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Ramon L. Carrasquillo and Josef Farbiarz

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16. Abstract

The main objective of this study was to determine the influences of the constituents of portland cement, aggregates, and mineral admixtures on alkali-silica reaction. The testing program included 3 natural aggregates, 3 Type I and 1 Type IP portland cements, 4 Type A and 5 Type B fly ashes, tap and distilled (low pH) water, and 1 source of silica fume.

ASTM C 227 was the primary guideline for the evaluation and comparison of these materials, most of which are available for use in highway projects in the state of Texas.

The results of this testing program demonstrated that:

(1) Each of the natural aggregates studied can be used safely in concrete without mineral admixtures, if the cement is chosen carefully with respect to alkali content.
(2) Each of the cements tested can be used in concrete with any of the aggregates tested, if a suitable mineral admixture is used as a partial replacement for cement in the proper proportion.
(3) The silica fume and seven of the nine fly ashes tested reduced expansions considerably when used in proper proportions as partial replacements for cement, and
(4) fineness of Type B fly ash does not affect significantly its effectiveness in reducing alkali-aggregate related mortar bar expansions.

17. Key Words

alkali-aggregate reaction, alkali-silica reaction, aggregates, mineral admixtures, portland cement, fly ashes, constituents, silica fume, proportion

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ALKALI-AGGREGATE REACTION IN CONCRETE CONTAINING FLY ASH
FINAL REPORT

by

Ramon L. Carrasquillo
and
Josef Farbiarz

Research Report No. 450-3F
Research Project 3-9-85-450
"Alkali-Aggregate Reaction in Concrete Containing Fly Ash"

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

by the

CENTER FOR TRANSPORTATION RESEARCH
BUREAU OF ENGINEERING RESEARCH
THE UNIVERSITY OF TEXAS AT AUSTIN

October 1989

There was no invention or discovery conceived or first actually reduced to practice in the course of or under this contract, including any art, method, process, machine, manufacture, design or composition of matter, or any new and useful improvement thereof, or any variety of plant which is or may be patentable under the patent laws of the United States of America or any foreign country.

PREFACE

This is the last in a series of reports summarizing the effect of fly ash on the alkali-aggregate mechanisms in concrete. The report described herein provides guidelines to the design and materials engineer for the selection of fly ash/cement combinations and their proportions to ensure long-term performance of the concrete.

This work is part of Research Project 3-9-85-450 entitled "Alkali-Aggregate Reaction in Concrete Containing Fly Ash". The study described in this report was jointly conducted by the Center for Transportation Research, Bureau of Engineering Research, the Phil M. Ferguson Structural Engineering Laboratory at the University of Texas and private industry. The work was co-sponsored by the Texas State Department of Highways and Public Transportation and the Federal Highway Administration.

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

SUMMARY

As the use of mineral admixtures in the concrete industry increases, so does the need for a complete understanding of their properties and their effects on the properties of fresh and hardened concrete. One of several beneficial attributes of mineral admixtures such as fly ash and silica fume when added to concrete mixtures is the potential for reduction of deleterious expansions within the hardened concrete. One such reaction occurs between minerals present in the aggregates and the alkalies present in the cement. The main objective of the research program described in this report is the need for guidelines relating to the proper use of mineral admixtures as a means of reducing the expansion due to alkali-aggregate reaction (AAR) in concrete.

Testing included different sources of aggregates, cements and fly ashes and one source of silica fume. The effect of fly ash fineness on alkali-aggregate reaction in concrete was also studied. ASTM C 227 was the primary guidelines for the evaluation and comparison of the materials.

Results indicate that the effectiveness of fly ash on reducing alkali-aggregate reaction expansion in concrete is dependent upon the chemical composition of the fly ash and the amount of cement being replaced with fly ash. Further, fineness of fly ash was not found to be a relevant factor governing the effectiveness of a fly ash in reducing alkali-aggregate expansion in concrete. Intergrinding of fly ash with cement clinker in the manufacture of a blended cement increases the effectiveness of fly ash.

IMPLEMENTATION

The results from this study clearly indicate that the effectiveness of a fly ash in reducing alkali-aggregate reaction expansions in concrete are dependent upon the chemical composition of the fly ash and the amount of cement being replaced. However, when properly selected and proportioned, the use of fly ash in concrete can prove to be an alternative to allow the use of high alkali cement or alkali reactive aggregates in concrete without concern for alkali-aggregate reaction damage occurring.

As a result of this study, the following guidelines are recommended for the selection of materials and their proportions in order to ensure a reduction in potential alkali-aggregate reaction.

1. If the fly ash is a TSDHPT Type A fly ash containing less than 1.7 percent available alkalies and less than 10 percent CaO, it can be used at any cement replacement level in cement.
2. For all other fly ashes, the fly ash should not be used in concrete at cement replacement levels of less than 25 percent by volume. Preferably, ASTM C 227 mortar bar expansion tests should be conducted using the proposed materials and proportion for a job in order to determine the adequacy of the 25 percent minimum replacement lower limit.

