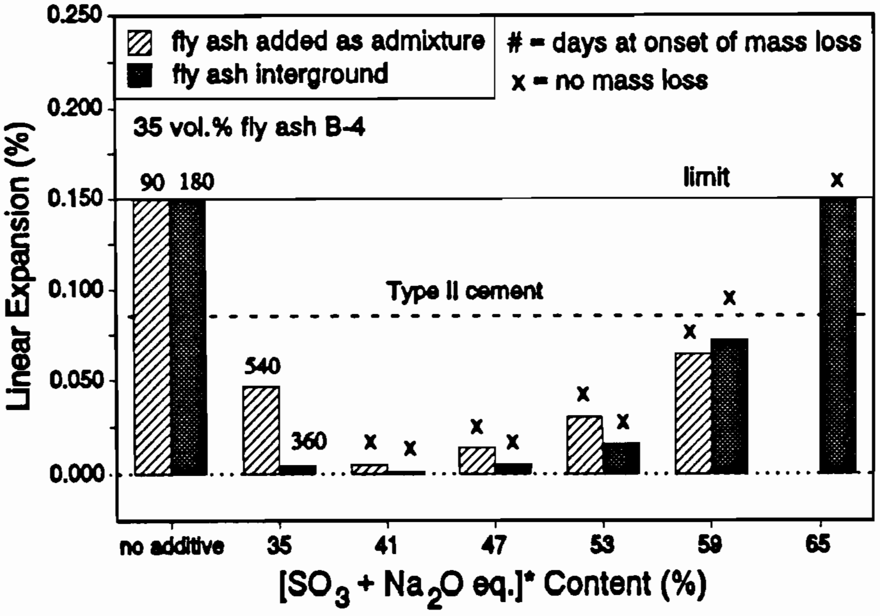


Figure 9.16 Linear Expansions of Type II Cement Concrete Containing Fly Ash B-4 and Various Proportions of Sodium Sulfate Additive

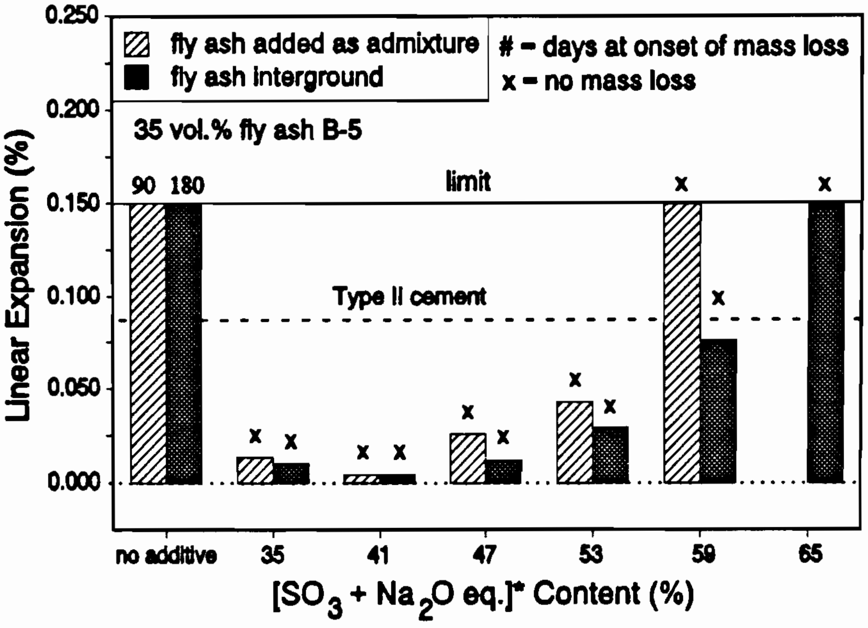


Figure 9.17 Linear Expansions of Type II Cement Concrete Containing Fly Ash B-5 and Various Proportions of Sodium Sulfate Additive

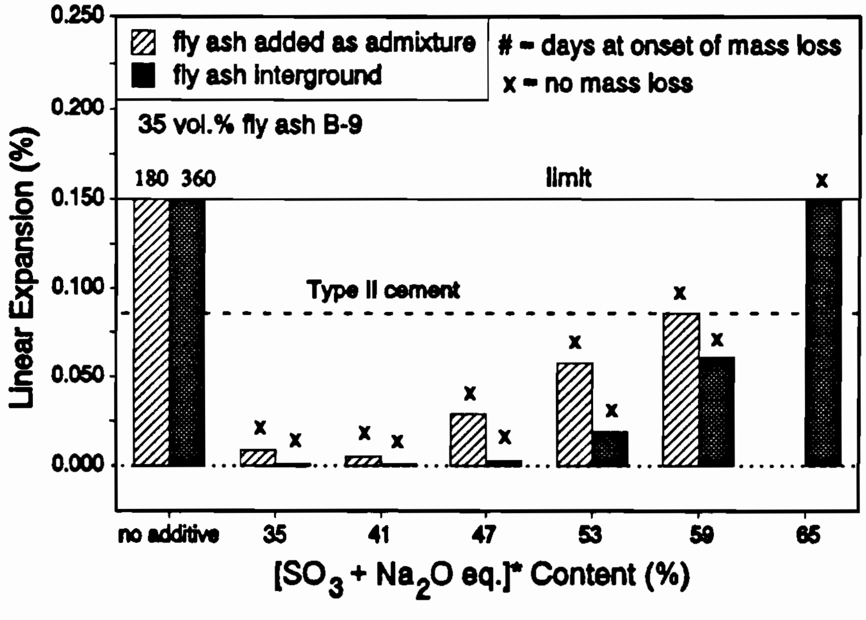


Figure 9.18 Linear Expansions of Type II Cement Concrete Containing Fly Ash B-9 and Various Proportions of Sodium Sulfate Additive

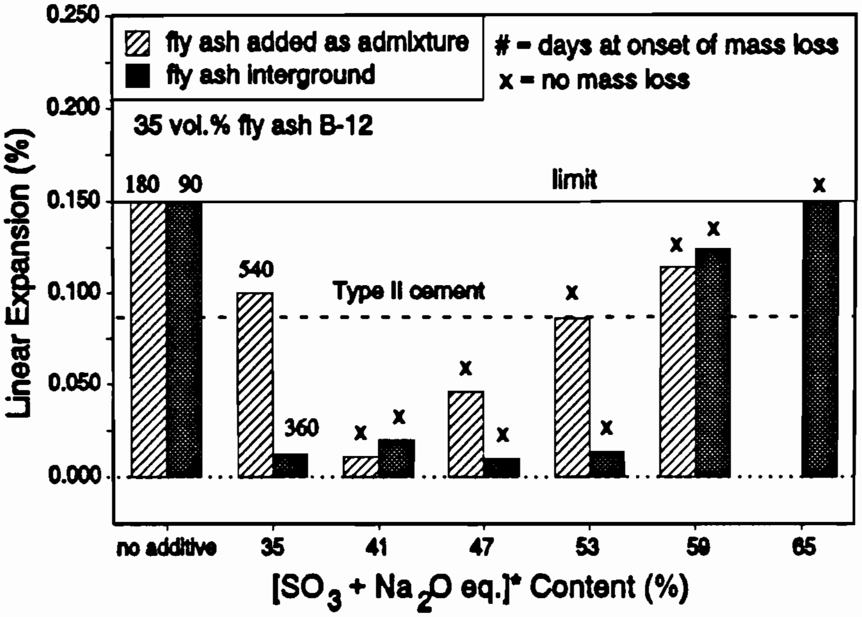


Figure 9.19 Linear Expansions of Type II Cement Concrete Containing Fly Ash B-12 and Various Proportions of Sodium Sulfate Additive

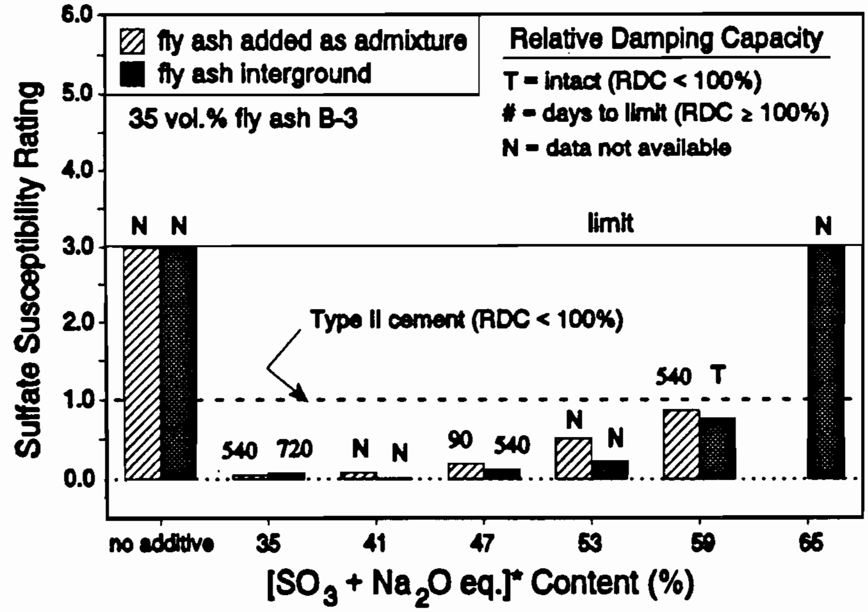


Figure 9.20 Sulfate Susceptibilities of Type II Cement Concrete Containing Fly Ash B-3 and Various Proportions of Sodium Sulfate Additive

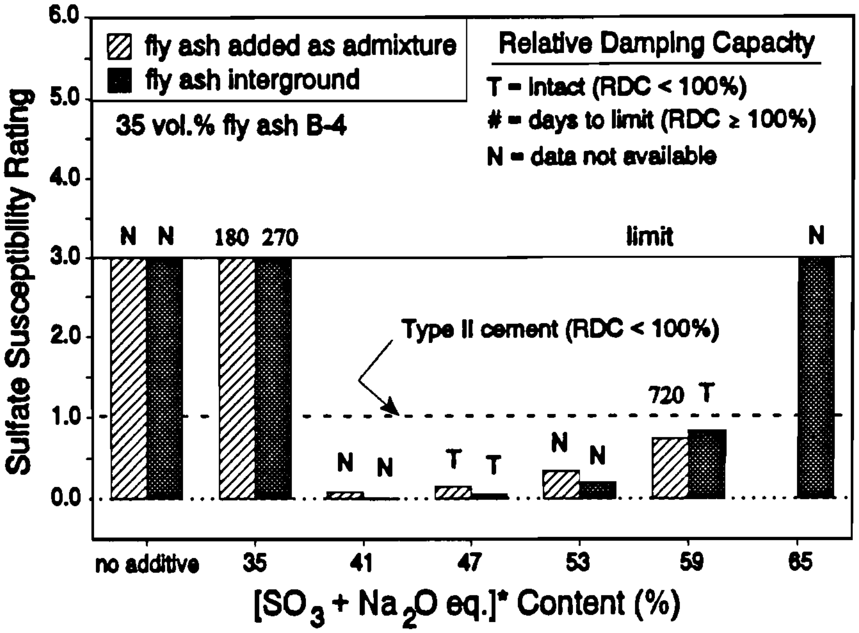


Figure 9.21 Sulfate Susceptibilities of Type II Cement Concrete Containing Fly Ash B-4 and Various Proportions of Sodium Sulfate Additive

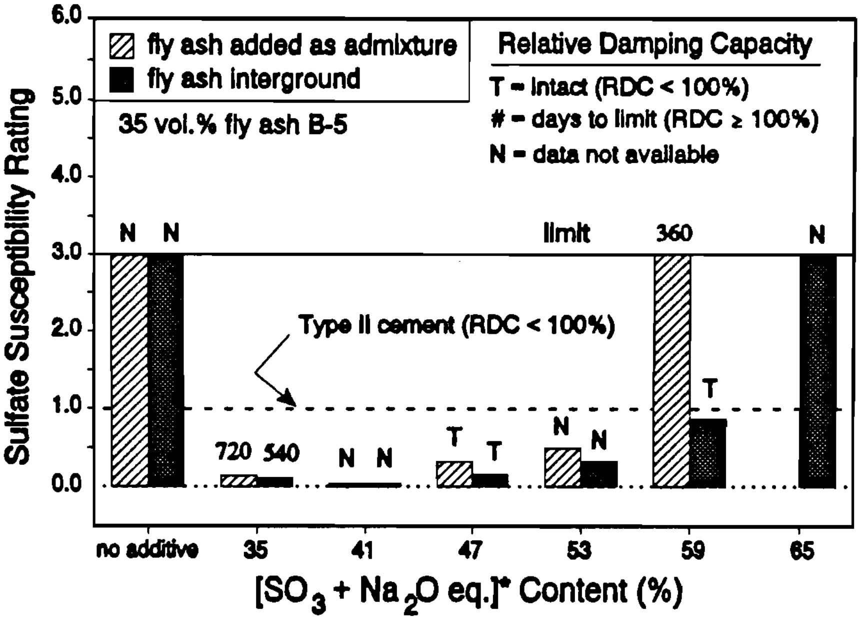


Figure 9.22 Sulfate Susceptibilities of Type II Cement Concrete Containing Fly Ash B-5 and Various Proportions of Sodium Sulfate Additive

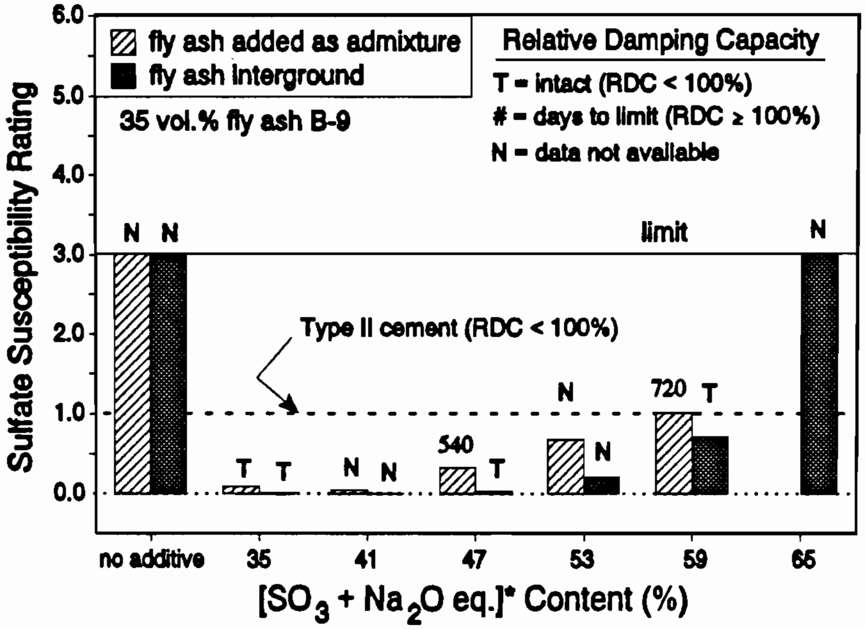


Figure 9.23 Sulfate Susceptibilities of Type II Cement Concrete Containing Fly Ash B-9 and Various Proportions of Sodium Sulfate Additive

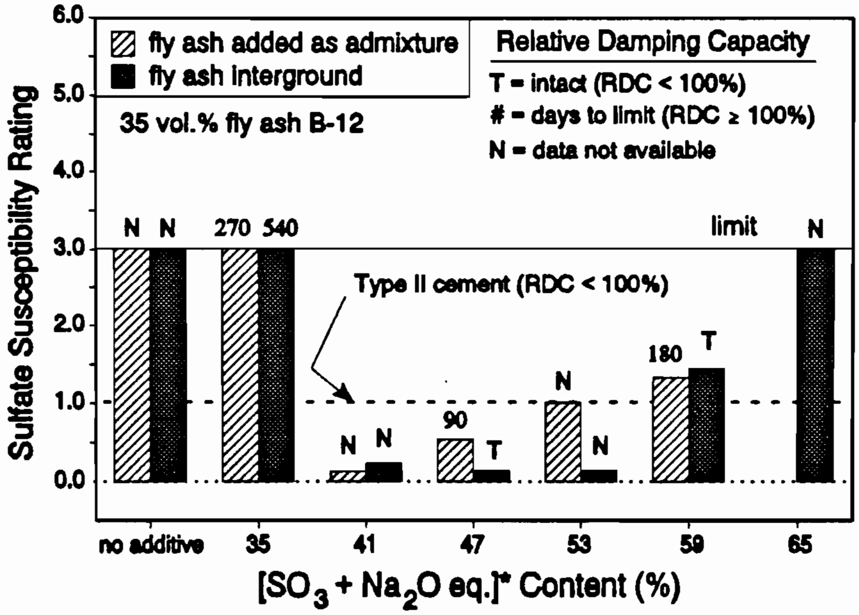


Figure 9.24 Sulfate Susceptibilities of Type II Cement Concrete Containing Fly Ash B-12 and Various Proportions of Sodium Sulfate Additive

Relative to mixtures in which fly ash was added as a mineral admixture, mixtures in which fly ash was interground were more likely to exhibit Relative Damping Capacities of less than 100 percent. For the concrete containing interground fly ash, either the mixture containing an [SO_3+Na_2O eq.]* content of 47 percent or 59 percent exhibited a Relative Damping Capacity of less than 100 percent. These mixtures contained 3.8 percent to 10.5 percent sodium sulfate by weight of cement.

Relative damping capacities were greater than 100 percent for all mixtures which lost mass. Damping capacities were not as effective in detecting deterioration by internal sulfate attack. Internal sulfate attack occured for the mixtures with the highest dosages of sodium sulfate. These expansions may not have been sufficient in all cases to cause extensive internal cracking.

9.3.6 PERMEABILITY

Due to the high sulfate resistance of mixtures containing moderate proportions of sodium sulfate additive, the effect of sodium sulfate additive on concrete permeability was also studied. Rapid chloride ion permeabilities were measured for mixtures containing fly ashes B-9 and B-12. The fly ash was interground at a cement replacement level of 35 percent. Permeabilities were measured after 13 and 91 days of curing at 100 percent relative humidity.

Inclusion of fly ash increased slightly the 13-day permeability of Type II cement concrete, as shown in Figure 9.25. However, inclusion of fly ash decreased the 91-day permeability of Type II cement concrete by 50 percent or more. Both early-age and long-term permeabilities of fly ash cement mixtures were reduced by the inclusion of sodium sulfate additive. Early-age permeabilities were improved most significantly with decreases of over 50 percent.

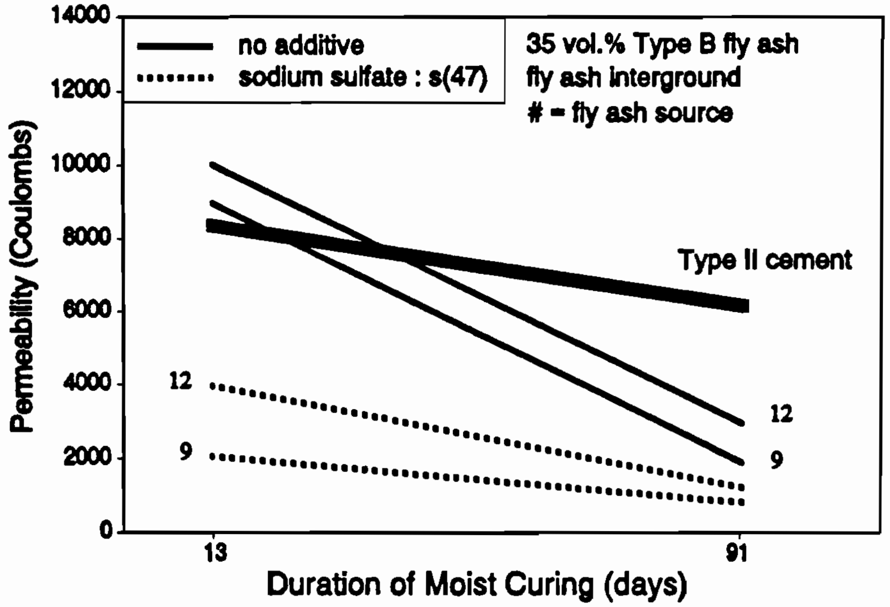


Figure 9.25 Permeabilities of Type II Cement Concrete Containing Interground Type B Fly Ash and Sodium Sulfate Additive

9.4 ADDITIONAL GYPSUM INTERGROUND AND SODIUM HYDROXIDE AS A CHEMICAL ADDITIVE

9.4.1 INTRODUCTION

Additions of gypsum and sodium hydroxide to fly ash concrete mixtures permitted individual adjustments in the total sulfate and total alkali contents within the concrete. Mixtures included partial replacement of Type II cement with two Type B fly ashes at a level of 35 percent by volume. Fly ash was interground as in the production of blended cement.

9.4.2 PROPORTIONS OF GYPSUM AND SODIUM HYDROXIDE

Total SO_3 and equivalent Na_2O contents of blended cements were used to control the proportions of added gypsum and sodium hydroxide. Mixtures included three levels of additional gypsum, three levels of sodium hydroxide additive, and all respective combinations (Figure 9.26). Three mixtures contained similar total proportions of SO_3 and equivalent Na_2O as mixtures which included sodium sulfate additive.

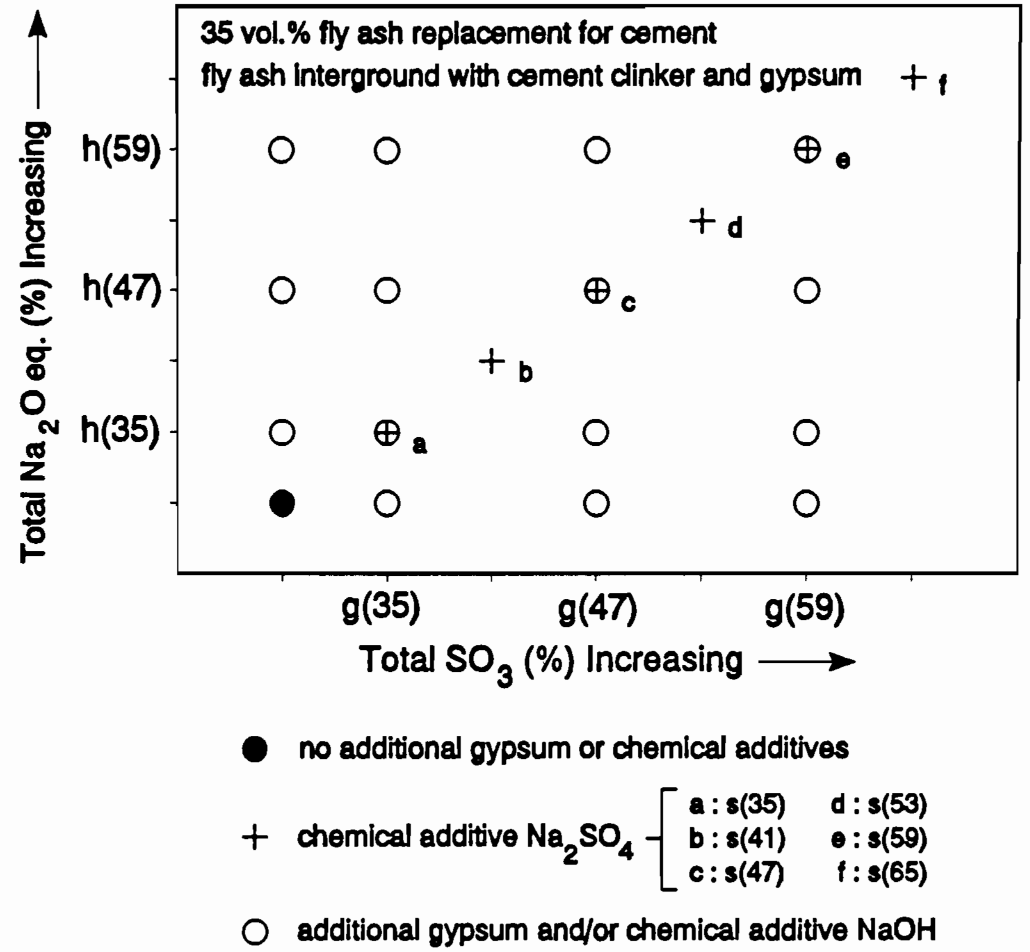


Figure 9.26 Illustration and Nomenclature for the Additions of Gypsum and Sodium Hydroxide

Mixture nomenclature is similar to that used for mixtures containing sodium sulfate. A "g" designates mixtures which contain additional gypsum. An "h" designates mixtures which contain sodium hydroxide. For mixtures containing additional gypsum (designated "g"), the number in parentheses indicates similar SO_3 contents as the sodium sulfate mixture with the same number. For mixtures containing sodium hydroxide additive (designated "h"), the number in parentheses indicates similar equivalent Na_2O as the sodium sulfate mixture with the same number. As examples of nomenclature:

1) g(35) contains additional gypsum and a total SO_3 content similar to s(35),
2) h(35) contains sodium hydroxide and an equivalent Na_2O content similar to s(35), and
3) g(35)h(35) contains additional gypsum and sodium hydroxide; its total SO_3 and equivalent Na_2O contents are similar to s(35).

With 100 percent pure gypsum, the proportions of gypsum required to obtain designated SO_3 contents in blended cements could be calculated from the molar mass ratio:

$$\frac{CaSO_4 \cdot 2H_2O}{SO_3} = 2.15 \ .$$

This ratio indicates that 2.15 percent gypsum is required for each 1.0 percent SO_3. This sulfur trioxide is in addition to that which is provided by the clinker.

However, while manufacturing the ordinary Type II cement, the effective gypsum/SO_3 mass ratio was determined to be larger. This indicates that the gypsum was not 100 percent pure. Five percent gypsum was required in order to attain a cement SO_3 content of 3.0 percent. Knowing the clinker SO_3 content (0.8 percent), the effective gypsum/SO_3 mass ratio was calculated:

$$0.8\%\ SO_3 \left[\frac{95}{100}\right] + z\%\ SO_3 \left[\frac{5}{100}\right] = 3.0\%\ SO_3, \text{ where}$$

$$x = \text{effective } SO_3 \text{ content of gypsum} = 44.8\% \ ,$$

$$\frac{\text{gypsum}}{SO_3} = \frac{1}{\frac{SO_3}{\text{gypsum}}} = \frac{1}{0.448} = 2.23 \ .$$

The gypsum supplied 96.1 percent of its calculated SO_3 content. This difference was attributed to impurities in the gypsum.

The commercially available NaOH was guaranteed to be 98$^+$ percent pure. For simplicity, it was assumed to be 100 percent pure. Two moles of NaOH were required for each mole of Na_2O:

$$2NaOH + H_2O \rightarrow Na_2O + 2H_2O .$$

Therefore, the mass ratio $NaOH/Na_2O$ was calculated as follows:

$$\frac{2(NaOH)}{Na_2O} = \frac{2(40)\ \frac{gm}{mol}}{62\ \frac{gm}{mol}} = 1.29 .$$

This mass ratio was used to determine the proportions of NaOH required to attain designated cement Na_2O contents.

The proportions of gypsum and sodium hydroxide which were added to mixtures containing fly ashes B-9 and B-12 are shown in Appendix C. Additions of gypsum and NaOH were as large as approximately 13 percent and 6 percent by weight of cement, respectively. Total and ternary weight percentages of equivalent Na_2O, SO_3, and equivalent C_3A are also provided in Appendix C. Sulfur trioxide contents ranged from 2.7 percent to 8.3 percent. Total alkali contents ranged from 0.9 to 5.4 percent.

9.4.3 MIXING WATER REQUIREMENT

Mixing water requirements were largest for mixtures containing high proportions of alkali and low proportions of sulfate, as shown in Figures 9.27 and 9.28. Water requirements of these mixtures decreased as sulfate contents increased.

Mixing water requirements were lowest for mixtures containing low proportions of both alkali and sulfates.

Mixing water requirements for mixtures containing gypsum and sodium hydroxide are compared with mixtures containing sodium sulfate additive in Figures 9.29 and 9.30. Comparisons involve mixtures with similar total sulfate and alkali contents. Relative to mixtures containing gypsum and sodium hydroxide, mixtures containing sodium sulfate additive required equal or smaller proportions of water. All these mixtures containing sulfate

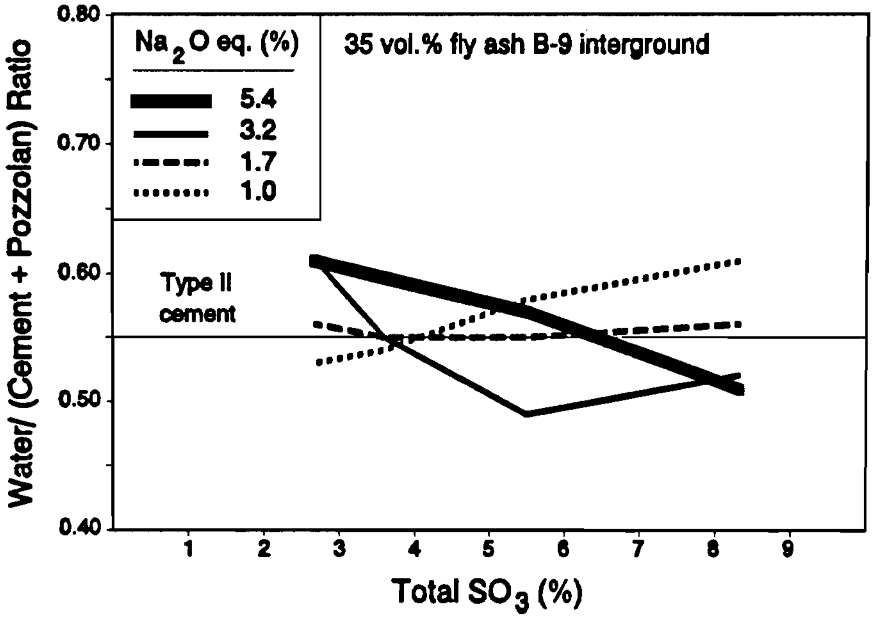


Figure 9.27 Mixing Water Requirements for Type II Cement Concrete Containing Interground Fly Ash B-9, Additional Gypsum, and Sodium Hydroxide Additive

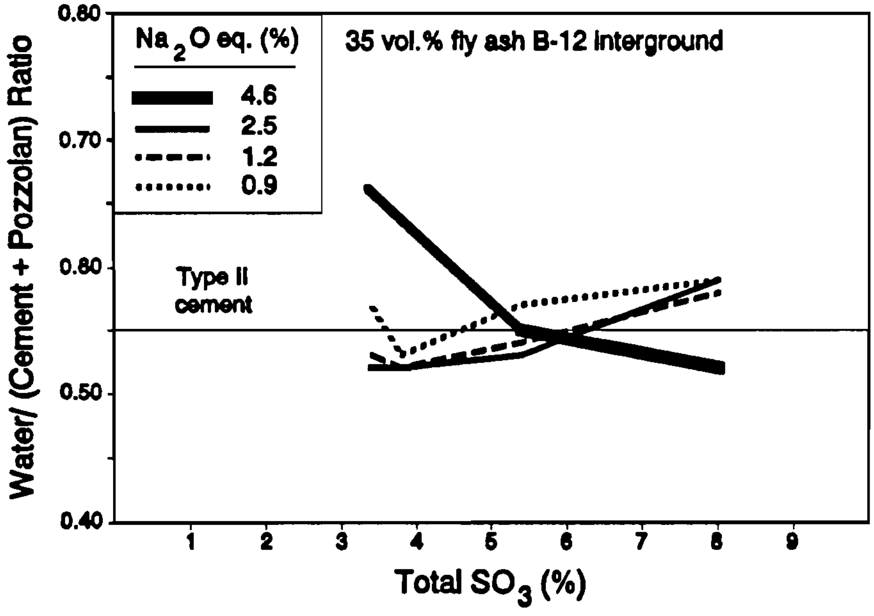


Figure 9.28 Mixing Water Requirements for Type II Cement Concrete Containing Interground Fly Ash B-12, Additional Gypsum, and Sodium Hydroxide Additive

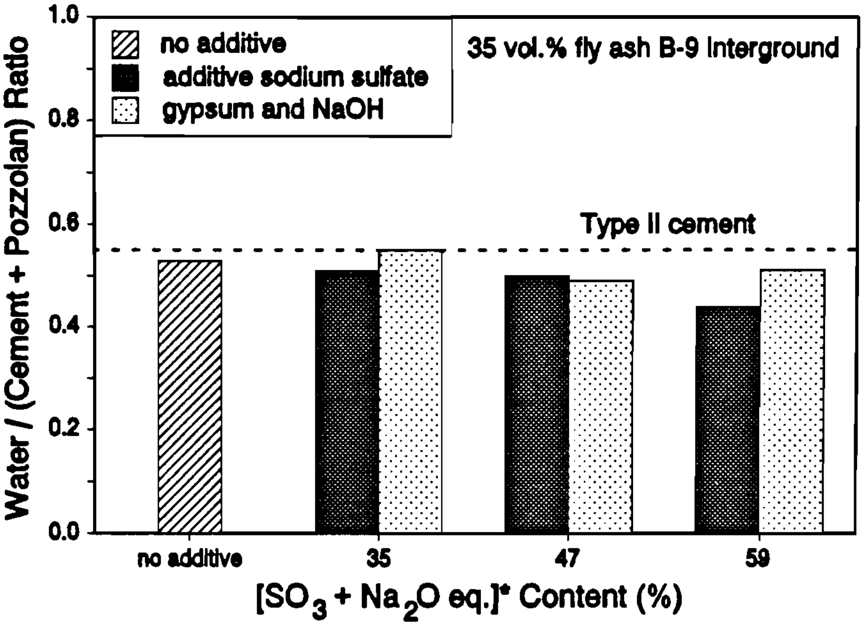


Figure 9.29 Mixing Water Requirements for Type II Cement Concrete Containing Interground Fly Ash B-9 and Various Mineral and Chemical Additives

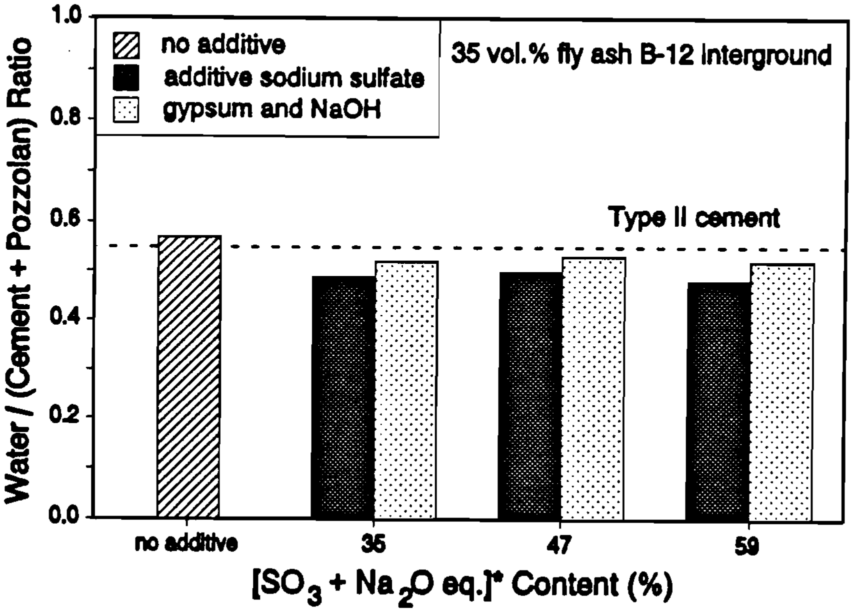


Figure 9.30 Mixing Water Requirements for Type II Cement Concrete Containing Interground Fly Ash B-12 and Various Mineral and Chemical Additives

and alkali additives required proportions of mixing water similar to or less than the mixtures containing fly ash without chemical additives.

9.4.4 COMPRESSIVE STRENGTH

Compressive strength at 28 days decreased with increases in alkali content, as shown in Figures 9.31 and 9.32. These decreases in strength were most significant for mixtures containing low proportions of sulfate.

Compressive strength was highest for mixtures containing low proportions of both alkali and sulfate.

The development of compressive strength for mixtures containing gypsum and sodium hydroxide are compared with mixtures containing sodium sulfate in Figures 9.33 through 9.36. In all cases, high levels of both alkali and sulfate either decreased long-term strength or had no significant effect. Decreases in strength were more extreme for mixtures containing gypsum and sodium hydroxide, as compared to mixtures containing sodium sulfate additive.

In all cases, high levels of both alkali and sulfate increased early-age strength. Increases were larger for mixtures containing sodium sulfate additive, as compared to mixtures containing gypsum and sodium hydroxide.

9.4.5 SULFATE SUSCEPTIBILITY

9.4.5.1 Linear Expansion and Mass Loss

Due to the extremely low strengths of mixtures containing the highest proportion of alkali [h(59)], these mixtures were considered impractical and were not included in the comparisons of sulfate susceptibility.

Low and moderate proportions of additional gypsum decreased the linear expansion of fly ash concrete, as shown in Figures 9.37 and 9.38. Slight increases in alkali content, along with these slight increases in sulfate content, resulted in the lowest expansions.

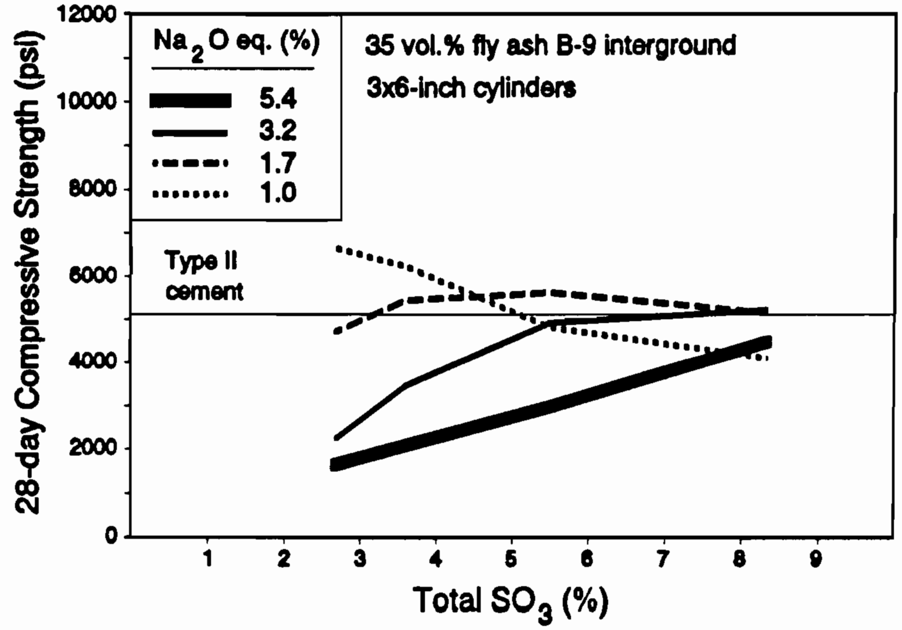


Figure 9.31 Compressive Strengths for Type II Cement Concrete Containing Interground Fly Ash B-9, Additional Gypsum, and Sodium Hydroxide Additive

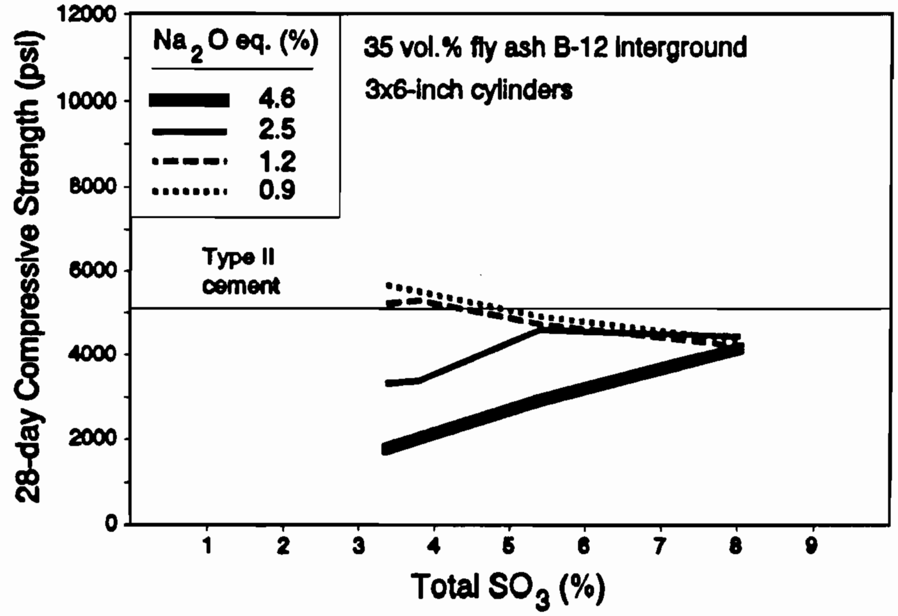


Figure 9.32 Compressive Strengths for Type II Cement Concrete Containing Interground Fly Ash B-12, Additional Gypsum, and Sodium Hydroxide Additive

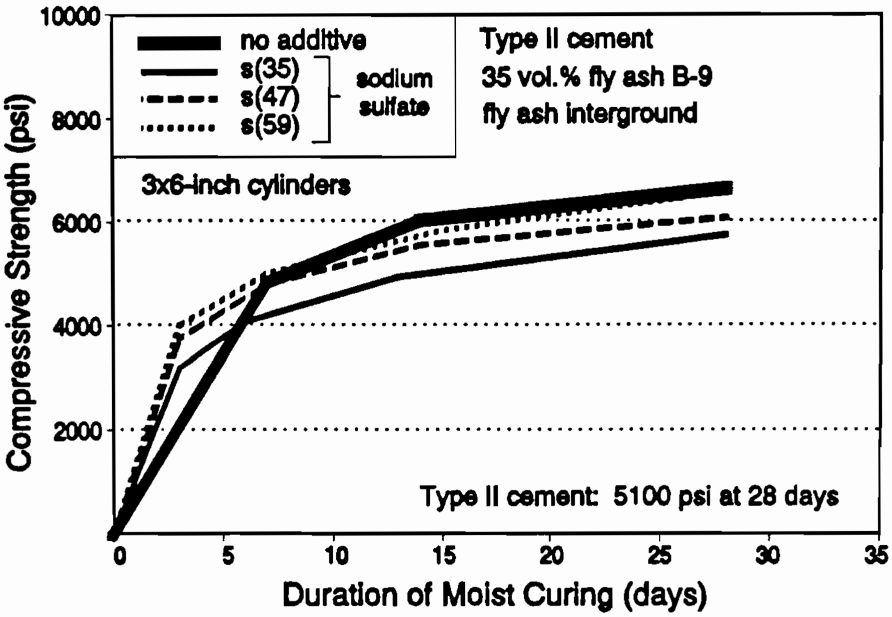


Figure 9.33 Compressive Strength Developments for Type II Cement Concrete Containing Interground Fly Ash B-9 and Sodium Sulfate Additive

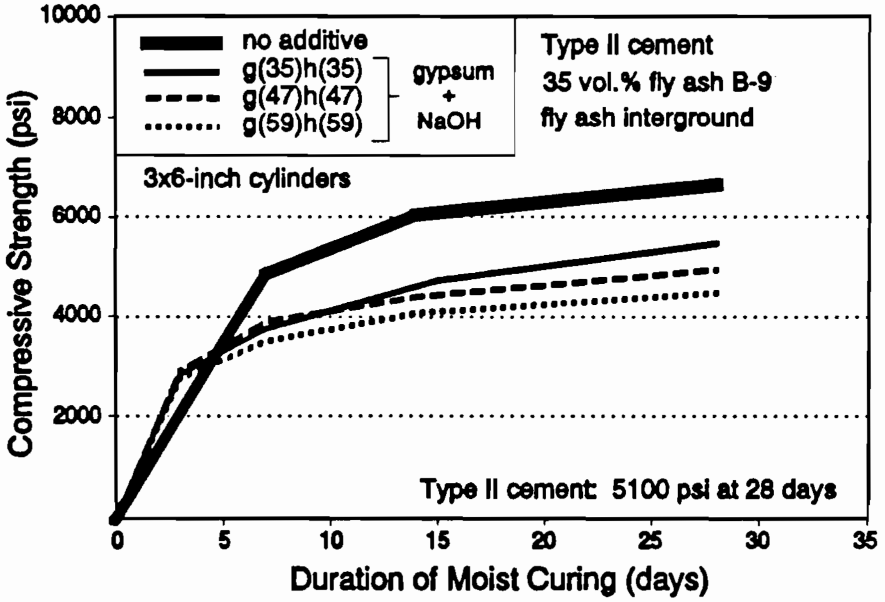


Figure 9.34 Compressive Strength Developments for Type II Cement Concrete Containing Interground Fly Ash B-9, Additional Gypsum, and Sodium Hydroxide Additive