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CHAPTER 1
INTRODUCTION

1.1 General

As the use of mineral admixtures in the concrete industry increases, so does the need for a complete understanding of their properties and their effects on the properties of fresh and hardened concrete. One of several beneficial attributes of mineral admixtures such as fly ash and silica fume when added to concrete mixtures is the potential for the reduction of deleterious expansions within the hardened concrete. One such reaction occurs between minerals present in the aggregates and the alkalies present in the cement. The main objective of the research program described in this report is a search for guidelines relating to the proper use of mineral admixtures as a means of reducing the expansion due to alkali-aggregate reaction (AAR) in concrete.

1.2 Background Information.

Since the early 1940's, AAR has been recognized as capable of degrading the strength and durability of concrete[1]. The use of aggregates whose reactivity with alkalies has proven to be negligible is the safest means of reducing the risk of damage to concrete due to AAR. However, this solution is not always available to the concrete user. As an alternative, the American Society for Testing and Materials (ASTM) has suggested a limit of 0.60 percent, by weight, on the alkali content of the cement for jobs where the alkali reactivity of the aggregate was either unknown or known to be deleterious[2]. However, factors such as moisture migration through the concrete section can raise the concentration level of alkalies beyond safe limits, even within concretes made with cements with a low alkali content[3].

The use of mineral admixtures to improve the properties of mortars dates back to the Greek and Roman eras. Both natural and artificial ashes had been used to increase the workability of fresh concrete and to increase the durability of hardened concrete[4].

Soon after AAR within concrete was identified as the cause of several important incidences of cracking and deformation of concrete structures such as dams and pavements, it was found that the use of certain mineral admixtures, such as pozzolanas, as a replacement of a portion of the cement in the concrete mixture can reduce, in some instances, the AAR related expansions of mortar bars compared to expansions of mortar bars made with a similar mixture containing no fly ash[5].

When alkali-aggregate reaction was first recognized, it was thought that this reaction occurred between the alkalies in the cement and the silica minerals in the aggregate. Later tests proved that AAR is only a generic term describing an expansive reaction involving alkalies in cement and certain minerals found in concrete aggregates, including, but not restricted to, silica minerals. Other minerals such as dolomite could be alkali reactive as well.

Although alkali-silica reaction is the most common type of AAR found worldwide, the fact that different aggregate minerals can cause deleterious expansions in hardened concrete makes even harder the determination of nonreactive aggregates as the solution to the AAR problem. Thus, the need to use mineral admixtures to reduce the risk of damages to hardened concrete due to such a reaction becomes more evident.

Both natural and artificial pozzolanas have been widely use as mineral admixtures in mortars and concrete. The two most common artificial pozzolanas are fly ash and silica fume[6]. Fly ash, also known as pulverized fuel ash, is a waste byproduct produced during the generation of electricity in coal burning power plants[6]. Silica fume is a byproduct of the manufacture of silicon or silicon alloys[7].

The widespread availability and cost effectiveness of fly ash makes it the most used mineral concrete admixture. The limited knowledge about some fly ash properties and their effects on concrete has led to a significant amount of research being made by investigators all around the world in the last decade.

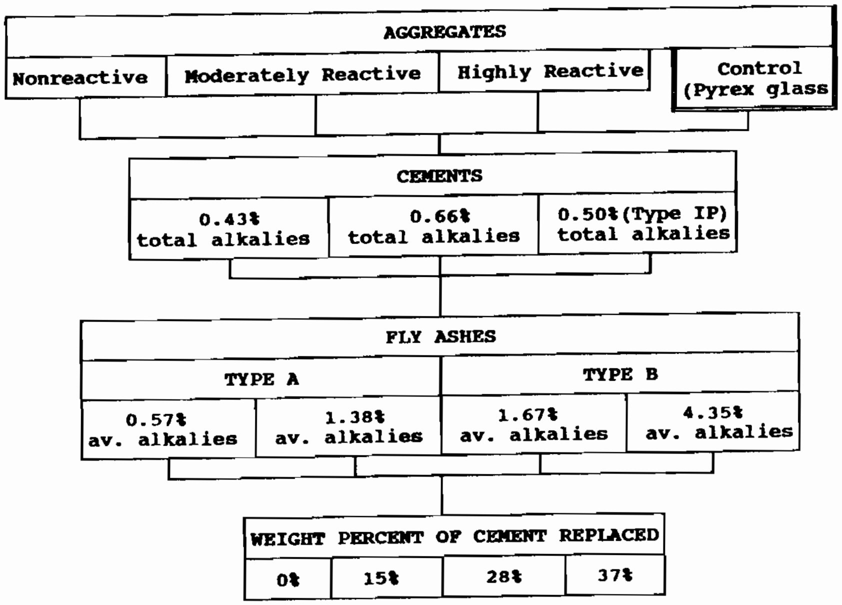
1.3 Scope Of Research.

As stated in Research Report 450-1[8], the main objective of this study is to determine the influence of the constituents of portland cement, aggregates, and mineral admixtures on alkali-silica reaction in concrete. With an understanding of these relationships, guidelines for proper, efficient, and economical use of mineral admixtures in concrete can be developed.