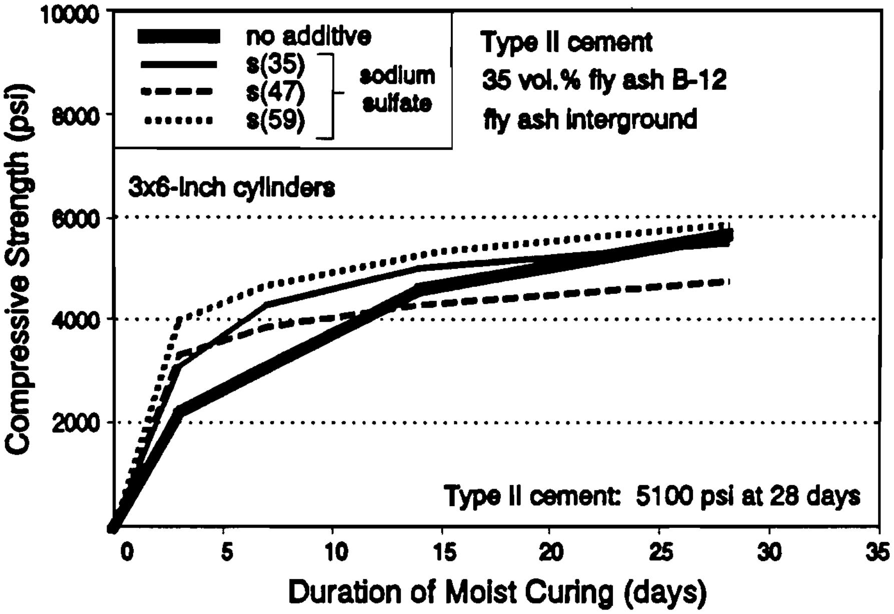


Figure 9.35 Compressive Strength Developments for Type II Cement Concrete Containing Interground Fly Ash B-12 and Sodium Sulfate Additive

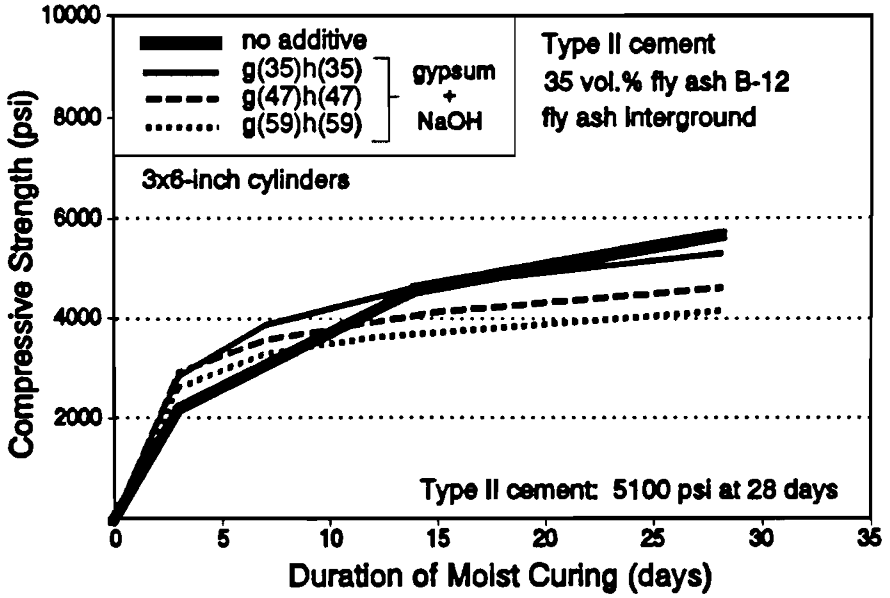


Figure 9.36 Compressive Strength Developments for Type II Cement Concrete Containing Interground Fly Ash B-12, Additional Gypsum, and Sodium Hydroxide Additive

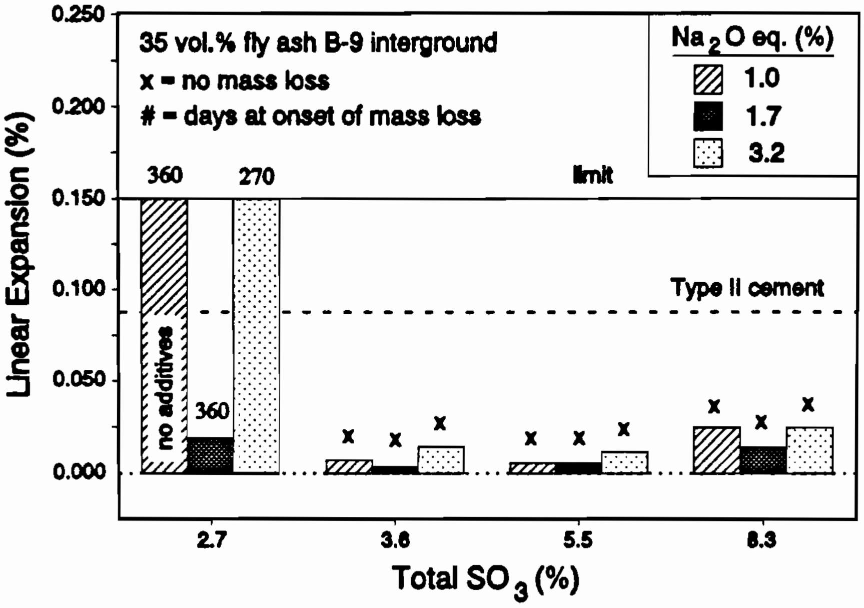


Figure 9.37 Linear Expansions of Type II Cement Concrete Containing Interground Fly Ash B-9, Additional Gypsum, and Sodium Hydroxide Additive

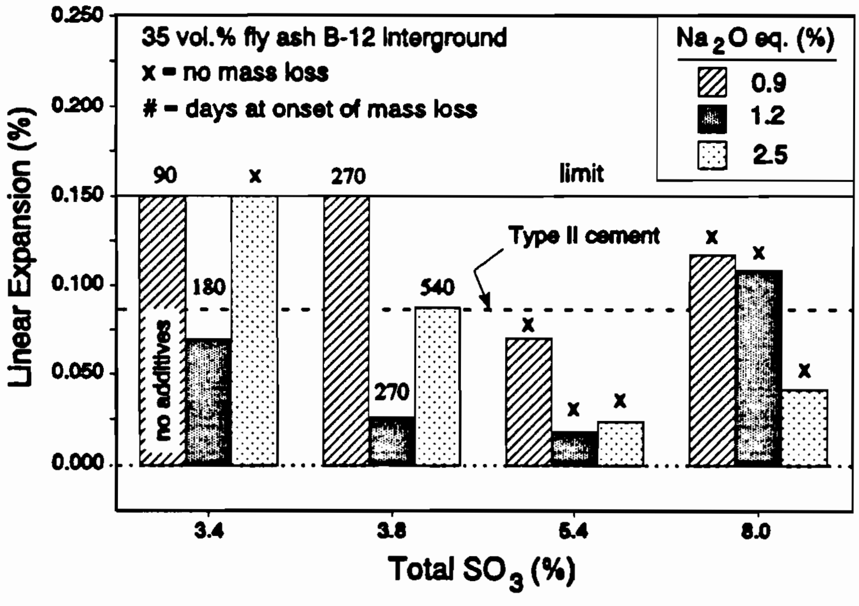


Figure 9.38 Linear Expansions of Type II Cement Concrete Containing Interground Fly Ash B-12, Additional Gypsum, and Sodium Hydroxide Additive

Although these fly ash concretes lost mass when they contained no additives, they did not lose mass when their total SO_3 contents were increased to approximately 5.5 percent.

Linear expansion and mass loss for mixtures containing sodium sulfate additive are compared with those containing gypsum and sodium hydroxide in Figures 9.39 and 9.40. Total sulfate and alkali contents were the same for mixtures with the same $[SO_3+Na_2O \text{ eq.}]^*$ content, independent of additives used. Although water requirements and strengths varied between mixtures with similar $[SO_3+Na_2O \text{ eq.}]^*$ contents, resistance to sulfates were very similar. Additions of gypsum and sodium hydroxide appear to be as effective in reducing expansions and eliminating mass loss as were the additions of sodium sulfate.

9.4.5.2 Sulfate Susceptibility Rating

The Sulfate Susceptibility Rating, as defined in Chapter 4, is a single-value parameter which depicts the rate of deterioration of concrete. This parameter includes deterioration in the forms of expansion and mass loss. It permits comparisons between the sulfate susceptibilities of all mixtures.

Mixtures containing fly ash B-9 were resistant to sulfate attack when total cement SO_3 contents were approximately 3.5 to 8.5 percent and total cement alkali contents were approximately 1.0 to 3.0 percent, as shown in Figure 9.41. Mixtures containing fly ash B-12 were resistant to sulfate attack when total cement SO_3 content was approximately 5.5 percent and total cement alkali contents were approximately 1.0 to 2.5 percent, as shown in Figure 9.42. Improvements in sulfate resistance were more significant for mixtures containing fly ash B-9 than for mixtures containing fly ash B-12. This may have been due to the higher glass content of fly ash B-9: proportions of crystalline material for fly ashes B-9 and B-12 were 19.0 percent and 38.5 percent, respectively. Alkali promotes the dissolution of the glassy portion of fly ash, which may then permit sulfate-related reactions to occur while concrete is plastic.

Relative Damping Capacity measurements were available only for mixtures containing additional gypsum or sodium hydroxide individually. Mixtures containing total sulfate contents of approximately 5.5 percent to 8 percent exhibited Relative Damping Capacities

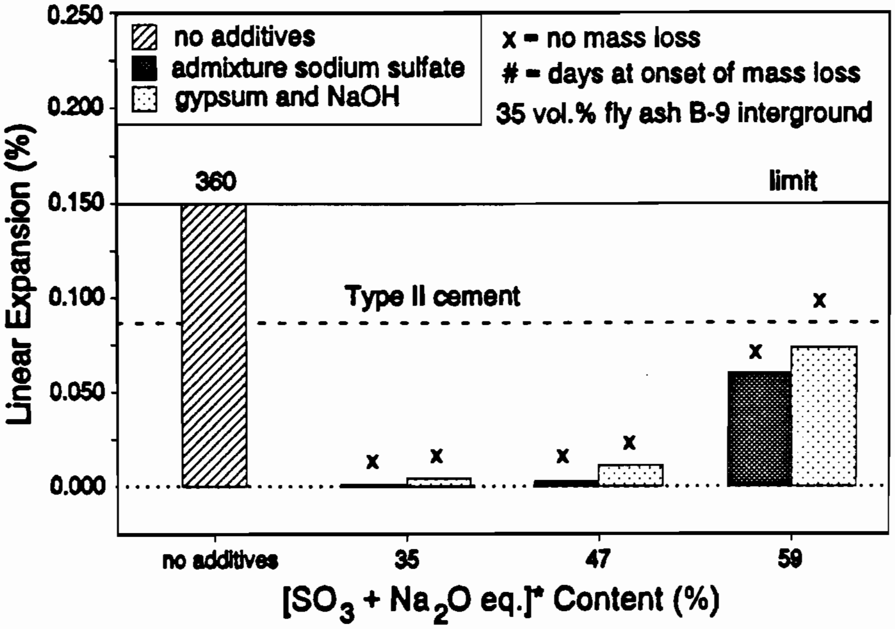


Figure 9.39 Linear Expansions of Type II Cement Concrete Containing Interground Fly Ash B-9 and Various Mineral and Chemical Additives

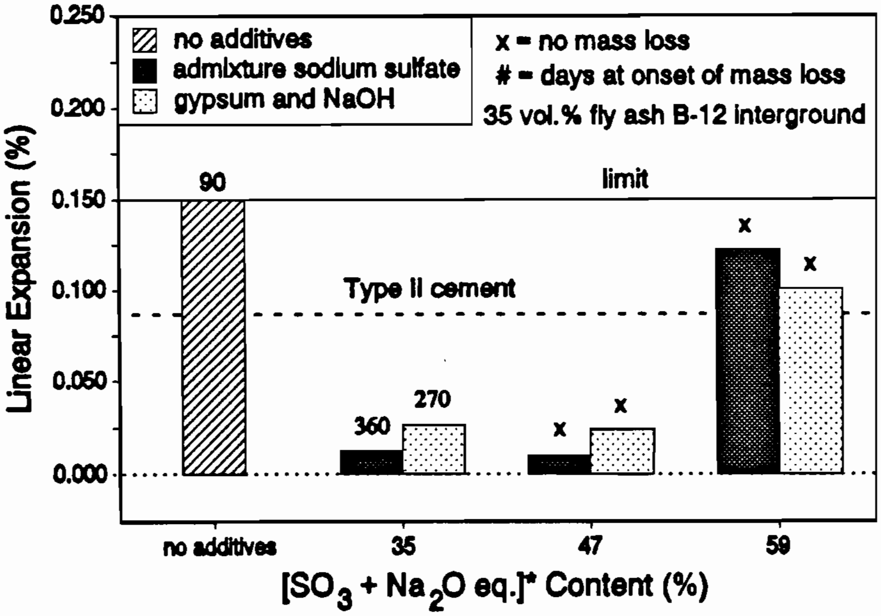


Figure 9.40 Linear Expansions of Type II Cement Concrete Containing Interground Fly Ash B-12 and Various Mineral and Chemical Additives

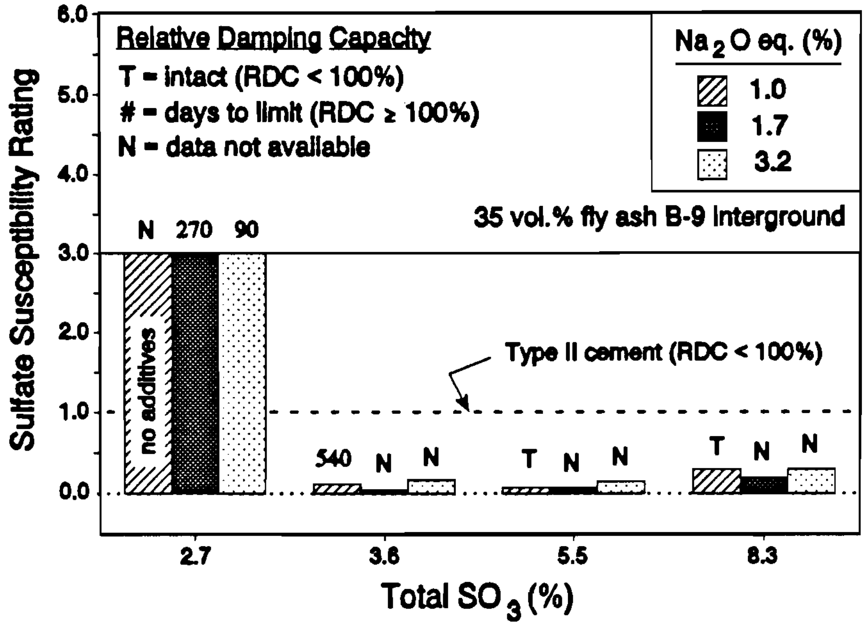


Figure 9.41 Sulfate Susceptibility Ratios of Type II Cement Concrete Containing Interground Fly Ash B-9, Additional Gypsum, and Sodium Hydroxide Additive

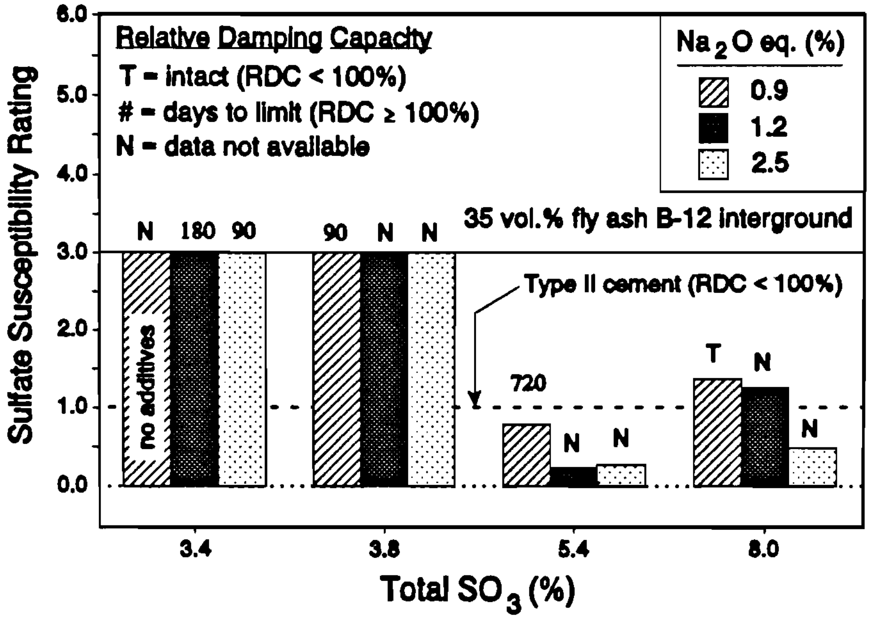


Figure 9.42 Sulfate Susceptibility Ratios of Type II Cement Concrete Containing Interground Fly Ash B-12, Additional Gypsum, and Sodium Hydroxide Additive

less than 100 percent. All mixtures which contained sodium hydroxide without additional gypsum exhibited relative damping capacities greater than 100 percent.

Sulfate Susceptibility Ratings and relative damping capacities for mixtures containing sodium sulfate additive are compared with those containing gypsum and sodium hydroxide in Figures 9.43 and 9.44. Total sulfate and alkali contents are the same for mixtures with the same [SO_3+Na_2O eq.]* content, independent of admixtures used. The use of gypsum and sodium hydroxide appears to be equally effective in reducing sulfate susceptibility. An [SO_3+Na_2O eq.]* content of 47 percent seems to be optimum in terms of sulfate resistance.

9.4.6 PERMEABILITY

Increasing the proportion of gypsum in fly ash cement without increasing alkali content did not influence concrete permeability, as shown in Figures 9.45 and 9.46. However, when sodium hydroxide additive accompanied the increased proportion of gypsum, concrete permeability at 13 days was reduced significantly and concrete permeability at 91 days was reduced slightly. The 91-day permeabilities of all fly ash cement concretes were less than half the permeability of Type II cement concrete without fly ash.

The permeability of mixtures containing additional gypsum and sodium hydroxide are compared with those of mixtures containing sodium sulfate additive in Figures 9.47 and 9.48. Total sulfate and alkali contents were the same for mixtures with the same [SO_3+Na_2O eq.]* content, independent of admixtures used. All mixtures containing mineral and chemical additives were less permeable than the plain fly ash cement concrete. Relative to additions of gypsum and sodium hydroxide, additions of sodium sulfate additive were more effective in reducing concrete permeability, particularly at 13 days.

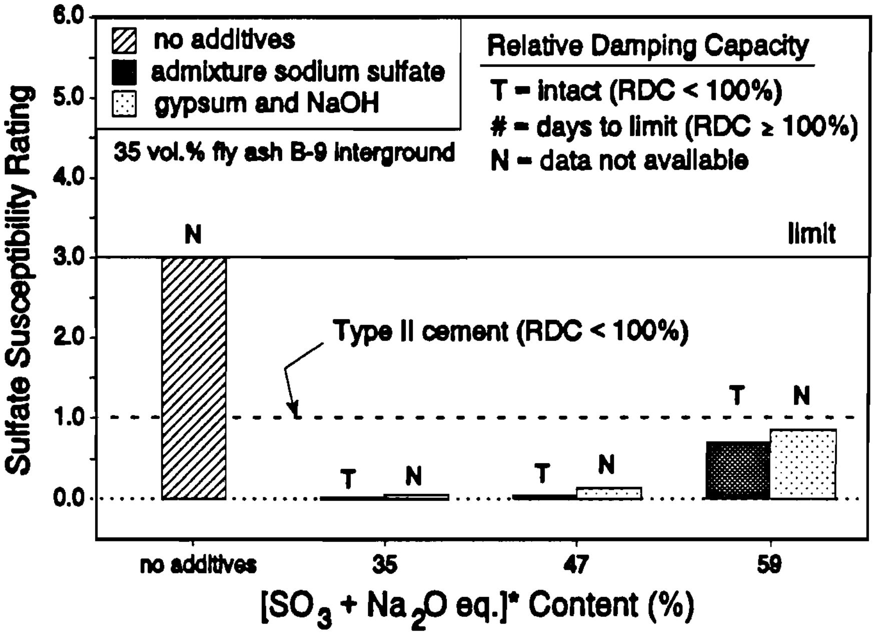


Figure 9.43 Sulfate Susceptibility Ratios of Type II Cement Concrete Containing Interground Fly Ash B-9 and Various Mineral and Chemical Additives

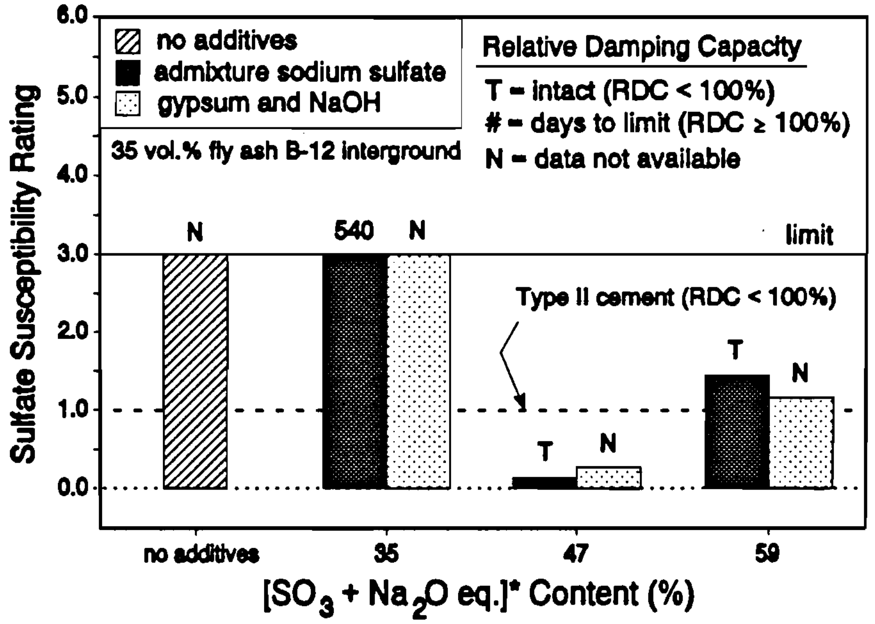


Figure 9.44 Sulfate Susceptibility Ratios of Type II Cement Concrete Containing Interground Fly Ash B-12 and Various Mineral and Chemical Additives

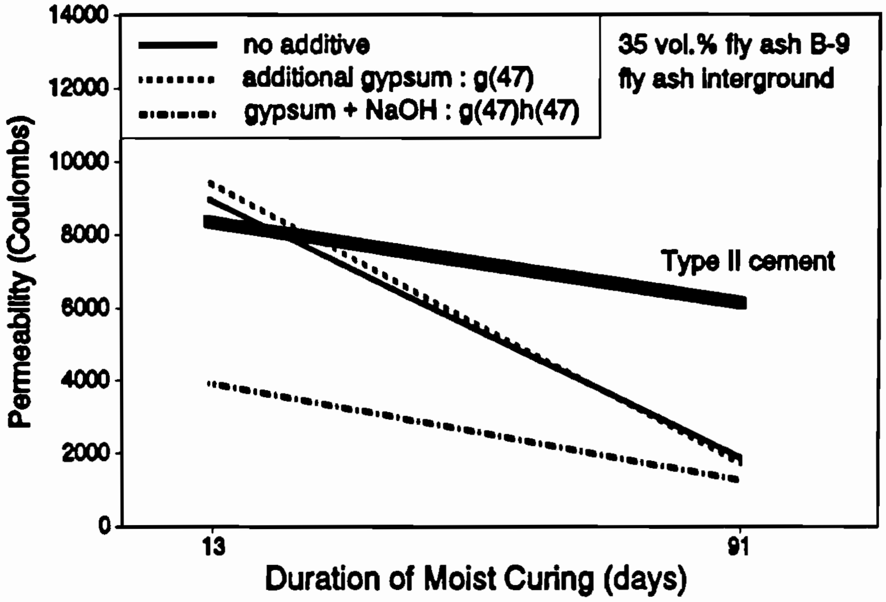


Figure 9.45 Permeabilities of Type II Cement Concrete Containing Interground Fly Ash B-9, Additional Gypsum, and Sodium Hydroxide Additive

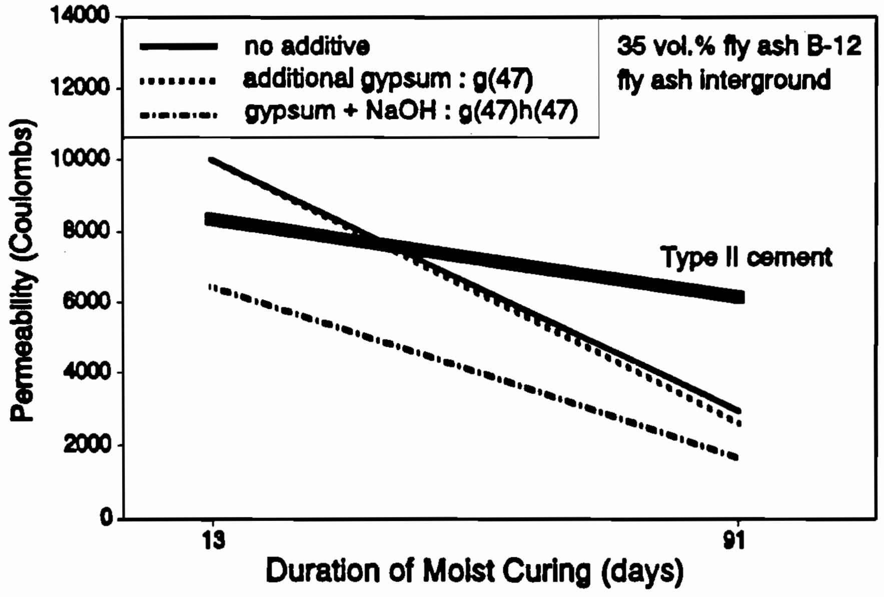


Figure 9.46 Permeabilities of Type II Cement Concrete Containing Interground Fly Ash B-12, Additional Gypsum, and Sodium Hydroxide Additive

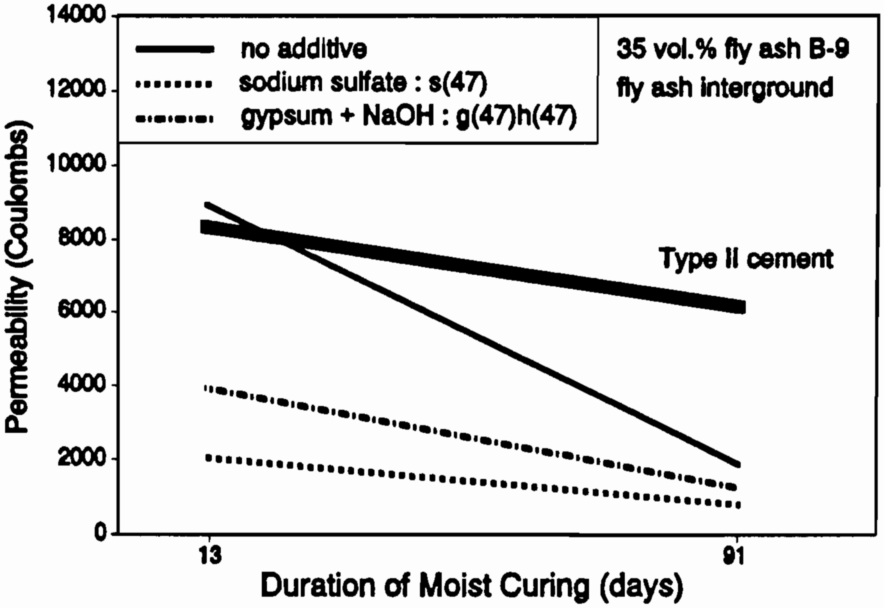


Figure 9.47 Permeabilities of Type II Cement Concrete Containing Interground Fly Ash B-9 and Various Mineral and Chemical Additives

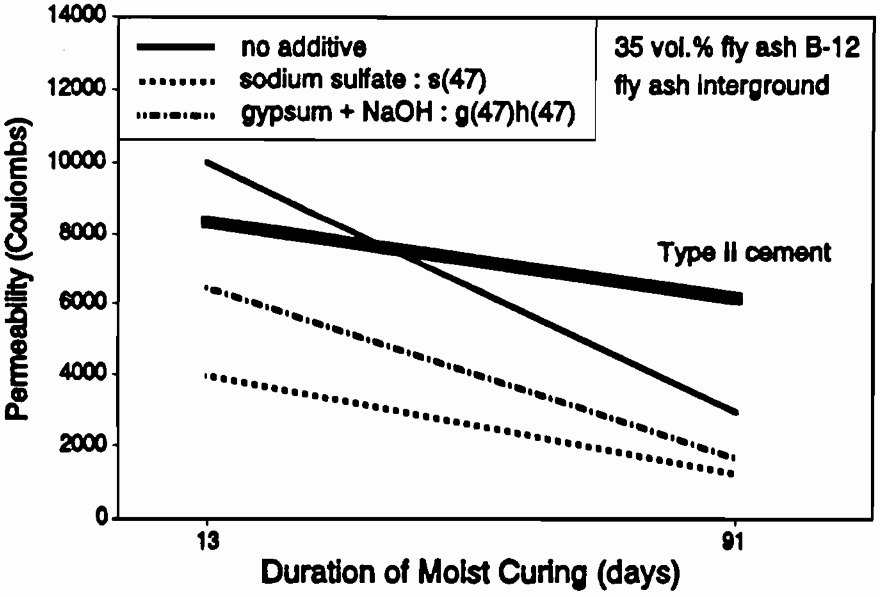


Figure 9.48 Permeabilities of Type II Cement Concrete Containing Interground Fly Ash B-12 and Various Mineral and Chemical Additives

9.5 SUMMARY

The primary objective of this portion of the study was to investigate the effects of high sulfate and/or high alkali contents on the sulfate resistance of fly ash cement concrete. The concrete mixtures included in this portion of the study were previously determined to be highly susceptible to sulfate attack when no adjustments were made in their sulfate or alkali contents. Mixtures consisted of Type II cement with partial replacement by five Type B fly ashes. The replacement level of fly ash for cement remained constant at 35 percent by volume. Concrete was designed for 5½ sacks of cement per cubic yard of concrete. Mixing water was added until a fresh concrete slump of 5 to 7 inches was attained.

Cement sulfate and alkali contents were increased concurrently by adding sodium sulfate as a chemical additive. Cement sulfate contents were increased individually by intergrinding additional gypsum. Cement alkali contents were increased individually by adding sodium hydroxide as a chemical additive.

Sodium sulfate additive generally decreased the mixing water requirements. The additive increased compressive strengths at 3 days and had variable effects on strengths at 28-days.

The sulfate resistance of Type B fly ash/Type II cement concrete was improved by adding sodium sulfate to the concrete mixing water. At optimum sulfate resistance, total SO_3 contents ranged from 4.2 percent to 6.7 percent and equivalent Na_2O contents ranged from 1.8 percent to 4.1 percent.

Mixing water requirements were increased if the chemically-modified cement contained high levels of alkali and low levels of sulfate. Mixing water requirements were also increased if the chemically-modified cement contained high levels of sulfate without high levels of alkali. Mixing water requirements were decreased if the cement contained high levels of both alkali and sulfate.

When alkali and sulfate were increased by adding sodium hydroxide and gypsum, compressive strengths were lower than the strengths of similar mixtures containing sodium sulfate additive. Strengths were particularly low for mixtures which contained high dosages of sodium hydroxide. The adverse effects of sodium hydroxide on strength may be attributed to the reduced solubility of calcium hydroxide (218).

Additions of gypsum and sodium hydroxide were as effective as additions of sodium sulfate in improving the sulfate resistance of fly ash concrete.

Type B fly ash/Type II cement concrete containing additional gypsum without additions of sodium hydroxide were also resistant to sulfate attack. Total SO_3 contents of these sulfate resistant mixtures ranged from 3.6 percent to 8.3 percent.

Relative to concrete containing fly ash B-12, the sulfate resistance of concrete containing fly ash B-9 was improved more significantly by increases in alkali and/or sulfate contents. Relative to fly ash B-12, fly ash B-9 contained a lower proportion of calcium and a higher proportion of glassy material. Fly ash B-9 was also characterized as having a lower Modified Calcium Aluminate Potential.

Moderate additions of both alkali and sulfate decreased concrete permeability, particularly at early ages. Therefore, the sulfate resistance of mixtures containing both alkali and sulfate additives may be partially attributable to changes in the physical properties of concrete.

When additional gypsum was interground with the fly ash cements and alkali contents remained unchanged, concrete permeability was not affected. Therefore, the improved resistance to sulfate attack of these mixtures were attributed to changes in the composition of hydration products.

CHAPTER 10

BLENDED FLY ASH CEMENT CONCRETE CONTAINING LARGE PROPORTIONS OF FLY ASH

10.1 INTRODUCTION

In order to maximize fly ash utilization, concrete with large proportions of fly ash has recently been a popular topic for research (94, 103, 149, 180, 236, 306, 416). These mixtures are often termed "high-volume fly ash concrete".

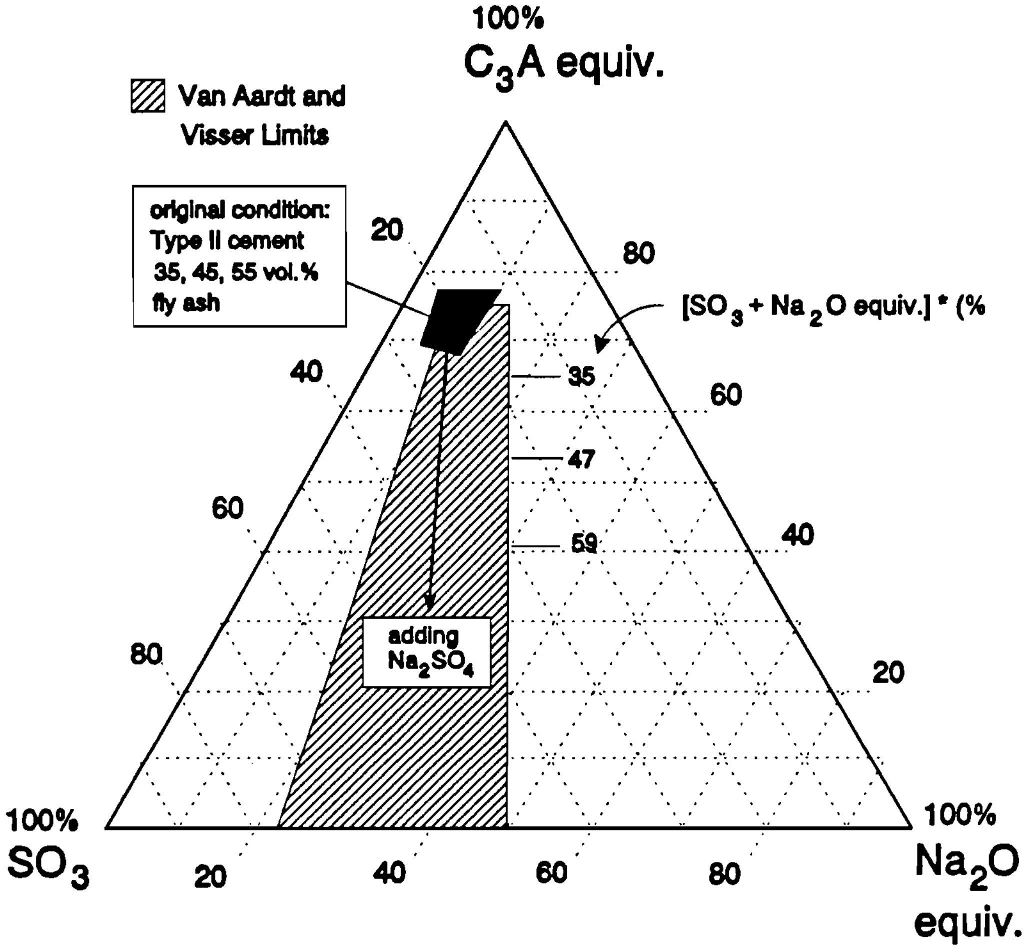
The objective of this portion of the study was to investigate the compressive strength, permeability, and sulfate resistance of mixtures containing large proportions of fly ash. Type II cement was partially replaced by two Type B ashes. The fly ash was interground with cement clinker and gypsum at replacement levels of 45 and 55 percent by volume. Mixtures containing 35 percent interground fly ash, which were presented in Chapter 8, are included in this chapter for comparison purposes.

All mixtures were designed for 5½ sacks of cement per cubic yard of concrete. Mixing water was added until a fresh concrete slump of 5 to 7 inches was attained.

Also, since the sulfate resistance and permeability characteristics of concrete containing 35 volume percent Type B fly ash were improved significantly by the addition of sodium sulfate as a chemical additive, the effects of sodium sulfate on mixtures with high fly ash contents were also investigated.

10.2 PROPORTIONS OF SODIUM SULFATE ADDITIVE

Additions of sodium sulfate were controlled by [SO_3 + Na_2O equiv.]* contents, similar to the procedure used for mixtures containing 35 volume percent fly ash (Chapter 9). Sodium sulfate dosages were designed to result in similar ternary weight percentages of



$$[SO_3 + Na_2O\ \text{equiv.}]^* = \frac{SO_3 + Na_2O\ \text{equiv.}}{C_3A\ \text{equiv.} + SO_3 + Na_2O\ \text{equiv.}} \times 100\%$$

Figure 10.1 Ternary (C_3A eq.-SO_3-Na_2O eq.) Compositions of Type B Fly Ash/Type II Cement Mixtures with High Proportions of Fly Ash equivalent C_3A as the fly ash cements containing 35 volume percent ash, as shown in Figure 10.1.

Since equivalent C_3A contents of fly ash cements increased with the proportion of fly ash, dosages of sodium sulfate also increased with the proportion of fly ash. Dosages of sodium sulfate required to attain [SO_3 + Na_2O equiv.]* contents of 35, 45, ang 59 percent are shown in Appendix C. Total weight percentages of equivalent Na_2O, SO_3, and equivalent C_3A are also shown in Appendix C.

10.3 EFFECTS OF BLENDING ON THE PHYSICAL PROPERTIES OF CEMENT

Specific gravities and fineness of blended cements were measured. These measured properties were compared with calculated properties of similar cements with fly ash added as a mineral admixture. The specific gravities of non-interground cements were calculated by the procedure recommended in ASTM C-127 for aggregate blends:

$$SG = \frac{W_1 + W_2}{V_1 + V_2} = \frac{100}{\frac{P_1}{G_1} + \frac{P_2}{G_2}}\text{, where} \qquad (10.1)$$

SG = average specific gravity,
W_i = weight in grams for solids 1 and 2,
V_i = volume in grams for solids 1 and 2,
P_i = weight percentage of solids 1 and 2, and
G_i = specific gravity of solids 1 and 2.

A simple weighted average was used for calculating the percent retained on #325 sieve for non-interground fly ash cements:

$$\text{Total Percent Retained} = P_1 (R_1) + P_2 (R_2)\text{ , where} \qquad (10.2)$$

P_i = weight percentage of solids 1 and 2 and
R_i = percent retained on #325 sieve for solids 1 and 2.

Intergrinding fly ash increased the specific gravity of fly ash cements, as shown in Figure 10.2. The effects of intergrinding were most prominent for fly ash B-9, which had the lowest specific gravity. The specific gravities of fly ashes B-9 and B-12 were 2.58 and 2.79, respectively. The effects of intergrinding increased in prominence with increases in the percent replacement of cement with fly ash.

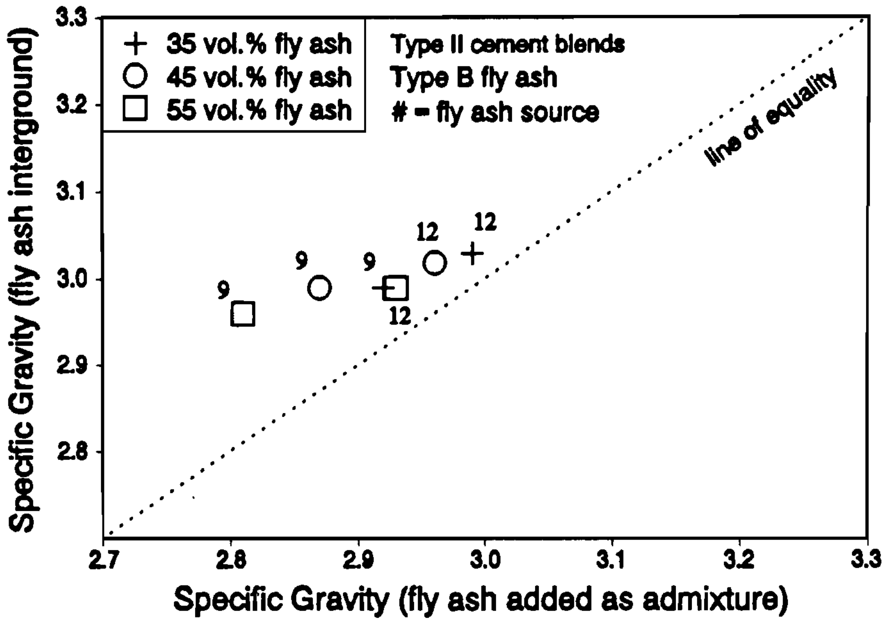


Figure 10.2 Specific Gravities of Type II Cement Containing High Proportions of Type B Fly Ash

Intergrinding fly ash decreased or had no significant effect on the fineness of fly ash cements, as shown in Figure 10.3. The effects of intergrinding were most prominent for fly ash B-9, which contained the highest proportion of coarse fly ash particles. The proportions of particles retained on the #325 sieve for fly ashes B-9 and B-12 were 22.0 percent and 10.4 percent, respectively. The effects of intergrinding increased in prominence with increases in the percent replacement of cement with fly ash.

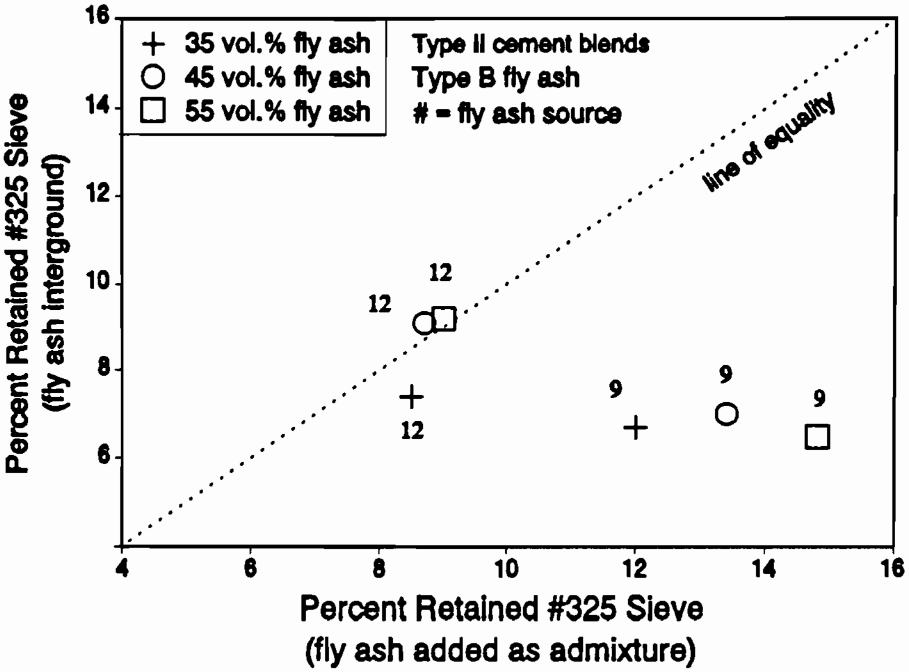


Figure 10.3 Fineness of Type II Cement Containing High Proportions of Type B Fly Ash

10.4 MIXING WATER REQUIREMENT

Mixing water requirements of mixtures containing 45 percent and 55 percent fly ash were either lower than or approximately equal to the mixing water requirements of mixtures containing 35 percent fly ash, as shown in Figures 10.4 and 10.5. Water requirements decreased slightly with increases in the additions of sodium sulfate. The effects of sodium sulfate on water requirements were most prominent for mixtures containing 35 volume percent fly ash.