This research project has been divided into three phases. The objectives of Phase I are:

1. to identify the most relevant components of fly ash, including type and amount, affecting the mechanism of alkali-silica reaction in concrete,
2. to establish a relationship, if possible, among relevant components of fly ash, portland cement, and concrete aggregates to be used in controlling alkali-silica reaction in concrete,
3. to provide further information on the adequacy of existing fly ash specifications to ensure satisfactory performance of concretes containing fly ash, especially in preventing alkali-silica reaction, and
4. to establish guidelines in a form useful to field engineers for the selection and use of fly ash in concrete to prevent alkali-silica reaction.

Table 1.1 Materials and test combinations used in Phase I of program.



To accomplish these objectives, mixtures comprising of 108 combinations of the materials listed in Table 1.1 were tested according to ASTM C 227 (Mortar Bar Method). The 90-day expansion test results were reported previously[8]. This report will include the results obtained from 90 days to 1440 days in Phase I of the program.

Phase II of the program was developed to further study several trends observed in Phase I and to investigate the behavior of additional materials. The topics under study in

Phase II are:

1. the behavior of fly ash treated with a chemical precipitating agent,
2. the effect of the pH of the mixing water,
3. the behavior of additional sources of fly ash and cement,
4. the effect of replacing different percentages of cement with fly ash,
5. the effect of replacing a portion of aggregate, rather than cement, with fly ash,
6. the effect of fineness and blending of Type IP cement, and
7. the behavior of mixtures containing silica fume.

A total of 94 mixtures were prepared in Phase II, utilizing the materials listed in Table 1.2.

Phase III was initiated as a result of the Phase II test results on the fineness and blending of Type IP cements. These test results led to the suggestion that the effect of the fineness of a particular fly ash on alkali- aggregate related expansions could be greater than anticipated, even when the "coarser" fly ash would pass the fineness requirements of specification ASTM C 618. Thus, a third Phase was conducted on the research program to study in more detail the effect that differences in the fineness of a particular fly ash would have on the mortar bar expansions.

A total of 37 mixtures were prepared in Phase III, utilizing the materials listed in Table 1.3. This report will discuss the results of the first 720 days of exposure testing comprising this part of the research program.

Table 1.2 Additional materials and mixture proportions used in Phase II of the program

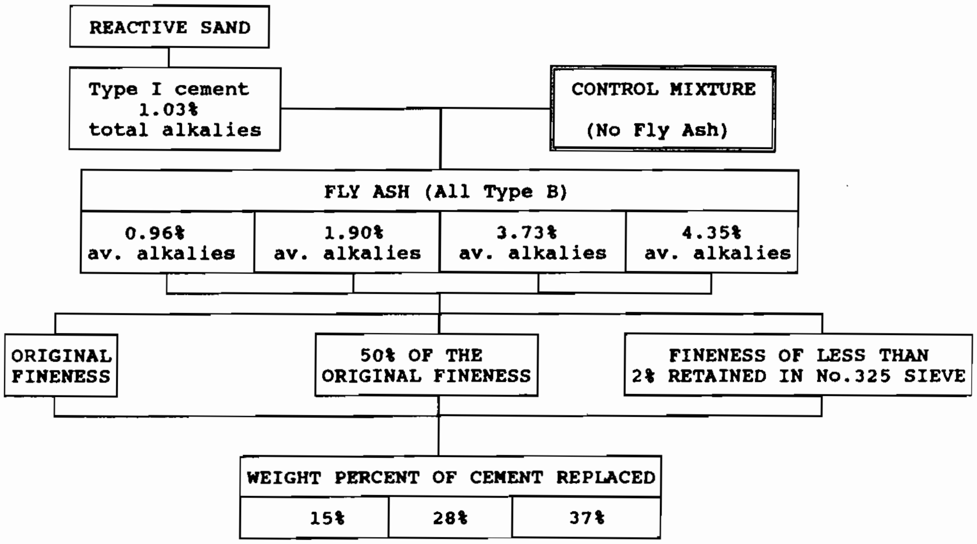
ADDITIONAL MATERIALS TESTED		
CEMENTS		FLY ASHES
1.03% total alkalies	0.53% total alkalies	0.13% av. alkalies
		1.76% av. alkalies
SILICA FUME		2.04% av. alkalies
75% - 98% SiO_2		2.35% av. alkalies
DISTILLED WATER		3.75% av. alkalies

ADDITIONAL MIXTURE PROPORTIONS TESTED				
WEIGHT PERCENT OF CEMENT REPLACED BY FLY ASH				
17.5%	26%	34.3%	45%	62.5%
AGGREGATE REPLACED BY FLY ASH				
Amount equal to 30% of the volume of cement				
VOLUME PERCENT OF CEMENT REPLACED BY SILICA FUME				
17.5%		34.4%		45%

Chapter 1 of this report contains a brief introduction and general description of the study. In Chapter 2 a review of pertinent literature is presented. Chapter 3 describes the testing procedures and materials used. Test results are provided in Chapter 4 and discussed in Chapter 5. In Chapter 6, a summary, conclusions, recommendations, and suggested topics for further research are presented.

This research program is part of a broad project entitled "Alkali-Aggregate Reaction in Concrete Containing Fly Ash". This program is being conducted jointly between the Center for Transportation Research and the Phil M. Ferguson Structural Engineering Laboratory at the University of Texas at Austin under the sponsorship

Table 1.3 Materials and test combinations used in Phase III of program.



of the Texas State Department of Highways and Public Transportation (TSDHPT), the Federal Highway Administration, and several industry representatives.

CHAPTER 2
LITERATURE REVIEW

2.1 General

At first, pozzolanas were used because of their cementitious properties in the presence of lime and water at ordinary temperatures[9]. With the introduction of Portland cement, pozzolanas lost most of their value as cementitious agents. However, it was later realized that blends of pozzolanas with Portland cements could improve durability, combined with some economy, to concrete in marine, hydraulic, and underground structures[10]. The reduction in heat evolution later provided another reason for their use in large mass concrete works[11]. Continued investigation led to the discovery that the use of pozzolanas in Portland cement mixtures, either in a blend or used as mineral admixtures in the concrete, often had a beneficial effect in both fresh and hardened concrete properties, such as workability and permeability. Furthermore, it was found that some pozzolanas reduced the expansions caused by AAR within the concrete[1].

The availability of waste by-products from industrial burning processes such as slag, fly ash, silica fume, and others, spurred the utilization of artificial pozzolanas for special situations. Extensive research conducted in the last two decades on the utilization of fly ash in concrete has led to the spread of its use in regular concrete operations due to factors such as heat evolution, lower water requirements, improved workability, reduced permeability, and increased durability.

The beneficial effects of mineral admixtures on expansions due to alkali-silica reaction were discovered by Stanton[1]. Natural pozzolanas, particularly finely ground portions of reactive aggregates, received much of the initial attention[1,12]. Later studies included artificial pozzolanas, as well[13].

Silica fume and rice husk ash, two extremely fine and highly siliceous by-products, have proven to be the most effective inhibitors of expansion[14]. Natural pozzolanas tend to be moderately effective[15]. Fly ash and blast furnace slag are the least effective of mineral admixtures, but are generally satisfactory if used in sufficient amounts. The environmental benefits of recycling by-products like fly ash and silica fume make their use even more attractive today. These two latter mineral admixtures were the only pozzolanas tested during this research program.

Research Report 450-2[16] of this program constituted an extensive review of the literature available on the AAR chemistry, mechanism, tests, and prevention. This chapter will first, present a summary of the main aspects of that literature survey, and second, will focus on the literature concerning the effect of the fineness of fly ash on alkali-aggregate related expansions in concrete.

2.2 Summary of Previous Literature Review

2.2.1 Chemistry of Alkali-Aggregate Reaction. Although it is called alkali-aggregate reaction, siliceous aggregates are not directly attacked by alkali ions. Instead, hydroxide ions (OH^-) have been found to initiate damaging reactions with susceptible aggregates[17]. The significance of alkalies in cement lies in the large concentrations of hydroxide ions produced in concrete containing alkali rich cements and the expansive properties of alkali-silicate reaction products. Virtually all of the soluble alkalies occur as sulfates which are derived more often from impurities in kiln fuel than from cement raw materials[15]. Changes in alkali concentration over time depend on several factors:

1. continuing hydration - which increases the number of alkali ions released,
2. evaporation of pore water - which increases the alkali ion concentration in the remaining water, and
3. addition of external water - which can either dilute the existing alkalies or introduce new alkalies to the solution.

Powers and Steinour have indicated that the ratio of calcium oxide (CaO) to alkali oxides (Na_2O, K_2O) in the reaction products serves as the indicator of a "safe" or "unsafe" reaction[18,19].

Research made by Chatterji revealed that little evidence of expansion or reaction occurs in specimens made with reactive material combinations when no calcium hydroxide ($Ca(OH)_2$) is present[20]. Most cement pastes are saturated or supersaturated with $Ca(OH)_2$[15]. Under normal conditions, these cement pastes contain a basic concentration of hydroxide ions which is attributable to pure $Ca(OH)_2$. Alkali ions can act to raise the level of hydroxide ions far above this basic level. It is these hydroxide ions which initiate the deleterious reactions with siliceous aggregates. In the presence of free $Ca(OH)_2$, sodium ions released from alkali salts, hydroxide ions from $Ca(OH)_2$ and from water molecules all penetrate reactive aggregate particles.

2.2.2 Mechanism of Alkali-Aggregate Reaction. Several theories have been proposed to explain the mechanism by which AAR causes deleterious expansion within the concrete. The first widely accepted theory, based on an osmotic cell, was proposed in 1944 by Hansen[21]. Later research[15,22] contradicted this theory by arguing that a "true" osmotic pressure cell could not exist because cracks that form in cement paste during the early stages of the alkali-silica reaction allow circumvention of the semi-permeable cement paste membrane.

Finally, Powers and Steinour[16,17] offered the opinion that neither theory of expansion was entirely satisfactory. Instead, they developed a theory combining aspects of the other two, presented below and illustrated in Figure 2.1

1. Structural discontinuities in a silica particle allow reactions at the particle surface between alkalies and silica. Alkali-silica "gel" containing colloidal silica is formed.
2. Alkalies penetrate deeper into the particle, continuing to participate in reactions with silica. Meanwhile, alkali hydroxides act as a peptizing agent, encouraging dispersion of colloidal silica in water drawn out of the cement paste. As the colloidal silica disperses, the resulting expansion is limited only by the strength of the peptizing agent. Water is drawn to the gel because the free energy of water is lower in a solution. Water naturally flows from a higher to lower energy state.
3. If enough water is imbibed, the alkali silica complex is transformed from a gel into a fluid. Expansion of the cement paste is then caused by hydraulic forces, as Hansen proposed. If the gel remains solid, expansion occurs due to swelling, even if cracks or cavities are present.