10.5 COMPRESSIVE STRENGTH DEVELOPMENT

In terms of compressive strength, mixtures behaved differently, depending on the calcium oxide content of the Type B fly ash. Relative to mixtures containing 35 and 45 percent of fly ash B-9, the compressive strength at 28 days for the mixture containing 55 percent fly ash was lower, as shown in Figure 10.6. For mixtures containing fly ash B-12, compressive strengths at 28 days were similar between mixtures containing different

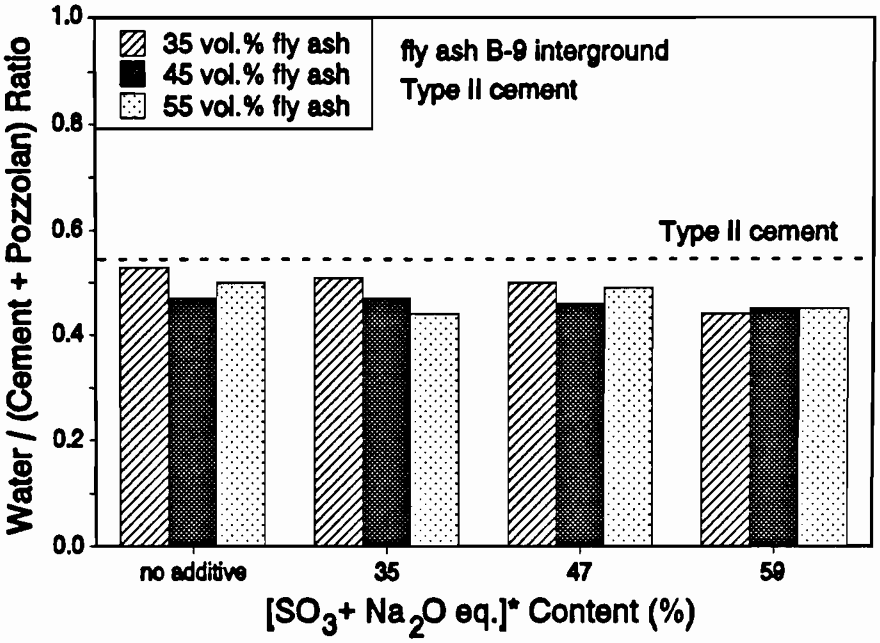


Figure 10.4 Mixing Water Requirements of Type II Cement Concrete Containing High Proportions of Interground Fly Ash B-9

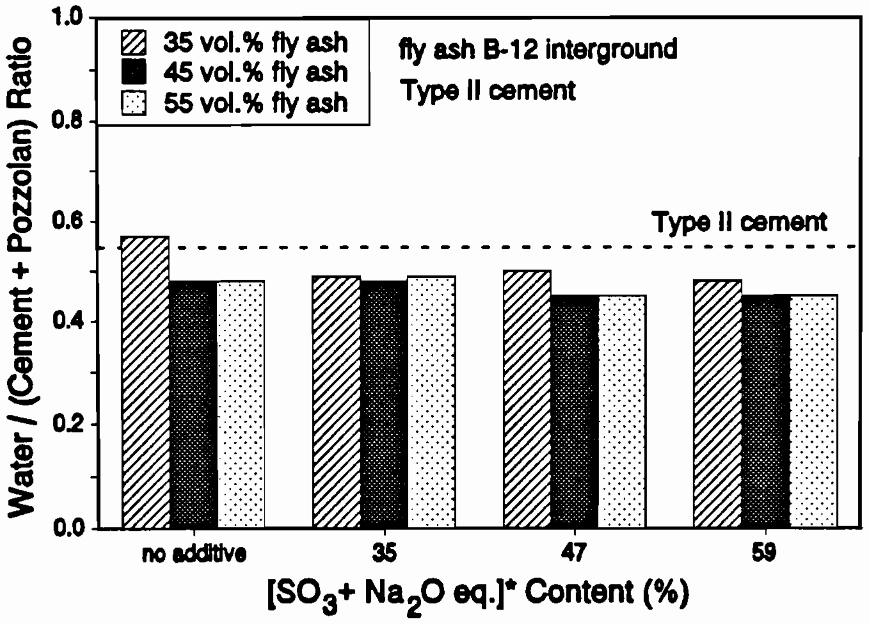


Figure 10.5 Mixing Water Requirements of Type II Cement Concrete Containing High Proportions of Interground Fly Ash B-12

proportions of fly ash, as shown in Figure 10.7. Fly ash B-9 and B-12 contained 23.1 percent and 33.9 percent calcium oxide, respectively.

The early strengths of mixtures which contained fly ash B-9 decreased as the proportion of fly ash increased. The early strengths of mixtures which contained fly ash B-12 were not significantly affected by the proportion of fly ash. The higher CaO content of fly ash B-12 promoted more cementitious activity.

Early-age compressive strengths were increased by the additions of sodium sulfate. These increases were most prominent for mixtures containing high proportions of the fly ash with the lower calcium content (ash B-9).

Compressive strengths at 28 days generally decreased with the inclusion of sodium sulfate. The rate at which strength was increasing at 28 days also decreased with the inclusion of sodium sulfate, particularly for mixtures containing large proportions of fly ash.

For mixtures containing 35 volume percent fly ash, the optimum dosage of sodium sulfate in terms of compressive strength was the highest dosage utilized. For mixtures containing 45 and 55 volume percent fly ash, the optimum dosage of sodium sulfate in terms of compressive strength was the lowest dosage utilized. These differences are related to the dependence of sodium sulfate dosage on the proportion of fly ash: the proportions of sodium sulfate that were required to attain designated [SO_3 + Na_2O eq.]* contents increased with increases in the proportion of fly ash.

10.6 SULFATE SUSCEPTIBILITY

10.6.1 Linear Expansion and Mass Loss

When sodium sulfate was not added to the mixing water, mixtures containing fly ash at levels of 45 percent and 55 percent expanded less than the mixtures containing fly ash at a level of 35 percent, as shown in Figures 10.8 and 10.9. The mixture containing 55 volume percent of the lower calcium Type B fly ash, B-9, had not experienced any expansion or mass loss by 720 days of exposure to 10 percent sodium sulfate solution.

All fly ash cement concrete containing low and moderate additions of sodium sulfate suffered minimal expansions. The highest level of sodium sulfate additive caused internal

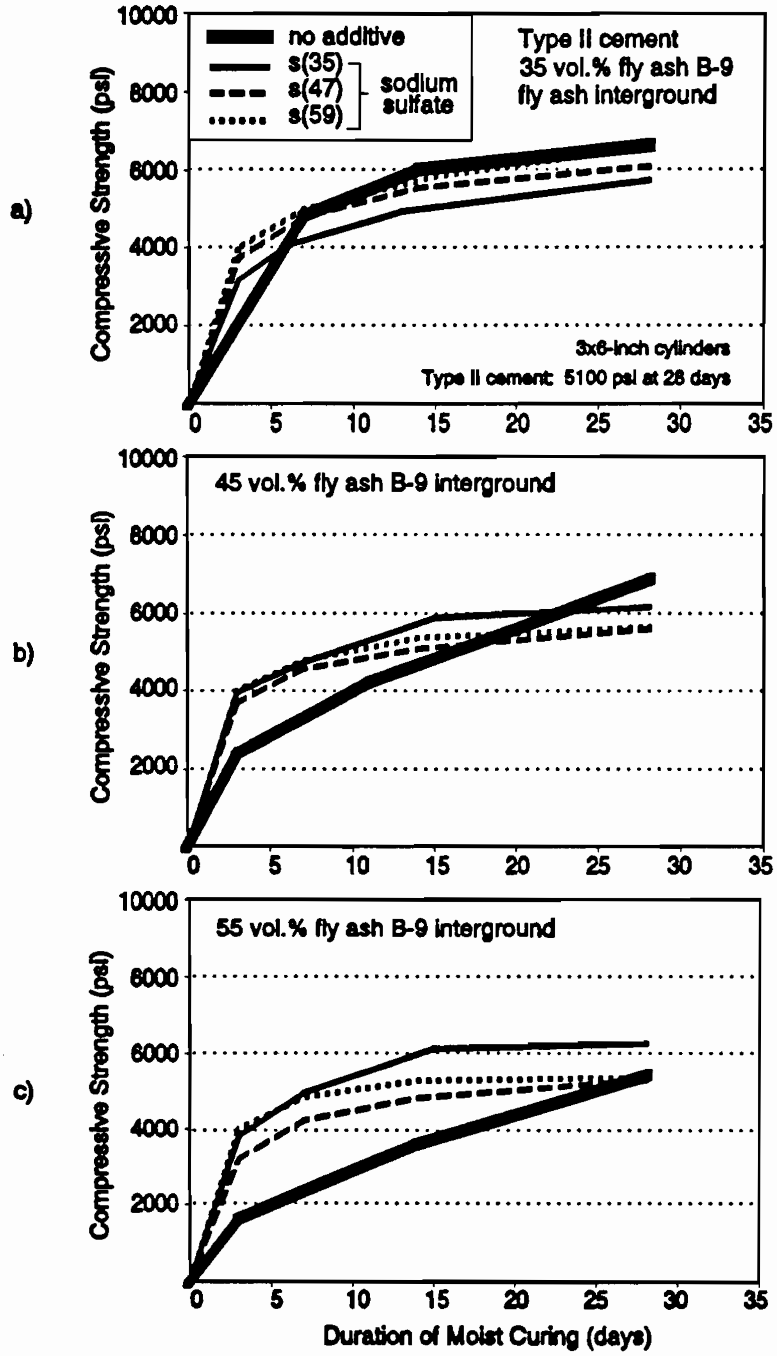


Figure 10.6 Compressive Strength Developments for Type II Cement Concrete Containing Interground Fly Ash B-9 at Levels of a) 35%, b) 45%, and c) 55% by Volume and Sodium Sulfate Additive

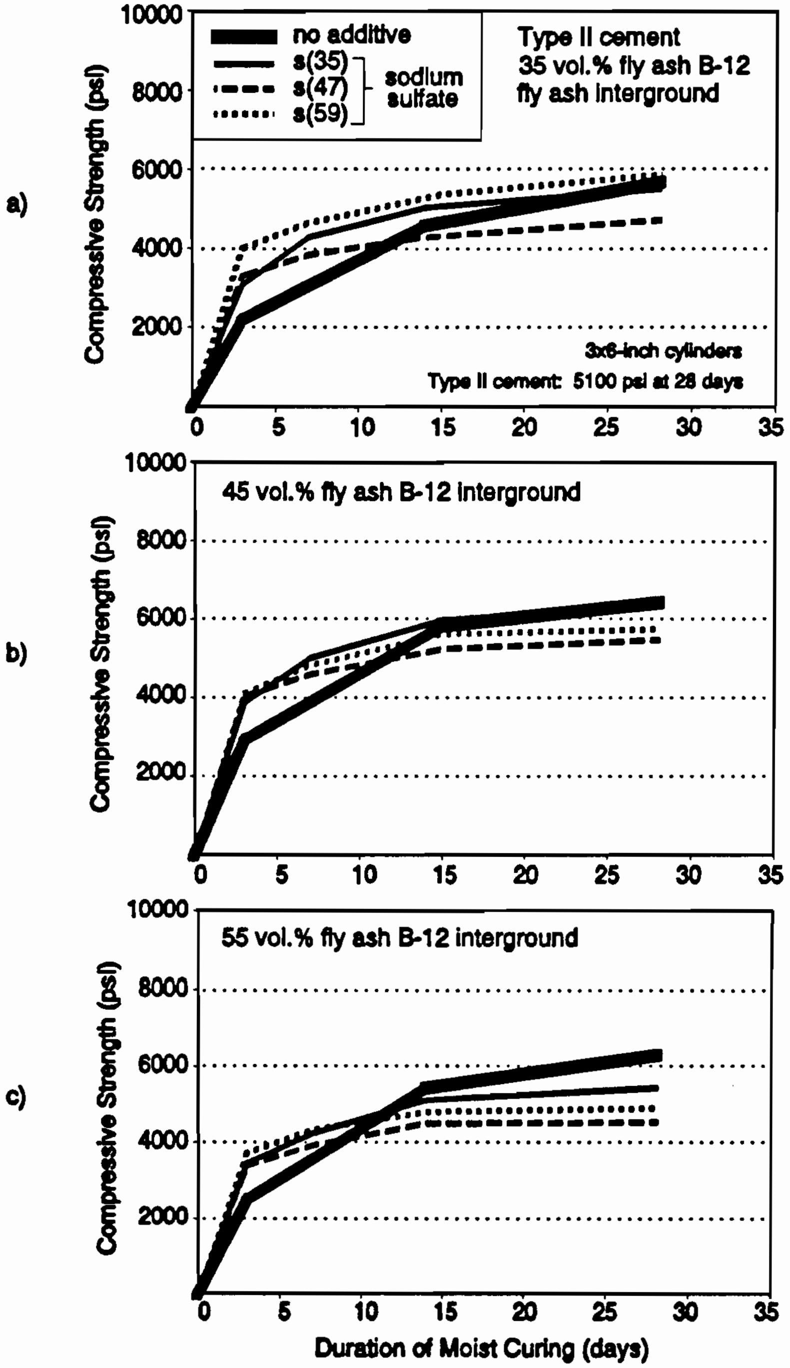


Figure 10.7 Compressive Strength Developments for Type II Cement Concrete Containing Interground Fly Ash B-12 at Levels of a) 35%, b) 45%, and c) 55% by Volume and Sodium Sulfate Additive

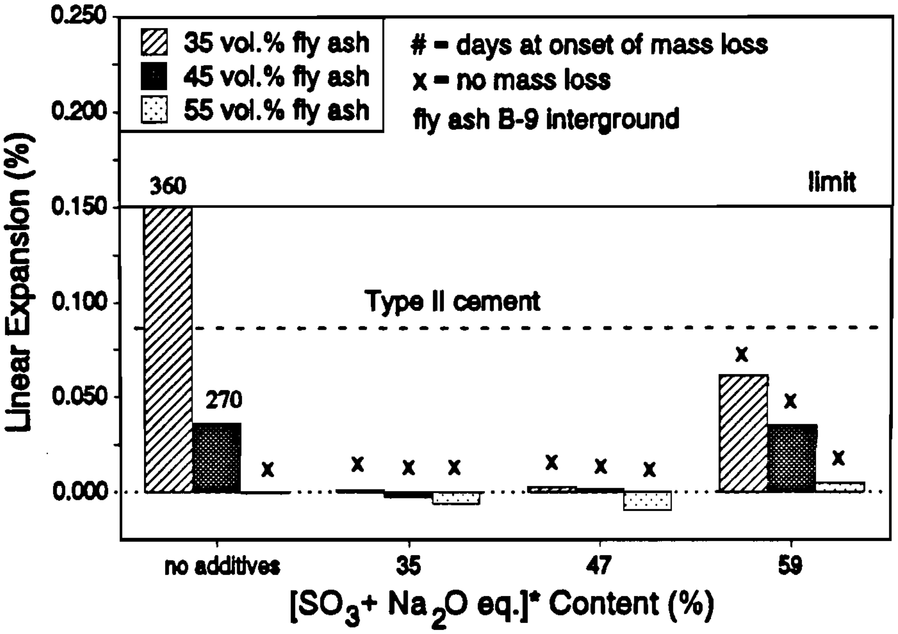


Figure 10.8 Linear Expansions of Type II Cement Concrete Containing High Proportions of Interground Fly Ash B-9 and Sodium Sulfate Additive

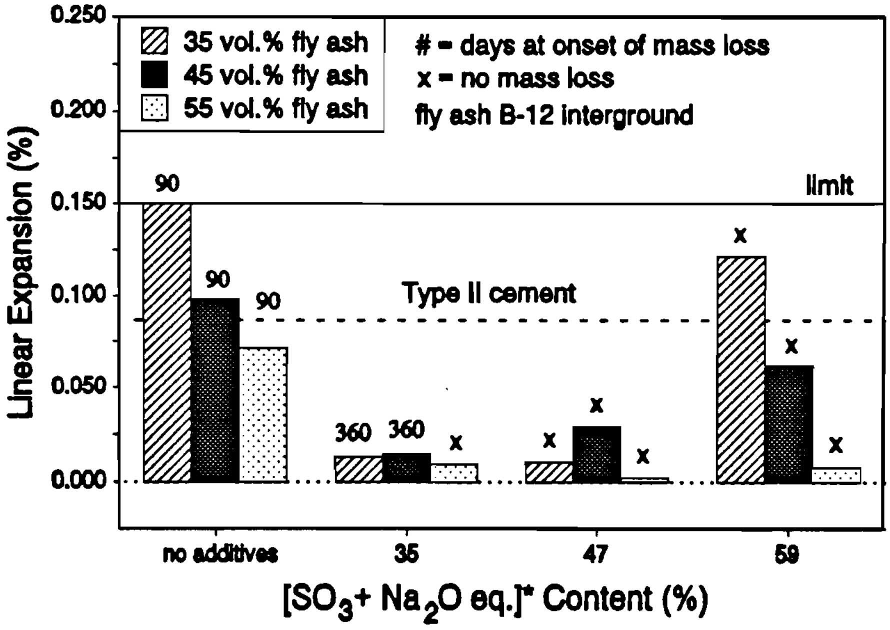


Figure 10.9 Linear Expansions of Type II Cement Concrete Containing High Proportions of Interground Fly Ash B-12 and Sodium Sulfate Additive

sulfate attack for mixtures containing low proportions of fly ash (35 and 45 percent by volume). The mixtures containing 55 percent fly ash and the highest proportion of sodium sulfate additive did not experience internal sulfate attack. Therefore, the portland cement portions of the fly ash cements may have been largely responsible for the slowly reacting calcium aluminates.

10.6.2 Sulfate Susceptibility Rating

The Sulfate Susceptibility Rating, as defined in Chapter 4, is a single-value parameter which depicts the rate of deterioration of concrete. This parameter includes deterioration in the forms of expansion and mass loss. It permits comparisons between the sulfate susceptibilities of all mixtures.

None of the fly ash cements with [SO_3+Na_2O eq.]* contents of 47 percent experienced significant sulfate deterioration, as shown in Figures 10.10 and 10.11. In terms of improving the sulfate resistance of all mixtures, this dosage seems to be optimum. Total SO_3 contents of these mixtures ranged from 5.4 percent to 6.6 percent. Equivalent Na_2O contents of these mixtures ranged from 2.5 percent to 4.3 percent.

The mixtures containing 35 percent fly ash and an [SO_3+Na_2O eq.]* content of 47 percent did not show deterioration in terms of Relative Damping Capacity. The mixture containing 55 percent fly ash B-9 without sodium sulfate additive also did not show deterioration in terms of Relative Damping Capacity.

10.7 PERMEABILITY

After 13 days of moist curing, the permeabilities of all fly ash cement mixtures without sodium sulfate were higher than the Type II cement mixture, as shown in Figures 10.12 and 10.13. After 91 days of moist curing, the permeabilities of all fly ash cement mixtures without sodium sulfate were lower than the Type II cement mixture.

The permeabilities of fly ash cement concrete decreased with the addition of sodium sulfate, particularly at 13 days. Decreases in permeability were most prominent for mixtures containing fly ash B-9. This may have been related to the high proportion of glass in fly ash B-9 (80.5 percent), relative to the proportion of glass in fly ash B-12 (61.2 percent).

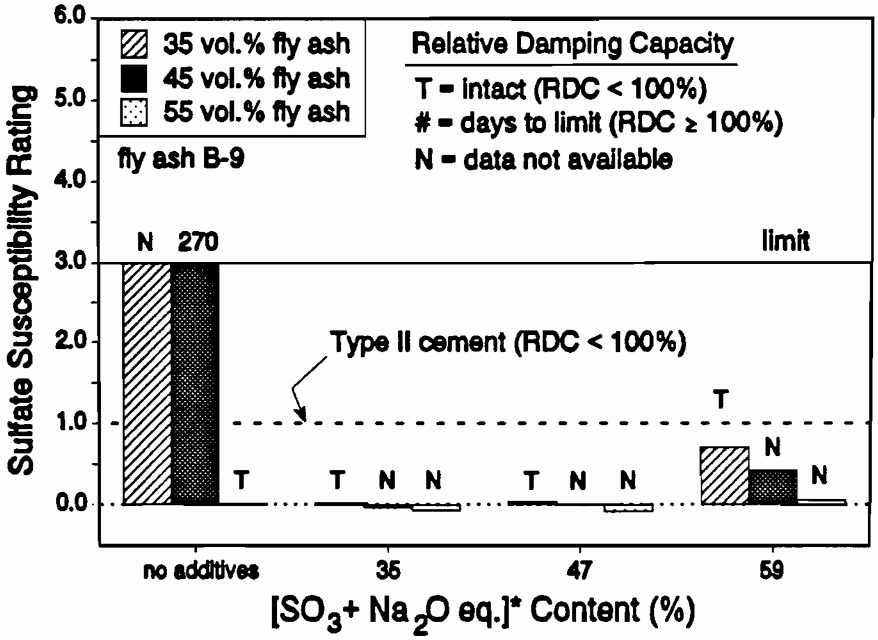


Figure 10.10 Sulfate Susceptibility Ratios of Type II Cement Concrete Containing High Proportions of Interground Fly Ash B-9 and Sodium Sulfate Additive

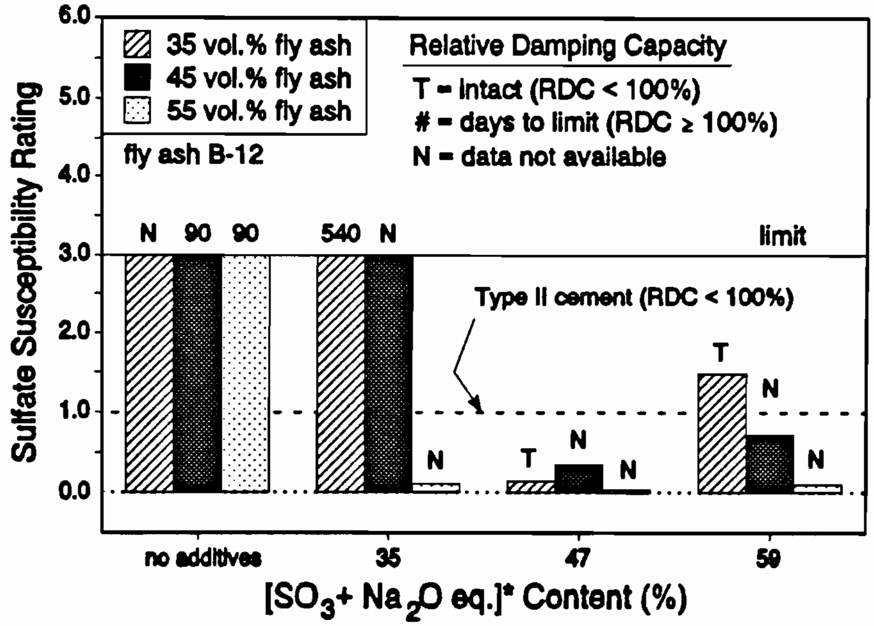


Figure 10.11 Sulfate Susceptibility Ratios of Type II Cement Concrete Containing High Proportions of Interground Fly Ash B-12 and Sodium Sulfate Additive

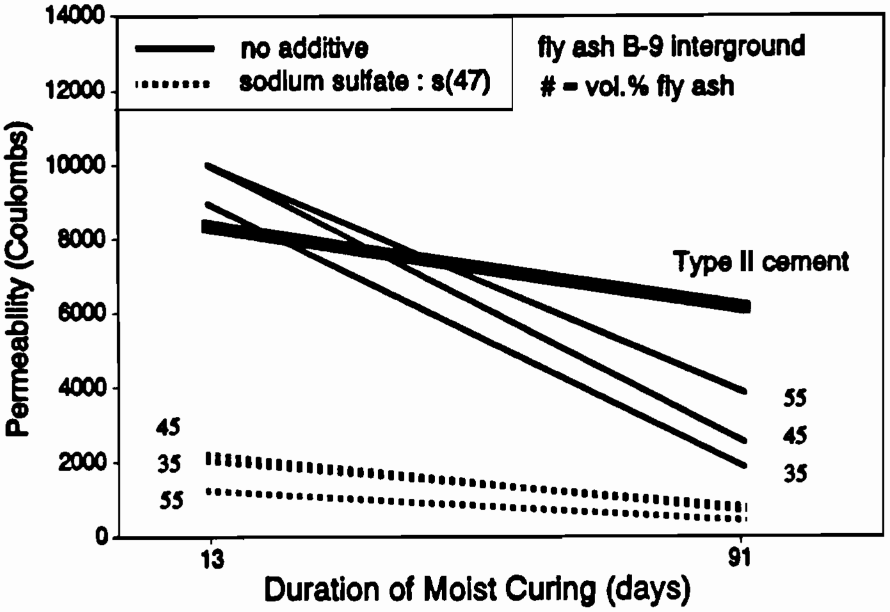


Figure 10.12 Permeabilities of Type II Cement Concrete Containing High Proportions of Interground Fly Ash B-9 and Sodium Sulfate Additive

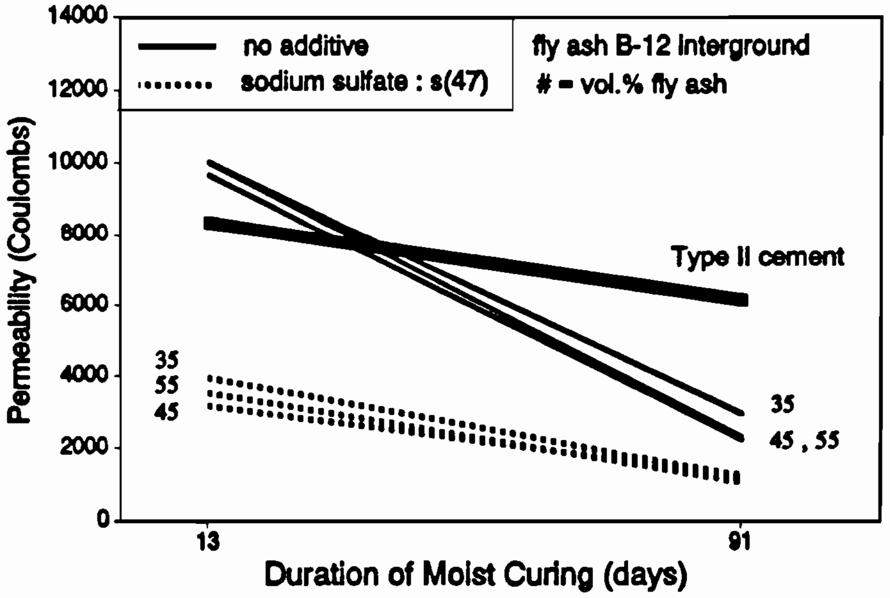


Figure 10.13 Permeabilities of Type II Cement Concrete Containing High Proportions of Interground Fly Ash B-12 and Sodium Sulfate Additive

10.8 SUMMARY

The objective of this portion of the study was to investigate the compressive strength, permeability, and sulfate resistance of concrete containing blended cements with large proportions of fly ash. Type II cement was partially replacement by two Type B ashes: B-9 and B-12. The fly ash was interground with cement clinker and gypsum at replacement levels of 45 and 55 percent by volume. Concrete which included 35 percent interground fly ash, as presented in Chapter 8, were included in this chapter for comparison purposes.

All mixtures were designed for 5½ sacks of cement per cubic yard of concrete. Mixing water was added until a fresh concrete slump of 5 to 7 inches was attained.

Since the sulfate resistance and permeability characteristics of concrete containing 35 volume percent Type B fly ash were improved significantly by the addition of sodium sulfate as a chemical additive, the effects of sodium sulfate on mixtures with high fly ash contents were also investigated.

Intergrinding fly ash with cement clinker and gypsum increased the specific gravity and decreased the proportion of coarse particles (+45 μm) in fly ash cements. Effects were most significant for the fly ash which was initially characterized as having the lowest specific gravity and the highest proportion of coarse particles.

Relative to blends containing 35 percent fly ash, blends containing 45 and 55 percent fly ash required equal or lesser quantities of mixing water.

Compressive strength, particularly at early ages, decreased as the proportion of fly ash B-9 increased. The proportion of fly ash B-12 did not significantly affect compressive strength. Fly ash B-12 had a higher CaO content than B-9 and therefore promoted more cementitious activity.

The only Type B fly ash/Type II cement concrete which was resistant to sulfate attack in the absence of sodium sulfate additive was the mixture containing fly ash B-9 at a level of 55 percent by volume. It had suffered no expansion and no mass loss within the 720-day test duration. Fly ash B-9 contained a moderately high calcium content, 23.1 percent, and a high proportion of glassy material, 80.5 percent.

Relative to the permeability of concrete containing 35 percent fly ash, the permeability of concrete containing 45 and 55 percent fly ash was either slightly higher or not significantly different.

Mixing water requirements for all blended cement concretes were either decreased or not significantly affected by the inclusion of the sodium sulfate additive.

Compressive strengths at 3 days were increased by the inclusion of the sodium sulfate additive, particularly for mixtures containing high proportions of fly ash. Compressive strengths at 28 days were generally decreased by the inclusion of sodium sulfate.

The sulfate resistance of these high-volume Type B fly ash concretes were improved by adding sodium sulfate to the mixing water. Total sulfate contents of cements ranged from 3.6 percent to 6.6 percent. Total alkali contents of cements ranged from 1.2 percent to 4.3 percent.

Relative to cement blends containing fly ash B-12, cement blends containing fly ash B-9 exhibited greater improvements in sulfate resistance by the inclusion of a sodium sulfate additive. Fly ash B-9 contained a lower proportion of bulk CaO and a higher proportion of glassy material.

Inclusion of the sodium sulfate additive significantly reduced the permeability of blended fly ash cement concrete, particular at early ages. Reduced permeability was at least partially responsible for the improvements in resistance to sulfate attack.

The susceptibility of blended cements to internal sulfate attack decreased as the proportion of Type B fly ash increased. Internal sulfate attack is caused by high concentrations of sulfate in the initial concrete mixture. If the sulfates are still available after the concrete has hardened, expansive reactions are possible. Therefore, in an alkaline environment, the reactive calcium aluminates which come from portland cement may be the portion which reacts slowly enough to still be available after the concrete has hardened.

CHAPTER 11

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

11.1 SUMMARY

11.1.1 RESEARCH OBJECTIVES

The primary objectives of this study were:

1) to recommend a criterion, based on physical and compositional characteristics, for selecting fly ash to be used in concrete in sulfate exposure environments;
2) to recommend an exposure test for future studies on the sulfate resistance of concrete; and
3) to recommend alternatives for improving the performance of non-sulfate resistant fly ash concrete mixtures.

11.1.2 EXPERIMENTAL PROCEDURE

The long-term resistance of concrete mixtures to sulfate attack was evaluated with a sulfate exposure laboratory test. Sulfate exposure in the laboratory involved immersion of 3x6-inch concrete cylinders in 10 percent sodium sulfate solution. The exposure cylinders were monitored for deterioration for durations of up to 4 years.

In order to satisfy the three primary objectives of this study, the experimental program included the concrete mixture design variables shown in Table 11.1.

Results of this study were presented and discussed in the following order:

1) evaluation of the sulfate exposure test, including repeatability and duration requirements,
2) ASTM Type II cement concrete containing fly ash as a mineral admixture,
3) ASTM Type I cement concrete containing fly ash as a mineral admixture,
4) fly ash cement concrete with a high cement factor,

5) blended fly ash cement concrete,
6) fly ash cement concrete containing high sulfate and/or high alkali contents, and
7) blended fly ash cement concrete containing large proportions of fly ash.

The presentation of results for concrete mixtures included mixing water requirements, compressive strength developments, permeabilities, and sulfate exposure data.

Table 11.1 Variables for Concrete Mixtures Exposed to Laboratory Sulfate Environment

Cement Type	Type II		Type I-L		Type I-H	
Fly Ash	12 Type A			12 Type B		
Proportion of Fly Ash (vol.%)	0	25	35		45	55
Method of Fly Ash Inclusion	as admixture			interground		
Mixture Design Cement Factor	5½ sacks/cu.yd.			7 sacks/cu.yd.		
Proportion of Gypsum in Blended Cements	4 levels					
Sodium Hydroxide Additive in Mixing Water	4 levels					
Sodium Sulfate Additive in Mixing Water	7 levels					

11.2 DISCUSSION OF RESULTS

11.2.1 PREDICTING THE EFFECTS OF FLY ASH ON THE SULFATE RESISTANCE OF CONCRETE

A parameter termed Modified Calcium Aluminate Potential was presented as a method for predicting the effects of fly ash on the sulfate resistance of concrete:

$$\text{Modified CAP} = \frac{CaO^{**} + Al_2O_3^{*}}{SiO_2^{*} + Fe_2O_3^{*}}\text{, where} \tag{11.1}$$

oxide* = proportion of bulk oxide in reactive components

= (weight percent in bulk chemical analysis) - (weight percent fixed in inert crystalline phases) and

CaO** = CaO* - (weight percent CaO which is reactive during early hydration) .

Oxides which were assumed to be fixed in inert phases include:

1) SiO_2 in quartz,
2) SiO_2 and Al_2O_3 in mullite, melilite, and merwinite,
3) Fe_2O_3 (FeO) in ferrite spinel and hematite, and
4) CaO in melilite and merwinite.

Phases of CaO which were assumed to be reactive during early hydration or to not participate in sulfate-related reactions include: lime, portlandite, anhydrite, C_2S, and C_3S.

Relative to the several options studied, this parameter was found to be the most accurate for predicting the effects of fly ash on the resistance of concrete to sulfate attack. The Modified CAP model requires mineralogical information, so a semi-quantitative X-ray diffraction analysis must be performed. Since cost or time constraints may not permit an

X-ray diffraction analysis, a parameter termed Bulk Chemical Modified Calcium Aluminate Potential was offered as an alternative:

$$\text{Bulk Chemical Modified CAP} = \frac{CaO + Al_2O_3}{SiO_2 + Fe_2O_3}\text{, where} \qquad (11.2)$$

oxide = weight percentage from bulk chemical analysis.

This parameter did not differentiate between reactive and nonreactive phases, so it did not predict the effects of fly ashes, included in this study, as accurately as the mineralogy-based Modified CAP. However, relative to all models which utilized only bulk chemical analyses, the Bulk Chemical Modified CAP was the best option. Other models which did not predict the effects of fly ash as accurately as the Bulk Chemical Modified CAP included the use of fly ash Texas Type and the use of fly ash bulk calcium oxide content alone.

The manner with which these Modified CAP models predict the effects of fly ash can be described with a ternary diagram, as shown in Figure 11.1. The relative proportions of SiO_2, CaO, and Al_2O_3 which are present in reactive phases in fly ash, are closely related to the effects of fly ash on the sulfate resistance of concrete.

Ferric oxide, which is not included in the ternary diagram, affects the morphology of ettringite crystals. Changes in crystal morphology influence the tendency for crystals to cause expansion.

If either Modified Calcium Aluminate Potential model (mineralogy-based or bulk chemical-based) is used to select fly ash for sulfate resistant concrete, the limits shown in Table 11.2 can be used as criteria. Although fly ash mineralogy was influential, the effects of mineralogy were not so significant that the criteria were changed. The criteria for fly ash were developed with the objective of attaining sulfate resistance comparable to ordinary Type II cement concrete. Fly ash replacements for cement included 25, 35, and 45 percent by volume.

Fly ash with low Modified Calcium Aluminate Potentials were able to improve the sulfate resistance of a Type II cement and a Type I cement with a relatively low C_3A content (9.9 percent). These fly ash/Type II cement and fly ash/Type I cement concrete mixtures were at least as resistant to sulfate attack as ordinary Type II cement concrete.

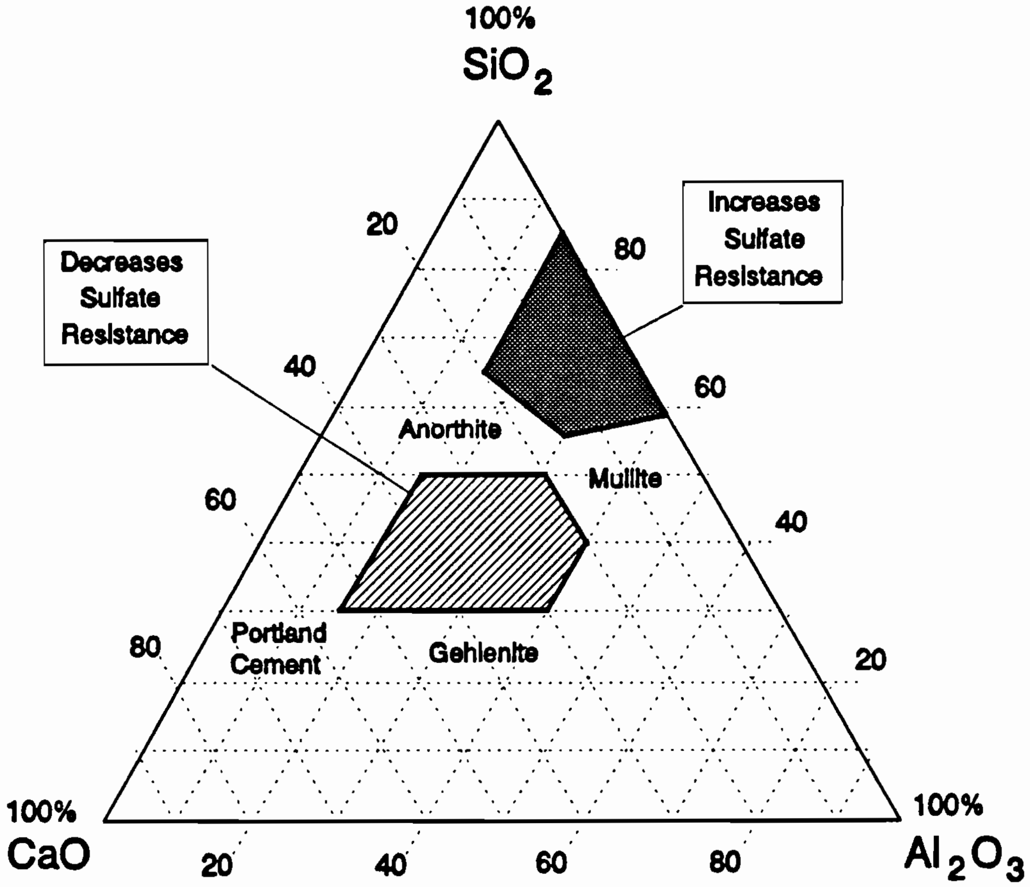


Figure 11.1 Ternary (SiO_2-CaO-Al_2O_3) Compositions of Sulfate Resistant and Non-Sulfate Resistant Fly Ashes

Fly ash, in almost all cases, was unable to significantly improve the sulfate resistance of the Type I cement with the relatively high C_3A content (11.2 percent).

The fly ash which was classified as "maybe" in Table 11.2 had variable effects on the sulfate resistance of Type II cement concrete. If a fly ash in this class is desirable in terms of cost or availability, its effects on sulfate resistance should be analyzed with a laboratory controlled exposure test.

These Modified Calcium Aluminate Potential models assume that fly ash meets the physical and chemical requirements of ASTM C-618. If a fly ash being considered does not meet this specification, it should be analyzed with a laboratory controlled exposure test. An example of these unique fly ashes would be one which contains sulfate in excess of the ASTM limit of 5.0 percent. The availability of sulfates during hydration may affect the composition of hydration products and, consequently, the resistance of hardened concrete to sulfate attack.

Table 11.2 Selection Criteria for Fly Ash to be Used in Sulfate Resistant Concrete

Cement	Modified Calcium Aluminate Potential of Fly Ash		
	≤ 0.6	0.6 < x ≤ 1.25	> 1.25
Type II (6.0% C_3A)	Yes	Maybe	No
Type I-L (9.9% C_3A)	Yes	No	No
Type I-H (11.2% C_3A)	No	No	No

Note: Fly ash replacement for cement included 25, 35, and 45 percent by volume.

Yes = sulfate resistance was comparable with ordinary Type II cement concrete
Maybe = sulfate exposure test is required
No = not as resistant to sulfate attack as ordinary Type II cement concrete

Another abnormality to look for in fly ash is excessive ferric oxide contents. Although typical ferric oxide contents of fly ash improve sulfate resistance, excessive ferric oxide contents, in conjunction with alumina, may be detrimental. This trend is analogous to the decreased sulfate resistance of portland cement when C_4AF contents exceed approximately 10 percent. The performance of fly ash cement using a fly ash which contains more than 20 percent ferric oxide should be evaluated on the basis of a laboratory controlled exposure test.

11.2.2 LABORATORY EXPOSURE TEST FOR EVALUATING THE SULFATE RESISTANCE OF CONCRETE

Even with a model available for predicting the effects of fly ash on the sulfate resistance of concrete, a standard laboratory exposure test is useful for several purposes:

1) testing the effects of fly ash which have intermediate Modified Calcium Aluminate Potentials,
2) testing the effects of fly ash which do not meet ASTM C-618 requirements,
3) testing the effects of fly ash which have ferric oxide contents in excess of 20 percent, and
4) continuing with the development of an understanding of the relationship between fly ash physical and compositional characteristics and the sulfate resistance of fly ash concrete.

The sulfate exposure test used in this study was a modification of U.S. Bureau of Reclamation Standard 4908. Concrete cylinders (3x6 inches) were continuously soaked in 10 percent sodium sulfate solution and were monitored for changes in length, mass, dynamic modulus of elasticity, and damping capacity.

This laboratory exposure test provided a uniform and repeatable sulfate susceptibility test for hardened concrete. In order to ensure uniformity and consistency, the following precautions were taken:

1) the exposure solution was changed periodically,
2) the ranges of temperature and solution/specimen volume ratios in exposure tanks were limited,
3) a single operator was employed for the assessment of the deterioration of exposure specimens, and
4) tight control was enforced over the procedures followed for assessing deterioration of exposure specimens.

Details of the test procedures were presented in Chapter 3.

A method for assessing deterioration based on changes in length and mass was presented. Measurements of length and mass were available for all mixtures for the full

2-year duration of exposure. The performances of these sulfate exposure specimens were evaluated with a parameter termed Sulfate Susceptibility Rating (SSR):

$$SSR_i = \frac{\text{linear expansion (\%) of mixture i}}{\text{linear expansion (\%) of control Type II cement concrete}} \,. \qquad (11.3)$$

The SSR of the control Type II cement concrete mixture was therefore 1.0.

Four-year exposure data revealed that any mixtures which exceeded an expansion of 0.15 percent or which lost mass within the first two years of exposure were more susceptible to long-term sulfate attack than the control Type II cement concrete. Mixtures which exceeded these limits were labelled with an SSR of 3.0 in order to identify their poor performance.

Dynamic modulus of elasticity and damping measurements were not available for all concrete mixtures. Therefore, they were not included in the SSR method for assessing deterioration.

However, damping measurements were shown to detect internal and external concrete deterioration more effectively than the combined use of expansion and mass loss. When damping measurements were available, the performance of mixtures were assessed on the basis of a parameter termed Relative Damping Capacity (RDC):

$$RDC_t = \frac{\delta_t}{\delta_o} \times 100\% \text{ , where}$$

δ_t = logarithmic decrement at time t and

δ_o = initial logarithmic decrement (after 7 days of exposure).

Details of the dynamic testing procedures and the method for calculating logarithmic decrement were discussed in Chapter 3.

Long-term exposure data permitted the evaluation of test duration requirements for mixtures meeting the following criteria:

1) mixture design cement contents of 5½ sacks cement per cubic yard of concrete,
2) fly ash replaced Type I and Type II cements at levels of 25, 35, and 45 percent by volume,

3) fly ash was added as a mineral admixture,
4) mixing water was added until a fresh concrete slump of 5 to 7 inches was attained, and
5) concrete cylinders (3x6 inches) were monitored for changes in length and for loss of mass.

Exposure duration requirements, for comparing the sulfate resistance of these fly ash concretes to that of ordinary Type II cement concrete, were dependent on fly ash content. Concrete which contained 35 or 45 percent fly ash required a test duration of one year. Concrete which contained 25 percent fly ash required a test duration of two years. The extended duration was required because in some cases low percentages of sulfate-susceptible fly ash did not show significant effects, in terms of concrete expansion or mass loss, until after one year.

Long-term exposure data was not available for specimens which were monitored for changes in dynamic properties. Therefore, test duration requirements could not be established. However, results clearly indicated that duration requirements would be reduced if concrete deterioration was monitored through measurements of damping capacity.

11.2.3 IMPROVEMENTS IN THE PERFORMANCE OF NON-SULFATE RESISTANT FLY ASH CONCRETE

11.2.3.1 Introduction

Many of the fly ashes which are available in Texas are harmful to the sulfate resistance of Type II cement concrete. However, these ashes are often desireable for use in concrete because of their cost, availability, and benefits to other properties of concrete, such as compressive strength. Therefore, several methods for improving the sulfate resistance of fly ash concretes were studied.

11.2.3.2 Physical Methods

Physical methods for improving the sulfate resistance of fly ash concrete included:

1) increasing the cement content and
2) intergrinding fly ash with cement clinker and gypsum.

Several non-sulfate resistant fly ash/Type II cement concrete mixtures were reproduced with an increased mixture design cement content. Cement content was increased from 5½ sacks cement to 7 sacks cement per cubic yard of concrete. The resulting increased strength and decreased permeability were anticipated to improve resistance to sulfate attack.

The sulfate resistance of fly ash concrete was improved by increasing the cement content, as long as two conditions were satisfied:

1) the Modified CAP of the fly ash was less than 1.25 and
2) fly ash replacement for cement was no greater than 25 percent by volume.