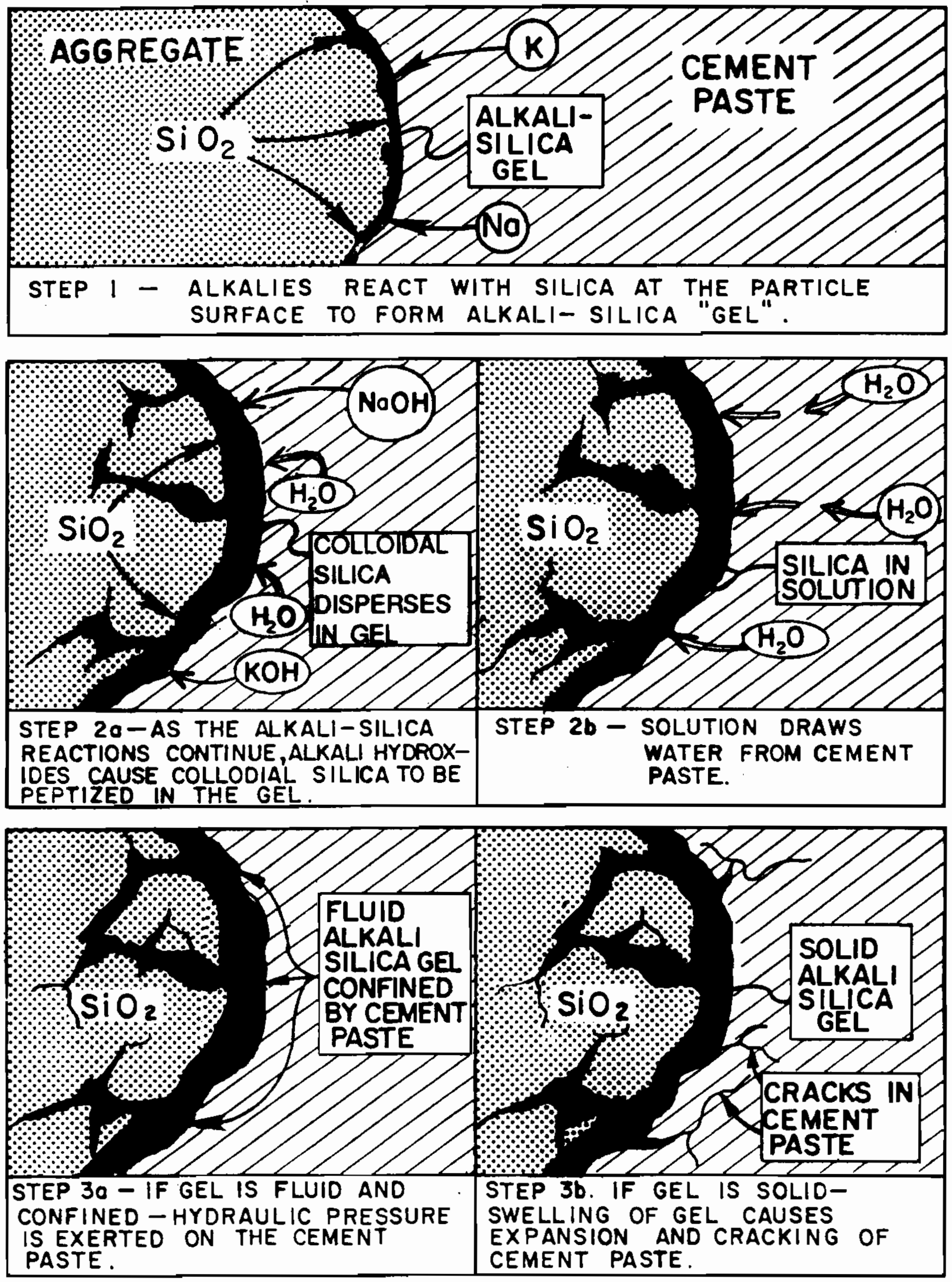


Figure 2.1 Illustration of expansion theory of Powers and Steinour[16,17]

2.2.3 Role of Concrete Constituents In Alkali-Aggregate Reaction.

2.2.3.1 Role of Aggregate. The reactivity of aggregate to attack by alkalies has been traced to some of the minerals that form the susceptible aggregate. The most common of the reactive minerals is silica. Silica is an important component of sedimentary rocks, and frequently occurs as quartz. Chert, flint, chalcedony, opal, cristobalite, and tridymite are much rarer forms of silica. The reactivity of silica depends in great part on its crystalline structure. Quartz, which has a well defined crystalline structure, causes very low expansions, if any[23]. Opal, on the other hand, is often defined as a "mineraloid" because it has no true crystalline structure and no definite chemical formula. Opal is a very alkali-reactive mineral.

Glasses, both natural and artificial, are also reactive[21]. Pyrex, an artificial glass, due to its constant composition and high silica content (≈80 percent), is specified as the "standard" reactive aggregate for use in ASTM C 441 "Test for Effectiveness of Mineral Admixtures in Preventing Excessive Expansion of Concrete Due to Alkali-Aggregate Reaction"[24].

Many variables affect the rate at which reactive aggregate participate in the AAR. Grain size, amount of aggregate present, amount of the reactive constituents present, etc. The amount of reactive material in an aggregate which results in the maximum expansion is known as the "pessimum" proportion[25]. However, this amount varies with particle size[26].

The Corps of Engineers[27] considers an aggregate to be "potentially deleteriously reactive" if it contains:

1. any opal,
2. more than 5 percent chert in which chalcedony is detected, or
3. more than 3 percent glassy igneous rocks in which acid or intermediate glass is detected.

Additionally, other constituents which can participate in "potentially deleterious reactions" in concrete include[28]:

4. strained quartz present as the predominant constituent of the aggregate,
5. tridymite present in an amount greater than 1 percent,

6. rhyolite, dacite, latite or andesite present in amounts greater than 3 percent, or

7. synthetic glass present in amounts over 1 percent.

2.2.3.2 Role of Cement. Cement is the main vehicle carrying the alkalies into the mixture to initiate the attack on the silica in the aggregate. The alkali content of cement is relatively small: it ranges typically from 0.2 to 1.3 percent by total weight of cement[29]. However, its effect upon several concrete properties is not minor. It affects, among other properties, drying shrinkage, setting time, response to admixtures, and strength.

Stanton observed that alkali-silica reaction was negligible when the alkali content of the cement used was less than 0.60 percent[30]. ASTM adopted this value as a recommended limit for total alkalies in cement used with reactive aggregates and included it in ASTM C 150. However, studies by Nixon et al.[31] indicated that evaporation of moisture from the top surface of concrete causes water to be drawn upward to the surface carrying soluble alkalies and concentrating them near the top of the concrete at levels far greater than would be expected.

2.2.3.3 Role of Water. Little attention is generally drawn to the composition of the mixing water. Traditionally, the only specification made on mixing water is for it to be potable. Sodium ions at a concentration of 1000 parts per million (ppm) in the mixing water will, at a water-cement ratio of 0.6, amount to 0.06 percent of cement weight, or 0.08 percent if expressed as sodium oxide. If reactive aggregates are used and cement alkalies are limited to 0.60 percent, the alkalies present in the water can comprise a significant portion of the alkalies in the concrete. Typical city water supplies, however, tend to contain alkali ions in much lower quantities than 1000 ppm. The Corps of Engineers states that water having a pH ranging from 6.0 to 8.0 is safe for use in concrete[32].

2.2.3.4 Role of Fly Ash. The term "fly ash" was coined by Davis et al.[33,34] in the first comprehensive report on the properties of concrete containing fly ash. The chemical characteristics of fly ash depend on the chemical characteristics of the coal which, in turn, are dependent on the geology and geography of the original coal deposit[35]. Fly ash is predominantly glassy due to rapid cooling during the collection process[36].

ASTM recognizes two classes of fly ash based on coal source: Class F from bituminous or anthracite coal and Class C from subbituminous or lignite coal. The chemical and physical requirements for each class of fly ash are presented in Table 2.1. The TSDHPT recognizes two types of fly ash, known as Type A and Type B, based on chemical composition[37]. The requirements for these two classifications are also presented in Table 2.1.

The use of fly ash in proper amounts has been found to reduce expansion in concrete due to alkali-silica reaction[13,38,39,40,41]. The mechanism by which this occurs is not exactly known[42]. However, it is suggested that a combination of both physical and chemical properties of fly ash contribute to this mechanism. On one hand, the use of fly ash in concrete significantly decreases its permeability[4,35]. As a result, the penetration of outside water into the concrete is restricted. Since less water is available to alkali-silica reaction products for imbibition and swelling, the magnitude of damage caused by the reaction is lessened. On the other hand, the presence of free $Ca(OH)_2$ is required for the development of an alkali-silica reaction[20]. The use of a sufficient quantity of fly ash, or other pozzolanas, results in the conversion of all of the free $Ca(OH)_2$ to C-S-H.

High calcium fly ashes - ASTM Class C or TSDPHT Type B - have been found to contain larger amounts of soluble alkalies, particularly sodium[15,43]. These fly ashes may contribute enough alkalies to the pore solution to increase the degree of reaction. ASTM C 618 contains an optional limit of 1.5 percent available alkalies, determined according to ASTM C 311, for fly ash used with a reactive cement-aggregate combination. Previous research has found that this limit might not be an accurate guideline when choosing a fly ash to help reduce the risk of AAR in concrete[8].

2.2.3.5 Role of Silica Fume. Silica fume is a recent addition to the category of mineral admixtures for concrete[44], and is regarded as the most efficient inhibitor of AAR. Studies conducted in Iceland[45] have demonstrated that this reaction can be suppressed by replacing as little as 7 percent of the cement in concrete with silica fume.