In summary, improvements in the resistance of fly ash concrete to sulfate attack were significant for mixtures containing small proportions of marginal fly ash. Improvements were not significant for mixtures containing large proportions of marginal fly ash or any proportion of very sulfate-susceptible fly ash.

The effects of intergrinding fly ash, as in the production of blended cements, were studied for concrete mixtures containing both Type A and Type B fly ashes and both Type II and Type I-H cements. Intergrinding was anticipated to increase fly ash reactivity and to improve cement homogeneity. Increased concrete strength and decreased concrete permeability were anticipated to improve resistance to sulfate attack.

Intergrinding fly ash increased the specific gravity and decreased the proportion of coarse (+45 μm) particles in fly ash cements. These effects were attributed to the crushing of large hollow and/or porous particles and to the dispersion of agglomerates of particles.

Intergrinding fly ash increased the compressive strength of concrete in almost all cases and increased the sulfate resistance of concrete in some cases. Improvements in sulfate resistance were not sufficient to alter the fly ash selection criteria, as shown in Table 11.2. However, the performances of Type II blended cement concretes containing fly ash with Modified CAPs less than approximately 0.6 were improved to a level comparable with ordinary Type V cement concrete.

Type II cement concrete containing interground fly ash with Modified CAPs between 0.6 and 1.25 performed as well as ordinary Type II cement concrete in some cases. However, the effects of these fly ashes were not consistent and, therefore, were not reliable.

The sulfate resistance of concrete containing Type II cement and fly ash with Modified CAPs greater than 1.25 was not improved by intergrinding.

Type I-H cement concrete containing interground fly ash with Modified CAPs less than approximately 0.6 performed as well as ordinary Type II cement concrete in some cases. However, the effects of these fly ashes were not consistent and, therefore, were not reliable.

The sulfate resistance of concrete containing Type I-H cement and fly ash with Modified CAPs greater than 0.6 was generally not improved by intergrinding.

In summary, the performance of moderately sulfate resistant fly ash concrete was significantly improved by intergrinding the fly ash. However, the performance of non-sulfate resistant fly ash concrete was not significantly improved by intergrinding.

11.2.3.3 Chemical Methods

Chemical methods for improving the sulfate resistance of fly ash concrete involved increasing the sulfate and/or alkali contents of fly ash cements. Sulfate contents were increased individually by intergrinding additional gypsum. Alkali contents were increased individually by addiing sodium hydroxide as a chemical additive. Sulfate and alkali contents were increased concurrently by adding sodium sulfate as a chemical additive.

High sulfate contents were anticipated to promote the formation and continued stability of ettringite during early hydration reactions. High alkali contents were anticipated to fascilitate fly ash dissolution and reactivity. Any reactive calcium aluminates which participated in the formation of ettringite while the concrete was plastic would not be available for the formation of ettringite after the concrete had hardened. It was hoped that these changes would increase the long-term sulfate resistance of fly ash concrete.

The presence of alkalies may also reduce the potential for ettringite to cause expansion by altering its morphology and its mechanism of crystallization. These characteristics of ettringite depend on the relative availability of ions with which it is formed. Alkalies reduce the solubility of calcium hydroxide, thereby reducing the concentration of calcium ions in solution.

In solutions of low calcium ion concentration, ettringite forms as large lath-like crystals, rather than as small rod-like crystals. The large crystals, with their low surface area to volume ratios, have a reduced ability to adsorb water molecules (64, 373). When surface area to volume ratios are high, adsorption of water is theorized to cause swelling.

In solutions of low calcium ion concentration, crystalline calcium aluminates are slightly soluble. Therefore, ettringite forms through-solution, rather than topochemically. Through-solution crystallization has been anticipated to not cause expansion (210).

Sodium sulfate was added to non-sulfate resistant Type B fly ash/Type II cement concrete. Mixtures included five Type B fly ashes which replaced the Type II cement at a level of 35 percent by volume. These fly ashes were added both as admixtures and interground.

Additional gypsum was interground with non-sulfate resistant Type B fly ash/Type II cement concrete. Mixtures included two Type B fly ashes which replaced the Type II cement at a level of 35 percent by volume. Fly ash was interground with the cement in all cases.

Low and moderate dosages of sodium sulfate additive, 1.6 percent to 7.4 percent by weight of cement, improved the sulfate resistance of Type B fly ash concrete to a level comparable with ordinary Type V cement concrete. Compressive strengths at 3 days were increased and compressive strengths at 28 days were decreased in most cases. Concrete permeability was decreased, particularly at early ages.

Concurrent additions of gypsum and sodium hydroxide were as effective as sodium sulfate additive in improving the sulfate resistance of Type B fly ash cement concrete. However, effects on compressive strength were even less desireable. Concrete permeability was decreased but not as effectively as with additions of sodium sulfate additive. Sodium hydroxide, particularly at high levels, seemed to interfere with the hydration of calcium silicates.

In some cases, sulfate resistance was improved by intergrinding additional gypsum without adding a sodium hydroxide additive. Total cement sulfate contents in these cases were 3.6 percent to 8.3 percent. The permeability of hardened concrete was not significantly affected, so the increased resistance to sulfate attack was purely a chemical effect, attributable to changes in the composition of the hydration products.

Two fly ashes were included in the mixtures with additional gypsum: one with a Modified CAP of 1.16 and one with a Modified CAP of 2.25. The proportions of amorphous phases for these two ashes were 80 percent and 60 percent, respectively. The fly ash with the lower Modified CAP and the higher glass content was much more susceptible to improvements in sulfate resistance.

11.2.3.4 Criteria for the Composition of Fly Ash Cement

Fly ash contains reactive calcium aluminates in various crystalline and glassy forms. Therefore, in order to compare the compositions of different fly ash cements, an equivalent C_3A parameter was developed. Approximately one-third of the bulk chemical alumina in high-calcium fly ash was assumed to be included in reactive calcium aluminate phases. These proportions of reactive alumina were converted to equivalent C_3A contents by multiplying reactive alumina by 2.65, which is the molar mass ratio C_3A/Al_2O_3.

Ternary (C_3A eq.-SO_3-Na_2O eq.) compositions of the unaltered Type B fly ash cements included in this portion of the study are shown in Figure 11.2. The ternary compositions of some of the modified cements which contained sulfate and alkali additives are shown as a region labelled "resistant to sulfate attack". The sulfate resistant modified cements met the following criteria:

$$1.5 < \frac{SO_3}{Na_2O\ \text{eq.}} < 9 \quad \text{and} \qquad (11.5)$$

$$0.5 < \frac{SO_3}{C_3A\ \text{eq.}} < 0.7\ . \qquad (11.6)$$

Some additional trends which were observed for mixtures containing high alkali and high sulfate contents are also shown in Figure 11.2. High alkali contents interfered with the normal hydration process of calcium silicates and caused low concrete compressive strengths. High sulfate contents resulted in internal sulfate attack, or unsoundness.

Unsoundness occured when all the calcium aluminates in cement could not react to form ettringite while the concrete was plastic. Consequently, they were available for expansive reactions after the concrete had hardened.

If all the calcium aluminates in fly ash cement mixtures are assumed to react with sulfate to form ettringite, the compositions from the ternary diagram may be used to determine the quantity of sulfate which is sufficient to react with all the equivalent C_3A. If gypsum is the only source of sulfate, each mole of C_3A consumes three moles of gypsum:

$$C_3A + 3C\bar{S}\ \text{(gypsum)} + 32H\ \text{(water)} \rightarrow C_3A \cdot 3C\bar{S} \cdot H_{32}\ \text{(ettringite)}\ .$$

The mass ratio SO_3/C_3A for complete consumption of C_3A can be estimated as follows:

$$\frac{3(C\bar{S})}{C_3A} \times \frac{SO_3}{C\bar{S}} = \frac{3(172)\ \text{gm/mol}}{270\ \text{gm/mol}} \times \frac{80.1\ \text{gm/mol}}{172\ \text{gm/mol}} = 0.9\ .$$

If sulfates are provided by a source other than gypsum (e.g. sodium sulfate), the reaction may be approximated as:

$$C_3A + 3CH + 3\bar{S} + 29H \rightarrow C_3A \cdot 3C\bar{S} \cdot H_{32}\ \text{(ettringite)}\ .$$

The mass ratio SO_3/C_3A for complete consumption of C_3A can still be estimated as 0.9.

The highest $SO_3/(C_3A$ eq.) ratio in the sulfate resistant region in the ternary diagram is 0.7. When the $SO_3/(C_3A$ eq.) ratio was as high as 0.9, internal sulfate attack occured. Therefore, even in the presence of alkalies, complete consumption of reactive calcium aluminates did not occur while the concrete was plastic. This may be partially attributable to the limited reactivity of C_3A provided by the Type II cement clinker. The reactivity of cement C_3A particles steadily decreases as reaction products form diffusion barriers.

11.2.4 BLENDED CEMENTS CONTAINING LARGE PROPORTIONS OF FLY ASH

In order to maximize the cost savings of using fly ash in concrete, high replacements of cement with fly ash have received considerable attention. In this study, several blended cements containing high proportions of fly ash were tested for their resistance to sulfate attack. Fly ash with relatively high Modified Calcium Aluminate Potentials were selected for this portion of the study in order to determine whether sulfate resistant concrete could be produced with high levels of non-sulfate resistant fly ash.

Two Texas Type B fly ashes replaced Type II cement at levels of 45 percent and 55 percent by volume. Fly ash was interground with cement clinker and gypsum. Intergrinding effectively reduced the total proportion of coarse particles (+45 μm). The increased surface area, along with the increased cement homogeneity, were anticipated to improve strength gain at early ages.

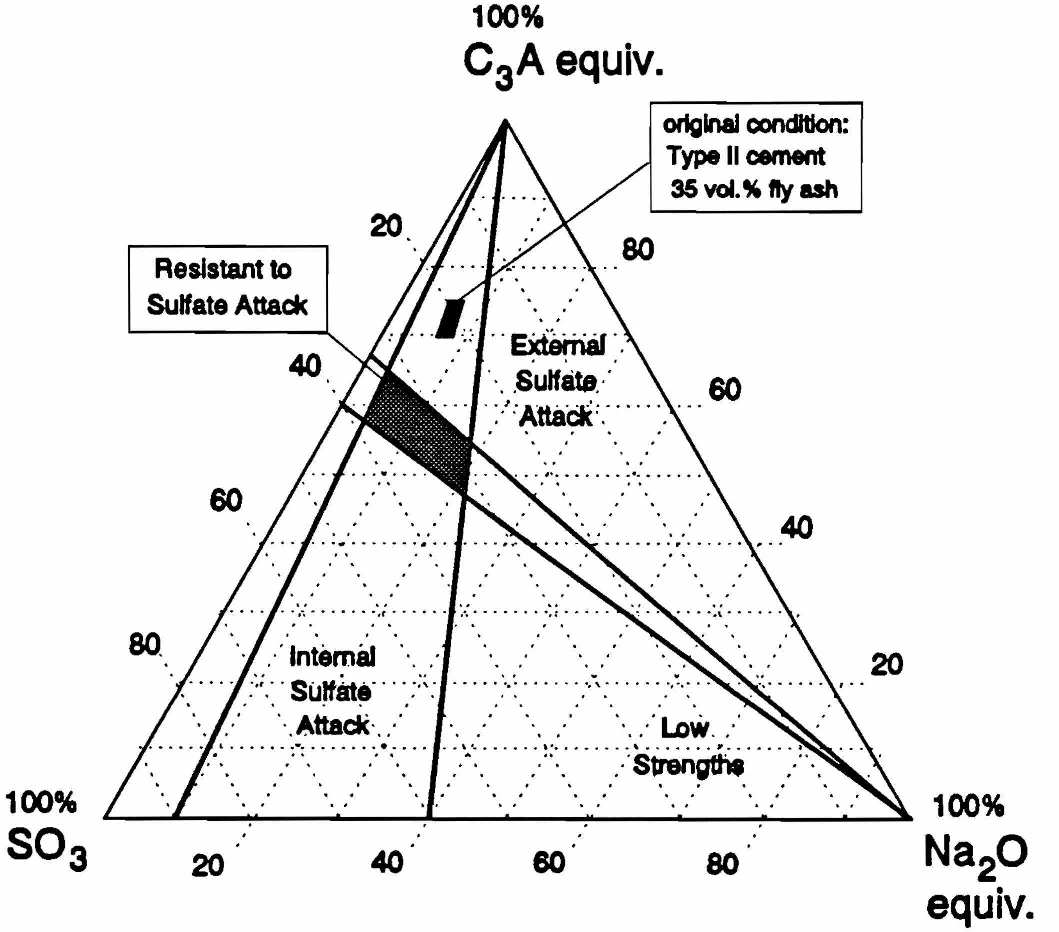


Figure 11.2 Range of Ternary (C_3A eq.-SO_3-Na_2O eq.) Compositions for Sulfate Resistant Fly Ash Concrete Containing Elevated Proportions of Sulfate and Alkali

One of the Type B ashes contained a moderate proportion of calcium oxide and a high proportion of glass, 23.1 percent and 80 percent, respectively. The other Type B ash contained a high proportion of calcium oxide and a moderate proportion of glass, 33.9 percent and 60 percent, respectively. These ashes performed very differently in this test series.

For concrete containing the high-calcium fly ash, compressive strength was not significantly affected by the proportion of fly ash. For concrete containing the moderate-calcium fly ash, compressive strength decreased with increasing ash content, particularly at early ages.

Concrete containing large proportions of the high-calcium ash was not resistant to sulfate attack. Concrete containing 55 percent of the moderate-calcium ash was resistant to sulfate attack. Since concrete permeability was not significantly affected by the proportion of fly ash, the sulfate resistance of the high fly ash content concrete may be attributable to increased consumption of calcium hydroxide and to effects on the composition of hydration products.

Inclusion of sodium sulfate additive in these mixtures improved sulfate resistance significantly. Improvements were most significant for the mixtures containing the moderate-calcium, high-glass fly ash. These improvements were attributed to the formation of ettringite while the concrete was plastic. The presence of alkalies may also have affected the expansive potential of ettringite.

Mixtures which contained 55 volume percent fly ash and $SO_3/(C_3A$ eq.) ratios of approximately 0.9 did not suffer expansions, due to internal or external sulfate attack, within the two-year test duration. Since an $SO_3/(C_3A$ eq.) ratio of 0.9 corresponds approximately to complete conversion of C_3A to ettringite, a large percentage of the calcium aluminates must have reacted while the concrete was plastic.

Fly ash cements which contain high percentages of fly ash also contain high proportions of calcium aluminates in amorphous form. In the presence of alakali, the glassy calcium aluminates in fly ash seem to be better able to react with sulfate to form ettringite, as compared to the crystalline calcium aluminates in cement. Therefore, high proportions of glassy fly ash may promote the formation of ettringite while the concrete is plastic and may decrease the risk of internal sulfate attack.

Similar to concrete containing 35 volume percent fly ash, inclusion of sodium sulfate additive in the high fly ash content mixtures increased compressive strength at early ages and decreased concrete permeability.

11.3 CONCLUSIONS

1) The mineralogy of fly ash was a significant factor governing the effects of fly ash on the sulfate resistance of concrete. A model termed Modified Calcium Aluminate Potential was presented as a method for predicting the effect of fly ash on the sulfate resistance of concrete. The Modified Calcium Aluminate Potential model accounts for fly ash mineralogy in its prediction of the potential for fly ash to contain reactive calcium aluminates.

2) Relative to adding fly ash as a mineral admixture, intergrinding fly ash with cement clinker and gypsum increased the specific gravity of fly ash cements and decreased the proportion of coarse particles. These effects were attributed to the crushing of hollow and porous particles and to the dispersion of agglomerates of fly ash particles.

3) Intergrinding fly ash was effective in increasing concrete compressive strength and in improving the performance of moderately-sulfate resistant fly ash concrete.

4) Physical methods for improving the performance of non-sulfate resistant fly ash concrete had limited success. These physical methods included intergrinding fly ash and increasing mixture design cement content. Decreases in concrete permeability often reduced the rate of intrusion of sulfates. However, expansions near the surface of concrete caused cracking and spalling.

5) Chemical methods for improving the performance of non-sulfate resistant fly ash concrete proved promising. These chemical methods included intergrinding additional gypsum in blended cements and using sodium hydroxide and sodium sulfate as chemical additives.

6) Improvements by chemical methods were closely related to achieving an optimum SO_3 content, in terms of sulfate resistance, for fly ash cement. When fly ash was added as a mineral admixture, optimum SO_3 content was attained only by chance. For the high-calcium fly ashes with typical SO_3 contents, combinations with the Type II cement seemed to result in total SO_3 contents which were lower than optimum. Low SO_3 contents during early hydration reactions promoted the conversion of ettringite to monosulfate hydrates. The monosulfate hydrates were then available for conversion back to ettringite once additional sulfates became available from the environment. By intergrinding additional gypsum or by including sodium sulfate additive, cement SO_3 contents were increased and ettringite remained stable during the early hydration reactions.

7) High alkali contents in fly ash cements increased the rates at which fly ash reacted. This was evident in both the increased compressive strengths and the decreased permeabilities at early ages. Increased rates of reaction were attributed to the fascilitation of the dissolution of fly ash by alkali hydroxides.

11.4 RECOMMENDATIONS FOR APPLICATION

1) When predicting the potential effects of fly ash on the sulfate resistance of concrete, use the Modified Calcium Aluminate Potential model. This model takes advantage of fly ash mineralogical information to estimate the average composition of glassy phases and to differentiate between reactive and nonreactive crystalline phases. If mineralogical information is not available, an option which requires only bulk chemical analyses is also offered. The Bulk Chemical Modified Calcium Aluminate Potential model is a more accurate option than using either fly ash Texas Type or fly ash bulk calcium oxide content.

2) If a fly ash to be used in concrete meets any of the following criteria, use a laboratory exposure test to evaluate its effects on the resistance of concrete to sulfate attack:

a) Modified Calcium Aluminate Potential (or Bulk Chemical Modified CAP) between 0.6 and 1.25,

b) non-conformance with ASTM C-618 physical or chemical requirements,

c) ferric oxide content greater than 20 percent.

The exposure test recommended in this study involves soaking 3x6-inch concrete cylinders continuously in 10 percent sodium sulfate solution.

3) When moderate sulfate resistance is required for a fly ash/Type I cement concrete, the Type I cement should contain no more than 10 percent C_3A. Inclusion of fly ash with a Type I cement containing more than 10 percent C_3A will not result in sulfate resistance comparable to Type II cement.

4) In general, decreasing concrete permeability will improve the performance of moderately sulfate resistant concrete. However, decreasing concrete permeability will not significantly improve the performance of concrete which is very susceptible to sulfate attack.

5) If a high-calcium fly ash is desireable in terms of cost or availability and is undesireable in terms of sulfate resistance, mineral and chemical additives may be used to improve its effects on the performance of concrete in sulfate environments. If the fly ash is to be interground with Type II cement, the gypsum content of the blend may be adjusted. If the fly ash is to be added to Type II cement as a mineral admixture, anhydrous sodium sulfate may be used as an additive in the concrete mixing water.

11.5 RECOMMENDATIONS FOR FUTURE RESEARCH

1) Continue the development of methods for predicting the effects of fly ash on the sulfate resistance of concrete. The performance of fly ash with intermediate Modified Calcium Aluminate Potentials seems to be difficult to predict. Physical effects of fly ash may also have to be considered. For example, two fly ashes with similar Modified Calcium Aluminate Potentials may have very different effects on concrete mixing water requirements and concrete permeability.

2) Continue studying the relationship between fly ash composition, cement composition, and optimum sulfate content. The optimum sulfate content may depend on the property of fly ash concrete being considered. For example, different total sulfate contents may optimize sulfate resistance, shrinkage, and compressive strength. This study should include the continued development of methods for quantifying reactive calcium aluminates in fly ash. For example, a simple equivalent C_3A content may be estimated from bulk chemical alumina contents. More precise methods may take advantage of mineralogical analyses.

3) Study the precise mechanism by which high sulfate and/or high alkali contents improve the sulfate resistance of concrete. This study should include comparisons between the quantities of ettringite formed, as a function of curing time. The effects of alkalies on the morphology of ettringite crystals could also be investigated, along with the relationship between ettringite morphology and potential for expansion.

4) In addition to effects on sulfate resistance, study other influences of high sulfate and/or high alkali contents in fly ash cement concrete. Topics may include temperature rise, set times, alkali-silica reactivity, and long-term compressive strength.

5) Determine a test duration requirement for concrete which is subjected to 10 percent sodium sulfate solution and which is monitored for changes in linear expansion and damping capacity. Material damping has been shown to be an efficient detector of concrete deterioration.

6) Continue studying the relationship between the deterioration of concrete in 2.1 percent sodium sulfate solution and the deterioration of concrete in 10 percent sodium sulfate solution. A solution containing 2.1 percent sodium sulfate simulates very severe, but realistic conditions. A solution containing 10 percent sodium sulfate provides an accelerated exposure test with the benefit of decreased exposure duration requirements. Therefore, comparisons between conclusions drawn from the two solutions would provide two types of valuable information:

a) the extent to which the mechanisms of sulfate attack are distorted in the 10 percent sodium sulfate solution, relative to realistic conditions and

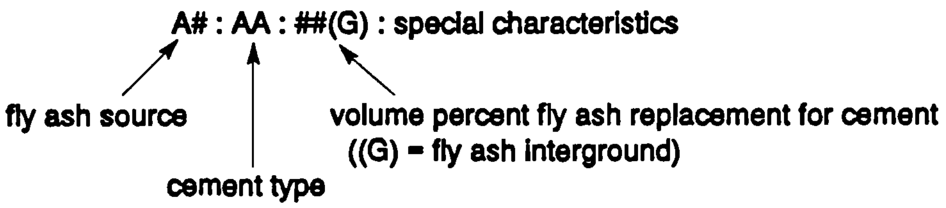
b) the extent to which the rate of deterioration of concrete is accelerated in the 10 percent sodium sulfate solution, relative to realistic conditions.

Conclusions drawn from these observations may vary depending on concrete constituents and concrete mixture design.

APPENDIX A

NOTATION

Table A.1 Mixture Designations



special characteristics

- 7sk = 7 sacks cement per cubic yard concrete
- 2.1% = exposure solution contains 2.1% sodium sulfate
- 5% = exposure solution contains 5% sodium sulfate
- s(##) = chemical admixture sodium sulfate
  - (##) refers to the cement composition ratio :

$$\frac{Na_2O \text{ eq.} + SO_3}{Na_2O \text{ eq.} + SO_3 + C_3A \text{ eq.}}$$

- g(##) = additional gypsum interground with cement
  - (##) indicates the cement contains the same proportion of SO_3 as s(##)
- h(##) = chemical admixture sodium hydroxide
  - (##) indicates the cement contains the same proportion of Na_2O eq. as s(##)

APPENDIX B

FLY ASH

Table B.1 Rankings of Fly Ash Physical Characteristics

Fly Ash	Specific Gravity	Blaine (cm^2/gm)	Retained #325 Sieve (%)	Pozzolanic Activity Index (%)
A-1	16	23	13	16
A-2	14, 15	17	6	17
A-3	22, 23	4	10	7
A-4	18	2	12	3
A-5	21	20	4, 5	23
A-6	12	14	23	2
A-7	19	24	3	22
A-8	20	16	1	24
A-9	17	18	17	8
A-10	24	22	4, 5	12
A-11	22, 23	15	2	18
A-12	14, 15	21	15	20
B-1	11	13	8	21
B-2	7	10, 11	22	19
B-3	5	3	16	10
B-4	8	5, 6	18	11
B-5	4	5, 6	9	14
B-6	6	10, 11	19	6
B-7	3	7	11	13
B-8	13	19	21	5
B-9	9	12	7	4
B-10	10	1	20	9
B-11	2	9	14	1
B-12	1	8	24	15

Note: twelve highest rankings are shaded

Table B.2 Rankings of Fly Ash Chemical Compositions

Fly Ash	Bulk Chemical Composition (percent by weight)						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	Na_2O equiv.	Loss on Ignition
A-1	5	17	1	21	15	3	6
A-2	2	23	3	16	16	18	15
A-3	9	3	20, 21	23	22	(1)	2
A-4	13	4	10	15	20, 21	(1)	4
A-5	10	5	5	19	17	7	11
A-6	7	14, 15	13	13	13	17	21
A-7	8	8, 9	24	14	19	2	3
A-8	4	20, 21	11	17	18	(1)	1
A-9	1	20, 21	23	20	24	19	23
A-10	6	2	12	22	23	9	9
A-11	3	14, 15	8, 9	18	20, 21	20	17, 18
A-12	12	1	2	24	14	(1)	5
B-1	11	24	4	12	12	15	22
B-2	23	12	22	4	1	1	16
B-3	19	6	15	6	8	12	7
B-4	21	18	18	5	7	14	19
B-5	20	10	16	3	5	10, 11	24
B-6	16	13	8, 9	7	4	16	10
B-7	18	22	7	8	3	5	12
B-8	14	19	19	10, 11	6	4	20
B-9	17	7	14	10, 11	10	6	8
B-10	15	8, 9	6	9	9	8	14
B-11	22	11	20, 21	2	11	10, 11	17, 18
B-12	24	16	17	1	2	13	13

Note: twelve highest rankings are shaded
(1) data not reported

Table B.3 Rankings of Fly Ash Mineralogical Compositions

Fly Ash	Mineralogical Composition (percent by weight)							
	C_3A	Ml	Mu	Mw	Qz	So	Sp	Total
A-1	a	a	9	a	15	a	1	9
A-2	a	a	11	a	2	a	9-11	13
A-3	a	a	1	a	6,7	a	12,13	6
A-4	a	a	3	a	9	a	20	15
A-5	a	a	7,8	a	11	a	21	19
A-6	a	13	4	a	5	a	4	7
A-7	a	a	a	a	14	a	18,19	24
A-8	12	a	10	a	3	a	17	11
A-9	a	a	7,8	a	1	a	22,23	12
A-10	a	a	2	a	6,7	a	18,19	10
A-11	a	a	6	a	18	a	5	18
A-12	a	14	5	a	19	a	2	8
B-1	7	11,12	a	a	22	a	3	23
B-2	a	5, 6	19	1	16,17	4	22,23	2
B-3	3,4,5	4	15-18	8	20	6,7	9,11	16
B-4	11	2	15-18	10	24	8,9	7	22
B-5	3,4,5	10	13	5	16,17	6,7	22	14
B-6	8	11,12	15-18	7	4	3	6	4,5
B-7	9,10	1	a	6	23	a	12,13	20
B-8	1	7	a	3	8	2	14,15	3
B-9	6	5,6	14	11	13	8,9	8	17
B-10	9,10	8,9	15-18	9	21	a	9-11	21
B-11	2	8,9	12	4	12	5	16	4,5
B-12	3,4,5	3	20	2	10	1	14,15	1

Note: twelve highest rankings are shaded
Ml = melilite, Mu = mullite, Mw = merwinite, Qz = quartz,
So = sodalite structures, Sp = ferrite spinel
a = less than 0.1 percent by weight

Table B.4 Rankings of Fly Ash Glass Compositions

Fly Ash	Glass Composition (percent by weight)				
	SiO_2	Al_2O_3	Fe_2O_3	CaO	Total
A-1	2	16	1	23	15
A-2	6	18, 19	3	16	12
A-3	13	24	17	22	22
A-4	12	14	5	15	10
A-5	8	9, 10	2	17	6
A-6	11	22	21	13	17
A-7	4	1	20	14	1
A-8	7	21	9	20	16
A-9	5	23	11	19	13
A-10	10	20	8	21	14
A-11	1	18, 19	18, 19	18	7
A-12	9	2	4	24	18
B-1	3	17	12	11	2
B-2	23	6	24	10	23
B-3	19	4	14	5	9
B-4	18	13	18, 19	2	3
B-5	20	7	10	1	11
B-6	21	8	13	7	20
B-7	15	9, 10	6, 7	8	5
B-8	16	11	15, 16	12	21
B-9	17	5	15, 16	19	8
B-10	14	3	6, 7	6	4
B-11	22	12	22	4	19
B-12	24	15	23	3	24

Note: twelve highest rankings are shaded

APPENDIX C

BLENDED CEMENTS

Table C.1 Fly Ash Cement Blend Designations and Constituents

Blend Number	Blend Designation	Cement Clinker Type	Fly Ash Type	Fly Ash (vol.%)	Dry Batch Weights (80 lbs. total)			
					Clinker (lbs)	Fly Ash (lbs)	Gypsum (lbs)	Anhydrite (lbs)
1	I-H blend A	I-H	---	---	76.3	---	2.59	1.11
2	I-H blend B	I-H	---	---	75.6	---	3.06	1.31
3	I-H blend C	I-H	---	---	73.1	---	4.85	2.08
4	I-H blend D	I-H	---	---	76.3	---	2.59	1.11
5	I-H blend E	I-H	---	---	76.8	---	2.25	1.00
6	I-H blend F	I-H	---	---	76.3	---	2.59	1.11
7	II blend A	II	---	---	76.2	---	3.85	---
8	II blend B	II	---	---	76.0	---	4.00	---
9	A1:I-H:25	I-H	A-1	25	61.3	16.1	1.79	.83
10	A1:I-H:35	I-H	A-1	35	54.5	23.2	1.59	.74
11	A1:II:25	II	A-1	25	60.4	16.4	3.18	---
12	A1:II:35	II	A-1	35	53.7	23.5	2.83	---
13	A2:I-H:25	I-H	A-2	25	61.0	16.4	1.78	.83
14	A2:I-H:35	I-H	A-2	35	54.2	23.5	1.58	.73
15	A2:II:25	II	A-2	25	60.2	16.6	3.17	---
16	A2:II:35	II	A-2	35	53.5	23.7	2.82	---
17	A6:I-H:25	I-H	A-6	25	60.7	16.7	1.77	.82
18	A6:I-H:35	I-H	A-6	35	53.8	23.9	1.57	.73
19	A6:II:25	II	A-6	25	59.9	16.9	3.16	---
20	A6:II:35	II	A-6	35	53.1	24.1	2.79	---
21	A7:I-H:25	I-H	A-7	25	62.0	15.4	1.81	.84
22	A7:I-H:35	I-H	A-7	35	55.3	22.3	1.62	.75
23	A7:II:25	II	A-7	25	61.2	15.6	3.22	---
24	A7:II:35	II	A-7	35	54.5	22.6	2.87	---
25	A9:I-H:25	I-H	A-9	25	61.7	15.7	1.80	.84
26	A9:I-H:35	I-H	A-9	35	55.0	22.7	1.60	.74
27	A9:II:25	II	A-9	25	60.8	16.0	3.20	---
28	A9:II:35	II	A-9	35	54.2	23.0	2.85	---
29	A11:I-H:25	I-H	A-11	25	62.3	15.0	1.82	.85
30	A11:I-H:35	I-H	A-11	35	55.9	21.7	1.63	.76
31	A11:II:25	II	A-11	25	61.6	15.2	3.24	---
32	A11:II:35	II	A-11	35	55.1	22.0	2.90	---
33	B1:I-H:25	I-H	B-1	25	60.4	17.0	1.76	.82
34	B1:I-H:35	I-H	B-1	35	53.5	24.2	1.56	.73
35	B1:II:25	II	B-1	25	59.7	17.2	3.14	---
36	B1:II:35	II	B-1	35	52.7	24.5	2.78	---
37	B3:I-H:25	I-H	B-3	25	59.6	17.8	1.74	.81
38	B3:I-H:35	I-H	B-3	35	52.5	25.3	1.53	.71
39	B3:II:25	II	B-3	25	58.9	18.0	3.10	---
40	B3:II:35	II	B-3	35	51.8	25.5	2.73	---
41	B4:I-H:25	I-H	B-4	25	60.1	17.3	1.76	.82
42	B4:I-H:35	I-H	B-4	35	53.1	24.6	1.55	.72
43	B4:II:25	II	B-4	25	59.4	17.5	3.13	---
44	B4:II:35	II	B-4	35	52.3	24.9	2.76	---
45	B5:I-H:25	I-H	B-5	25	59.6	17.8	1.74	.81
46	B5:I-H:35	I-H	B-5	35	52.5	25.3	1.53	.71
47	B5:II:25	II	B-5	25	58.9	18.0	3.10	---
48	B5:II:35	II	B-5	35	51.8	25.5	2.73	---
49	B7:I-H:25	I-H	B-7	25	59.6	17.8	1.74	.81
50	B7:I-H:35	I-H	B-7	35	52.5	25.3	1.53	.71
51	B7:II:25	II	B-7	25	58.8	18.1	3.10	---
52	B7:II:35	II	B-7	35	51.7	25.6	2.72	---

Table C.1 (continued)

Blend Number	Blend Designation	Cement Clinker Type	Fly Ash Type	Fly Ash (vol.%)	Dry Batch Weights (80 lbs. total)			
					Clinker (lbs)	Fly Ash (lbs)	Gypsum (lbs)	Anhydrite (lbs)
53	B9:I-H:25	I-H	B-9	25	60.2	17.2	1.76	.82
54	B9:I-H:35	I-H	B-9	35	53.2	24.5	1.55	.72
55	B9:II:25	II	B-9	25	59.5	17.4	3.13	---
56	B9:II:35	II	B-9	35	52.5	24.9	2.77	---
57	B9:II:35:g(35)	II	B-9	35	50.8	24.9	4.26	---
58	B9:II:35:g(47)	II	B-9	35	47.3	24.9	7.71	---
59	B9:II:35:g(59)	II	B-9	35	42.2	24.9	12.80	---
60	B9:II:45	II	B-9	45	45.2	32.4	2.38	---
61	B9:II:55	II	B-9	55	37.7	40.3	1.99	---
62	B10:II:25	II	B-10	25	59.6	17.3	3.14	---
63	B10:II:35	II	B-10	35	52.5	24.7	2.77	---
64	B12:I-H:25	I-H	B-12	25	59.3	18.2	1.73	.80
65	B12:I-H:35	I-H	B-12	35	52.0	25.8	1.52	.70
66	B12:II:25	II	B-12	25	58.4	18.5	3.08	---
67	B12:II:35	II	B-12	35	53.9	26.2	2.70	---
68	B12:II:35:g(35)	II	B-12	35	50.4	26.2	3.28	---
69	B12:II:35:g(47)	II	B-12	35	47.6	26.2	6.20	---
70	B12:II:35:g(59)	II	B-12	35	42.8	26.2	10.90	---
71	B12:II:45	II	B-12	45	43.8	33.9	2.31	---
72	B12:II:55	II	B-12	55	36.2	41.9	1.91	---

Table C.2 Fly Ash Cement Blend Physical Properties

Blend Number	Blend Designation	Fly Ash		Specific Gravity *		Retained #325 Sieve (%) *		Blaine Air Perm. (sq cm/gm)
		vol.%	wt.%	calc.	mea.	calc.	mea.	
1	I-H blend A	---	---	---	---	---	---	---
2	I-H blend B	---	---	---	---	---	---	---
3	I-H blend C	---	---	---	---	---	---	---
4	I-H blend D	---	---	---	---	---	---	---
5	I-H blend E	---	---	3.15	3.12	11.7	14.8	3900
6	I-H blend F	---	---	---	---	---	---	---
7	II blend A	---	---	---	---	---	---	---
8	II blend B	---	---	3.10	3.06	7.5	11.3	3340
9	A1:I-H:25	25	20.2	2.96	3.01	---	---	4270
10	A1:I-H:35	35	29.0	2.88	2.96	---	---	4420
11	A1:II:25	25	20.4	2.92	3.01	---	---	3440
12	A1:II:35	35	29.3	2.85	2.98	10.1	8.0	3480
13	A2:I-H:25	25	20.5	2.97	3.01	---	---	4040
14	A2:I-H:35	35	29.4	2.90	2.95	---	---	4150
15	A2:II:25	25	20.7	2.93	2.98	---	---	3440
16	A2:II:35	35	29.7	2.87	2.94	12.3	6.7	3480
17	A6:I-H:25	25	20.9	2.99	3.02	---	---	4190
18	A6:I-H:35	35	29.9	2.92	2.99	---	---	4350
19	A6:II:25	25	21.1	2.95	3.01	---	---	3530
20	A6:II:35	35	30.2	2.89	2.98	8.4	6.8	3810
21	A7:I-H:25	25	19.3	2.93	3.03	---	---	4110
22	A7:I-H:35	35	27.9	2.84	2.98	---	---	4130
23	A7:II:25	25	19.6	2.89	3.05	---	---	3460
24	A7:II:35	35	28.2	2.81	3.02	13.3	10.0	3790
25	A9:I-H:25	25	19.7	2.94	2.97	---	---	4040
26	A9:I-H:35	35	28.4	2.86	2.92	---	---	4170
27	A9:II:25	25	20.0	2.91	2.97	---	---	3460
28	A9:II:35	35	28.7	2.83	2.94	9.2	7.0	3560
29	A11:I-H:25	25	18.7	2.91	3.01	---	---	4330
30	A11:I-H:35	35	27.2	2.81	2.95	---	---	4500
31	A11:II:25	25	19.0	2.87	3.00	---	---	3510
32	A11:II:35	35	27.5	2.78	2.94	13.9	6.7	3650
33	B1:I-H:25	25	21.2	3.00	3.02	---	---	4090
34	B1:I-H:35	35	30.3	2.94	2.95	---	---	4130
35	B1:II:25	25	21.5	2.96	3.02	---	---	3480
36	B1:II:35	35	30.6	2.90	2.98	11.8	7.2	3580
37	B3:I-H:25	25	22.2	3.04	3.06	---	---	4230
38	B3:I-H:35	35	31.5	2.99	3.02	---	---	4460
39	B3:II:25	25	22.4	3.00	3.03	---	---	3580
40	B3:II:35	35	31.9	2.96	3.05	9.9	5.7	3670
41	B4:I-H:25	25	21.6	3.01	3.05	---	---	3920
42	B4:I-H:35	35	30.8	2.96	3.03	---	---	4150
43	B4:II:25	25	21.9	2.98	3.08	---	---	3560
44	B4:II:35	35	31.1	2.93	3.02	9.6	7.9	3630
45	B5:I-H:25	25	22.2	3.04	3.06	---	---	4130
46	B5:I-H:35	35	31.6	2.99	3.02	---	---	4190
47	B5:II:25	25	22.5	3.00	3.01	---	---	3580
48	B5:II:35	35	31.9	2.96	3.06	11.1	7.7	3760
49	B7:I-H:25	25	22.3	3.04	3.07	---	---	3900
50	B7:I-H:35	35	31.7	3.00	3.03	---	---	4040
51	B7:II:25	25	22.6	3.00	3.06	---	---	3480

Table C.2 (continued)

Blend Number	Blend Designation	Fly Ash		Specific Gravity *		Retained #325 Sieve (%) *		Blaine Air Perm. (sq cm/gm)
		vol.%	wt.%	calc.	mea.	calc.	mea.	
52	B7:II:35	35	32.0	2.96	3.01	10.6	7.5	3510
53	B9:I-H:25	25	21.5	3.01	3.04	---	---	3960
54	B9:I-H:35	35	30.6	2.95	3.02	---	---	4270
55	B9:II:25	25	21.7	2.97	3.04	---	---	3510
56	B9:II:35	35	31.0	2.92	2.99	12.0	6.7	3630
57	B9:II:35:g(35)	35	31.0	---	---	---	---	---
58	B9:II:35:g(47)	35	31.0	---	---	---	---	---
59	B9:II:35:g(59)	35	31.0	---	---	---	---	---
60	B9:II:45	45	40.5	2.87	2.99	13.4	7.0	3670
61	B9:II:55	55	50.4	2.81	2.96	14.8	6.5	3830
62	B10:II:25	25	21.5	2.96	3.04	---	---	3510
63	B10:II:35	35	30.7	2.91	3.02	9.0	6.9	3810
64	B12:I-H:25	25	22.8	3.06	3.02	---	---	3830
65	B12:I-H:35	35	32.3	3.02	3.04	---	---	4110
66	B12:II:25	25	23.1	3.02	3.05	---	---	3410
67	B12:II:35	35	32.6	2.99	3.03	8.5	7.4	3480
68	B12:II:35:g(35)	35	32.6	---	---	---	---	---
69	B12:II:35:g(47)	35	32.6	---	---	---	---	---
70	B12:II:35:g(59)	35	32.6	---	---	---	---	---
71	B12:II:45	45	42.4	2.96	3.02	8.7	9.1	3530
72	B12:II:55	55	52.4	2.93	2.99	9.0	9.2	3530

* calc. = calculated using physical properties of fly ash and cement
mea. = measured physical property of cement or interground fly ash cement

Table C.2 (continued)

Fly Ash Percent by Weight

$$W_x = \frac{(SG_x)(V_x)}{(SG_x)(V_x) + (SG_y)(V_y)} \times 100\% \text{ , where}$$

W_x = percent by weight of constituent x,

SG_x, SG_y = specific gravity of constituents x and y, and

V_x, V_y = percent by volume of constituents x and y.

Calculated Specific Gravity

$$SG_t = \frac{100\%}{\frac{W_x}{SG_x} + \frac{W_y}{SG_Y}} \text{ , where}$$

SG_t = specific gravity of fly ash cement blend,

W_x, W_y = percent by weight of constituents x and y, and

SG_x, SG_y = specific gravity of constituents x and y.

Calculated Percent Retained on #325 Sieve

$$P_t = \frac{P_x(W_x) + P_y(W_y)}{100\%} \text{ , where}$$

P_t = percent by weight retained on #325 sieve for fly ash cement blend,

P_x, P_y = percent by weight retained on #325 sieve for constituents x and y, and

W_x, W_y = percent by weight of constituents x and y.

Table C.3 Alkali, Sulfate, and Equivalent Tricalcium Aluminate Contents of Type II Cement Concrete Containing Fly Ash B-3 and Sodium Sulfate Additive

Type II Cement Fly Ash B-3 (35 vol.%)	Na_2SO_4 Added (%) *	Total wt.% *			Ternary wt.% **			$\frac{SO_3}{C_3A\ eq.}$
		Na_2O equiv.	SO_3	C_3A equiv.	Na_2O equiv.	SO_3	C_3A equiv.	
no additive	0	0.9	2.7	10.4	6.4	19	74	0.26
s(35)	1.8	1.7	3.7	10.2	11	24	65	0.37
s(41)	3.4	2.4	4.5	10.1	14	27	59	0.46
s(47)	5.3	3.2	5.6	9.9	17	30	53	0.57
s(53)	7.4	4.1	6.7	9.6	20	33	47	0.70
s(59)	10.5	5.4	8.3	9.3	24	36	41	0.88
s(65)	13.8	6.8	10.1	9.0	26	39	35	1.11

* percent by weight of cement

** Na_2O equiv. + SO_3 + C_3A equiv. = 100%

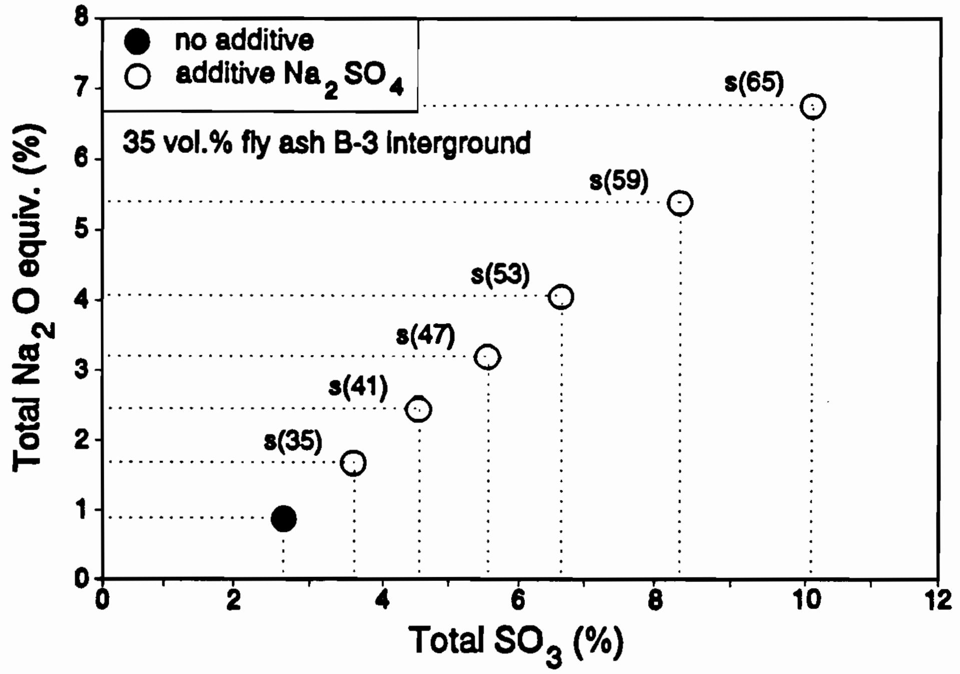


Figure C.1 Alkali and Sulfate Contents of Type II Cement Concrete Containing Fly Ash B-3 and Sodium Sulfate Additive

Table C.4 Alkali, Sulfate, and Equivalent Tricalcium Aluminate Contents of Type II Cement Concrete Containing Fly Ash B-4 and Sodium Sulfate Additive

Type II Cement Fly Ash B-4 (35 vol.%)	Na_2SO_4 Added (%) *	Total wt.% *			Ternary wt.% **			$\frac{SO_3}{C_3A\ eq.}$
		Na_2O equiv.	SO_3	C_3A equiv.	Na_2O equiv.	SO_3	C_3A equiv.	
no additive	0	0.8	2.7	9.6	6.1	21	73	0.29
s(35)	1.4	1.4	3.4	9.5	10	24	65	0.37
s(41)	2.8	2.0	4.2	9.3	13	27	59	0.46
s(47)	4.6	2.8	5.1	9.2	16	30	53	0.57
s(53)	6.5	3.6	6.2	9.0	19	33	47	0.70
s(59)	9.5	4.9	7.8	8.7	23	37	41	0.90
s(65)	12.7	6.3	9.5	8.4	26	39	35	1.11

* percent by weight of cement

** Na_2O equiv. + SO_3 + C_3A equiv. = 100%

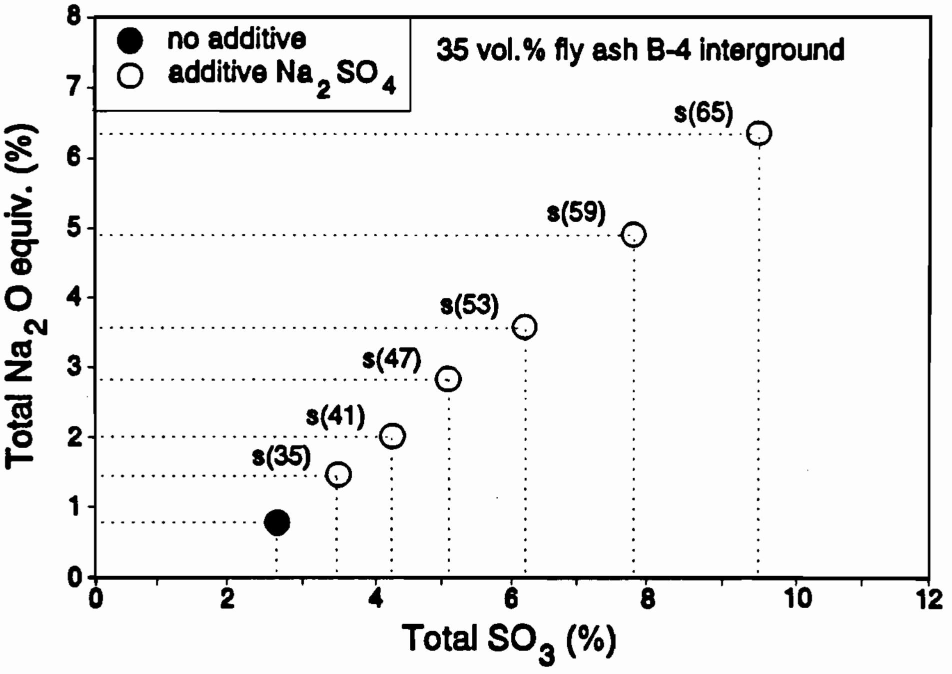


Figure C.2 Alkali and Sulfate Contents of Type II Cement Concrete Containing Fly Ash B-4 and Sodium Sulfate Additive

Table C.5 Alkali, Sulfate, and Equivalent Tricalcium Aluminate Contents of Type II Cement Concrete Containing Fly Ash B-5 and Sodium Sulfate Additive

Type II Cement Fly Ash B-5 (35 vol.%)	Na_2SO_4 Added (%) *	Total wt.% *			Ternary wt.% **			$\frac{SO_3}{C_3A\text{ eq.}}$
		Na_2O equiv.	SO_3	C_3A	Na_2O equiv.	SO_3	C_3A	
no additive	0	1.0	2.8	10.3	7.1	20	73	0.27
s(35)	1.8	1.7	3.7	10.1	11	24	65	0.37
s(41)	3.2	2.4	4.5	10.0	14	27	59	0.46
s(47)	5.1	3.2	5.5	9.8	17	30	53	0.57
s(53)	7.2	4.1	6.6	9.6	20	33	47	0.70
s(59)	10.3	5.4	8.3	9.2	23	36	41	0.88
s(65)	13.5	6.8	10.0	8.9	26	39	35	1.11

* percent by weight of cement

** Na_2O equiv. + SO_3 + C_3A equiv. = 100%

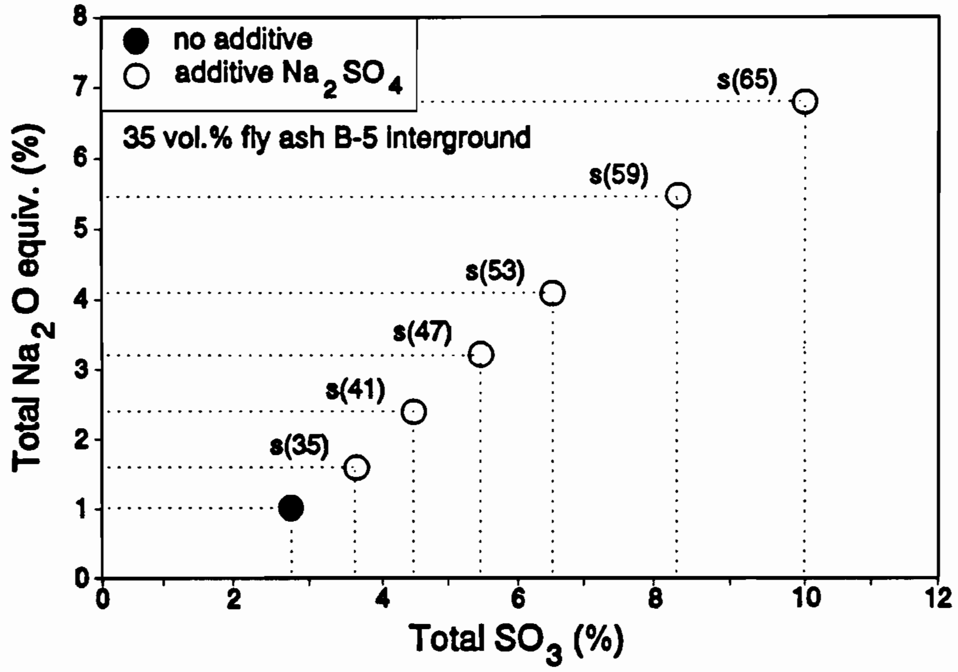


Figure C.3 Alkali and Sulfate Contents of Type II Cement Concrete Containing Fly Ash B-5 and Sodium Sulfate Additive

Table C.6 Alkali, Sulfate, and Equivalent Tricalcium Aluminate Contents of Type II Cement Concrete Containing Fly Ash B-9 and Sodium Sulfate Additive

Type II Cement Fly Ash B-9 (35 vol.%)	Na_2SO_4 Added (%) *	Total wt.% *			Ternary wt.% **			$\frac{SO_3}{C_3A\ eq.}$
		Na_2O equiv.	SO_3	C_3A equiv.	Na_2O equiv.	SO_3	C_3A equiv.	
no additive	0	1.0	2.7	10.3	7.1	19	74	0.26
s(35)	1.6	1.7	3.6	10.1	11	23	65	0.35
s(41)	3.4	2.4	4.5	10.0	14	27	59	0.46
s(47)	5.2	3.2	5.5	9.8	17	30	53	0.57
s(53)	7.3	4.1	6.6	9.6	20	33	47	0.70
s(59)	10.4	5.4	8.3	9.2	23	36	41	0.88
s(65)	13.6	6.8	10.0	8.9	26	39	35	1.11

* percent by weight of cement
** Na_2O equiv. + SO_3 + C_3A equiv. = 100%

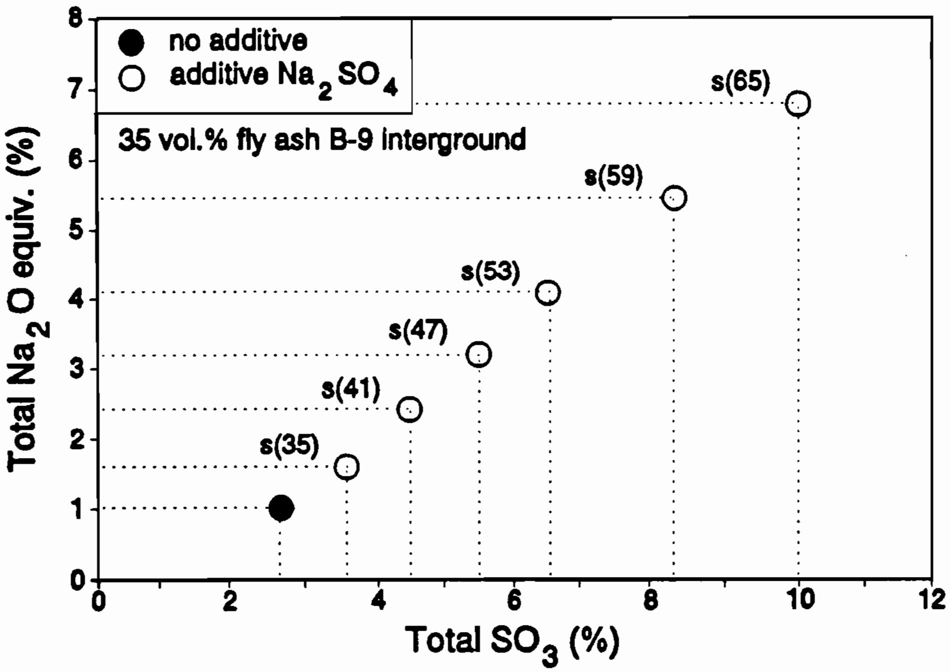


Figure C.4 Alkali and Sulfate Contents of Type II Cement Concrete Containing Fly Ash B-9 and Sodium Sulfate Additive

Table C.7 Alkali, Sulfate, and Equivalent Tricalcium Aluminate Contents of Type II Cement Concrete Containing Fly Ash B-12 and Sodium Sulfate Additive

Type II Cement Fly Ash B-12 (35 vol.%)	Na_2SO_4 Added (%) *	Total wt.% *			Ternary wt.% **			$\frac{SO_3}{C_3A\ eq.}$
		Na_2O equiv.	SO_3	C_3A equiv.	Na_2O equiv.	SO_3	C_3A equiv.	
no additive	0	0.9	3.4	9.8	6.4	24	70	0.34
s(35)	0.8	1.2	3.8	9.7	8.4	26	65	0.40
s(41)	2.1	1.8	4.5	9.6	11	29	59	0.49
s(47)	3.8	2.5	5.4	9.4	15	31	53	0.58
s(53)	5.8	3.4	6.5	9.2	18	34	47	0.72
s(59)	8.7	4.6	8.0	9.0	21	37	41	0.90
s(65)	12.4	6.2	9.9	8.6	25	40	35	1.14

* percent by weight of cement

** Na_2O equiv. + SO_3 + C_3A equiv. = 100%

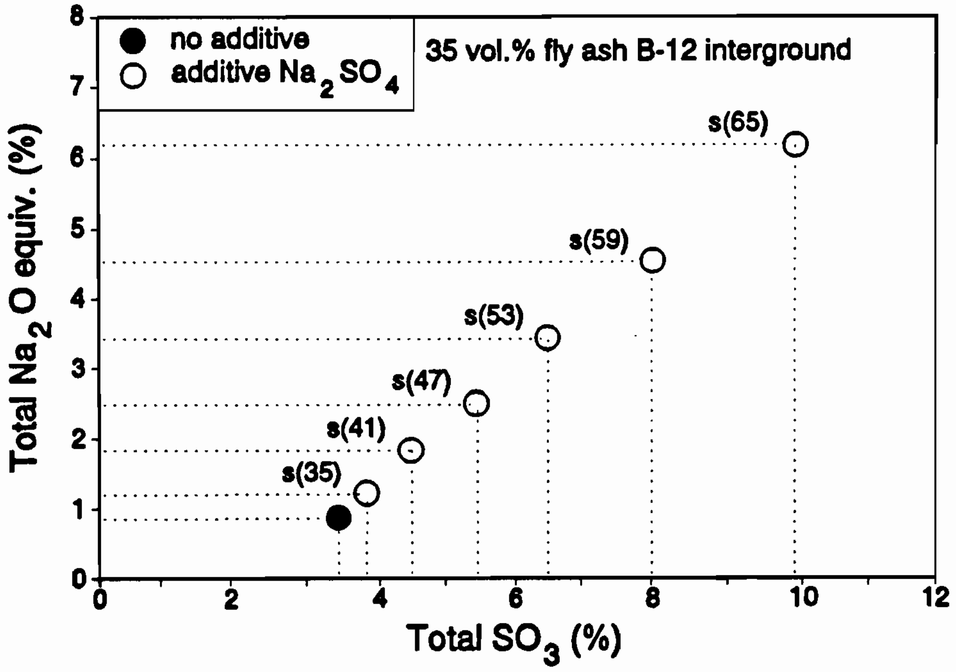


Figure C.5 Alkali and Sulfate Contents of Type II Cement Concrete Containing Fly Ash B-12 and Sodium Sulfate Additive

Table C.8 Alkali, Sulfate, and Equivalent Tricalcium Aluminate Contents of Type II Cement Concrete Containing Interground Fly Ash B-9, Additional Gypsum, and Sodium Hydroxide Additive

Type II Cement Fly Ash B-9 (35 vol.%)	add'l gypsum (%) *	NaOH (%) *	Total wt.% **			Ternary wt.% **		
			Na_2O equiv.	SO_3	C_3A equiv.	Na_2O equiv.	SO_3	C_3A equiv.
no additives	0	0	1.0	2.7	10.3	7.1	19	74
h(35)	0	0.93	1.7	2.7	10.3	12	18	70
h(47)	0	2.93	3.2	2.7	10.3	20	17	64
h(59)	0	5.86	5.4	2.7	10.3	29	15	56
g(35)	1.98	0	1.0	3.6	10.1	6.8	24	69
g(35)h(35)	1.98	0.93	1.7	3.6	10.1	11	23	65
g(35)h(47)	1.98	2.93	3.2	3.6	10.1	19	21	60
g(35)h(59)	1.98	5.86	5.4	3.6	10.1	28	19	53
g(47)	6.53	0	1.0	5.5	9.8	6.1	34	60
g(47)h(35)	6.53	0.93	1.7	5.5	9.8	10	32	58
g(47)h(47)	6.53	2.93	3.2	5.5	9.8	17	30	53
g(47)h(59)	6.53	5.86	5.4	5.5	9.8	26	27	47
g(59)	13.3	0	1.0	8.3	9.2	5.4	45	50
g(59)h(35)	13.3	0.93	1.7	8.3	9.2	8.9	43	48
g(59)h(47)	13.3	2.93	3.2	8.3	9.2	15	40	44
g(59)h(59)	13.3	5.86	5.4	8.3	9.2	23	36	41

* percent by weight of blended fly ash cement

** Na_2O equiv. + SO_3 + C_3A equiv. = 100%

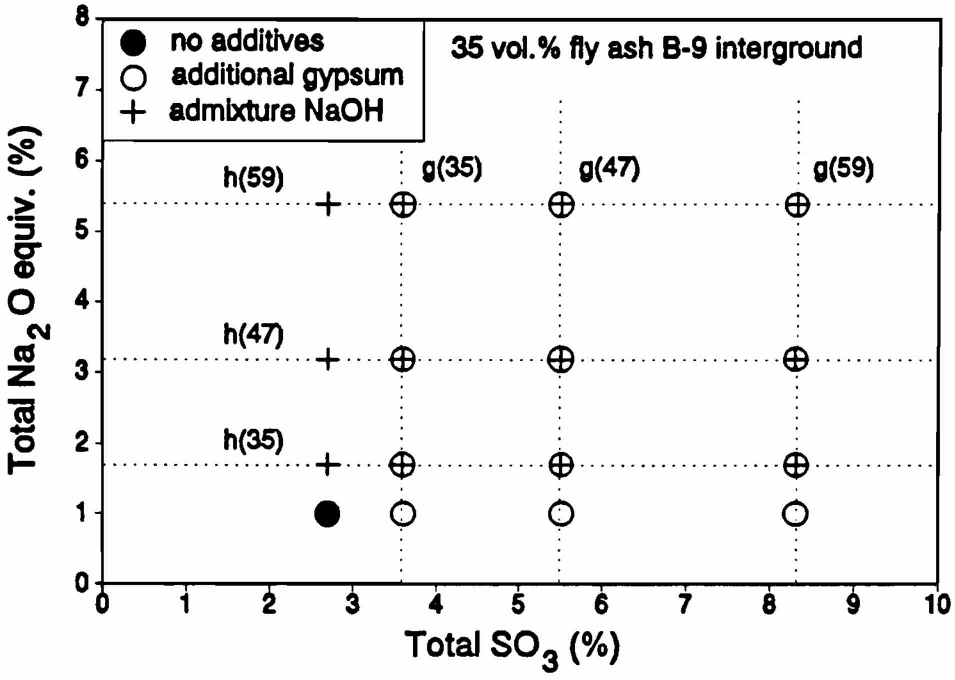


Figure C.6 Alkali and Sulfate Contents of Type II Cement Concrete Containing Fly Ash B-9, Additional Gypsum, and Sodium Hydroxide Additive

Table C.9 Alkali, Sulfate, and Equivalent Tricalcium Aluminate Contents of Type II Cement Concrete Containing Interground Fly Ash B-12, Additional Gypsum, and Sodium Hydroxide Additive

Type II Cement Fly Ash B-12 (35 vol.%)	add'l gypsum (%) *	NaOH (%) *	Total wt.% **			Ternary wt.% **		
			Na_2O equiv.	SO_3	C_3A equiv.	Na_2O equiv.	SO_3	C_3A equiv.
no additives	0	0	0.9	3.4	9.8	6.4	24	70
h(35)	0	0.45	1.2	3.4	9.8	8.3	24	68
h(47)	0	2.15	2.5	3.4	9.8	16	22	62
h(59)	0	4.90	4.6	3.4	9.8	26	19	55
g(35)	0.78	0	0.9	3.8	9.7	6.3	26	67
g(35)h(35)	0.78	0.45	1.2	3.8	9.7	8.4	26	65
g(35)h(47)	0.78	2.15	2.5	3.8	9.7	16	24	61
g(35)h(59)	0.78	4.90	4.6	3.8	9.7	25	21	54
g(47)	4.61	0	0.9	5.4	9.4	5.7	34	60
g(47)h(35)	4.61	0.45	1.2	5.4	9.4	7.5	34	59
g(47)h(47)	4.61	2.15	2.5	5.4	9.4	15	31	53
g(47)h(59)	4.61	4.90	4.6	5.4	9.4	24	28	48
g(59)	10.8	0	0.9	8.0	9.0	5.0	45	50
g(59)h(35)	10.8	0.45	1.2	8.0	9.0	6.6	44	49
g(59)h(47)	10.8	2.15	2.5	8.0	9.0	13	41	46
g(59)h(59)	10.8	4.90	4.6	8.0	9.0	21	37	41

* percent by weight of blended fly ash cement

** Na_2O equiv. + SO_3 + C_3A equiv. = 100%

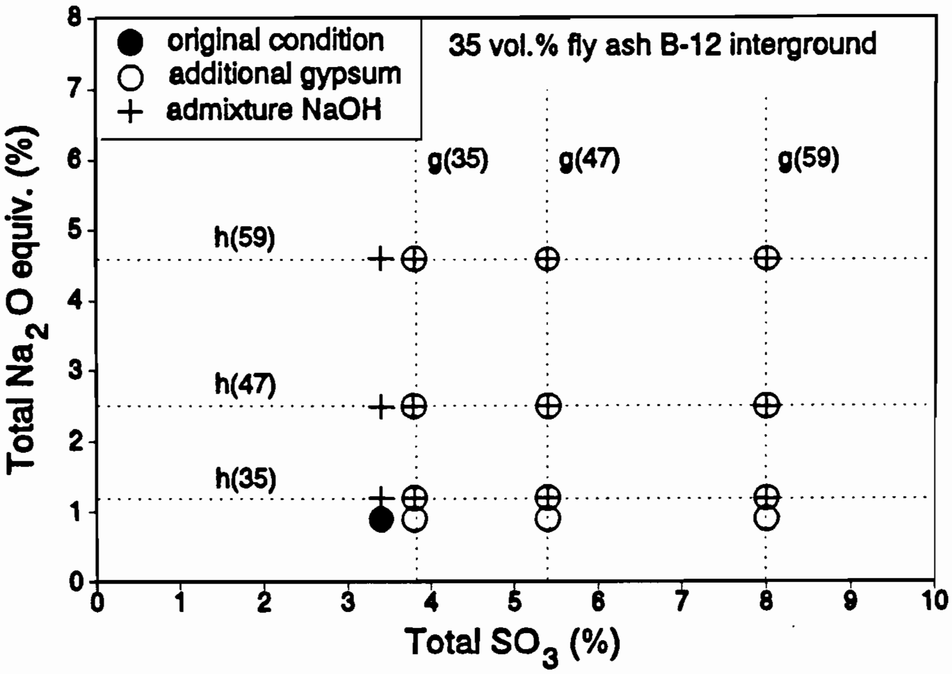


Figure C.7 Alkali and Sulfate Contents of Type II Cement Concrete Containing Fly Ash B-12, Additional Gypsum, and Sodium Hydroxide Additive

Table C.10 Alkali, Sulfate, and Equivalent Tricalcium Aluminate Contents of Type II Cement Concrete Containing High Proportions of Interground Fly Ash B-9 and Sodium Sulfate Additive

Mixture Designation	Na_2SO_4 Added (%) *	Total wt.% *			Ternary wt.% **		
		Na_2O equiv.	SO_3	C_3A equiv.	Na_2O equiv.	SO_3	C_3A equiv.
B9:II:35G	0	1.0	2.7	10.3	7.1	19	74
B9:II:45G	0	1.2	2.6	11.6	7.6	17	75
B9:II:55G	0	1.3	2.5	13.0	7.7	15	77
B9:II:35G:s(35)	1.6	1.7	3.6	10.1	11	23	65
B9:II:45G:s(35)	2.3	2.2	3.8	11.3	13	22	65
B9:II:55G:s(35)	3.0	2.6	4.1	12.6	13	21	65
B9:II:35G:s(47)	5.2	3.2	5.5	9.8	17	30	53
B9:II:45G:s(47)	6.0	3.8	5.8	11	18	29	53
B9:II:55G:s(47)	7.0	4.3	6.3	12	19	28	53
B9:II:35G:s(59)	10.4	5.4	8.3	9.2	23	36	41
B9:II:45G:s(59)	11.9	6.3	9.0	10	24	35	41
B9:II:55G:s(59)	13.5	7.1	9.8	11	25	34	41

* percent by weight of cement

** Na_2O equiv. + SO_3 + C_3A equiv. = 100%

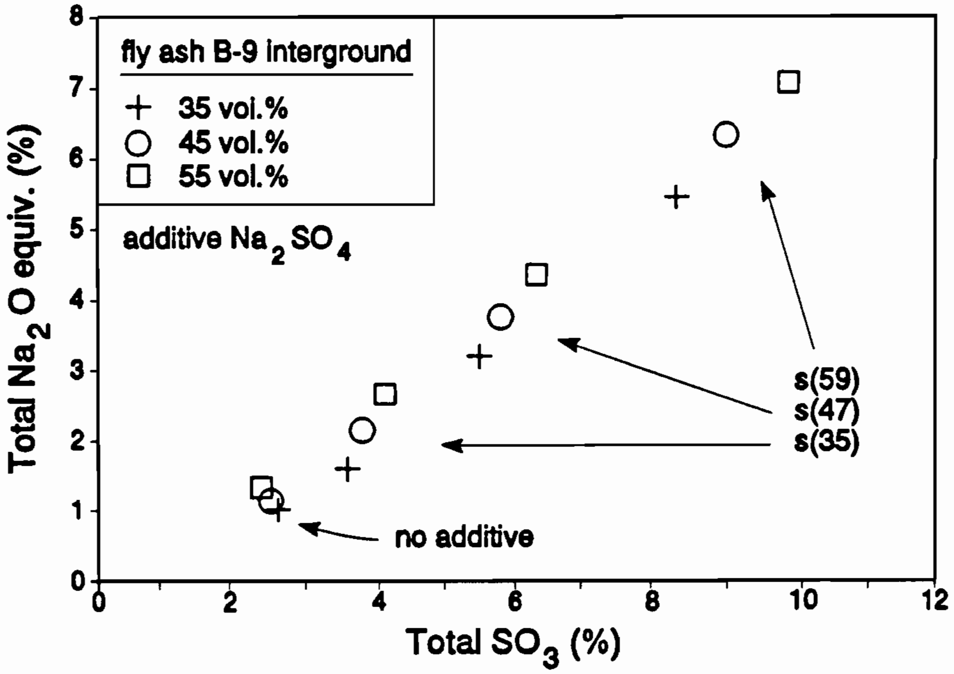


Figure C.8 Alkali and Sulfate Contents of Type II Cement Concrete Containing High Proportions of Interground Fly Ash B-9 and Sodium Sulfate Additive

Table C.11 Alkali, Sulfate, and Equivalent Tricalcium Aluminate Contents of Type II Cement Concrete Containing High Proportions of Interground Fly Ash B-12 and Sodium Sulfate Additive

Mixture Designation	Na_2SO_4 Added (%) *	Total wt.% *			Ternary wt.% **		
		Na_2O equiv.	SO_3	C_3A equiv.	Na_2O equiv.	SO_3	C_3A equiv.
B12:II:35G	0	0.9	3.4	9.8	6.4	24	70
B12:II:45G	0	1.0	3.6	11.0	6.4	23	71
B12:II:55G	0	1.1	3.7	12.2	6.5	22	72
B12:II:35G:s(35)	0.8	1.2	3.8	9.7	8.4	26	65
B12:II:45G:s(35)	1.2	1.5	4.2	10.9	9.1	26	65
B12:II:55G:s(35)	1.6	1.8	4.5	12.0	9.7	25	65
B12:II:35G:s(47)	3.8	2.5	5.4	9.4	15	31	53
B12:II:45G:s(47)	4.8	3.1	6.1	10.5	16	31	53
B12:II:55G:s(47)	5.5	3.4	6.6	11.6	16	31	53
B12:II:35G:s(59)	8.7	4.6	8.0	9.0	21	37	41
B12:II:45G:s(59)	10.5	5.5	9.2	10.0	22	37	41
B12:II:55G:s(59)	11.7	6.1	9.9	10.9	22	37	41

* percent by weight of cement
** Na_2O equiv. + SO_3 + C_3A equiv. = 100%

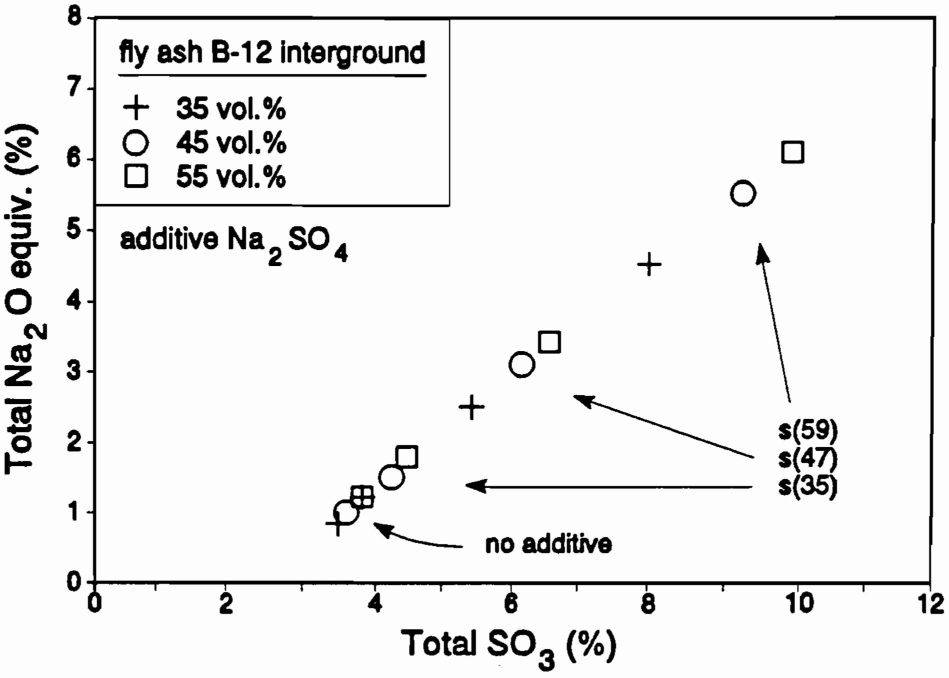


Figure C.9 Alkali and Sulfate Contents of Type II Cement Concrete Containing High Proportions of Interground Fly Ash B-12 and Sodium Sulfate Additive

APPENDIX D

CONCRETE MIXTURES

Table D.1 Concrete Mixture Designations and Descriptions

Mixture Number	Mixture Designation	Cement or Cement Clinker	Cement Factor (sacks/CY)	Fly Ash Type	Volume Percent Fly Ash	Mineral or Chemical Admixture
1	I-L	I-L	5.5	---	0	---
2	I-H	I-H	5.5	---	0	---
3	I-H	I-H	5.5	---	0	---
4	I-H blend A	I-H	5.5	---	0	---
5	I-H blend B	I-H	5.5	---	0	---
6	I-H blend C	I-H	5.5	---	0	---
7	I-H blend D	I-H	5.5	---	0	---
8	I-H blend E	I-H	5.5	---	0	---
9	I-H blend F	I-H	5.5	---	0	---
10	II	II	5.5	---	0	---
11	II	II	5.5	---	0	---
12	II	II	5.5	---	0	---
13	II	II	5.5	---	0	---
14	II	II	5.5	---	0	---
15	II	II	5.5	---	0	---
16	II blend A	II	5.5	---	0	---
17	II blend B	II	5.5	---	0	---
18	II blend B	II	5.5	---	0	---
19	II:7sk	II	7.0	---	0	---
20	II:7sk	II	7.0	---	0	---
21	II:7sk	II	7.0	---	0	---
22	V	V	5.5	---	0	---
23	0%L	0%-L	5.5	---	0	---
24	0%H	0%-H	5.5	---	0	---
25	A1:I-H:25	I-H	5.5	A-1	25	---
26	A1:I-H:35	I-H	5.5	A-1	35	---
27	A1:I-H:25G	I-H	5.5	A-1	25	---
28	A1:I-H:35G	I-H	5.5	A-1	35	---
29	A1:II:25	II	5.5	A-1	25	---
30	A1:II:35	II	5.5	A-1	35	---
31	A1:II:45	II	5.5	A-1	45	---
32	A1:II:25G	II	5.5	A-1	25	---
33	A1:II:35G	II	5.5	A-1	35	---
34	A2:I-L:25	I-L	5.5	A-2	25	---
35	A2:I-H:25	I-H	5.5	A-2	25	---
36	A2:I-H:35	I-H	5.5	A-2	35	---
37	A2:I-H:25G	I-H	5.5	A-2	25	---
38	A2:I-H:35G	I-H	5.5	A-2	35	---
39	A2:II:25	II	5.5	A-2	25	---
40	A2:II:35	II	5.5	A-2	35	---
41	A2:II:45	II	5.5	A-2	45	---
42	A2:II:25G	II	5.5	A-2	25	---
43	A2:II:35G	II	5.5	A-2	35	---
44	A3:II:25	II	5.5	A-3	25	---
45	A3:II:45	II	5.5	A-3	45	---
46	A4:II:25	II	5.5	A-4	25	---
47	A4:II:45	II	5.5	A-4	45	---
48	A5:I-L:25	I-L	5.5	A-5	25	---
49	A5:II:35	II	5.5	A-5	35	---
50	A6:I-H:25	I-H	5.5	A-6	25	---
51	A6:I-H:35	I-H	5.5	A-6	35	---
52	A6:I-H:25G	I-H	5.5	A-6	25	---
53	A6:I-H:35G	I-H	5.5	A-6	35	---
54	A6:II:25	II	5.5	A-6	25	---
55	A6:II:35	II	5.5	A-6	35	---
56	A6:II:45	II	5.5	A-6	45	---

Table D.1 (continued)

Mixture Number	Mixture Designation	Cement or Cement Clinker	Cement Factor (sacks/CY)	Fly Ash Type	Volume Percent Fly Ash	Mineral or Chemical Admixture
57	A6:II:25G	II	5.5	A-6	25	---
58	A6:II:35G	II	5.5	A-6	35	---
59	A7:I-H:25	I-H	5.5	A-7	25	---
60	A7:I-H:35	I-H	5.5	A-7	35	---
61	A7:I-H:25G	I-H	5.5	A-7	25	---
62	A7:I-H:35G	I-H	5.5	A-7	35	---
63	A7:II:25	II	5.5	A-7	25	---
64	A7:II:35	II	5.5	A-7	35	---
65	A7:II:45	II	5.5	A-7	45	---
66	A7:II:25G	II	5.5	A-7	25	---
67	A7:II:35G	II	5.5	A-7	35	---
68	A8:II:25	II	5.5	A-8	25	---
69	A8:II:45	II	5.5	A-8	45	---
70	A9:IL:25	IL	5.5	A-9	25	---
71	A9:I-L:35	I-L	5.5	A-9	35	---
72	A9:I-H:25	I-H	5.5	A-9	25	---
73	A9:I-H:35	I-H	5.5	A-9	35	---
74	A9:I-H:25G	I-H	5.5	A-9	25	---
75	A9:I-H:35G	I-H	5.5	A-9	35	---
76	A9:II:25	II	5.5	A-9	25	---
77	A9:II:35	II	5.5	A-9	35	---
78	A9:II:45	II	5.5	A-9	45	---
79	A9:II:25G	II	5.5	A-9	25	---
80	A9:II:35G	II	5.5	A-9	35	---
81	A10:I-L:25	I-L	5.5	A-10	25	---
82	A10:II:35	II	5.5	A-10	35	---
83	A11:I-L:25	I-L	5.5	A-11	25	---
84	A11:I-L:35	I-L	5.5	A-11	35	---
85	A11:I-H:25	I-H	5.5	A-11	25	---
86	A11:I-H:35	I-H	5.5	A-11	35	---
87	A11:I-H:25G	I-H	5.5	A-11	25	---
88	A11:I-H:35G	I-H	5.5	A-11	35	---
89	A11:II:25	II	5.5	A-11	25	---
90	A11:II:35	II	5.5	A-11	35	---
91	A11:II:45	II	5.5	A-11	45	---
92	A11:II:25G	II	5.5	A-11	25	---
93	A11:II:35G	II	5.5	A-11	35	---
94	A12:II:35	II	5.5	A-12	35	---
95	B1:I-H:25	I-H	5.5	B-1	25	---
96	B1:I-H:35	I-H	5.5	B-1	35	---
97	B1:I-H:25G	I-H	5.5	B-1	25	---
98	B1:I-H:35G	I-H	5.5	B-1	35	---
99	B1:II:25	II	5.5	B-1	25	---
100	B1:II:35	II	5.5	B-1	35	---
101	B1:II:45	II	5.5	B-1	45	---
102	B1:II:25G	II	5.5	B-1	25	---
103	B1:II:35G	II	5.5	B-1	35	---
104	B2:II:35	II	5.5	B-2	35	---
105	B3:I-L:25	I-L	5.5	B-3	25	---
106	B3:I-H:25	I-H	5.5	B-3	25	---
107	B3:I-H:35	I-H	5.5	B-3	35	---
108	B3:I-H:25G	I-H	5.5	B-3	25	---
109	B3:I-H:35G	I-H	5.5	B-3	35	---
110	B3:II:25	II	5.5	B-3	25	---
111	B3:II:35	II	5.5	B-3	35	---
112	B3:II:45	II	5.5	B-3	45	---

Table D.1 (continued)

Mixture Number	Mixture Designation	Cement or Cement Clinker	Cement Factor (sacks/CY)	Fly Ash Type	Volume Percent Fly Ash	Mineral or Chemical Admixture
113	B3:II:25G	II	5.5	B-3	25	---
114	B3:II:35G	II	5.5	B-3	35	---
115	B3:II:35:S(35)	II	5.5	B-3	35	Na2SO4
116	B3:II:35:S(41)	II	5.5	B-3	35	Na2SO4
117	B3:II:35:S(47)	II	5.5	B-3	35	Na2SO4
118	B3:II:35:S(53)	II	5.5	B-3	35	Na2SO4
119	B3:II:35:S(59)	II	5.5	B-3	35	Na2SO4
120	B3:II:35G:S(35)	II	5.5	B-3	35	Na2SO4
121	B3:II:35G:S(41)	II	5.5	B-3	35	Na2SO4
122	B3:II:35G:S(47)	II	5.5	B-3	35	Na2SO4
123	B3:II:35G:S(53)	II	5.5	B-3	35	Na2SO4
124	B3:II:35G:S(59)	II	5.5	B-3	35	Na2SO4
125	B3:II:35G:S(65)	II	5.5	B-3	35	Na2SO4
126	B3:II:25:7sk	II	7.0	B-3	25	---
127	B3:II:35:7sk	II	7.0	B-3	35	---
128	B3:II:45:7sk	II	7.0	B-3	45	---
129	B4:I-H:25	I-H	5.5	B-4	25	---
130	B4:I-H:35	I-H	5.5	B-4	35	---
131	B4:I-H:25G	I-H	5.5	B-4	25	---
132	B4:I-H:35G	I-H	5.5	B-4	35	---
133	B4:II:25	II	5.5	B-4	25	---
134	B4:II:35	II	5.5	B-4	35	---
135	B4:II:45	II	5.5	B-4	45	---
136	B4:II:25G	II	5.5	B-4	25	---
137	B4:II:35G	II	5.5	B-4	35	---
138	B4:II:35:S(35)	II	5.5	B-4	35	Na2SO4
139	B4:II:35:S(41)	II	5.5	B-4	35	Na2SO4
140	B4:II:35:S(47)	II	5.5	B-4	35	Na2SO4
141	B4:II:35:S(53)	II	5.5	B-4	35	Na2SO4
142	B4:II:35:S(59)	II	5.5	B-4	35	Na2SO4
143	B4:II:35G:S(35)	II	5.5	B-4	35	Na2SO4
144	B4:II:35G:S(41)	II	5.5	B-4	35	Na2SO4
145	B4:II:35G:S(47)	II	5.5	B-4	35	Na2SO4
146	B4:II:35G:S(53)	II	5.5	B-4	35	Na2SO4
147	B4:II:35G:S(59)	II	5.5	B-4	35	Na2SO4
148	B4:II:35G:S(65)	II	5.5	B-4	35	Na2SO4
149	B4:II:25:7sk	II	7.0	B-4	25	---
150	B4:II:35:7sk	II	7.0	B-4	35	---
151	B4:II:45:7sk	II	7.0	B-4	45	---
152	B5:I-L:25	I-L	5.5	B-5	25	---
153	B5:I-L:35	I-L	5.5	B-5	35	---
154	B5:I-H:25	I-H	5.5	B-5	25	---
155	B5:I-H:35	I-H	5.5	B-5	35	---
156	B5:I-H:25G	I-H	5.5	B-5	25	---
157	B5:I-H:35G	I-H	5.5	B-5	35	---
158	B5:II:25	II	5.5	B-5	25	---
159	B5:II:35	II	5.5	B-5	35	---
160	B5:II:45	II	5.5	B-5	45	---
161	B5:II:25G	II	5.5	B-5	25	---
162	B5:II:35G	II	5.5	B-5	35	---
163	B5:II:35:S(35)	II	5.5	B-5	35	Na2SO4
164	B5:II:35:S(41)	II	5.5	B-5	35	Na2SO4
165	B5:II:35:S(47)	II	5.5	B-5	35	Na2SO4
166	B5:II:35:S(53)	II	5.5	B-5	35	Na2SO4
167	B5:II:35:S(59)	II	5.5	B-5	35	Na2SO4
168	B5:II:35G:S(35)	II	5.5	B-5	35	Na2SO4

Table D.1 (continued)

Mixture Number	Mixture Designation	Cement or Cement Clinker	Cement Factor (sacks/CY)	Fly Ash Type	Volume Percent Fly Ash	Mineral or Chemical Admixture
169	B5:II:35G:S(41)	II	5.5	B-5	35	Na2SO4
170	B5:II:35G:S(47)	II	5.5	B-5	35	Na2SO4
171	B5:II:35G:S(53)	II	5.5	B-5	35	Na2SO4
172	B5:II:35G:S(59)	II	5.5	B-5	35	Na2SO4
173	B5:II:35G:S(65)	II	5.5	B-5	35	Na2SO4
174	B5:II:25:7sk	II	7.0	B-5	25	---
175	B5:II:35:7sk	II	7.0	B-5	35	---
176	B5:II:45:7sk	II	7.0	B-5	45	---
177	B6:I-L:25	I-L	5.5	B-6	25	---
178	B6:II:25	II	5.5	B-6	25	---
179	B6:II:35	II	5.5	B-6	35	---
180	B6:II:45	II	5.5	B-6	45	---
181	B7:I-H:25	I-H	5.5	B-7	25	---
182	B7:I-H:35	I-H	5.5	B-7	35	---
183	B7:I-H:25G	I-H	5.5	B-7	25	---
184	B7:I-H:35G	I-H	5.5	B-7	35	---
185	B7:II:25	II	5.5	B-7	25	---
186	B7:II:35	II	5.5	B-7	35	---
187	B7:II:45	II	5.5	B-7	45	---
188	B7:II:25G	II	5.5	B-7	25	---
189	B7:II:35G	II	5.5	B-7	35	---
190	B7:II:25:7sk	II	7.0	B-7	25	---
191	B7:II:35:7sk	II	7.0	B-7	35	---
192	B7:II:45:7sk	II	7.0	B-7	45	---
193	B8:II:25	II	5.5	B-8	25	---
194	B8:II:35	II	5.5	B-8	35	---
195	B8:II:45	II	5.5	B-8	45	---
196	B9:I-L:25	I-L	5.5	B-9	25	---
197	B9:I-L:35	I-L	5.5	B-9	35	---
198	B9:I-H:25	I-H	5.5	B-9	25	---
199	B9:I-H:35	I-H	5.5	B-9	35	---
200	B9:I-H:25G	I-H	5.5	B-9	25	---
201	B9:I-H:35G	I-H	5.5	B-9	35	---
202	B9:II:25	II	5.5	B-9	25	---
203	B9:II:35	II	5.5	B-9	35	---
204	B9:II:45	II	5.5	B-9	45	---
205	B9:II:25G	II	5.5	B-9	25	---
206	B9:II:35G	II	5.5	B-9	35	---
207	B9:II:45G	II	5.5	B-9	45	---
208	B9:II:55G	II	5.5	B-9	55	---
209	B9:II:35:S(35)	II	5.5	B-9	35	Na2SO4
210	B9:II:35:S(41)	II	5.5	B-9	35	Na2SO4
211	B9:II:35:S(47)	II	5.5	B-9	35	Na2SO4
212	B9:II:35:S(53)	II	5.5	B-9	35	Na2SO4
213	B9:II:35:S(59)	II	5.5	B-9	35	Na2SO4
214	B9:II:35G:S(35)	II	5.5	B-9	35	Na2SO4
215	B9:II:35G:S(41)	II	5.5	B-9	35	Na2SO4
216	B9:II:35G:S(47)	II	5.5	B-9	35	Na2SO4
217	B9:II:35G:S(53)	II	5.5	B-9	35	Na2SO4
218	B9:II:35G:S(59)	II	5.5	B-9	35	Na2SO4
219	B9:II:35G:S(65)	II	5.5	B-9	35	Na2SO4
220	B9:II:45G:S(35)	II	5.5	B-9	45	Na2SO4
221	B9:II:45G:S(47)	II	5.5	B-9	45	Na2SO4
222	B9:II:45G:S(59)	II	5.5	B-9	45	Na2SO4
223	B9:II:55G:S(35)	II	5.5	B-9	55	Na2SO4
224	B9:II:55G:S(47)	II	5.5	B-9	55	Na2SO4

Table D.1 (continued)