Depending on the silicon alloy produced and furnace design, different types of silica fume are produced. Aitcin et al.[7] recognize seven types of silica fume which

Table 2.1 ASTM and TSDHPT specifications for fly ash composition[24,37]

FLY ASH CHEMICAL COMPOSITION REQUIREMENTS	ASTM C 618-84		TSDHPT D-9-8900	
	Class F	Class C	Type A	Type B
Si + Al + Fe oxides minimum %	70	50	65	50
Ca oxide maximum %	–	–	*	*
Mg Oxide maximum %	–	–	5.0	5.0
SO_3 maximum %	–	–	5.0	5.0
Available alkalies (expressed as Na_2O) maximum %	1.5	1.5	1.5	1.5
Loss on ignition maximum %	6.0	6.0	3.0	3.0
Moisture content maximum %	3.0	3.0	2.0	2.0
Amount retained on #325 sieve maximum %	34	34	30	30
Pozzolanic activity index	75	75	75	75
Shrinkage maximum %	0.03	0.03	0.03	0.03

* 4% maximum variation from previous 10 samples

are presented in Table 2.2. The information which has been published shows that the silica fume in use typically falls in the "Si" and both "SiFe-75 percent" categories

Table 2.2 Proposed classification of silica fumes by chemical composition[7]

	AMOUNT OF COMPONENT IN EACH CLASS OF SILICA FUME (by weight, in percent						
	PROPOSED CLASSES OF SILICA FUME						
COMPONENT	Si	FeSi-75%	** FeSi-75%	FeSi-50%	FeCrSi	CaSi	SiMn
SiO_2	94	89	90	83	83	53.7	25
Fe_2O_3	0.03	0.6	2.9	2.5	1.0	0.7	1.8
Al_2O_3	0.06	0.4	1.0	2.5	2.5	0.9	2.5
CaO	0.5	0.2	0.1	0.8	0.8	23.2	4.0
MgO	1.1	1.7	0.2	3.0	7.0	3.3	2.7
Na_2O	0.04	0.2	0.9	0.3	1.0	0.6	2.0
K_2O	0.05	1.2	1.3	2.0	1.8	2.4	8.5
C	1.0	1.4	0.6	1.8	1.6	3.4	2.5
S	0.2	–	0.1	–	–	–	2.5
MnO	–	0.06	–	0.2	0.2	–	36.0
Loss on Ignition	2.5	2.7	–	3.6	2.2	7.9	10.0

** produced by heat recovery system

of Table 2.2. Some qualities that could make the use of some silica fumes in concrete undesirable are presented in Table 2.3.

2.2.4 Tests for Determining Potential Reactivity of Materials. The test procedures most commonly used throughout the world for determining potential reactivity of materials are ASTM C 227, ASTM C 289, ASTM C 295. and ASTM C

Table 2.3 Unusual characteristics of several classes of silica fume[7]

CLASS	CHARACTERISTICS
CaSI	The calcium carbide in this type of silica fume reacts with water in a cement mixture to form enough highly explosive acetylene gas to comprise 3 percent to 4 percent of the volume of the concrete. Some danger is associated with the use of this silica fume in concrete.
SiMn	This type of silica fume contains a much higher amount of manganese and much smaller amount of silica than the other types of silica fume. Careful investigation will be required to determine the suitability of this type of silica fume for use in concrete.
FeSi-50%	This silica fume has also bee found to produce a small amount of gas in concrete. The nature of this gas is unknown except for the fact that it is not acetylene.

441. Typically, ASTM C 227 is the first test conducted to determine if a particular cement- aggregate combination is compatible. Mortar bars are prepared using a specified gradation of aggregate and a high alkali cement. The specimens are stored above water in sealed containers at 100°F (38°C). At certain time intervals, their lengths are measured. The average expansion of all specimens of a given material combination should not exceed 0.05 percent at three months or 0.10 percent at six months. The three- month criteria is for use only when six-month data is not available.

If the results of ASTM C 227 indicate that an aggregate is potentially reactive, a skilled petrographer can use ASTM C 295 to determine the potentially reactive materials present[43]. If suspect materials are found, a chemical test, ASTM C 289, can be run to classify an aggregate as "innocuous" or "deleterious" as a function of the percentage of silica dissolved in a NaOH solution compared to a reduction in the alkalinity of the solution. Excess silica in solution is considered to be related to the formation of gel in concrete.

ASTM C 441 is used to test the effectiveness of mineral admixtures in reducing expansions due to alkali- aggregate reactions. It is similar to ASTM C 227 in that mortar bars, formed and stored under identical conditions, are used in the test. This test uses Pyrex glass as the aggregate for the mixture combinations, which include a control mixture with no admixture added, a test mixture with a cement containing more than 1.0 percent available alkalies, and a job mixture if a particular cement to be used in a job is to be tested. For a mineral admixture to meet the requirements of this standard, the expansions of the test specimens must be less than one-fourth of the expansions of corresponding control specimens. Additionally, the expansion of the job specimens may not exceed 0.02 percent at 14 days.