Mixture Number	Mixture Designation	Cement or Cement Clinker	Cement Factor (sacks/CY)	Fly Ash Type	Volume Percent Fly Ash	Mineral or Chemical Admixture
225	B9:II:55G:S(59)	II	5.5	B-9	55	Na2SO4
226	B9:II:35G:g(35)	II	5.5	B-9	35	gypsum
227	B9:II:35G:g(35)h(35)	II	5.5	B-9	35	gyp., NaOH
228	B9:II:35G:g(35)h(47)	II	5.5	B-9	35	gyp., NaOH
229	B9:II:35G:g(47)	II	5.5	B-9	35	gypsum
230	B9:II:35G:g(47)h(35)	II	5.5	B-9	35	gyp., NaOH
231	B9:II:35G:g(47)h(47)	II	5.5	B-9	35	gyp., NaOH
232	B9:II:35G:g(47)h(59)	II	5.5	B-9	35	gyp., NaOH
233	B9:II:35G:g(59)	II	5.5	B-9	35	gypsum
234	B9:II:35G:g(59)h(35)	II	5.5	B-9	35	gyp., NaOH
235	B9:II:35G:g(59)h(47)	II	5.5	B-9	35	gyp., NaOH
236	B9:II:35G:g(59)h(59)	II	5.5	B-9	35	gyp., NaOH
237	B9:II:35G:h(35)	II	5.5	B-9	35	NaOH
238	B9:II:35G:h(47)	II	5.5	B-9	35	NaOH
239	B9:II:35G:h(59)	II	5.5	B-9	35	NaOH
240	B9:II:25:7sk	II	7.0	B-9	25	---
241	B9:II:35:7sk	II	7.0	B-9	35	---
242	B9:II:45:7sk	II	7.0	B-9	45	---
243	B10:I-L:25	I-L	5.5	B-10	25	---
244	B10:I-L:35	I-L	5.5	B-10	35	---
245	B10:II:25	II	5.5	B-10	25	---
246	B10:II:35	II	5.5	B-10	35	---
247	B10:II:45	II	5.5	B-10	45	---
248	B10:II:25G	II	5.5	B-10	25	---
249	B10:II:35G	II	5.5	B-10	35	---
250	B11:II:25	II	5.5	B-11	25	---
251	B11:II:35	II	5.5	B-11	35	---
252	B11:II:45	II	5.5	B-11	45	---
253	B12:I-H:25	I-H	5.5	B-12	25	---
254	B12:I-H:35	I-H	5.5	B-12	35	---
255	B12:I-H:25G	I-H	5.5	B-12	25	---
256	B12:I-H:35G	I-H	5.5	B-12	35	---
257	B12:II:25	II	5.5	B-12	25	---
258	B12:II:35	II	5.5	B-12	35	---
259	B12:II:45	II	5.5	B-12	45	---
260	B12:II:25G	II	5.5	B-12	25	---
261	B12:II:35G	II	5.5	B-12	35	---
262	B12:II:45G	II	5.5	B-12	45	---
263	B12:II:55G	II	5.5	B-12	55	---
264	B12:II:35:S(35)	II	5.5	B-12	35	Na2SO4
265	B12:II:35:S(41)	II	5.5	B-12	35	Na2SO4
266	B12:II:35:S(47)	II	5.5	B-12	35	Na2SO4
267	B12:II:35:S(53)	II	5.5	B-12	35	Na2SO4
268	B12:II:35:S(59)	II	5.5	B-12	35	Na2SO4
269	B12:II:35G:S(35)	II	5.5	B-12	35	Na2SO4
270	B12:II:35G:S(41)	II	5.5	B-12	35	Na2SO4
271	B12:II:35G:S(47)	II	5.5	B-12	35	Na2SO4
272	B12:II:35G:S(53)	II	5.5	B-12	35	Na2SO4
273	B12:II:35G:S(59)	II	5.5	B-12	35	Na2SO4
274	B12:II:35G:S(65)	II	5.5	B-12	35	Na2SO4
275	B12:II:45G:S(35)	II	5.5	B-12	45	Na2SO4
276	B12:II:45G:S(47)	II	5.5	B-12	45	Na2SO4
277	B12:II:45G:S(59)	II	5.5	B-12	45	Na2SO4
278	B12:II:55G:S(35)	II	5.5	B-12	55	Na2SO4
279	B12:II:55G:S(47)	II	5.5	B-12	55	Na2SO4
280	B12:II:55G:S(59)	II	5.5	B-12	55	Na2SO4

Table D.1 (continued)

Mixture Number	Mixture Designation	Cement or Cement Clinker	Cement Factor (sacks/CY)	Fly Ash Type	Volume Percent Fly Ash	Mineral or Chemical Admixture
281	B12:II:35G:g(35)	II	5.5	B-12	35	gypsum
282	B12:II:35G:g(35)h(35)	II	5.5	B-12	35	gyp., NaOH
283	B12:II:35G:g(35)h(47)	II	5.5	B-12	35	gyp., NaOH
284	B12:II:35G:g(47)	II	5.5	B-12	35	gypsum
285	B12:II:35G:g(47)h(35)	II	5.5	B-12	35	gyp., NaOH
286	B12:II:35G:g(47)h(47)	II	5.5	B-12	35	gyp., NaOH
287	B12:II:35G:g(47)h(59)	II	5.5	B-12	35	gyp., NaOH
288	B12:II:35G:g(59)	II	5.5	B-12	35	gypsum
289	B12:II:35G:g(59)h(35)	II	5.5	B-12	35	gyp., NaOH
290	B12:II:35G:g(59)h(47)	II	5.5	B-12	35	gyp., NaOH
291	B12:II:35G:g(59)h(59)	II	5.5	B-12	35	gyp., NaOH
292	B12:II:35G:h(35)	II	5.5	B-12	35	NaOH
293	B12:II:35G:h(47)	II	5.5	B-12	35	NaOH
294	B12:II:35G:h(59)	II	5.5	B-12	35	NaOH
295	B12:II:25:7sk	II	7.0	B-12	25	---
296	B12:II:35:7sk	II	7.0	B-12	35	---
297	B12:II:45:7sk	II	7.0	B-12	45	---
298	I-H:2.1%	I-H	5.5	---	0	---
299	I-H:5%	I-H	5.5	---	0	---
300	A2:I-H:25:2.1%	I-H	5.5	A-2	25	---
301	A2:I-H:25:5%	I-H	5.5	A-2	25	---
302	A2:I-H:25G:2.1%	I-H	5.5	A-2	25	---
303	A2:I-H:25G:5%	I-H	5.5	A-2	25	---
304	A9:I-H:25:2.1%	I-H	5.5	A-9	25	---
305	A9:I-H:25:5%	I-H	5.5	A-9	25	---
306	A9:I-H:25G:2.1%	I-H	5.5	A-9	25	---
307	A9:I-H:25G:5%	I-H	5.5	A-9	25	---
308	B4:I-H:35:2.1%	I-H	5.5	B-4	35	---
309	B4:I-H:35:5%	I-H	5.5	B-4	35	---
310	B4:I-H:35G:2.1%	I-H	5.5	B-4	35	---
311	B4:I-H:35G:5%	I-H	5.5	B-4	35	---
312	B9:I-H:35:2.1%	I-H	5.5	B-9	35	---
313	B9:I-H:35:5%	I-H	5.5	B-9	35	---
314	B9:I-H:35G:2.1%	I-H	5.5	B-9	35	---
315	B9:I-H:35G:5%	I-H	5.5	B-9	35	---
316	B12:I-H:35:2.1%	I-H	5.5	B-12	35	---
317	B12:I-H:35:5%	I-H	5.5	B-12	35	---
318	B12:I-H:35G:2.1%	I-H	5.5	B-12	35	---
319	B12:I-H:35G:5%	I-H	5.5	B-12	35	---

Table D.2 Concrete Mixture Constituents and Water/(Cement + Pozzolan) Ratios, by Weight

Mixture Number	Saturated Surface Dry Weights (lbs); 1 Cubic Yard Concrete							
	Cement	Fly Ash	Rock	Sand	Water	NaOH	Na2SO4	W/(C+P)
1	516.9	---	1568	1544	266.3	---	---	.52
2	516.9	---	1543	1571	253.3	---	---	.49
3	516.9	---	1563	1490	303.9	---	---	.59
4	516.9	---	1714	1469	253.3	---	---	.49
5	516.9	---	1714	1453	259.8	---	---	.50
6	516.9	---	1714	1446	257.7	---	---	.50
7	516.9	---	1714	1461	249.0	---	---	.48
8	516.9	---	1714	1414	274.9	---	---	.53
9	516.9	---	1714	1455	258.7	---	---	.50
10	516.9	---	1568	1521	274.9	---	---	.53
11	516.9	---	1568	1521	274.9	---	---	.53
12	516.9	---	1568	1408	326.2	---	---	.63
13	516.9	---	1568	1552	263.4	---	---	.51
14	516.9	---	1714	1424	268.5	---	---	.52
15	516.9	---	1563	1509	293.8	---	---	.57
16	516.9	---	1568	1486	296.5	---	---	.57
17	516.9	---	1568	1475	300.9	---	---	.58
18	516.9	---	1714	1407	274.9	---	---	.53
19	657.5	---	1542	1363	285.5	---	---	.43
20	657.5	---	1542	1385	276.9	---	---	.42
21	657.5	---	1713	1326	260.7	---	---	.40
22	516.9	---	1568	1570	256.6	---	---	.50
23	516.9	---	1568	1474	292.9	---	---	.57
24	516.9	---	1568	1457	299.2	---	---	.58
25	387.7	98.0	1714	1397	281.4	---	---	.58
26	336.0	137.3	1714	1430	268.5	---	---	.57
27	516.9	---	1714	1411	268.5	---	---	.52
28	516.9	---	1714	1415	264.1	---	---	.51
29	387.7	99.6	1568	1544	274.9	---	---	.56
30	336.0	139.5	1568	1544	274.9	---	---	.58
31	284.3	179.3	1568	1583	259.8	---	---	.56
32	516.9	---	1714	1433	259.8	---	---	.50
33	516.9	---	1714	1456	249.0	---	---	.48
34	387.7	101.3	1568	1602	244.4	---	---	.50
35	387.7	99.7	1618	1474	291.1	---	---	.60
36	336.0	139.6	1714	1430	268.5	---	---	.56
37	516.9	---	1714	1472	244.7	---	---	.47
38	516.9	---	1714	1424	259.8	---	---	.50
39	387.7	101.3	1568	1571	256.0	---	---	.52
40	336.0	141.8	1568	1612	240.4	---	---	.50
41	284.3	182.3	1568	1571	256.0	---	---	.55
42	516.9	---	1714	1434	257.7	---	---	.50
43	516.9	---	1714	1434	255.5	---	---	.49
44	387.7	90.7	1568	1441	305.2	---	---	.64
45	284.3	163.6	1568	1438	306.3	---	---	.68
46	387.7	95.0	1568	1521	274.9	---	---	.57
47	284.3	171.1	1568	1521	274.9	---	---	.60
48	387.7	92.5	1568	1454	300.6	---	---	.63
49	336.0	129.6	1568	1600	245.2	---	---	.53
50	387.7	102.2	1714	1425	270.6	---	---	.55
51	336.0	143.0	1714	1475	251.2	---	---	.52
52	516.9	---	1714	1473	244.7	---	---	.47
53	516.9	---	1714	1441	255.5	---	---	.49
54	387.7	103.8	1568	1605	251.5	---	---	.51

Table D.2 (continued)

Mixture Number	Saturated Surface Dry Weights (lbs); 1 Cubic Yard Concrete							
	Cement	Fly Ash	Rock	Sand	Water	NaOH	Na2SO4	W/(C+P)
55	336.0	145.3	1568	1629	242.5	---	---	.50
56	284.3	186.9	1568	1605	251.5	---	---	.53
57	516.9	---	1714	1394	274.9	---	---	.53
58	516.9	---	1714	1418	264.1	---	---	.51
59	387.7	92.7	1714	1425	270.6	---	---	.56
60	336.0	129.8	1714	1414	274.9	---	---	.59
61	516.9	---	1714	1419	266.3	---	---	.52
62	516.9	---	1714	1429	259.8	---	---	.50
63	387.7	94.2	1568	1572	264.1	---	---	.55
64	336.0	131.9	1568	1629	242.5	---	---	.52
65	284.3	169.6	1568	1615	247.9	---	---	.55
66	516.9	---	1714	1478	244.7	---	---	.47
67	516.9	---	1714	1412	268.5	---	---	.52
68	387.7	92.9	1568	1497	284.1	---	---	.59
69	284.3	167.3	1568	1488	287.4	---	---	.64
70	387.7	96.7	1568	1509	279.5	---	---	.58
71	336.0	135.4	1568	1594	247.4	---	---	.52
72	387.7	95.2	1618	1487	285.7	---	---	.59
73	336.0	133.2	1714	1467	254.2	---	---	.54
74	516.9	---	1714	1427	259.8	---	---	.50
75	516.9	---	1714	1442	251.2	---	---	.49
76	387.7	96.7	1568	1620	237.7	---	---	.49
77	336.0	135.4	1568	1604	243.6	---	---	.52
78	284.3	174.1	1568	1593	247.9	---	---	.54
79	516.9	---	1714	1466	244.7	---	---	.47
80	516.9	---	1714	1500	229.6	---	---	.44
81	387.7	84.2	1568	1436	307.1	---	---	.65
82	336.0	117.9	1568	1538	268.5	---	---	.59
83	387.7	95.9	1568	1454	300.6	---	---	.62
84	336.0	134.2	1568	1521	274.9	---	---	.58
85	387.7	89.4	1618	1476	290.1	---	---	.61
86	336.0	125.2	1714	1453	259.8	---	---	.56
87	516.9	---	1714	1450	253.3	---	---	.49
88	516.9	---	1714	1441	253.3	---	---	.49
89	387.7	90.9	1714	1440	262.0	---	---	.55
90	336.0	134.2	1568	1600	245.2	---	---	.52
91	284.3	163.6	1714	1407	274.9	---	---	.61
92	516.9	---	1714	1454	251.2	---	---	.49
93	516.9	---	1714	1406	266.3	---	---	.52
94	336.0	141.8	1568	1528	272.2	---	---	.57
95	387.7	104.2	1714	1469	253.3	---	---	.52
96	336.0	145.9	1714	1458	257.7	---	---	.53
97	516.9	---	1714	1407	270.6	---	---	.52
98	516.9	---	1714	1430	257.7	---	---	.50
99	387.7	105.9	1568	1585	259.1	---	---	.53
100	336.0	148.3	1568	1629	242.5	---	---	.50
101	284.3	190.6	1568	1639	238.9	---	---	.50
102	516.9	---	1714	1429	262.0	---	---	.51
103	516.9	---	1714	1445	253.3	---	---	.49
104	336.0	150.2	1568	1521	274.9	---	---	.57
105	387.7	112.7	1568	1558	260.9	---	---	.52
106	387.7	110.7	1714	1430	268.5	---	---	.54
107	336.0	155.1	1543	1616	236.1	---	---	.48
108	516.9	---	1714	1404	273.9	---	---	.53

Table D.2 (continued)

Mixture	Saturated Surface Dry Weights (lbs); 1 Cubic Yard Concrete							
Number	Cement	Fly Ash	Rock	Sand	Water	NaOH	Na2SO4	W/(C+P)
109	516.9	---	1714	1446	255.5	---	---	.49
110	387.7	112.6	1568	1543	266.8	---	---	.53
111	336.0	157.5	1568	1554	262.5	---	---	.53
112	284.3	202.6	1568	1600	245.2	---	---	.50
113	516.9	---	1714	1364	287.9	---	---	.56
114	516.9	---	1714	1406	272.8	---	---	.53
115	329.9	154.7	1563	1648	239.8	---	8.92	.49
116	324.5	152.2	1563	1648	239.8	---	16.83	.49
117	318.2	149.2	1563	1648	239.8	---	26.17	.49
118	311.2	145.9	1563	1683	226.3	---	36.47	.46
119	304.1	142.6	1563	1674	229.6	---	46.90	.47
120	507.6	---	1563	1551	273.5	---	9.34	.53
121	499.3	---	1563	1595	256.6	---	17.62	.50
122	489.5	---	1563	1569	266.8	---	27.41	.52
123	478.7	---	1563	1595	256.6	---	38.20	.50
124	467.8	---	1563	1629	243.1	---	49.12	.47
125	454.3	---	1563	1621	246.5	---	62.64	.48
126	493.1	143.2	1542	1463	246.6	---	---	.39
127	427.4	200.4	1542	1469	244.5	---	---	.39
128	361.6	257.7	1542	1491	235.8	---	---	.38
129	387.7	106.7	1714	1406	278.2	---	---	.56
130	336.0	149.4	1543	1616	236.1	---	---	.49
131	516.9	---	1714	1472	246.9	---	---	.48
132	516.9	---	1714	1469	246.9	---	---	.48
133	387.7	108.4	1563	1501	297.1	---	---	.60
134	336.0	151.7	1563	1570	270.1	---	---	.55
135	284.3	195.1	1714	1457	255.5	---	---	.53
136	516.9	---	1714	1404	274.9	---	---	.53
137	516.9	---	1714	1396	274.9	---	---	.53
138	331.4	149.6	1563	1657	236.4	---	6.69	.48
139	326.4	147.4	1563	1579	266.8	---	13.88	.55
140	320.7	144.8	1563	1579	266.8	---	22.20	.55
141	314.3	141.9	1563	1579	266.8	---	31.44	.55
142	306.8	138.6	1563	1674	229.6	---	42.31	.47
143	509.8	---	1563	1556	270.1	---	7.09	.52
144	502.2	---	1563	1591	256.6	---	14.71	.50
145	493.4	---	1563	1617	246.5	---	23.53	.48
146	483.6	---	1563	1599	253.3	---	33.32	.49
147	472.1	---	1563	1634	239.8	---	44.85	.46
148	458.7	---	1563	1651	233.0	---	58.25	.45
149	493.1	142.5	1713	1340	255.3	---	---	.40
150	427.4	199.4	1713	1356	248.8	---	---	.40
151	361.6	256.4	1713	1384	238.0	---	---	.39
152	387.7	112.6	1568	1509	279.5	---	---	.56
153	336.0	157.5	1568	1597	246.3	---	---	.50
154	387.7	110.7	1714	1430	268.5	---	---	.54
155	336.0	155.1	1543	1660	218.8	---	---	.45
156	516.9	---	1714	1446	257.7	---	---	.50
157	516.9	---	1714	1435	259.8	---	---	.50
158	387.7	112.6	1568	1521	274.9	---	---	.55
159	336.0	157.5	1568	1542	267.0	---	---	.54
160	284.3	199.8	1568	1578	253.3	---	---	.52
161	516.9	---	1714	1329	303.0	---	---	.59
162	516.9	---	1714	1394	274.9	---	---	.53

Table D.2 (continued)

Mixture Number	Saturated Surface Dry Weights (lbs); 1 Cubic Yard Concrete							
	Cement	Fly Ash	Rock	Sand	Water	NaOH	Na2SO4	W/(C+P)
163	330.3	154.9	1563	1640	243.1	---	8.39	.49
164	325.2	152.5	1563	1544	280.3	---	15.91	.57
165	318.9	149.5	1563	1605	256.6	---	25.15	.52
166	311.9	146.3	1563	1640	243.1	---	35.37	.49
167	304.6	142.8	1563	1692	222.9	---	46.09	.45
168	508.1	---	1563	1535	280.3	---	8.79	.54
169	500.2	---	1563	1622	246.5	---	16.66	.48
170	490.6	---	1563	1618	248.2	---	26.34	.48
171	479.9	---	1563	1596	256.6	---	37.05	.50
172	468.6	---	1563	1648	236.4	---	48.27	.46
173	455.5	---	1563	1587	260.0	---	61.40	.50
174	493.1	143.2	1542	1452	250.9	---	---	.39
175	427.4	200.4	1542	1485	238.0	---	---	.38
176	361.6	257.7	1542	1496	233.7	---	---	.38
177	387.7	110.5	1568	1472	293.6	---	---	.59
178	387.7	110.5	1568	1550	264.1	---	---	.53
179	336.0	154.6	1568	1593	247.9	---	---	.51
180	284.3	198.8	1568	1539	268.2	---	---	.56
181	387.7	111.2	1714	1414	274.9	---	---	.55
182	336.0	155.6	1714	1480	249.0	---	---	.51
183	516.9	---	1714	1481	244.7	---	---	.47
184	516.9	---	1714	1458	251.2	---	---	.49
185	387.7	113.0	1568	1458	307.3	---	---	.61
186	336.0	158.2	1568	1515	285.7	---	---	.58
187	284.3	203.4	1568	1544	274.9	---	---	.56
188	516.9	---	1714	1446	257.7	---	---	.50
189	516.9	---	1714	1461	249.0	---	---	.48
190	493.1	143.7	1713	1317	263.9	---	---	.41
191	427.4	201.2	1713	1356	248.8	---	---	.40
192	361.6	258.7	1713	1395	233.7	---	---	.38
193	387.7	102.9	1568	1563	267.7	---	---	.55
194	336.0	144.1	1568	1548	273.1	---	---	.57
195	284.3	185.3	1568	1590	257.4	---	---	.55
196	387.7	107.6	1568	1456	299.8	---	---	.61
197	336.0	150.6	1568	1564	258.7	---	---	.53
198	387.7	105.9	1714	1414	274.9	---	---	.56
199	336.0	148.2	1543	1632	229.6	---	---	.47
200	516.9	---	1714	1465	249.0	---	---	.48
201	516.9	---	1714	1446	255.5	---	---	.49
202	387.7	107.6	1568	1543	266.8	---	---	.54
203	336.0	150.6	1568	1546	265.5	---	---	.55
204	284.3	193.6	1568	1575	254.7	---	---	.53
205	516.9	---	1714	1443	257.7	---	---	.50
206	516.9	---	1714	1391	274.9	---	---	.53
207	516.9	---	1563	1619	243.1	---	---	.47
208	516.9	---	1563	1570	260.0	---	---	.50
209	330.5	148.1	1563	1648	239.8	---	7.94	.49
210	324.7	145.5	1563	1685	225.3	---	16.32	.46
211	318.4	142.7	1563	1703	218.5	---	25.41	.45
212	311.4	139.6	1563	1720	211.8	---	35.54	.44
213	304.3	136.4	1563	1631	246.5	---	45.83	.51
214	508.5	---	1563	1573	263.4	---	8.44	.51
215	499.6	---	1563	1599	253.3	---	17.34	.49
216	489.9	---	1563	1591	256.6	---	26.99	.50

Table D.2 (continued)

Mixture Number	Saturated Surface Dry Weights (lbs); 1 Cubic Yard Concrete							
	Cement	Fly Ash	Rock	Sand	Water	NaOH	Na2SO4	W/(C+P)
217	479.1	---	1563	1599	253.3	---	37.76	.49
218	468.2	---	1563	1660	229.6	---	48.69	.44
219	455.0	---	1563	1634	239.8	---	61.88	.46
220	505.2	---	1563	1619	243.1	---	11.67	.47
221	487.6	---	1563	1628	239.8	---	29.26	.46
222	461.9	---	1563	1645	233.0	---	54.97	.45
223	502.1	---	1563	1657	226.3	---	14.81	.44
224	483.1	---	1563	1588	253.3	---	33.82	.49
225	455.4	---	1563	1640	233.0	---	61.48	.45
226	516.9	---	1563	1538	276.9	---	---	.54
227	516.9	---	1563	1512	287.0	4.76	---	.55
228	516.9	---	1563	1495	293.8	14.71	---	.55
229	516.9	---	1563	1478	300.5	---	---	.58
230	516.9	---	1563	1512	287.0	4.76	---	.55
231	516.9	---	1563	1582	260.0	14.71	---	.49
232	516.9	---	1563	1452	310.6	28.61	---	.57
233	516.9	---	1563	1434	317.4	---	---	.61
234	516.9	---	1563	1495	293.8	4.76	---	.56
235	516.9	---	1563	1538	276.9	14.71	---	.52
236	516.9	---	1563	1530	280.3	28.61	---	.51
237	516.9	---	1563	1504	290.4	4.76	---	.56
238	516.9	---	1563	1417	324.1	14.71	---	.61
239	516.9	---	1563	1391	334.3	28.61	---	.61
240	493.1	141.4	1713	1378	240.1	---	---	.38
241	427.4	197.9	1713	1390	235.8	---	---	.38
242	361.6	254.5	1713	1398	232.6	---	---	.38
243	387.7	107.1	1568	1543	266.6	---	---	.54
244	336.0	150.0	1568	1557	261.4	---	---	.54
245	387.7	107.1	1568	1607	242.5	---	---	.49
246	336.0	150.0	1568	1535	269.5	---	---	.55
247	284.3	192.8	1568	1551	263.6	---	---	.55
248	516.9	---	1714	1421	266.3	---	---	.52
249	516.9	---	1714	1457	251.2	---	---	.49
250	387.7	113.8	1568	1559	260.5	---	---	.52
251	336.0	159.3	1568	1521	274.9	---	---	.56
252	284.3	204.8	1568	1535	269.5	---	---	.55
253	387.7	114.4	1714	1425	270.6	---	---	.54
254	336.0	160.2	1543	1604	240.4	---	---	.48
255	516.9	---	1714	1462	249.0	---	---	.48
256	516.9	---	1714	1424	265.2	---	---	.51
257	387.7	116.3	1568	1521	274.9	---	---	.55
258	336.0	162.8	1568	1545	265.9	---	---	.53
259	284.3	209.3	1568	1564	258.7	---	---	.52
260	516.9	---	1543	1468	287.9	---	---	.56
261	516.9	---	1543	1454	292.2	---	---	.57
262	516.9	---	1563	1615	246.5	---	---	.48
263	516.9	---	1563	1601	249.9	---	---	.48
264	333.3	161.5	1563	1640	243.1	---	4.01	.49
265	329.1	159.5	1563	1706	217.3	---	10.26	.44
266	323.1	156.6	1563	1687	224.5	---	19.19	.45
267	316.7	153.5	1563	1700	219.5	---	28.68	.44
268	309.1	149.8	1563	1613	253.3	---	39.92	.51
269	512.8	---	1563	1599	253.3	---	4.51	.49
270	506.3	---	1563	1634	239.8	---	10.63	.46

Table D.2 (continued)

Mixture Number	Saturated Surface Dry Weights (lbs); 1 Cubic Yard Concrete							
	Cement	Fly Ash	Rock	Sand	Water	NaOH	Na2SO4	W/(C+P)
271	497.2	---	1563	1591	256.6	---	19.69	.50
272	487.2	---	1563	1591	256.6	---	29.72	.50
273	475.5	---	1563	1617	246.5	---	41.37	.48
274	459.9	---	1563	1591	256.6	---	57.03	.50
275	510.7	---	1563	1606	249.9	---	6.23	.48
276	493.4	---	1563	1650	233.0	---	23.53	.45
277	467.8	---	1563	1650	233.0	---	49.12	.45
278	508.8	---	1563	1592	253.3	---	8.09	.49
279	490.0	---	1563	1644	233.0	---	26.90	.45
280	462.6	---	1563	1644	233.0	---	54.31	.45
281	516.9	---	1563	1547	273.5	---	---	.53
282	516.9	---	1563	1556	270.1	2.32	---	.52
283	516.9	---	1563	1538	276.9	10.88	---	.52
284	516.9	---	1563	1495	293.8	---	---	.57
285	516.9	---	1563	1530	280.3	2.32	---	.54
286	516.9	---	1563	1530	280.3	10.88	---	.53
287	516.9	---	1563	1486	297.1	24.15	---	.55
288	516.9	---	1563	1469	303.9	---	---	.59
289	516.9	---	1563	1478	300.5	2.32	---	.58
290	516.9	---	1563	1443	314.0	10.88	---	.59
291	516.9	---	1563	1521	283.6	24.15	---	.52
292	516.9	---	1563	1538	276.9	2.32	---	.53
293	516.9	---	1563	1538	276.9	10.88	---	.52
294	516.9	---	1563	1330	357.9	24.15	---	.66
295	493.1	147.9	1542	1431	258.9	---	---	.40
296	427.4	207.1	1542	1483	238.9	---	---	.38
297	361.6	266.3	1542	1478	240.9	---	---	.38

Table D.3 Concrete Compressive Strengths and Age at Exposure

	Compressive Strength (psi)					
Mixture Number	(3x6-inch cylinders)				(6x12-inch)	Age at Exposure (days)
	(days) fc	(days) fc	(days) fc	28 days	28 days	
1	(5) 2370	(12) 3640	---	4050	---	12
2	(3) 3220	(7) 4170	(14) 4850	5330	---	7
3	(3) 2600	(8) 3920	(13) 4190	4780	4780	8
4	(3) 3830	(7) 4790	(14) 5250	5580 *	5300	3
5	(3) 3720	(7) 4610	(14) 5130	5260 *	4990	3
6	(3) 3300	(5) 4030	(14) 4850	5560 *	5280	5
7	(3) 3420	(5) 3910	(14) 4650	5310 *	5040	5
8	(3) 3090	(5) 3570	(14) 4300	4580 *	4320	5
9	(3) 3710	(7) 4320	(14) 4950	5660 *	5380	3
10	(7) 3460	---	---	4310	---	7
11	(3) 2550	(5) 3320	(15) 4690	5120	---	6
12	(3) 3360	(6) 4520	---	6070	---	4
13	(5) 3260	(6) 3460	(8) 3650	4910 *	4640	8
14	(1) 2410	(3) 3400	(4) 3680	5800 *	5520	4
15	(3) 2290	(8) 3370	(13) 3790	4390 *	4890	10
16	(1) 2140	(7) 3680	(15) 4380	4700 *	4440	7
17	(1) 1840	(9) 3500	(13) 3680	4750 *	4490	9
18	(3) 3540	(7) 4200	(14) 4690	5590 *	5310	3
19	(2) 3700	(7) 5270	(14) 5890	6850 *	6560	2
20	(2) 3870	(7) 5440	(14) 6190	6750 *	6460	2
21	(3) 5220	(7) 6120	(14) 7020	6980 *	6680	3
22	(8) 3730	---	---	4520	---	8
23	(4) 2960	(9) 3450	---	4040	---	9
24	(5) 2800	(12) 3310	---	3920	---	14
25	(3) 2200	(9) 3110	(14) 3420	4260 *	4000	20
26	(3) 2350	(10) 3120	(16) 3630	4120 *	3870	16
27	(3) 3740	(7) 4530	(14) 5260	6140 *	5850	3
28	(3) 3110	(7) 3980	(14) 4790	5840 *	5560	7
29	(6) 2180	(13) 2770	(21) 3190	4260 *	4000	28
30	(6) 1740	(13) 2350	(21) 2760	4010 *	3760	28
31	(6) 1680	(13) 2200	(21) 2620	3800 *	3550	28
32	(4) 3590	(8) 4360	(14) 4830	5550 *	5270	4
33	(3) 2630	(8) 3850	(14) 4530	5380 *	5110	8
34	(7) 2670	(14) 2930	---	3710	---	28
35	(3) 2680	(7) 3630	(14) 4350	5040 *	4770	7
36	(3) 2620	(11) 3670	(14) 3870	4730 *	4470	11
37	(3) 3920	(8) 5090	(14) 5460	6570	6320	3
38	(3) 3760	(8) 4890	(10) 5150	6650	6230	3
39	(7) 2830	(12) 3010	(19) 3670	4200	---	19
40	(7) 3130	(11) 3400	---	4110	---	12
41	(7) 2310	(12) 2710	(21) 3340	3660	---	26
42	(3) 3680	(7) 4790	(14) 5530	6610 *	6320	3
43	(3) 3410	(5) 3800	(14) 5170	6370 *	6080	5
44	(7) 2810	(20) 3330	---	3470	---	28
45	(7) 1820	---	---	2510	---	28
46	(7) 3240	(14) 4000	---	4200	---	14
47	(7) 2400	(20) 3530	---	3810	---	20
48	(5) 2400	(12) 3220	---	4250	---	28
49	(5) 2250	(12) 2910	---	3690	---	28
50	(3) 2810	(9) 4020	(14) 4380	5370 *	5100	9
51	(3) 2930	(10) 4300	(14) 4800	5460 *	5190	10
52	(3) 4050	(7) 5210	(14) 5980	6730 *	6440	3

Table D.3 (continued)

Mixture Number	Compressive Strength (psi)					Age at Exposure (days)
	(3x6-inch cylinders)				(6x12-inch)	
	(days) fc	(days) fc	(days) fc	28 days	28 days	
53	(3) 3870	(7) 4990	(14) 6040	6770 *	6480	3
54	(6) 2870	(11) 3310	(13) 3770	4900 *	4630	13
55	(6) 2670	(13) 3610	(18) 3930	5160 *	4890	13
56	(6) 2130	(13) 3170	(18) 3500	4620 *	4360	18
57	(3) 3820	(5) 4180	(14) 5560	6260 *	5970	3
58	(3) 3460	(5) 3930	(14) 5780	6590 *	6300	5
59	(4) 2570	(10) 3270	(13) 3570	4630 *	4370	13
60	(3) 2520	(10) 3460	(13) 3600	4360 *	4100	13
61	(4) 3860	(7) 4710	(14) 5250	6560 *	6270	4
62	(4) 3620	(7) 4370	(14) 5190	6240 *	5950	4
63	(7) 2510	(14) 3020	(22) 3590	4470 *	4210	22
64	(7) 2240	(14) 2750	(22) 3230	4060 *	3810	28
65	(7) 1720	(14) 2310	(22) 2720	3740 *	3490	28
66	(4) 3640	(7) 4260	(14) 4920	5750 *	5470	4
67	(4) 3830	(7) 4210	(14) 5130	5680 *	5400	4
68	(7) 3300	(14) 3870	---	4280	---	14
69	(7) 1880	---	---	2740	---	28
70	(5) 2440	(12) 3270	---	3900	---	28
71	(5) 1560	(12) 2280	---	2550	---	28
72	(3) 2150	(7) 2950	(14) 3690	4160 *	3910	14
73	(3) 2440	(10) 3450	(13) 3730	4990 *	4720	13
74	(5) 3760	(7) 4150	(14) 5040	6310 *	6020	5
75	(5) 3850	(7) 4290	(14) 5290	5920 *	5640	5
76	(7) 3710	---	---	5010	---	7
77	(7) 2880	(12) 3190	(19) 3620	4200	---	19
78	(6) 2340	(14) 3020	(23) 3500	3760	---	23
79	(3) 2020	(11) 3410	(14) 3580	5060 *	4790	14
80	(4) 2880	(11) 4110	(14) 4450	5780 *	5500	11
81	(5) 2350	(12) 3000	---	3990	---	28
82	(5) 2180	(12) 2780	---	3360	---	28
83	(5) 2290	(12) 2900	---	4040	---	28
84	---	---	---	2680	---	28
85	(3) 2760	(7) 3970	(14) 4410	5130 *	4860	7
86	(3) 2410	(11) 3380	(14) 3510	4440 *	4180	14
87	(5) 4380	(7) 4740	(14) 5700	6840 *	6550	5
88	(5) 4030	(7) 4400	(14) 5380	6370 *	6080	5
89	(3) 2440	(8) 3760	(14) 4350	5000 *	4730	8
90	(5) 2270	(12) 2960	---	3600	---	28
91	(3) 1450	(8) 2390	(19) 3230	3890 *	3640	28
92	(3) 3730	(7) 4470	(14) 5380	6590 *	6300	3
93	(4) 3430	(7) 4060	(14) 5060	6510 *	6220	7
94	(5) 1630	(20) 2550	---	2960	---	28
95	(4) 3010	(8) 3790	(14) 4310	5090 *	4820	8
96	(3) 2850	(10) 3800	(14) 4310	5180 *	4910	10
97	(4) 4210	(7) 5020	(14) 5700	6630 *	6340	4
98	(4) 3950	(7) 4670	(14) 5640	6460 *	6170	4
99	(5) 2840	(8) 3150	(11) 3550	4580 *	4320	11
100	(5) 2430	(8) 2850	(11) 3260	4880 *	4610	28
101	(5) 2050	(11) 2710	(21) 3320	4220 *	3960	28
102	(3) 3790	(7) 4690	(14) 5620	6140 *	5860	3
103	(3) 3550	(7) 4550	(14) 5370	6200 *	5920	7
104	(5) 3280	(12) 3800	---	4120	---	8

Table D.3 (continued)

Mixture Number	Compressive Strength (psi)					Age at Exposure (days)
	(3x6-inch cylinders)				(6x12-inch)	
	(days) fc	(days) fc	(days) fc	28 days	28 days	
105	(5) 3030	(12) 4100	---	5210	---	9
106	(3) 3450	(4) 4040	(13) 5370	5830 *	5550	4
107	(3) 3110	(6) 4240	(14) 5450	6400 *	6110	6
108	(3) 4250	(7) 5110	(14) 6270	6590 *	6300	3
109	(3) 4010	(7) 5080	(14) 6300	6930 *	6630	3
110	(6) 3900	(14) 4810	---	5380	---	6
111	(6) 4180	(14) 5300	---	6130	---	6
112	(6) 3490	(14) 5010	---	5940	---	7
113	(7) 5250	(14) 6190	(21) 6600	6420 *	6130	7
114	(7) 5100	(14) 6470	(21) 7180	6970 *	6670	7
115	(3) 2950	(7) 4050	(14) 4760	5480	5500	7
116	(3) 3770	(7) 4720	(14) 5780	6190	5430	3
117	(3) 3780	(7) 4670	(14) 5390	5690	5310	3
118	(3) 3980	(7) 4930	(14) 5830	6170	5790	3
119	(3) 3950	(7) 4690	(15) 5360	5820	5350	3
120	(3) 2920	(7) 3830	(13) 4730	5560	5490	7
121	(3) 3880	(7) 5100	(14) 6000	6770	6300	3
122	(3) 4180	(7) 5370	(14) 6300	6870	6610	3
123	(3) 4500	(7) 5600	(14) 6500	6890	6640	3
124	(3) 4380	(7) 5470	(15) 6030	7000	6280	3
125	(3) 3950	(7) 4920	(15) 5800	6630	5710	3
126	(4) 5020	(7) 6160	(14) 6930	7500 *	7200	4
127	(4) 5150	(7) 6280	(14) 7190	7920 *	7610	4
128	(4) 4350	(7) 5650	(14) 7010	8200 *	7890	4
129	(3) 3750	(7) 4450	(14) 5010	5810 *	5530	3
130	(3) 3280	(6) 4200	(14) 5170	6040 *	5760	6
131	(3) 4430	(7) 5430	(14) 6220	6860 *	6570	3
132	(3) 4250	(7) 5130	(14) 6380	6980 *	6680	3
133	(3) 2500	(7) 3830	(14) 4690	5380	5510	7
134	(3) 1990	(7) 3460	(14) 4650	5510	5610	9
135	(4) 3110	(8) 4420	(14) 5070	6300 *	6010	8
136	(7) 5370	(14) 6000	(20) 6290	6210 *	5930	7
137	(7) 5460	(14) 6500	(20) 6860	6820 *	6530	7
138	(3) 2360	(8) 3780	(14) 4540	5060	4950	8
139	(3) 3120	(6) 3810	(14) 4690	4950	4720	6
140	(3) 3520	(7) 4210	(14) 5000	5230	5130	3
141	(3) 3580	(7) 4400	(14) 5000	5480	4990	3
142	(3) 3680	(7) 4290	(14) 4920	5430	5050	3
143	(3) 3030	(7) 3920	(13) 4680	5640	5400	7
144	(3) 3640	(7) 4620	(14) 5030	5750	5350	3
145	(3) 3870	(7) 4710	(14) 5350	5910	5670	3
146	(3) 3830	(7) 4770	(14) 5260	5920	5570	3
147	(3) 4260	(7) 5010	(15) 5810	6360	5700	3
148	(3) 3390	(5) 3990	(15) 4950	5610	5110	5
149	(3) 5280	(7) 6940	(14) 7580	8620 *	8300	3
150	(3) 5330	(7) 7160	(14) 8660	9060 *	8730	3
151	(3) 4880	(7) 6730	(14) 8280	9000 *	8670	3
152	(7) 3320	(14) 3960	---	4930	---	14
153	(5) 2080	(12) 3280	---	4310	---	15
154	(3) 3600	(8) 4560	(13) 4880	5430 *	5160	3
155	(3) 2900	(7) 4030	(14) 4950	5640 *	5360	7
156	(3) 3610	(7) 4450	(14) 5600	6450 *	6160	3

Table D.3 (continued)

	Compressive Strength (psi)					
	(3x6-inch cylinders)				(6x12-inch)	
Mixture Number	(days) fc	(days) fc	(days) fc	28 days	28 days	Age at Exposure (days)
157	(3) 3420	(7) 4530	(14) 5800	6640 *	6350	7
158	(7) 4140	(14) 4820	---	5270	---	7
159	(5) 2600	(9) 3200	---	4560	---	20
160	(5) 3000	(12) 4110	---	5250	---	9
161	(7) 4770	(14) 5500	(20) 5810	5950 *	5670	7
162	(7) 5550	(14) 6000	(20) 6320	6560 *	6270	7
163	(3) 2810	(7) 3640	(14) 4160	4740	4630	7
164	(3) 2860	(7) 3420	(13) 3910	4430	4280	9
165	(3) 3160	(6) 3490	(13) 4120	4710	4500	7
166	(3) 3300	(7) 3870	(14) 4600	4930	4530	7
167	(3) 3300	(7) 3960	(14) 4480	5020	4390	3
168	(3) 2900	(7) 3730	(13) 4550	5210	5100	7
169	(3) 3460	(5) 4130	(15) 5270	5680	5470	5
170	(3) 3770	(7) 4680	(15) 5450	5800	5580	3
171	(3) 4010	(7) 4810	(15) 6610	6130	5730	3
172	(3) 4080	(7) 4800	(15) 5540	6140	5490	3
173	(3) 3680	(7) 4320	(15) 5100	5800	5010	3
174	(4) 4640	(7) 5600	(14) 6540	7330 *	7030	4
175	(4) 4890	(7) 6050	(14) 7240	7580 *	7270	4
176	(4) 4220	(7) 5350	(14) 6600	7690 *	7380	4
177	(5) 3540	(12) 4560	---	5890	---	5
178	(5) 2970	(9) 3640	---	5010	---	9
179	(5) 2970	(9) 3840	---	5050	---	9
180	(5) 2450	(9) 3310	---	5030	---	11
181	(3) 3160	(7) 3900	(14) 4400	4910 *	4640	7
182	(3) 3680	(7) 4780	(14) 5600	5820 *	5540	3
183	(3) 4800	(8) 5870	(14) 6500	7370	6020	3
184	(3) 4270	(8) 5560	(14) 6540	7270	6170	3
185	(8) 3060	(11) 3350	(13) 3490	4890 *	4620	14
186	(8) 3280	(10) 3550	(14) 4150	5460 *	5190	10
187	(8) 3090	(11) 3680	(14) 4030	5610 *	5330	11
188	(3) 3650	(7) 5020	(14) 5480	6300 *	6010	3
189	(3) 3720	(7) 5140	(14) 6100	6540 *	6250	3
190	(3) 4700	(7) 6020	(14) 7170	7120 *	6820	3
191	(3) 4640	(7) 6070	(14) 7350	7470 *	7170	3
192	(3) 4290	(7) 6000	(14) 7510	7960 *	7650	3
193	(8) 3540	(10) 4010	(14) 4450	5140 *	4870	8
194	(8) 3490	(10) 3730	(14) 4190	5520 *	5250	10
195	(8) 2820	(14) 3590	(21) 4170	5270 *	5000	14
196	(7) 3220	(14) 3940	---	4560	---	14
197	(5) 1930	(12) 3260	---	4220	---	15
198	(3) 3750	(7) 4530	(14) 5150	5610 *	5330	3
199	(3) 2640	(8) 4090	(14) 5000	5490 *	5220	8
200	(3) 4220	(7) 5530	(14) 6560	7300 *	7000	3
201	(3) 3270	(7) 5140	(14) 6280	7030 *	6730	7
202	(5) 2790	(9) 3280	---	4380	---	11
203	(5) 2440	(9) 3060	(14) 3360	4620	---	17
204	(7) 3280	(11) 3900	---	5020	---	11
205	(7) 5280	(14) 6310	(21) 6700	6900 *	6600	7
206	(7) 4850	(14) 6040	(21) 6520	6650 *	6360	7
207	(3) 2400	(7) 3470	(11) 4210	6870 *	6580	11
208	(3) 1640	(7) 2730	(14) 3620	5430 *	5160	14

Table D.3 (continued)

Mixture Number	Compressive Strength (psi)					Age at Exposure (days)
	(3x6-inch cylinders)				(6x12-inch)	
	(days) fc	(days) fc	(days) fc	28 days	28 days	
209	(3) 2420	(8) 3870	(14) 4330	5100	4840	8
210	(3) 3320	(5) 3640	(14) 4650	5380	5350	5
211	(3) 3900	(8) 4760	(14) 5190	5990	5720	3
212	(3) 4110	(8) 4750	(14) 5330	6380	5840	3
213	(3) 3620	(7) 4400	(14) 4960	5500	4980	3
214	(3) 3180	(6) 4070	(13) 4960	5760	5560	6
215	(3) 3330	(5) 3910	(14) 5070	5710	5370	5
216	(3) 3740	(7) 4810	(14) 5580	6100	5860	3
217	(3) 3640	(7) 4720	(14) 5410	5960	5570	3
218	(3) 4000	(7) 5010	(15) 5860	6590	6210	3
219	(3) 3510	(7) 4570	(15) 5220	5810	5120	3
220	(3) 3940	(7) 4750	(15) 5890	6180 *	5900	3
221	(3) 4000	(7) 4790	(14) 5390	5660 *	5380	3
222	(3) 3690	(7) 4580	(14) 5110	5610 *	5330	3
223	(3) 3830	(7) 4980	(15) 6120	6260 *	5970	3
224	(3) 4020	(7) 4870	(14) 5290	5380 *	5110	3
225	(3) 3220	(7) 4240	(14) 4850	5310 *	5040	7
226	(3) 2780	(7) 3930	(15) 5290	6240	6030	7
227	(3) 2830	(7) 3750	(15) 4720	5460	5100	7
228	(3) 1890	(7) 2370	(15) 3190	3480	2960	28
229	(3) 1950	(7) 3040	(14) 3910	4820	5170	14
230	(3) 2770	(7) 3840	(14) 4740	5630	5420	7
231	(3) 2900	(7) 3880	(14) 4380	4930	4790	7
232	(3) 1690	(7) 2240	(14) 2590	2990	2660	28
233	(3) 1300	(7) 1810	(14) 3220	4110	4330	28
234	(3) 1730	(7) 2910	(15) 4640	5180	5010	15
235	(3) 2000	(7) 4000	(14) 4630	5240	5110	7
236	(3) 2740	(7) 3490	(14) 4060	4470	4150	8
237	(3) 2330	(7) 3260	(15) 4250	4740	4740	15
238	(3) 1180	(7) 1590	(19) 2100	2270	1960	28
239	(3) 740	(7) 1040	(19) 1490	1660	1450	---
240	(3) 5570	(7) 7190	(14) 8060	8240 *	7930	3
241	(3) 5220	(7) 6940	(14) 8400	8640 *	8320	3
242	(3) 4320	(7) 6130	(14) 7810	8070 *	7760	3
243	(7) 3510	(14) 3990	---	4850	---	7
244	(5) 1650	(12) 2900	---	3800	---	28
245	(6) 4050	(14) 5200	---	5870	---	6
246	(5) 3370	(12) 4380	---	5140	---	7
247	(7) 3690	(12) 4550	---	5680	---	7
248	(3) 4200	(7) 5140	(14) 6030	6600 *	6310	3
249	(3) 3830	(7) 5090	(14) 6060	6940 *	6640	3
250	(3) 2520	(5) 3350	---	4720	---	6
251	(3) 2010	(6) 3140	(10) 4290	4710	---	10
252	(3) 1860	(10) 3900	---	5480	---	10
253	(3) 3670	(8) 4450	(13) 4950	5570 *	5290	3
254	(3) 3000	(7) 3950	(14) 4690	5400 *	5130	7
255	(3) 4330	(7) 5270	(14) 5930	6410 *	6120	3
256	(3) 4260	(7) 5220	(14) 5910	6560 *	6270	3
257	(3) 2330	(6) 2940	(10) 3850	5220	---	10
258	(3) 2100	(6) 2910	(10) 3580	3950	---	10
259	(5) 2630	(9) 3440	---	4580	---	10
260	(3) 2560	(11) 4460	(14) 4770	5670 *	5390	11

Table D.3 (continued)

Mixture Number	Compressive Strength (psi)					Age at Exposure (days)
	(3x6-inch cylinders)				(6x12-inch)	
	(days) fc	(days) fc	(days) fc	28 days	28 days	
261	(3) 2190	(11) 4360	(14) 4580	5660 *	5380	11
262	(3) 2930	(7) 4270	(15) 5840	6430 *	6140	7
263	(3) 2510	(7) 4060	(14) 5440	6300 *	6010	7
264	(3) 2450	(8) 3820	(14) 4450	5010	5070	8
265	(3) 3720	(6) 4320	(13) 4970	5600	5230	3
266	(3) 3980	(6) 4480	(13) 5100	5970	5400	3
267	(3) 4140	(6) 4520	(13) 5150	5890	5540	3
268	(3) 3840	(7) 4360	(14) 4790	5420	5100	3
269	(3) 3070	(7) 4280	(14) 5040	5500	5480	7
270	(3) 3270	(7) 3700	(14) 4390	4790	4450	7
271	(3) 3300	(7) 3840	(14) 4280	4720	4270	7
272	(3) 3460	(7) 4250	(14) 4800	5310	4920	7
273	(3) 3980	(7) 4650	(15) 5370	5860	5350	3
274	(3) 3540	(7) 4300	(15) 4860	5550	4850	3
275	(3) 3880	(7) 5030	(15) 5980	6330 *	6040	3
276	(3) 4110	(7) 4840	(15) 5630	5760 *	5480	3
277	(3) 4040	(7) 4610	(15) 5260	5480 *	5210	3
278	(3) 3460	(7) 4240	(14) 5120	5440 *	5170	4
279	(3) 3730	(7) 4330	(14) 4820	4920 *	4650	3
280	(3) 3400	(7) 3910	(14) 4520	4550 *	4290	7
281	(3) 2760	(7) 3880	(14) 4950	5520	5750	7
282	(3) 2840	(7) 3860	(14) 4630	5300	5200	7
283	(3) 2060	(7) 2660	(14) 2940	3390	3000	28
284	(3) 2250	(7) 3220	(11) 3950	4920	5010	11
285	(3) 2660	(7) 3490	(14) 4170	4730	4650	8
286	(3) 2910	(7) 3560	(15) 4130	4600	4260	7
287	(3) 1750	(7) 2160	(15) 2590	2920	2770	28
288	(3) 1250	(7) 1810	(15) 3610	4370	4520	15
289	(3) 1180	(7) 1670	(14) 3390	4220	4290	28
290	(3) 2380	(7) 3360	(12) 3890	4440	4430	12
291	(3) 2610	(7) 3290	(12) 3610	4140 *	3890	12
292	(3) 2640	(7) 3690	(15) 4760	5230	5070	7
293	(3) 2020	(7) 2400	(19) 3100	3330	2880	28
294	(3) 940	(7) 1220	(19) 1580	1800	1490	---
295	(3) 4300	(7) 5890	(13) 6700	7640 *	7330	3
296	(3) 4370	(7) 6080	(13) 7000	7600 *	7290	3
297	(3) 3850	(7) 5700	(13) 6500	7560 *	7260	3

* estimated from the strength of 6x12-inch cylinders
- regression: $y = 1.015x + 196$, where
y = 3x6-inch cylinder strength (psi)
x = 6x12-inch cylinder strength (psi)
$R^2 = 0.94$ for 88 observations

APPENDIX E

SULFATE EXPOSURE TEST DATA

Table E.1 Linear Expansion (%) of Sulfate Exposure Specimens

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
1	I-L	.000	.014	.025	.039	.076	.217	.503
2	I-H	.000	.007	.101	.752	fracture	---	---
3	I-H	.000	.018	.195	fracture	---	---	---
4	I-H blend A	.000	.008	.023	.094	.320	1.675	fracture
5	I-H blend B	.000	.012	.070	.351	.987	2.848	fracture
6	I-H blend C	.000	.086	.425	.829	1.109	1.461	1.670
7	I-H blend D	.000	.017	.122	.803	fracture	---	---
8	I-H blend E	.000	.022	.236	1.541	fracture	---	---
9	I-H blend F	.000	.010	.040	.243	.937	3.618	fracture
10	II	.000	.013	.017	.026	.036	.057	.086
11	II	.000	.006	.015	.032	.044	.064	.091
12	II	.000	.005	.016	.033	.046	.066	.080
13	II	.000	-.003	-.003	-.003	.007	.029	.080
14	II	.000	.001	.010	.010	.017	.044	.090
15	II	.000	.003	.006	.006	.014	.039	.079
16	II blend A	.000	.002	-.004	.006	.017	.042	.080
17	II blend B	.000	.001	.003	.020	.040	.091	.145
18	II blend B	.000	.002	.015	.018	.029	.078	.143
19	II:7sk	.000	-.004	-.006	.001	-.002	.003	.005
20	II:7sk	.000	-.003	-.006	.002	.000	.005	.008
21	II:7sk	.000	-.005	-.004	.000	-.004	-.006	-.004
22	V	.000	.008	.022	.034	.043	.054	.066
23	0%L	.000	.011	.019	.027	.034	.051	.060
24	0%H	.000	.013	.027	.040	.050	.075	.100
25	A1:I-H:25	.000	.007	.011	.015	.018	.051	.096
26	A1:I-H:35	.000	.001	.013	.010	.014	.032	.051
27	A1:I-H:25G	.000	-.001	.001	.005	-.002	.001	-.002
28	A1:I-H:35G	.000	-.002	.002	.003	.000	.004	.000
29	A1:II:25	.000	.000	-.008	.002	-.001	-.001	.002
30	A1:II:35	.000	.001	-.005	.006	.002	.003	.001
31	A1:II:45	.000	.003	-.007	.004	.000	-.003	-.004
32	A1:II:25G	.000	.001	.008	.007	.002	.003	-.001
33	A1:II:35G	.000	-.002	.004	-.001	.000	.002	-.004
34	A2:I-L:25	.000	.003	.003	.002	.010	-.001	-.002
35	A2:I-H:25	.000	.000	.000	.006	.004	.012	.029
36	A2:I-H:35	.000	.007	.025	.059	.162	.461	fracture
37	A2:I-H:25G	.000	.007	-.002	.005	.002	.005	.007
38	A2:I-H:35G	.000	-.001	-.005	.000	-.003	.001	.003
39	A2:II:25	.000	.007	.019	.022	.034	.048	.067
40	A2:II:35	.000	.008	.015	.024	.033	.040	.051
41	A2:II:45	.000	.007	.018	.020	.028	.032	.040
42	A2:II:25G	.000	.000	.010	.004	.003	.004	.003
43	A2:II:35G	.000	-.001	.004	.001	.004	.000	-.003
44	A3:II:25	.000	.014	.020	.023	.032	.032	.037
45	A3:II:45	.000	.012	.015	.021	.029	.037	.034
46	A4:II:25	.000	.023	.032	.041	.061	.100	.175
47	A4:II:45	.000	.007	.019	.023	.031	.037	.052
48	A5:I-L:25	.000	.007	.015	.020	.025	.035	.074
49	A5:II:35	.000	.004	.007	.005	.008	-.004	-.005
50	A6:I-H:25	.000	.001	.008	.024	.084	fracture	---
51	A6:I-H:35	.000	.004	.013	.019	.058	fracture	---
52	A6:I-H:25G	.000	-.001	.000	.004	-.002	.000	.000
53	A6:I-H:35G	.000	-.001	.000	.006	-.002	.000	-.003
54	A6:II:25	.000	-.002	-.002	.000	.003	.019	.054

Table E.1 (continued)

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
55	A6:II:35	.000	.001	-.005	-.003	.001	.005	.024
56	A6:II:45	.000	-.002	-.005	-.002	.002	.012	.027
57	A6:II:25G	.000	.000	.010	.006	.007	.009	.010
58	A6:II:35G	.000	.001	.006	.003	.003	.003	.001
59	A7:I-H:25	.000	.010	.040	.133	.299	fracture	---
60	A7:I-H:35	.000	.013	.026	.072	.155	fracture	---
61	A7:I-H:25G	.000	.000	.005	.007	.001	.004	.005
62	A7:I-H:35G	.000	-.001	.004	.007	.001	.007	.005
63	A7:II:25	.000	.000	.001	.012	.025	.055	.109
64	A7:II:35	.000	-.001	.008	.021	.033	.074	.115
65	A7:II:45	.000	.000	.001	.013	.017	.033	.044
66	A7:II:25G	.000	.002	.009	.004	.003	.007	.002
67	A7:II:35G	.000	.007	.009	.006	.004	.010	.008
68	A8:II:25	.000	.012	.020	.030	.043	.064	.099
69	A8:II:45	.000	.010	.018	.024	.031	.030	.037
70	A9:IL:25	.000	.009	.018	.019	.019	.008	.015
71	A9:I-L:35	.000	.003	.006	.004	.009	.003	.000
72	A9:I-H:25	.000	.002	.002	.010	.016	.039	.140
73	A9:I-H:35	.000	.005	.011	.013	.020	.057	.101
74	A9:I-H:25G	.000	-.002	.006	.005	.001	.002	.003
75	A9:I-H:35G	.000	-.002	.003	.001	-.002	-.002	-.002
76	A9:II:25	.000	.007	.013	.019	.026	.037	.037
77	A9:II:35	.000	.013	.019	.019	.029	.039	.039
78	A9:II:45	.000	.020	.019	.021	.026	.030	.028
79	A9:II:25G	.000	-.003	.007	.002	.000	.001	-.006
80	A9:II:35G	.000	.001	.009	.005	-.001	.000	-.003
81	A10:I-L:25	.000	.000	.005	.003	.012	.002	.004
82	A10:II:35	.000	.007	.009	.006	.010	-.001	-.003
83	A11:I-L:25	.000	.004	.007	.004	.012	.003	.005
84	A11:I-L:35	.000	.022	.028	.032	.035	.049	.070
85	A11:I-H:25	.000	-.001	.000	.007	.013	.036	.085
86	A11:I-H:35	.000	.003	.007	.008	.011	.034	.061
87	A11:I-H:25G	.000	-.001	.005	.008	.003	.001	.000
88	A11:I-H:35G	.000	-.004	.000	.000	-.002	-.002	-.004
89	A11:II:25	.000	.001	.009	.006	.004	.005	.004
90	A11:II:35	.000	.005	.008	.002	.007	-.005	-.005
91	A11:II:45	.000	.009	.009	.008	.003	.007	.005
92	A11:II:25G	.000	.002	.008	.004	.006	.004	.000
93	A11:II:35G	.000	.001	.006	.001	-.001	.002	-.002
94	A12:II:35	.000	.009	.021	.026	.039	.046	.060
95	B1:I-H:25	.000	.003	.006	.008	.011	.034	.072
96	B1:I-H:35	.000	.002	.010	.009	.011	.019	.043
97	B1:I-H:25G	.000	-.002	.003	.003	.001	.004	.004
98	B1:I-H:35G	.000	-.001	.004	.007	.000	.002	.002
99	B1:II:25	.000	.005	.003	.002	.004	.000	.011
100	B1:II:35	.000	-.002	-.004	-.004	-.005	-.009	-.003
101	B1:II:45	.000	.000	.000	-.002	.001	-.006	-.004
102	B1:II:25G	.000	.002	.009	.007	.004	.005	.002
103	B1:II:35G	.000	-.001	.005	.002	.001	.005	-.001
104	B2:II:35	.000	.006	.010	.011	.017	.020	.020
105	B3:I-L:25	.000	.012	.017	.019	.029	.074	.267
106	B3:I-H:25	.000	.015	fracture	---	---	---	---
107	B3:I-H:35	.000	.004	.010	.030	.103	fracture	---
108	B3:I-H:25G	.000	.002	.002	.018	.043	fracture	---

Table E.1 (continued)

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
109	B3:I-H:35G	.000	-.001	-.003	.005	.020	.060	fracture
110	B3:II:25	.000	.004	.009	.019	.033	.055	.097
111	B3:II:35	.000	.010	.015	.027	.045	.107	.596
112	B3:II:45	.000	.006	.011	.030	.063	.203	fracture
113	B3:II:25G	.000	-.001	.005	.025	.063	.264	fracture
114	B3:II:35G	.000	-.001	.002	.009	.018	.065	fracture
115	B3:II:35:S(35)	.000	.000	.000	.000	.002	.001	.005
116	B3:II:35:S(41)	.000	.006	.003	.002	.008	.008	.008
117	B3:II:35:S(47)	.000	.007	.004	.004	.012	.014	.017
118	B3:II:35:S(53)	.000	.009	.011	.013	.027	.033	.045
119	B3:II:35:S(59)	.000	.012	.021	.031	.044	.055	.075
120	B3:II:35G:S(35)	.000	.004	.006	.002	.006	.004	.006
121	B3:II:35G:S(41)	.000	.002	.000	-.001	-.001	-.003	.000
122	B3:II:35G:S(47)	.000	.005	.004	.005	.006	.007	.010
123	B3:II:35G:S(53)	.000	.006	.009	.010	.012	.014	.020
124	B3:II:35G:S(59)	.000	.008	.016	.023	.033	.047	.067
125	B3:II:35G:S(65)	.000	.022	.032	.047	.063	.101	.158
126	B3:II:25:7sk	.000	-.002	-.003	.008	.005	.006	.006
127	B3:II:35:7sk	.000	-.002	.005	.006	.002	.001	.000
128	B3:II:45:7sk	.000	-.003	.004	.006	.002	.003	.018
129	B4:I-H:25	.000	.067	fracture	---	---	---	---
130	B4:I-H:35	.000	.007	.027	fracture	---	---	---
131	B4:I-H:25G	.000	.000	-.003	.010	.022	.098	fracture
132	B4:I-H:35G	.000	.002	.000	.038	.101	fracture	---
133	B4:II:25	.000	.008	.027	.111	fracture	---	---
134	B4:II:35	.000	.003	.013	.197	fracture	---	---
135	B4:II:45	.000	.003	.015	.026	.063	fracture	---
136	B4:II:25G	.000	.001	.003	.015	.033	.134	.595
137	B4:II:35G	.000	.003	.002	.012	.018	.068	fracture
138	B4:II:35:S(35)	.000	.002	.004	.004	.008	.015	.042
139	B4:II:35:S(41)	.000	.006	.004	.003	.005	.005	.007
140	B4:II:35:S(47)	.000	.006	.009	.007	.007	.008	.014
141	B4:II:35:S(53)	.000	.011	.014	.015	.016	.022	.030
142	B4:II:35:S(59)	.000	.013	.018	.026	.037	.045	.063
143	B4:II:35G:S(35)	.000	-.001	-.001	-.001	.001	.002	.005
144	B4:II:35G:S(41)	.000	.003	.003	.002	.002	.000	.001
145	B4:II:35G:S(47)	.000	.004	.004	.006	.004	.005	.005
146	B4:II:35G:S(53)	.000	.006	.010	.010	.013	.014	.017
147	B4:II:35G:S(59)	.000	.011	.020	.032	.039	.052	.073
148	B4:II:35G:S(65)	.000	.021	.037	.056	.075	.135	.215
149	B4:II:25:7sk	.000	-.001	.002	.008	.003	.008	.013
150	B4:II:35:7sk	.000	.003	.004	.010	.005	.015	.013
151	B4:II:45:7sk	.000	-.002	.004	.013	.018	.070	fracture
152	B5:I-L:25	.000	.007	.014	.011	.016	.035	.091
153	B5:I-L:35	.000	.013	.131	.645	fracture	---	---
154	B5:I-H:25	.000	.043	fracture	---	---	---	---
155	B5:I-H:35	.000	.010	.062	fracture	---	---	---
156	B5:I-H:25G	.000	-.003	.001	.025	.099	fracture	---
157	B5:I-H:35G	.000	.003	.000	.015	.045	fracture	---
158	B5:II:25	.000	.007	.021	.042	.127	.726	fracture
159	B5:II:35	.000	.023	.121	.637	fracture	---	---
160	B5:II:45	.000	.013	.027	.073	.263	fracture	---
161	B5:II:25G	.000	.006	.034	.154	.835	fracture	---
162	B5:II:35G	.000	.001	.003	.014	.027	.158	fracture

Table E.1 (continued)

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
163	B5:II:35:S(35)	.000	.001	.002	.001	.006	.006	.013
164	B5:II:35:S(41)	.000	.002	.003	-.001	.002	.002	.004
165	B5:II:35:S(47)	.000	.007	.010	.012	.015	.018	.026
166	B5:II:35:S(53)	.000	.005	.007	.012	.018	.030	.041
167	B5:II:35:S(59)	.000	.018	.029	.045	.066	.107	.160
168	B5:II:35G:S(35)	.000	.005	.006	.003	.006	.006	.010
169	B5:II:35G:S(41)	.000	.005	.002	.003	.002	.002	.004
170	B5:II:35G:S(47)	.000	.006	.008	.006	.006	.009	.012
171	B5:II:35G:S(53)	.000	.010	.017	.013	.016	.021	.028
172	B5:II:35G:S(59)	.000	.014	.023	.033	.042	.055	.074
173	B5:II:35G:S(65)	.000	.025	.037	.055	.078	.145	.239
174	B5:II:25:7sk	.000	.000	-.003	.009	.009	.009	.016
175	B5:II:35:7sk	.000	-.003	-.003	.007	.004	.005	.005
176	B5:II:45:7sk	.000	.000	-.002	.009	.007	.013	.025
177	B6:I-L:25	.000	.006	.008	.010	.015	.005	.006
178	B6:II:25	.000	.003	.016	.031	.048	.082	.157
179	B6:II:35	.000	.008	.021	.045	.078	.167	.478
180	B6:II:45	.000	.002	.013	.041	.083	.349	fracture
181	B7:I-H:25	.000	.014	.130	.695	fracture	---	---
182	B7:I-H:35	.000	.003	.004	.010	.016	.028	.090
183	B7:I-H:25G	.000	.001	-.001	.003	.004	.014	.029
184	B7:I-H:35G	.000	.003	-.003	.004	.004	.018	.044
185	B7:II:25	.000	.002	.006	.020	.042	.134	.306
186	B7:II:35	.000	.001	.002	.006	.020	.064	.229
187	B7:II:45	.000	-.001	.004	.011	.026	.062	.102
188	B7:II:25G	.000	.001	-.002	.006	.003	.006	.007
189	B7:II:35G	.000	.002	-.002	.005	.003	.006	.009
190	B7:II:25:7sk	.000	-.001	-.003	.001	-.003	-.005	-.007
191	B7:II:35:7sk	.000	-.001	-.004	.000	.002	-.006	-.005
192	B7:II:45:7sk	.000	-.005	-.009	-.002	-.005	-.011	-.011
193	B8:II:25	.000	.009	.007	.026	.064	.321	.593
194	B8:II:35	.000	.010	.017	.040	.083	.289	fracture
195	B8:II:45	.000	.013	.033	.092	.293	fracture	---
196	B9:I-L:25	.000	.005	.006	.007	.011	.003	.007
197	B9:I-L:35	.000	.009	.018	.041	.153	fracture	---
198	B9:I-H:25	.000	.017	.689	fracture	---	---	---
199	B9:I-H:35	.000	.003	.006	.038	fracture	---	---
200	B9:I-H:25G	.000	-.005	-.006	.004	.010	.115	fracture
201	B9:I-H:35G	.000	-.003	.000	.002	.000	.014	.037
202	B9:II:25	.000	.011	.021	.042	.073	.140	.268
203	B9:II:35	.000	.013	.024	.052	.109	.834	fracture
204	B9:II:45	.000	.008	.024	.072	.471	fracture	---
205	B9:II:25G	.000	-.003	.000	.010	.012	.047	.118
206	B9:II:35G	.000	.004	.002	.012	.016	.049	.153
207	B9:II:45G	.000	-.001	-.002	.001	.008	.011	.036
208	B9:II:55G	.000	-.002	-.002	-.001	.002	-.004	.000
209	B9:II:35:S(35)	.000	.002	.002	.000	.003	.004	.009
210	B9:II:35:S(41)	.000	.004	.001	-.001	.003	.002	.006
211	B9:II:35:S(47)	.000	.012	.013	.013	.014	.022	.029
212	B9:II:35:S(53)	.000	.014	.016	.021	.029	.044	.059
213	B9:II:35:S(59)	.000	.015	.019	.030	.044	.062	.087
214	B9:II:35G:S(35)	.000	.000	.000	-.002	.001	-.001	.001
215	B9:II:35G:S(41)	.000	.001	.003	-.001	-.001	.000	.001
216	B9:II:35G:S(47)	.000	.003	.003	.002	.002	.003	.003

Table E.1 (continued)

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
217	B9:II:35G:S(53)	.000	.007	.011	.011	.013	.014	.018
218	B9:II:35G:S(59)	.000	.010	.020	.025	.033	.042	.060
219	B9:II:35G:S(65)	.000	.019	.033	.049	.067	.112	.167
220	B9:II:45G:S(35)	.000	.000	-.002	.003	.002	-.005	-.002
221	B9:II:45G:S(47)	.000	.001	.000	.001	.004	.000	.002
222	B9:II:45G:S(59)	.000	.009	.013	.018	.023	.024	.034
223	B9:II:55G:S(35)	.000	-.003	-.005	-.003	-.004	-.008	-.007
224	B9:II:55G:S(47)	.000	-.005	-.009	-.034	-.004	-.011	-.009
225	B9:II:55G:S(59)	.000	.003	-.013	.004	.006	-.002	.004
226	B9:II:35G:g(35)	.000	.002	.002	.003	.006	.006	.008
227	B9:II:35G:g(35)h(35)	.000	.002	.003	.005	.007	.003	.004
228	B9:II:35G:g(35)h(47)	.000	.005	.006	.008	.010	.006	.014
229	B9:II:35G:g(47)	.000	.001	.001	.004	.006	.007	.006
230	B9:II:35G:g(47)h(35)	.000	.004	.005	.007	.011	.004	.006
231	B9:II:35G:g(47)h(47)	.000	.003	.004	.008	.012	.008	.011
232	B9:II:35G:g(47)h(59)	.000	.008	.020	.041	.071	fracture	---
233	B9:II:35G:g(59)	.000	.007	.013	.015	.018	.017	.025
234	B9:II:35G:g(59)h(35)	.000	.009	.008	.013	.017	.011	.015
235	B9:II:35G:g(59)h(47)	.000	.008	.008	.014	.016	.019	.025
236	B9:II:35G:g(59)h(59)	.000	.013	.020	.031	.039	.056	.073
237	B9:II:35G:h(35)	.000	.003	.004	.009	.014	.008	.019
238	B9:II:35G:h(47)	.000	.002	.005	.010	.021	.067	fracture
239	B9:II:35G:h(59)	---	---	---	---	---	---	---
240	B9:II:25:7sk	.000	-.003	.001	.001	-.002	-.005	-.005
241	B9:II:35:7sk	.000	-.003	-.005	-.001	-.003	-.006	-.006
242	B9:II:45:7sk	.000	-.009	-.006	-.002	-.004	-.008	-.008
243	B10:I-L:25	.000	.005	.008	.006	.006	.001	.003
244	B10:I-L:35	.000	.005	.016	.031	.061	.210	.671
245	B10:II:25	.000	.010	.014	.020	.029	.038	.049
246	B10:II:35	.000	.006	.008	.015	.026	.047	.065
247	B10:II:45	.000	.007	.013	.016	.026	.036	.044
248	B10:II:25	.000	-.003	.008	.006	.007	.012	.022
249	B10:II:35G	.000	.000	.010	.010	.009	.014	.026
250	B11:II:25	.000	.001	.021	.053	.100	.255	fracture
251	B11:II:35	.000	.012	.025	.064	.186	fracture	---
252	B11:II:45	.000	.019	.050	.432	fracture	---	---
253	B12:I-H:25	.000	.046	.882	fracture	---	---	---
254	B12:I-H:35	.000	.028	fracture	---	---	---	---
255	B12:I-H:25G	.000	.009	.016	.065	fracture	---	---
256	B12:I-H:35G	.000	.002	.003	.012	.026	fracture	---
257	B12:II:25	.000	.022	.075	.242	fracture	---	---
258	B12:II:35	.000	.028	.111	.555	fracture	---	---
259	B12:II:45	.000	.016	fracture	---	---	---	---
260	B12:II:25G	.000	.019	.275	1.456	fracture	---	---
261	B12:II:35G	.000	.041	fracture	---	---	---	---
262	B12:II:45G	.000	.004	.006	.011	.019	.036	.097
263	B12:II:55G	.000	.012	.019	.023	.029	.044	.072
264	B12:II:35:S(35)	.000	.002	.006	.006	.013	.028	.097
265	B12:II:35:S(41)	.000	.009	.007	.008	.005	.011	.010
266	B12:II:35:S(47)	.000	.013	.014	.014	.017	.031	.045
267	B12:II:35:S(53)	.000	.014	.017	.020	.027	.050	.086
268	B12:II:35:S(59)	.000	.017	.026	.038	.053	.079	.115
269	B12:II:35G:S(35)	.000	.000	.002	.003	.005	.006	.012
270	B12:II:35G:S(41)	.000	.001	.003	.004	.010	.017	.020

Table E.1 (continued)

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
271	B12:II:35G:S(47)	.000	.001	.001	-.001	.007	.008	.010
272	B12:II:35G:S(53)	.000	.006	.007	.005	.012	.011	.013
273	B12:II:35G:S(59)	.000	.016	.030	.043	.060	.089	.124
274	B12:II:35G:S(65)	.000	.038	.074	.126	.202	.499	fracture
275	B12:II:45G:S(35)	.000	.001	.006	.006	.008	.006	.014
276	B12:II:45G:S(47)	.000	.005	.008	.014	.014	.014	.029
277	B12:II:45G:S(59)	.000	.015	.023	.031	.038	.048	.062
278	B12:II:55G:S(35)	.000	.004	.005	.005	.007	.005	.009
279	B12:II:55G:S(47)	.000	-.002	-.001	.000	.001	-.002	.002
280	B12:II:55G:S(59)	.000	.003	.004	.006	.006	.003	.008
281	B12:II:35G:g(35)	.000	.001	.005	.010	.018	.046	.161
282	B12:II:35G:g(35)h(35)	.000	.001	.002	.007	.009	.011	.026
283	B12:II:35G:g(35)h(47)	.000	.004	.011	.016	.022	.039	.088
284	B12:II:35G:g(47)	.000	.009	.012	.021	.028	.039	.068
285	B12:II:35G:g(47)h(35)	.000	.006	.006	.010	.013	.014	.018
286	B12:II:35G:g(47)h(47)	.000	.006	.007	.012	.017	.018	.023
287	B12:II:35G:g(47)h(59)	.000	.015	.040	.079	.146	.590	fracture
288	B12:II:35G:g(59)	.000	.018	.033	.046	.065	.090	.119
289	B12:II:35G:g(59)h(35)	.000	.017	.027	.041	.057	.079	.109
290	B12:II:35G:g(59)h(47)	.000	.010	.012	.019	.025	.032	.041
291	B12:II:35G:g(59)h(59)	.000	.011	.015	.025	.038	.065	.101
292	B12:II:35G:h(35)	.000	.006	.009	.012	.018	.026	.069
293	B12:II:35G:h(47)	.000	.003	.006	.011	.023	.043	.160
294	B12:II:35G:h(59)	---	---	---	---	---	---	---
295	B12:II:25:7sk	.000	.000	-.004	.008	.006	.011	.012
296	B12:II:35:7sk	.000	.001	-.002	.009	.005	.010	.012
297	B12:II:45:7sk	.000	.002	.002	.011	.011	.014	.019
298	I-H:2.1%	.000	.009	.008	.009	.011	.012	.021
299	I-H:5%	.000	.010	.012	.015	.026	.084	.638
300	A2:I-H:25:2.1%	.000	.007	.003	.001	-.001	.001	-.002
301	A2:I-H:25:5%	.000	.004	.003	.001	-.002	.000	.015
302	A2:I-H:25G:2.1%	.000	.008	.007	.004	.001	.002	-.001
303	A2:I-H:25G:5%	.000	.006	.006	.002	-.001	-.001	-.001
304	A9:I-H:25:2.1%	.000	.008	.004	.003	.002	.003	-.001
305	A9:I-H:25:5%	.000	.007	.005	.003	.000	.002	.007
306	A9:I-H:25G:2.1%	.000	.007	.003	.002	-.002	.001	-.004
307	A9:I-H:25G:5%	.000	.005	.003	.002	-.001	.001	-.002
308	B4:I-H:35:2.1%	.000	.008	.007	.006	.006	.004	.003
309	B4:I-H:35:5%	.000	.004	.004	.001	.002	.001	.014
310	B4:I-H:35G:2.1%	.000	.009	.008	.006	.006	.005	.003
311	B4:I-H:35G:5%	.000	.008	.007	.004	.004	.005	.007
312	B9:I-H:35:2.1%	.000	.007	.004	.004	.005	.002	.004
313	B9:I-H:35:5%	.000	.009	.007	.006	.010	.007	.010
314	B9:I-H:35G:2.1%	.000	.006	.004	.002	.001	-.001	-.003
315	B9:I-H:35G:5%	.000	.008	.006	.002	.000	.001	.001
316	B12:I-H:35:2.1%	.000	.009	.008	.008	.009	.007	.010
317	B12:I-H:35:5%	.000	.010	.010	.011	.016	.021	fracture
318	B12:I-H:35G:2.1%	.000	.008	.008	.008	.010	.007	.009
319	B12:I-H:35G:5%	.000	.010	.010	.007	.012	.009	.012

Table E.2 Incremental Mass Change (%) of Sulfate Exposure Specimens

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
1	I-L	.000	.211	.079	.193	.244	.611	.757
2	I-H	.000	.211	-.002	1.187	fracture	---	---
3	I-H	.000	.301	.513	fracture	---	---	---
4	I-H blend A	.000	.201	-.225	.013	.132	1.547	fracture
5	I-H blend B	.000	.189	.207	.663	.815	1.594	fracture
6	I-H blend C	.000	.236	.288	.666	.512	.692	.426
7	I-H blend D	.000	.217	.268	.694	fracture	---	---
8	I-H blend E	.000	.285	-.050	-3.169	fracture	---	---
9	I-H blend F	.000	.173	.253	.618	.283	.508	fracture
10	II	.000	.161	.096	.260	.225	.363	.264
11	II	.000	.133	.119	.266	.127	.214	.138
12	II	.000	.076	.123	.295	.168	.256	.124
13	II	.000	.110	.062	.252	.329	.395	.175
14	II	.000	.118	.093	.195	.168	.432	.100
15	II	.000	.087	.052	.261	.103	.423	.262
16	II blend A	.000	.130	.127	.287	.234	.366	.148
17	II blend B	.000	.131	.100	.313	.282	.385	.218
18	II blend B	.000	.122	.064	.229	.244	.285	.203
19	II:7sk	.000	.089	.074	.151	.147	.323	.283
20	II:7sk	.000	.089	.081	.199	.213	.313	.227
21	II:7sk	.000	.140	.072	.184	.161	.189	.091
22	V	.000	.121	.078	.190	.144	.214	.098
23	0%L	.000	.170	.050	.145	.200	.164	.192
24	0%H	.000	.107	.111	.280	.161	.302	.143
25	A1:I-H:25	.000	.162	.135	.437	.320	.393	-.272
26	A1:I-H:35	.000	.109	.062	.122	.192	.324	.221
27	A1:I-H:25G	.000	.101	.063	.237	.193	.215	.143
28	A1:I-H:35G	.000	.114	.083	.273	.167	.189	.070
29	A1:II:25	.000	.063	.046	.167	.225	.289	.243
30	A1:II:35	.000	.031	.034	.144	.203	.249	.146
31	A1:II:45	.000	.037	.038	.106	.163	.191	.106
32	A1:II:25G	.000	.047	.074	.224	.146	.183	.199
33	A1:II:35G	.000	.105	.075	.166	.158	.123	.163
34	A2:I-L:25	.000	.030	-.010	.083	.095	.296	.199
35	A2:I-H:25	.000	.180	-.011	-.242	.070	.275	.258
36	A2:I-H:35	.000	-.106	.039	-.030	.261	.393	fracture
37	A2:I-H:25G	.000	-.058	.059	.141	-.487	.160	-.668
38	A2:I-H:35G	.000	.002	.073	.133	.028	.101	-.156
39	A2:II:25	.000	.100	.058	.178	.159	.241	.180
40	A2:II:35	.000	.085	.060	.140	.156	.206	.119
41	A2:II:45	.000	.103	.034	-.033	.051	.090	.071
42	A2:II:25G	.000	.064	.022	.134	.173	.169	.154
43	A2:II:35G	.000	.059	.026	.088	.113	.128	.148
44	A3:II:25	.000	.049	.032	.060	.059	.123	.060
45	A3:II:45	.000	.059	.036	.061	.064	.104	.056
46	A4:II:25	.000	.148	.100	.179	.191	.331	.308
47	A4:II:45	.000	.113	.059	.098	.077	.163	.078
48	A5:I-L:25	.000	.181	.041	.160	.140	.339	.367
49	A5:II:35	.000	.007	-.030	.032	.069	.217	.185
50	A6:I-H:25	.000	.046	-.279	-2.145	-1.732	fracture	---
51	A6:I-H:35	.000	-.164	-.358	-1.279	-.524	fracture	---
52	A6:I-H:25G	.000	.040	.023	.155	.023	.163	-.428
53	A6:I-H:35G	.000	.044	.035	.080	.108	-.531	-.299
54	A6:II:25	.000	.147	.095	.363	.256	.389	.066

Table E.2 (continued)

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
55	A6:II:35	.000	.118	.062	.284	.230	.338	.129
56	A6:II:45	.000	.073	.027	-.096	-.280	-.291	-.850
57	A6:II:25G	.000	.069	.013	.123	.187	.172	.072
58	A6:II:35G	.000	.065	.024	.058	.078	.112	.184
59	A7:I-H:25	.000	.186	-.271	-1.984	-.544	fracture	---
60	A7:I-H:35	.000	-.004	-.037	.021	-1.631	fracture	---
61	A7:I-H:25G	.000	.051	.053	.307	.199	-.461	-.115
62	A7:I-H:35G	.000	.082	.087	.253	.167	-.010	.043
63	A7:II:25	.000	.148	.075	.236	.214	.481	.353
64	A7:II:35	.000	.080	.042	.181	.205	.375	.292
65	A7:II:45	.000	.052	.036	.159	.190	.224	.152
66	A7:II:25G	.000	.045	.027	.056	.122	.138	.180
67	A7:II:35G	.000	.068	.025	.047	.163	.160	.112
68	A8:II:25	.000	.118	.089	.190	.146	.269	.166
69	A8:II:45	.000	.063	.017	.088	-.010	.078	.015
70	A9:IL:25	.000	.190	.033	.145	.117	.242	.249
71	A9:I-L:35	.000	.102	-.009	-.010	.040	.150	.180
72	A9:I-H:25	.000	.156	.090	.005	.108	.420	-1.093
73	A9:I-H:35	.000	-.029	.066	.218	.158	.200	-.433
74	A9:I-H:25G	.000	.083	.028	.305	.237	.089	-.033
75	A9:I-H:35G	.000	.029	.075	.266	.182	.153	.073
76	A9:II:25	.000	.085	.076	.137	.112	.138	.057
77	A9:II:35	.000	.151	.048	.100	.123	.145	.121
78	A9:II:45	.000	.094	.046	.093	.067	.088	.087
79	A9:II:25G	.000	.080	.074	.188	.139	.131	.188
80	A9:II:35G	.000	.092	.082	.205	.138	.152	.171
81	A10:I-L:25	.000	.034	.015	.235	.129	.363	.332
82	A10:II:35	.000	.003	-.036	.023	.056	.216	.127
83	A11:I-L:25	.000	.028	.008	.180	.179	.355	.245
84	A11:I-L:35	.000	.111	.046	.130	.159	.265	.255
85	A11:I-H:25	.000	.161	.091	.222	.170	-.046	-.088
86	A11:I-H:35	.000	.017	.028	-.018	.038	-.238	.085
87	A11:I-H:25G	.000	.091	.094	.128	-.220	.189	-1.560
88	A11:I-H:35G	.000	.036	.066	.257	.166	.122	-.238
89	A11:II:25	.000	.132	.089	.224	.192	.183	.239
90	A11:II:35	.000	.002	-.027	.022	.069	.259	.152
91	A11:II:45	.000	.093	.069	.130	.100	.134	.207
92	A11:II:25G	.000	.056	.014	.097	.089	.129	.137
93	A11:II:35G	.000	.077	.030	.104	.164	.195	.188
94	A12:II:35	.000	.069	.070	.213	.140	.132	.182
95	B1:I-H:25	.000	.149	.141	.327	-.673	-.525	-1.520
96	B1:I-H:35	.000	.121	.086	.159	.171	.182	-.839
97	B1:I-H:25G	.000	.004	.072	.293	.195	-.239	-.715
98	B1:I-H:35G	.000	.076	.065	.256	.209	.187	.113
99	B1:II:25	.000	.139	.066	.256	.166	.318	.137
100	B1:II:35	.000	.103	.067	.293	.132	.276	.144
101	B1:II:45	.000	.089	.053	.240	.137	.219	.043
102	B1:II:25G	.000	.088	.058	.174	.149	.117	.134
103	B1:II:35G	.000	.089	.035	.188	.149	.150	.180
104	B2:II:35	.000	.152	.075	.124	.071	.202	.302
105	B3:I-L:25	.000	.189	.072	-.191	-1.578	-1.054	-2.104
106	B3:I-H:25	.000	-2.354	fracture	---	---	---	---
107	B3:I-H:35	.000	-.952	-3.058	-3.042	-3.056	fracture	---
108	B3:I-H:25G	.000	-.184	-1.152	-2.591	-1.870	fracture	---

Table E.2 (continued)

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
109	B3:I-H:35G	.000	-.845	-.884	-2.705	-3.775	-6.414	fracture
110	B3:II:25	.000	.131	.085	-.344	-.057	-.878	-1.629
111	B3:II:35	.000	.061	.085	-.405	-.401	-2.719	-.966
112	B3:II:45	.000	-.368	-.354	-1.610	-1.981	-1.930	fracture
113	B3:II:25G	.000	.144	-.328	-1.035	-.571	-.965	fracture
114	B3:II:35G	.000	-.005	-.002	-.046	-1.071	-.008	fracture
115	B3:II:35:S(35)	.000	.124	.076	.184	.022	.198	.204
116	B3:II:35:S(41)	.000	.062	.074	.135	.089	.186	.107
117	B3:II:35:S(47)	.000	.066	.038	.131	.074	.186	.146
118	B3:II:35:S(53)	.000	.063	.061	.124	.051	.169	.102
119	B3:II:35:S(59)	.000	.073	.044	.150	.009	.183	.119
120	B3:II:35G:S(35)	.000	.103	.051	.127	.013	.152	.162
121	B3:II:35G:S(41)	.000	.072	.064	.206	.091	.136	.132
122	B3:II:35G:S(47)	.000	.077	.059	.189	.072	.086	.128
123	B3:II:35G:S(53)	.000	.081	.054	.192	.071	.089	.121
124	B3:II:35G:S(59)	.000	.071	.042	.127	.000	.140	.132
125	B3:II:35G:S(65)	.000	.058	.018	.032	.026	.196	.206
126	B3:II:25:7sk	.000	.132	.060	.206	.655	-.497	-1.517
127	B3:II:35:7sk	.000	.045	-.110	-.660	-.525	-.708	-1.247
128	B3:II:45:7sk	.000	-.082	-.227	-.621	-1.518	-1.152	-.350
129	B4:I-H:25	.000	-3.700	fracture	---	---	---	---
130	B4:I-H:35	.000	-1.946	-5.070	fracture	---	---	---
131	B4:I-H:25G	.000	-.267	-.610	-.848	-1.898	-7.007	fracture
132	B4:I-H:35G	.000	-.736	-1.270	-2.109	-2.233	fracture	---
133	B4:II:25	.000	.131	-.737	-1.890	fracture	---	---
134	B4:II:35	.000	-.300	-.383	-3.029	fracture	---	---
135	B4:II:45	.000	-1.546	-2.136	-3.411	-3.815	fracture	---
136	B4:II:25G	.000	.255	.013	-.462	-.658	-2.884	-5.434
137	B4:II:35G	.000	.177	-.172	-1.060	-.334	-1.385	fracture
138	B4:II:35:S(35)	.000	.125	.052	.126	.002	-.737	.197
139	B4:II:35:S(41)	.000	.070	.048	.107	.077	.256	.179
140	B4:II:35:S(47)	.000	.081	.039	.195	.009	.271	.158
141	B4:II:35:S(53)	.000	.077	.040	.188	.025	.210	.139
142	B4:II:35:S(59)	.000	.083	.041	.149	.010	.199	.184
143	B4:II:35G:S(35)	.000	.170	.062	.174	-.149	.211	.143
144	B4:II:35G:S(41)	.000	.074	.047	.171	.180	.209	.177
145	B4:II:35G:S(47)	.000	.070	.058	.140	.147	.188	.177
146	B4:II:35G:S(53)	.000	.074	.051	.157	.156	.163	.151
147	B4:II:35G:S(59)	.000	.072	.042	.121	.007	.142	.108
148	B4:II:35G:S(65)	.000	.076	.043	.074	.028	.243	.215
149	B4:II:25:7sk	.000	.042	.043	.170	.216	.046	-.647
150	B4:II:35:7sk	.000	-.084	-.028	-.058	-.341	-.967	-2.302
151	B4:II:45:7sk	.000	-.193	-.102	-.502	-.479	-2.620	fracture
152	B5:I-L:25	.000	.070	.035	-.184	-1.355	-.211	-.760
153	B5:I-L:35	.000	.031	-1.426	-5.754	fracture	---	---
154	B5:I-H:25	.000	-2.705	fracture	---	---	---	---
155	B5:I-H:35	.000	-2.850	-3.685	fracture	---	---	---
156	B5:I-H:25G	.000	-.468	-.766	-2.751	-4.139	fracture	---
157	B5:I-H:35G	.000	-.781	-1.219	-3.744	-2.899	fracture	---
158	B5:II:25	.000	.121	.145	.437	-.389	-2.148	fracture
159	B5:II:35	.000	-1.067	-1.330	-2.296	fracture	---	---
160	B5:II:45	.000	.061	-.560	-2.673	-3.476	fracture	---
161	B5:II:25G	.000	.096	-.757	-1.593	-4.638	fracture	---
162	B5:II:35G	.000	.025	-.489	-1.007	-1.483	-2.834	fracture

Table E.2 (continued)

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
163	B5:II:35:S(35)	.000	.123	.068	.185	.020	.251	.271
164	B5:II:35:S(41)	.000	.061	.028	.103	-.009	.165	.212
165	B5:II:35:S(47)	.000	.045	.044	.121	.012	.232	.189
166	B5:II:35:S(53)	.000	.074	.060	.166	.089	.187	.176
167	B5:II:35:S(59)	.000	.084	.048	.157	.041	.193	.205
168	B5:II:35G:S(35)	.000	.086	.078	.145	.019	.205	.240
169	B5:II:35G:S(41)	.000	.072	.046	.169	.083	.077	.170
170	B5:II:35G:S(47)	.000	.071	.038	.202	.084	.136	.130
171	B5:II:35G:S(53)	.000	.075	.035	.173	.074	.130	.143
172	B5:II:35G:S(59)	.000	.082	.044	.117	.015	.148	.113
173	B5:II:35G:S(65)	.000	.079	.014	.066	.046	.249	.262
174	B5:II:25:7sk	.000	.163	.035	.090	-.092	-1.976	.224
175	B5:II:35:7sk	.000	.054	-.096	-.252	.108	-.485	-1.532
176	B5:II:45:7sk	.000	-.077	-.043	-.504	-.413	-1.103	-3.582
177	B6:I-L:25	.000	.046	.013	.162	.176	.234	-.728
178	B6:II:25	.000	.126	.083	.223	.122	.304	.374
179	B6:II:35	.000	.140	.116	-.302	-.589	-.999	-2.509
180	B6:II:45	.000	-.075	-.387	-1.103	-.818	-.397	fracture
181	B7:I-H:25	.000	-.955	-1.255	-4.603	fracture	---	---
182	B7:I-H:35	.000	-.060	-.002	-.202	-1.279	-.710	-.998
183	B7:I-H:25G	.000	-.199	-.184	-1.131	-.410	-.666	-1.794
184	B7:I-H:35G	.000	-.195	-.042	-.791	-1.280	-1.047	-2.353
185	B7:II:25	.000	.195	.061	.228	.256	.669	.139
186	B7:II:35	.000	.208	.138	.325	.307	.498	.125
187	B7:II:45	.000	.161	-.285	-.737	-.352	-.619	-.557
188	B7:II:25G	.000	.101	.050	.085	.119	.228	.083
189	B7:II:35G	.000	.102	.070	.105	.130	.218	.076
190	B7:II:25:7sk	.000	.125	.060	.164	.046	.248	-.045
191	B7:II:35:7sk	.000	.109	.064	.202	.230	.180	.077
192	B7:II:45:7sk	.000	.101	.050	.198	.202	.221	-.330
193	B8:II:25	.000	.167	.107	.387	.411	.732	.403
194	B8:II:35	.000	.200	.028	-.097	-.262	-6.798	fracture
195	B8:II:45	.000	-.001	-1.387	-1.867	-.132	fracture	---
196	B9:I-L:25	.000	.044	.004	.124	.201	-.986	-1.038
197	B9:I-L:35	.000	.141	-.262	-.408	-2.529	fracture	---
198	B9:I-H:25	.000	-1.731	-1.109	fracture	---	---	---
199	B9:I-H:35	.000	-2.001	-2.248	-4.462	fracture	---	---
200	B9:I-H:25G	.000	-.160	-.251	-.212	-.921	-3.408	fracture
201	B9:I-H:35G	.000	-.151	-1.366	-2.622	-2.133	-3.449	-3.599
202	B9:II:25	.000	.125	.101	.239	.253	.493	.545
203	B9:II:35	.000	.124	-.686	-2.551	-1.346	-.849	fracture
204	B9:II:45	.000	-.198	-.677	-2.045	-2.137	fracture	---
205	B9:II:25G	.000	.181	.093	.279	.080	-.156	-.060
206	B9:II:35G	.000	.133	.053	.230	-.682	-.894	-4.167
207	B9:II:45G	.000	.066	.023	-.254	-.182	-1.389	-1.760
208	B9:II:55G	.000	.054	.094	.110	-.003	-.018	.394
209	B9:II:35:S(35)	.000	.122	.079	.202	.068	.146	.183
210	B9:II:35:S(41)	.000	.076	.093	.206	.132	.102	.151
211	B9:II:35:S(47)	.000	.077	.086	.178	.153	.163	.175
212	B9:II:35:S(53)	.000	.091	.095	.142	.162	.106	.131
213	B9:II:35:S(59)	.000	.079	.049	.124	-.003	.229	.176
214	B9:II:35G:S(35)	.000	.119	.072	.176	.013	.185	.116
215	B9:II:35G:S(41)	.000	.052	.038	.176	.084	.150	.142
216	B9:II:35G:S(47)	.000	.063	.039	.139	.144	.170	.123

Table E.2 (continued)

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
217	B9:II:35G:S(53)	.000	.047	.038	.147	.134	.160	.144
218	B9:II:35G:S(59)	.000	.063	.040	.132	.003	.151	.112
219	B9:II:35G:S(65)	.000	.049	.038	.030	.005	.185	.189
220	B9:II:45G:S(35)	.000	.044	.049	.120	.036	.186	.159
221	B9:II:45G:S(47)	.000	.061	.051	.089	.004	.135	.138
222	B9:II:45G:S(59)	.000	.059	.047	.089	.006	.112	.138
223	B9:II:55G:S(35)	.000	.029	.040	.081	-.009	.087	.142
224	B9:II:55G:S(47)	.000	.056	.038	.084	.004	.127	.116
225	B9:II:55G:S(59)	.000	.024	.057	.094	.010	.172	.132
226	B9:II:35G:g(35)	.000	.084	.085	.174	.072	.218	.212
227	B9:II:35G:g(35)h(35)	.000	.080	.081	.148	.054	.241	.186
228	B9:II:35G:g(35)h(47)	.000	.119	.071	.173	.065	.229	.414
229	B9:II:35G:g(47)	.000	.060	.011	.017	.061	.350	.215
230	B9:II:35G:g(47)h(35)	.000	.072	.039	.025	.062	.224	.157
231	B9:II:35G:g(47)h(47)	.000	.069	.027	.026	.052	.180	.170
232	B9:II:35G:g(47)h(59)	.000	-.062	-.470	-.133	-.352	fracture	---
233	B9:II:35G:g(59)	.000	.067	.082	.110	.039	.166	.106
234	B9:II:35G:g(59)h(35)	.000	.066	.062	.108	.016	.148	.097
235	B9:II:35G:g(59)h(47)	.000	.053	.026	.043	-.017	.189	.134
236	B9:II:35G:g(59)h(59)	.000	.097	.037	.063	.004	.289	.149
237	B9:II:35G:h(35)	.000	.154	.110	.252	-.111	.111	-.226
238	B9:II:35G:h(47)	.000	.055	-.002	-.511	-.095	-.392	fracture
239	B9:II:35G:h(59)	---	---	---	---	---	---	---
240	B9:II:25:7sk	.000	.105	.071	.179	.149	.166	.014
241	B9:II:35:7sk	.000	.100	.036	.165	.091	.058	-.694
242	B9:II:45:7sk	.000	-.014	-.133	-.417	-.055	-.283	-.775
243	B10:I-L:25	.000	.052	.010	.089	.137	.279	.238
244	B10:I-L:35	.000	.129	-.156	-.662	-1.149	-3.577	-.563
245	B10:II:25	.000	.135	.044	.138	.130	.237	.078
246	B10:II:35	.000	.148	.059	-.083	.089	.121	.090
247	B10:II:45	.000	.094	.045	.066	.066	.094	.056
248	B10:II:25G	.000	.093	.077	.197	.197	.164	.246
249	B10:II:35G	.000	.045	.065	.027	.123	-.598	-.605
250	B11:II:25	.000	.154	.134	.286	.280	.685	fracture
251	B11:II:35	.000	.099	-1.892	-2.199	-3.658	fracture	---
252	B11:II:45	.000	.056	-.161	-1.242	fracture	---	---
253	B12:I-H:25	.000	-1.420	-5.168	fracture	---	---	---
254	B12:I-H:35	.000	-2.730	fracture	---	---	---	---
255	B12:I-H:25G	.000	-.406	-.496	-2.824	fracture	---	---
256	B12:I-H:35G	.000	-1.054	-.843	-1.832	-1.357	fracture	---
257	B12:II:25	.000	-.264	.022	-2.342	fracture	---	---
258	B12:II:35	.000	.192	-1.864	-3.309	fracture	---	---
259	B12:II:45	.000	-1.328	fracture	---	---	---	---
260	B12:II:25G	.000	.302	-1.486	-7.697	fracture	---	---
261	B12:II:35G	.000	-1.645	fracture	---	---	---	---
262	B12:II:45G	.000	-.145	-.310	-.369	-.972	-.514	-1.640
263	B12:II:55G	.000	-.284	-.373	-1.123	-1.450	-.846	-.631
264	B12:II:35:S(35)	.000	.177	.080	.319	.168	-.830	-.288
265	B12:II:35:S(41)	.000	.074	.098	.144	.219	-.035	.085
266	B12:II:35:S(47)	.000	.075	.106	.164	.153	.163	.197
267	B12:II:35:S(53)	.000	.078	.084	.242	.216	.224	.216
268	B12:II:35:S(59)	.000	.111	.045	.144	.029	.228	.198
269	B12:II:35G:S(35)	.000	.130	.068	.146	-.097	.238	.237
270	B12:II:35G:S(41)	.000	.072	.061	.174	.098	.192	.159

Table E.2 (continued)

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
271	B12:II:35G:S(47)	.000	.071	.064	.158	.088	.183	.162
272	B12:II:35G:S(53)	.000	.093	.078	.192	.111	.227	.211
273	B12:II:35G:S(59)	.000	.083	.046	.140	.013	.167	.130
274	B12:II:35G:S(65)	.000	.113	.074	.122	.136	.575	fracture
275	B12:II:45G:S(35)	.000	.041	.040	.080	-.113	-.128	-.710
276	B12:II:45G:S(47)	.000	.061	.059	.092	.019	.159	.224
277	B12:II:45G:S(59)	.000	.053	.059	.062	.002	.175	.110
278	B12:II:55G:S(35)	.000	-.029	.036	.080	.012	.128	.044
279	B12:II:55G:S(47)	.000	.028	.050	.081	.015	.133	.084
280	B12:II:55G:S(59)	.000	.033	.050	.071	.012	.151	.080
281	B12:II:35G:g(35)	.000	.131	-.040	-1.470	-.221	-.773	.108
282	B12:II:35G:g(35)h(35)	.000	-.025	-.014	-.096	.004	.468	.006
283	B12:II:35G:g(35)h(47)	.000	.084	.078	.164	.059	-.217	-.412
284	B12:II:35G:g(47)	.000	.116	.044	.081	.098	.308	.218
285	B12:II:35G:g(47)h(35)	.000	.083	.021	.039	.044	.269	.197
286	B12:II:35G:g(47)h(47)	.000	.069	.028	.043	.052	.242	.178
287	B12:II:35G:g(47)h(59)	.000	.004	.120	.327	-.005	.097	fracture
288	B12:II:35G:g(59)	.000	.115	.039	.072	.030	.240	.201
289	B12:II:35G:g(59)h(35)	.000	.122	.082	.170	.053	.224	.182
290	B12:II:35G:g(59)h(47)	.000	.065	.020	.033	.030	.204	.177
291	B12:II:35G:g(59)h(59)	.000	.070	.012	.057	.056	.260	.216
292	B12:II:35G:h(35)	.000	.127	-.141	.296	-.523	-1.086	-.781
293	B12:II:35G:h(47)	.000	.095	.133	.131	.183	.449	-.016
294	B12:II:35G:h(59)	---	---	---	---	---	---	---
295	B12:II:25:7sk	.000	.194	-.026	-.400	.042	.118	-.096
296	B12:II:35:7sk	.000	.048	-.166	-.526	.089	-1.793	-.017
297	B12:II:45:7sk	.000	-.076	-.092	-.729	-.625	-1.390	.206
298	I-H:2.1%	.000	.066	.036	.109	.123	.172	.313
299	I-H:5%	.000	.104	.109	.251	.239	.544	.846
300	A2:I-H:25:2.1%	.000	.053	.018	.048	.040	.035	.061
301	A2:I-H:25:5%	.000	.080	.076	.141	.120	.112	.157
302	A2:I-H:25G:2.1%	.000	.070	.041	.084	.067	.010	.058
303	A2:I-H:25G:5%	.000	.080	.046	.149	.106	.090	.163
304	A9:I-H:25:2.1%	.000	.054	.025	.054	.052	.024	.080
305	A9:I-H:25:5%	.000	.062	.063	.117	.092	.091	.134
306	A9:I-H:25G:2.1%	.000	.057	.036	.067	.053	.025	.074
307	A9:I-H:25G:5%	.000	.068	.063	.164	.101	.073	.144
308	B4:I-H:35:2.1%	.000	.076	.035	.098	.092	.073	.164
309	B4:I-H:35:5%	.000	.121	-.085	-.055	.127	-.055	-1.209
310	B4:I-H:35G:2.1%	.000	.077	.047	.125	.117	.009	.056
311	B4:I-H:35G:5%	.000	.075	.027	.119	-.042	-.455	-.543
312	B9:I-H:35:2.1%	.000	.058	.031	.076	.090	.067	.141
313	B9:I-H:35:5%	.000	.085	.056	.084	.126	-.125	.102
314	B9:I-H:35G:2.1%	.000	.063	.025	.088	.069	.017	.115
315	B9:I-H:35G:5%	.000	.099	.030	.085	.038	-.080	-.001
316	B12:I-H:35:2.1%	.000	.073	.041	.035	.109	.176	.277
317	B12:I-H:35:5%	.000	.098	-.103	.122	-.534	-1.744	fracture
318	B12:I-H:35G:2.1%	.000	.054	.029	.078	.098	.072	.116
319	B12:I-H:35G:5%	.000	.071	.034	.121	-.202	.109	.122

Table E.3 Sulfate Susceptibility Ratings for Exposure Specimens

Mixture Number	Mixture Designation	Sulfate Susceptibility Rating 720-day exposure
1	I-L	3.00
2	I-H	3.00
3	I-H	3.00
4	I-H blend A	3.00
5	I-H blend B	3.00
6	I-H blend C	3.00
7	I-H blend D	3.00
8	I-H blend E	3.00
9	I-H blend F	3.00
10	II	1.00
11	II	1.04
12	II	.93
13	II	.93
14	II	1.05
15	II	.92
16	II blend A	.94
17	II blend B	1.75
18	II blend B	1.66
19	II:7sk	.06
20	II:7sk	.10
21	II:7sk	-.05
22	V	.77
23	0%L	.70
24	0%H	1.16
25	A1:I-H:25	3.00
26	A1:I-H:35	.59
27	A1:I-H:25G	-.03
28	A1:I-H:35G	.00
29	A1:II:25	.02
30	A1:II:35	.01
31	A1:II:45	-.05
32	A1:II:25G	-.02
33	A1:II:35G	-.04
34	A2:I-L:25	-.02
35	A2:I-H:25	3.00
36	A2:I-H:35	3.00
37	A2:I-H:25G	3.00
38	A2:I-H:35G	3.00
39	A2:II:25	.78
40	A2:II:35	.59
41	A2:II:45	.46
42	A2:II:25G	.03
43	A2:II:35G	-.03
44	A3:II:25	.43
45	A3:II:45	.39
46	A4:II:25	3.00
47	A4:II:45	.60
48	A5:I-L:25	.85
49	A5:II:35	-.05
50	A6:I-H:25	3.00
51	A6:I-H:35	3.00
52	A6:I-H:25G	3.00
53	A6:I-H:35G	3.00
54	A6:II:25	.63

Table E.3 (continued)

Mixture Number	Mixture Designation	Sulfate Susceptibility Rating 720-day exposure
55	A6:II:35	.28
56	A6:II:45	3.00
57	A6:II:25G	.12
58	A6:II:35G	.01
59	A7:I-H:25	3.00
60	A7:I-H:35	3.00
61	A7:I-H:25G	3.00
62	A7:I-H:35G	.06
63	A7:II:25	1.26
64	A7:II:35	1.34
65	A7:II:45	.51
66	A7:II:25G	.02
67	A7:II:35G	.09
68	A8:II:25	1.15
69	A8:II:45	.43
70	A9:IL:25	.18
71	A9:I-L:35	.00
72	A9:I-H:25	3.00
73	A9:I-H:35	3.00
74	A9:I-H:25G	.03
75	A9:I-H:35G	-.03
76	A9:II:25	.42
77	A9:II:35	.45
78	A9:II:45	.33
79	A9:II:25G	-.07
80	A9:II:35G	-.03
81	A10:I-L:25	.05
82	A10:II:35	-.03
83	A11:I-L:25	.06
84	A11:I-L:35	.81
85	A11:I-H:25	3.00
86	A11:I-H:35	3.00
87	A11:I-H:25G	3.00
88	A11:I-H:35G	3.00
89	A11:II:25	.04
90	A11:II:35	-.06
91	A11:II:45	.06
92	A11:II:25G	.00
93	A11:II:35G	-.03
94	A12:II:35	.70
95	B1:I-H:25	3.00
96	B1:I-H:35	3.00
97	B1:I-H:25G	3.00
98	B1:I-H:35G	.02
99	B1:II:25	.13
100	B1:II:35	-.03
101	B1:II:45	-.05
102	B1:II:25G	.03
103	B1:II:35G	-.01
104	B2:II:35	.24
105	B3:I-L:25	3.00
106	B3:I-H:25	3.00
107	B3:I-H:35	3.00
108	B3:I-H:25G	3.00

Table E.3 (continued)

Mixture Number	Mixture Designation	Sulfate Susceptibility Rating 720-day exposure
109	B3:I-H:35G	3.00
110	B3:II:25	3.00
111	B3:II:35	3.00
112	B3:II:45	3.00
113	B3:II:25G	3.00
114	B3:II:35G	3.00
115	B3:II:35:S(35)	.06
116	B3:II:35:S(41)	.09
117	B3:II:35:S(47)	.20
118	B3:II:35:S(53)	.52
119	B3:II:35:S(59)	.87
120	B3:II:35G:S(35)	.07
121	B3:II:35G:S(41)	.00
122	B3:II:35G:S(47)	.12
123	B3:II:35G:S(53)	.23
124	B3:II:35G:S(59)	.78
125	B3:II:35G:S(65)	3.00
126	B3:II:25:7sk	3.00
127	B3:II:35:7sk	3.00
128	B3:II:45:7sk	3.00
129	B4:I-H:25	3.00
130	B4:I-H:35	3.00
131	B4:I-H:25G	3.00
132	B4:I-H:35G	3.00
133	B4:II:25	3.00
134	B4:II:35	3.00
135	B4:II:45	3.00
136	B4:II:25G	3.00
137	B4:II:35G	3.00
138	B4:II:35:S(35)	3.00
139	B4:II:35:S(41)	.08
140	B4:II:35:S(47)	.16
141	B4:II:35:S(53)	.35
142	B4:II:35:S(59)	.73
143	B4:II:35G:S(35)	3.00
144	B4:II:35G:S(41)	.01
145	B4:II:35G:S(47)	.06
146	B4:II:35G:S(53)	.20
147	B4:II:35G:S(59)	.85
148	B4:II:35G:S(65)	3.00
149	B4:II:25:7sk	3.00
150	B4:II:35:7sk	3.00
151	B4:II:45:7sk	3.00
152	B5:I-L:25	3.00
153	B5:I-L:35	3.00
154	B5:I-H:25	3.00
155	B5:I-H:35	3.00
156	B5:I-H:25G	3.00
157	B5:I-H:35G	3.00
158	B5:II:25	3.00
159	B5:II:35	3.00
160	B5:II:45	3.00
161	B5:II:25G	3.00
162	B5:II:35G	3.00

Table E.3 (continued)

Mixture Number	Mixture Designation	Sulfate Susceptibility Rating 720-day exposure
163	B5:II:35:S(35)	.15
164	B5:II:35:S(41)	.05
165	B5:II:35:S(47)	.30
166	B5:II:35:S(53)	.48
167	B5:II:35:S(59)	3.00
168	B5:II:35G:S(35)	.12
169	B5:II:35G:S(41)	.05
170	B5:II:35G:S(47)	.14
171	B5:II:35G:S(53)	.33
172	B5:II:35G:S(59)	.86
173	B5:II:35G:S(65)	3.00
174	B5:II:25:7sk	3.00
175	B5:II:35:7sk	3.00
176	B5:II:45:7sk	3.00
177	B6:I-L:25	3.00
178	B6:II:25	3.00
179	B6:II:35	3.00
180	B6:II:45	3.00
181	B7:I-H:25	3.00
182	B7:I-H:35	3.00
183	B7:I-H:25G	3.00
184	B7:I-H:35G	3.00
185	B7:II:25	3.00
186	B7:II:35	3.00
187	B7:II:45	3.00
188	B7:II:25G	.08
189	B7:II:35G	.10
190	B7:II:25:7sk	-.08
191	B7:II:35:7sk	-.06
192	B7:II:45:7sk	3.00
193	B8:II:25	3.00
194	B8:II:35	3.00
195	B8:II:45	3.00
196	B9:I-L:25	3.00
197	B9:I-L:35	3.00
198	B9:I-H:25	3.00
199	B9:I-H:35	3.00
200	B9:I-H:25G	3.00
201	B9:I-H:35G	3.00
202	B9:II:25	3.00
203	B9:II:35	3.00
204	B9:II:45	3.00
205	B9:II:25G	3.00
206	B9:II:35G	3.00
207	B9:II:45G	3.00
208	B9:II:55G	.00
209	B9:II:35:S(35)	.10
210	B9:II:35:S(41)	.07
211	B9:II:35:S(47)	.34
212	B9:II:35:S(53)	.69
213	B9:II:35:S(59)	1.01
214	B9:II:35G:S(35)	.01
215	B9:II:35G:S(41)	.01
216	B9:II:35G:S(47)	.03

Table E.3 (continued)

Mixture Number	Mixture Designation	Sulfate Susceptibility Rating 720-day exposure
217	B9:II:35G:S(53)	.21
218	B9:II:35G:S(59)	.70
219	B9:II:35G:S(65)	3.00
220	B9:II:45G:S(35)	-.02
221	B9:II:45G:S(47)	.02
222	B9:II:45G:S(59)	.40
223	B9:II:55G:S(35)	-.08
224	B9:II:55G:S(47)	-.10
225	B9:II:55G:S(59)	.05
226	B9:II:35G:g(35)	.09
227	B9:II:35G:g(35)h(35)	.05
228	B9:II:35G:g(35)h(47)	.16
229	B9:II:35G:g(47)	.07
230	B9:II:35G:g(47)h(35)	.07
231	B9:II:35G:g(47)h(47)	.13
232	B9:II:35G:g(47)h(59)	3.00
233	B9:II:35G:g(59)	.29
234	B9:II:35G:g(59)h(35)	.17
235	B9:II:35G:g(59)h(47)	.29
236	B9:II:35G:g(59)h(59)	.85
237	B9:II:35G:h(35)	3.00
238	B9:II:35G:h(47)	3.00
239	B9:II:35G:h(59)	---
240	B9:II:25:7sk	-.06
241	B9:II:35:7sk	3.00
242	B9:II:45:7sk	3.00
243	B10:I-L:25	.04
244	B10:I-L:35	3.00
245	B10:II:25	.57
246	B10:II:35	3.00
247	B10:II:45	.51
248	B10:II:25G	.25
249	B10:II:35G	3.00
250	B11:II:25	3.00
251	B11:II:35	3.00
252	B11:II:45	3.00
253	B12:I-H:25	3.00
254	B12:I-H:35	3.00
255	B12:I-H:25G	3.00
256	B12:I-H:35G	3.00
257	B12:II:25	3.00
258	B12:II:35	3.00
259	B12:II:45	3.00
260	B12:II:25G	3.00
261	B12:II:35G	3.00
262	B12:II:45G	3.00
263	B12:II:55G	3.00
264	B12:II:35:S(35)	3.00
265	B12:II:35:S(41)	.12
266	B12:II:35:S(47)	.52
267	B12:II:35:S(53)	1.00
268	B12:II:35:S(59)	1.34
269	B12:II:35G:S(35)	3.00
270	B12:II:35G:S(41)	.23

Table E.3 (continued)

Mixture Number	Mixture Designation	Sulfate Susceptibility Rating 720-day exposure
271	B12:II:35G:S(47)	.12
272	B12:II:35G:S(53)	.15
273	B12:II:35G:S(59)	1.44
274	B12:II:35G:S(65)	3.00
275	B12:II:45G:S(35)	3.00
276	B12:II:45G:S(47)	.34
277	B12:II:45G:S(59)	.72
278	B12:II:55G:S(35)	.10
279	B12:II:55G:S(47)	.02
280	B12:II:55G:S(59)	.09
281	B12:II:35G:g(35)	3.00
282	B12:II:35G:g(35)h(35)	3.00
283	B12:II:35G:g(35)h(47)	3.00
284	B12:II:35G:g(47)	.79
285	B12:II:35G:g(47)h(35)	.21
286	B12:II:35G:g(47)h(47)	.27
287	B12:II:35G:g(47)h(59)	3.00
288	B12:II:35G:g(59)	1.38
289	B12:II:35G:g(59)h(35)	1.27
290	B12:II:35G:g(59)h(47)	.48
291	B12:II:35G:g(59)h(59)	1.17
292	B12:II:35G:h(35)	3.00
293	B12:II:35G:h(47)	3.00
294	B12:II:35G:h(59)	---
295	B12:II:25:7sk	3.00
296	B12:II:35:7sk	3.00
297	B12:II:45:7sk	3.00
298	I-H:2.1%	.24
299	I-H:5%	3.00
300	A2:I-H:25:2.1%	-.02
301	A2:I-H:25:5%	.17
302	A2:I-H:25G:2.1%	-.01
303	A2:I-H:25G:5%	-.01
304	A9:I-H:25:2.1%	-.01
305	A9:I-H:25:5%	.08
306	A9:I-H:25G:2.1%	-.05
307	A9:I-H:25G:5%	-.02
308	B4:I-H:35:2.1%	.03
309	B4:I-H:35:5%	3.00
310	B4:I-H:35G:2.1%	.03
311	B4:I-H:35G:5%	3.00
312	B9:I-H:35:2.1%	.05
313	B9:I-H:35:5%	3.00
314	B9:I-H:35G:2.1%	-.03
315	B9:I-H:35G:5%	3.00
316	B12:I-H:35:2.1%	.12
317	B12:I-H:35:5%	3.00
318	B12:I-H:35G:2.1%	.10
319	B12:I-H:35G:5%	3.00

Table E.4 Relative Dynamic Modulus of Elasticity (%) of Sulfate Exposure Specimens

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
3	I-H	100.0	101.7	no rdg.	---	---	---	---
15	II	100.0	106.7	108.7	109.0	108.6	108.1	106.9
115	B3:II:35:S(35)	100.0	105.6	106.3	106.7	106.8	106.6	106.0
117	B3:II:35:S(47)	100.0	103.3	103.6	103.4	103.2	103.0	102.3
119	B3:II:35:S(59)	100.0	103.7	104.1	104.5	104.3	103.7	102.9
120	B3:II:35G:S(35)	100.0	107.1	108.6	109.1	109.3	109.5	109.6
122	B3:II:35G:S(47)	100.0	104.0	103.5	103.7	103.7	103.6	103.7
124	B3:II:35G:S(59)	100.0	103.7	104.1	104.4	104.2	103.7	102.8
133	B4:II:25	100.0	107.3	no rdg.	---	---	---	---
134	B4:II:35	100.0	110.5	no rdg.	---	---	---	---
138	B4:II:35:S(35)	100.0	107.1	107.8	108.2	no rdg.	---	---
140	B4:II:35:S(47)	100.0	104.6	106.0	106.1	105.8	105.7	105.3
142	B4:II:35:S(59)	100.0	103.8	104.6	104.7	104.7	103.8	102.6
143	B4:II:35G:S(35)	100.0	108.3	109.5	109.5	110.3	109.5	109.5
145	B4:II:35G:S(47)	100.0	105.5	105.5	105.7	105.4	105.1	104.9
147	B4:II:35G:S(59)	100.0	103.6	103.9	104.2	104.0	103.6	102.7
163	B5:II:35:S(35)	100.0	106.1	107.2	107.7	107.5	107.1	107.0
165	B5:II:35:S(47)	100.0	104.5	106.0	106.7	106.8	106.4	106.2
167	B5:II:35:S(59)	100.0	103.4	104.0	103.4	102.1	98.8	95.1
168	B5:II:35G:S(35)	100.0	107.3	108.9	109.6	109.6	109.6	108.6
170	B5:II:35G:S(47)	100.0	104.4	104.1	104.5	104.7	104.5	104.7
172	B5:II:35G:S(59)	100.0	104.2	104.7	105.0	104.8	104.5	103.6
207	B9:II:45G	100.0	111.5	113.0	114.0	114.4	114.1	no rdg.
208	B9:II:55G	100.0	118.4	120.4	121.3	121.5	122.6	123.0
209	B9:II:35:S(35)	100.0	107.3	108.1	108.6	108.8	108.5	108.4
211	B9:II:35:S(47)	100.0	105.0	105.3	104.9	104.8	103.9	103.1
213	B9:II:35:S(59)	100.0	103.9	104.5	104.7	104.4	102.9	101.2
214	B9:II:35G:S(35)	100.0	107.8	108.6	109.3	109.3	109.6	109.7
216	B9:II:35G:S(47)	100.0	105.1	105.1	105.1	104.7	104.5	104.7
218	B9:II:35G:S(59)	100.0	104.0	104.2	104.5	104.3	103.9	102.9
226	B9:II:35G:g(35)	100.0	109.7	111.5	111.7	111.6	111.4	111.3
229	B9:II:35G:g(47)	100.0	108.5	110.5	111.2	111.1	111.0	110.7
233	B9:II:35G:g(59)	100.0	106.5	107.3	107.8	107.8	107.5	107.5
237	B9:II:35G:h(35)	100.0	106.1	106.5	106.6	106.8	no rdg.	---
238	B9:II:35G:h(47)	100.0	103.8	104.5	106.0	106.0	no rdg.	---
262	B12:II:45G	100.0	109.3	112.0	113.4	114.9	no rdg.	---
263	B12:II:55G	100.0	109.7	112.8	115.2	119.4	118.3	117.6
264	B12:II:35:S(35)	100.0	107.1	108.6	110.7	no rdg.	---	---
266	B12:II:35:S(47)	100.0	104.5	105.1	105.0	104.8	103.6	101.9
268	B12:II:35:S(59)	100.0	103.3	104.1	104.1	103.6	101.7	no rdg.
269	B12:II:35G:S(35)	100.0	107.0	108.3	109.0	109.0	108.4	107.2
271	B12:II:35G:S(47)	100.0	105.1	105.9	106.0	106.1	106.3	106.4
273	B12:II:35G:S(59)	100.0	104.0	104.3	104.4	103.9	102.9	101.7
281	B12:II:35G:g(35)	100.0	107.7	no rdg.	---	---	---	---
284	B12:II:35G:g(47)	100.0	108.0	109.6	110.1	109.7	107.7	105.0
288	B12:II:35G:g(59)	100.0	108.0	109.4	109.1	108.4	106.6	105.2
292	B12:II:35G:h(35)	100.0	106.9	108.9	108.2	107.5	no rdg.	---
293	B12:II:35G:h(47)	100.0	102.9	103.9	103.5	no rdg.	---	---
298	I-H:2.1%	100.0	105.7	106.4	106.7	106.9	106.3	no rdg.
299	I-H:5%	100.0	105.3	105.6	105.9	105.0	96.7	no rdg.
300	A2:I-H:25:2.1%	100.0	108.5	110.5	111.3	111.8	112.3	112.8
301	A2:I-H:25:5%	100.0	107.7	109.0	109.7	110.0	110.1	109.3
302	A2:I-H:25G:2.1%	100.0	110.2	111.7	112.2	112.7	113.3	113.9
303	A2:I-H:25G:5%	100.0	110.1	111.3	111.7	111.9	112.1	112.4

Table E.4 (continued)

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
304	A9:I-H:25:2.1%	100.0	108.0	109.8	110.5	110.9	111.2	111.7
305	A9:I-H:25:5%	100.0	108.4	109.7	110.4	110.6	110.9	112.8
306	A9:I-H:25G:2.1%	100.0	108.2	109.6	110.2	110.6	111.1	111.8
307	A9:I-H:25G:5%	100.0	108.5	109.5	110.0	110.2	110.2	110.5
308	B4:I-H:35:2.1%	100.0	108.3	109.8	110.5	110.9	111.8	113.0
309	B4:I-H:35:5%	100.0	107.9	109.5	110.4	111.1	no rdg.	---
310	B4:I-H:35G:2.1%	100.0	109.6	111.0	111.4	111.6	112.6	112.6
311	B4:I-H:35G:5%	100.0	109.5	110.5	111.4	112.0	112.9	114.6
312	B9:I-H:35:2.1%	100.0	110.1	111.9	112.6	113.2	114.1	114.3
313	B9:I-H:35:5%	100.0	109.9	111.3	112.0	112.0	111.8	115.4
314	B9:I-H:35G:2.1%	100.0	111.2	112.8	113.5	114.1	114.2	115.0
315	B9:I-H:35G:5%	100.0	110.6	111.8	112.5	113.0	113.3	no rdg.
316	B12:I-H:35:2.1%	100.0	108.3	110.1	111.0	112.7	112.0	no rdg.
317	B12:I-H:35:5%	100.0	108.0	109.5	110.5	114.7	no rdg.	---
318	B12:I-H:35G:2.1%	100.0	108.5	109.7	110.2	110.6	111.6	111.8
319	B12:I-H:35G:5%	100.0	107.8	108.8	109.6	110.2	109.9	no rdg.

Table E.5 Relative Damping Capacity (%) of Sulfate Exposure Specimens

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
3	I-H	100.0	113.3	no rdg.	---	---	---	---
15	II	100.0	81.2	74.5	76.7	80.0	83.4	88.7
115	B3:II:35:S(35)	100.0	84.3	87.5	88.9	88.8	105.2	115.6
117	B3:II:35:S(47)	100.0	101.4	104.5	107.5	111.8	124.4	128.9
119	B3:II:35:S(59)	100.0	93.2	97.3	96.5	94.4	112.0	117.4
120	B3:II:35G:S(35)	100.0	82.0	77.7	75.5	76.9	84.3	101.7
122	B3:II:35G:S(47)	100.0	88.0	90.8	91.3	92.3	100.2	100.8
124	B3:II:35G:S(59)	100.0	89.2	88.9	86.1	90.3	91.1	95.9
133	B4:II:25	100.0	124.5	no rdg.	---	---	---	---
134	B4:II:35	100.0	125.0	no rdg.	---	---	---	---
138	B4:II:35:S(35)	100.0	98.5	120.6	187.9	no rdg.	---	---
140	B4:II:35:S(47)	100.0	87.6	82.1	84.3	86.4	93.1	95.4
142	B4:II:35:S(59)	100.0	90.8	91.2	90.3	90.5	97.1	101.0
143	B4:II:35G:S(35)	100.0	77.6	76.0	131.4	145.0	173.4	168.4
145	B4:II:35G:S(47)	100.0	82.2	84.9	85.9	87.8	95.1	99.0
147	B4:II:35G:S(59)	100.0	90.2	86.7	86.3	85.5	91.0	90.1
163	B5:II:35:S(35)	100.0	84.3	86.5	81.0	82.8	93.3	211.8
165	B5:II:35:S(47)	100.0	87.9	82.3	81.2	80.0	85.9	84.1
167	B5:II:35:S(59)	100.0	90.6	89.5	93.4	101.4	117.2	132.2
168	B5:II:35G:S(35)	100.0	82.5	80.8	78.4	82.6	115.1	167.9
170	B5:II:35G:S(47)	100.0	81.3	82.4	83.6	83.4	90.7	94.4
172	B5:II:35G:S(59)	100.0	87.8	87.1	78.4	87.6	91.0	90.3
207	B9:II:45G	100.0	77.1	86.0	117.1	178.0	241.6	no rdg.
208	B9:II:55G	100.0	59.9	59.9	60.6	61.4	60.7	85.0
209	B9:II:35:S(35)	100.0	83.1	80.1	82.6	81.2	87.8	89.7
211	B9:II:35:S(47)	100.0	85.9	87.7	96.2	98.5	101.7	238.9
213	B9:II:35:S(59)	100.0	76.1	88.5	88.1	86.7	98.2	104.0
214	B9:II:35G:S(35)	100.0	77.8	80.3	77.9	79.5	81.9	80.8
216	B9:II:35G:S(47)	100.0	77.9	80.2	80.0	82.1	83.3	85.5
218	B9:II:35G:S(59)	100.0	80.9	80.2	80.6	83.1	84.6	86.9
226	B9:II:35G:g(35)	100.0	78.9	74.7	77.8	85.1	115.8	208.8
229	B9:II:35G:g(47)	100.0	71.9	64.8	64.3	65.5	68.9	70.9
233	B9:II:35G:g(59)	100.0	84.5	82.9	80.4	85.6	81.7	79.1
237	B9:II:35G:h(35)	100.0	82.7	98.0	162.4	227.9	no rdg.	---
238	B9:II:35G:h(47)	100.0	106.7	150.6	189.8	321.1	no rdg.	---
262	B12:II:45G	100.0	124.3	138.2	194.6	288.7	no rdg.	---
263	B12:II:55G	100.0	102.2	125.3	187.9	142.5	131.1	162.2
264	B12:II:35:S(35)	100.0	85.2	91.6	181.4	no rdg.	---	---
266	B12:II:35:S(47)	100.0	102.9	103.7	112.2	119.4	134.0	180.8
268	B12:II:35:S(59)	100.0	98.2	112.3	103.3	103.5	106.4	no rdg.
269	B12:II:35G:S(35)	100.0	90.6	93.5	88.6	82.7	107.4	159.1
271	B12:II:35G:S(47)	100.0	77.7	79.4	80.9	81.2	82.7	85.9
273	B12:II:35G:S(59)	100.0	86.6	86.4	87.8	94.0	94.5	94.8
281	B12:II:35G:g(35)	100.0	108.7	no rdg.	---	---	---	---
284	B12:II:35G:g(47)	100.0	81.1	78.8	77.3	81.9	96.7	103.7
288	B12:II:35G:g(59)	100.0	83.9	78.5	78.8	78.8	83.3	80.7
292	B12:II:35G:h(35)	100.0	92.8	111.2	175.8	252.3	no rdg.	---
293	B12:II:35G:h(47)	100.0	105.9	125.8	176.3	no rdg.	---	---
298	I-H:2.1%	100.0	84.2	82.2	79.7	80.0	85.4	no rdg.
299	I-H:5%	100.0	87.7	88.7	88.8	98.0	155.1	no rdg.
300	A2:I-H:25:2.1%	100.0	83.0	78.1	77.1	75.3	69.3	77.3
301	A2:I-H:25:5%	100.0	58.3	56.3	57.8	57.9	86.4	79.7
302	A2:I-H:25G:2.1%	100.0	65.5	60.3	61.1	59.7	60.2	59.4
303	A2:I-H:25G:5%	100.0	65.5	62.3	60.4	60.5	65.2	63.5

Table E.5 (continued)

Mixture Number	Mixture Designation	Time of Exposure (days)						
		0	90	180	270	360	540	720
304	A9:I-H:25:2.1%	100.0	73.2	71.6	67.9	68.0	69.0	67.8
305	A9:I-H:25:5%	100.0	70.4	71.3	70.3	68.3	67.3	68.6
306	A9:I-H:25G:2.1%	100.0	69.7	66.8	66.4	65.4	65.6	64.4
307	A9:I-H:25G:5%	100.0	67.8	66.1	65.8	64.4	64.3	62.7
308	B4:I-H:35:2.1%	100.0	78.2	73.2	73.9	76.7	120.5	237.2
309	B4:I-H:35:5%	100.0	78.8	116.3	127.8	140.1	no rdg.	---
310	B4:I-H:35G:2.1%	100.0	75.7	68.5	75.8	82.6	81.6	115.7
311	B4:I-H:35G:5%	100.0	79.5	85.9	114.0	147.9	154.8	214.8
312	B9:I-H:35:2.1%	100.0	69.7	66.5	65.7	66.0	79.0	115.0
313	B9:I-H:35:5%	100.0	74.1	74.9	83.0	139.2	141.1	290.3
314	B9:I-H:35G:2.1%	100.0	74.3	69.6	69.8	72.1	82.1	108.5
315	B9:I-H:35G:5%	100.0	75.6	80.7	83.2	82.2	101.4	no rdg.
316	B12:I-H:35:2.1%	100.0	66.4	66.5	69.6	144.0	247.9	no rdg.
317	B12:I-H:35:5%	100.0	74.4	94.8	154.4	374.9	no rdg.	---
318	B12:I-H:35G:2.1%	100.0	80.2	76.3	84.8	90.6	96.6	122.0
319	B12:I-H:35G:5%	100.0	77.8	89.0	118.4	130.6	167.5	no rdg.

APPENDIX F

PERMEABILITY TEST DATA

Table F.1 Chloride Ion Permeability (milliamperes) After 13 Days of Moist Curing

Mixture Designation	Duration of Permeability Test (hours)													Total Coulombs
	0	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	
II	249	284	314	341	361	379	395	410	428	443	455	466	475	8350
B9:II:35G	255	319	354	385	408	426	437	445	456	458	461	464	464	8950
B9:II:35G:s(47)	72	79	84	89	92	95	97	99	101	102	104	104	104	2050
B9:II:35G:g(47)	281	337	371	398	413	424	431	443	463	486	511	542	546	9420
B9:II:35G:g(47)h(47)	127	145	157	168	177	185	191	195	198	199	198	197	196	3910
B9:II:45G	371	488	557	606	634	673	768	877	877	877	877	877	877	15720
B9:II:45G:s(47)	78	86	91	96	100	103	106	108	110	112	113	114	115	2220
B9:II:55G	366	507	593	640	650	698	781	879	896	896	896	896	896	16130
B9:II:55G:s(47)	46	50	52	53	55	57	59	60	61	62	63	63	64	1240
B12:II:35G	297	359	404	433	462	483	509	535	563	603	626	659	686	11030
B12:II:35G:s(47)	133	149	162	173	182	188	193	195	196	197	196	194	192	3940
B12:II:35G:g(47)	302	367	417	452	475	491	504	517	542	583	640	676	713	11110
B12:II:35G:g(47)h(47)	194	228	252	272	290	300	310	318	323	331	337	344	349	6440
B12:II:45G	270	334	378	409	429	444	454	461	470	483	508	549	611	9650
B12:II:45G:s(47)	104	117	125	133	142	147	152	156	159	162	162	163	163	3150
B12:II:55G	336	437	529	578	610	641	685	772	802	802	802	802	802	14460
B12:II:55G:s(47)	95	111	121	131	141	153	166	176	186	196	204	211	214	3510

Table F.2 Chloride Ion Permeability (milliamperes) After 91 Days of Moist Curing

Mixture Designation	Duration of Permeability Test (hours)													Total Coulombs
	0	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	
II	194	223	241	259	275	287	296	304	310	315	320	324	321	6140
B9:II:35G	72	75	79	82	85	87	90	91	93	95	95	96	97	1890
B9:II:35G:s(47)	34	34	35	36	37	38	39	40	40	40	40	41	41	820
B9:II:35G:g(47)	73	75	76	78	80	80	81	82	83	83	83	83	83	1730
B9:II:35G:g(47)h(47)	52	55	56	58	59	59	60	60	60	60	60	59	59	1260
B9:II:45G	91	98	104	109	114	117	121	124	126	128	129	131	131	2540
B9:II:45G:s(47)	28	30	31	31	32	32	32	33	33	33	33	33	33	690
B9:II:55G	120	137	149	161	171	158	188	194	201	205	209	211	214	3870
B9:II:55G:s(47)	19	19	19	20	20	20	20	20	20	20	20	20	20	420
B12:II:35G	104	112	118	125	130	136	141	145	147	150	151	153	154	2950
B12:II:35G:s(47)	49	51	53	54	55	56	58	59	59	60	60	60	60	1220
B12:II:35G:g(47)	100	105	110	114	118	121	123	126	128	129	129	130	131	2610
B12:II:35G:g(47)h(47)	68	71	72	75	76	77	78	80	80	82	82	82	82	1670
B12:II:45G	92	96	98	101	103	105	106	107	108	107	107	107	106	2240
B12:II:45G:s(47)	54	56	57	58	58	58	59	59	59	59	59	59	58	1250
B12:II:55G	89	94	99	102	105	107	109	111	111	112	113	113	113	2300
B12:II:55G:s(47)	41	44	46	47	48	49	50	50	51	51	52	52	52	1060

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