Sims[46,47] believes that the intent of these tests has been misunderstood. Frequently, test results are seen as being definitive and are used in a strict pass-fail basis, when in fact they are intended only as guidelines to assist concrete designers in making judgments regarding material selection. ASTM C 33 states that test methods "... do not provide quantitative information on the degree of reactivity to be expected..." and that "...reactivity of an aggregate should be based upon judgement and interpretation of test data and examination of concrete structures...".

2.3 Fineness

2.3.1 General. Portland cement is manufactured by burning a mixture of limestone and clay at temperatures ranging from 1400 to 1600°C (2550 to 2900°F)[4]. At these temperatures, the chemical reactions that occur between the two raw materials result in the silicates that will later react with water to provide the strength of concrete. However, the product that comes out of the kiln is not as yet ready to use in the making of concrete. This product, called clinker, is a stony matter fused together in coarse grain sizes, larger than 5 mm ($\frac{1}{5}$ in) in diameter[4]. Although most of the chemical reaction needed to produce the cement have already occurred, the clinker has to undergo further processing to become Portland cement. Gypsum has to be interground with the clinker to prevent the tricalcium aluminate (C3A) from causing flash set of the ground clinker when it comes in contact with water.

Also, the clinker has to be ground to fine powder particle size so its cementitious properties are enhanced.

This improvement is explained first, because of the fact that a fine powder covers more completely the grains of sand than a coarse one, and second, because hydration occurs only at the surface of the cement solid particles, so the more and the finer these solid particles, the faster the rate of hydration[10]. When Portland cement was patented, no specification on the fineness to which the clinker had to be ground was set. Up to the second world war there was a steady increase in the fineness of cements. Since then, it was somewhat stabilized changing very little in the last 35 years[10].

Similarly, when lime-pozzolana mortars were made in the past, no attention was paid to the fineness in which the pozzolana was added to the mixture. Still today, pozzolanas for building mortars are used in a relatively coarse state in places such as Italy, where it is specified that natural pozzolanas for use in building mortars shall contain maximum size grains not exceeding 5 mm ($\frac{1}{5}$ in)[11].

The coarser particles act as relatively inert aggregate and only the finer material, which grades down to a fine dust, acts as an active pozzolana. With the development of the use of pozzolanas with Portland cement the practice has become common of grinding them to cement fineness. As for fly ash, it consists of the finer particles of the ash produced by the coal combustion in power plants, thus having an initial fineness similar to that of Portland cement.

2.3.2 Methods for the Determination of Fineness.

2.3.2.1. Fineness of Cements. The most basic method of determining fineness is the use of sieves having meshes of a particular size through which the material whose fineness is to be measured is sifted by shaking. The percent weight of the amount of material retained in the sieve is the measure of fineness.

Other methods involve a parameter called the specific surface area, i.e. the total surface area of the particles in a unit weight of cement. Neither the sieve analysis nor the specific surface area give an indication of the actual particle size distribution of the material. Moreover, different methods of measuring the specific surface area give different results. Methods for analyzing particle size distribution are based on elutriation or sedimentation processes that make use of Stoke's law on particles falling through a gaseous or liquid medium[10].

The two most commonly used methods to measure specific surface area are the Wagner turbidimeter method and the Blaine air permeability method. The first method is a sedimentation process which can give a size-weight distribution curve but that is generally used only to calculate the specific surface area of the particles. The second method, as stated by Lea[10], "...depends on the fact that the resistance offered to gas flow by a plug of powder compacted to a known volume and porosity depends on the specific surface area of the powder". Although both the Wagner and the Blaine tests are supposed to measure specific surface area their results differ. maybe because the concepts in which they are based are radically different. Generally, Blaine test results average a value 1.8 times greater than averaged results of the Wagner test on the same samples[4].

Originally, the sieve analysis was used to measure fineness of cements. Presently, most specifications for cements include specific surface area as the measure of fineness. For example, the fineness requirement specified in ASTM C 150 Standard Specification for Portland Cement is, alternatively, a minimum value of 160 m^2/kg as measured by the turbidimeter test, or a minimum value of 280 m^2/kg as measured by the air-permeability test.

2.3.2.2. Fineness of Fly Ash. Although fly ash is produced in a fine powder state, its fineness is seldom consistent between power plants. Moreover, there are variations in fineness with time for a fly ash produced at a particular power plant.

The same methods used to measure cement fineness can be applied to measure fly ash fineness. Up to 1977, the ASTM C 618 included a requirement on the specific surface of fly ash. but it was since then deleted[48]. Presently, ASTM C 618 specifies a maximum of 20 percent of the sample weight to be retained in No. 325 sieve.

2.3.3. Effect of Cement Fineness on Alkali-Aggregate Reaction. Fineness of cement might affect concrete AAR in two ways:

1. As the cement is ground finer, the rate of hydration increases and the cement particles react more thoroughly. The more thoroughly the cement

particles react, the more alkalies are readily available to react with the aggregates.

2. In general, there is an increase in strength of mortars and concretes as the cement they contain is ground finer, as illustrated in Figure 2.2[10]. This increase in strength can be attributed to the faster and more complete hydration which also results in a denser and less permeable matrix. The lower the permeability, the less water available for AAR. The stronger the concrete, the better it withstands pressures exerted by the AAR.

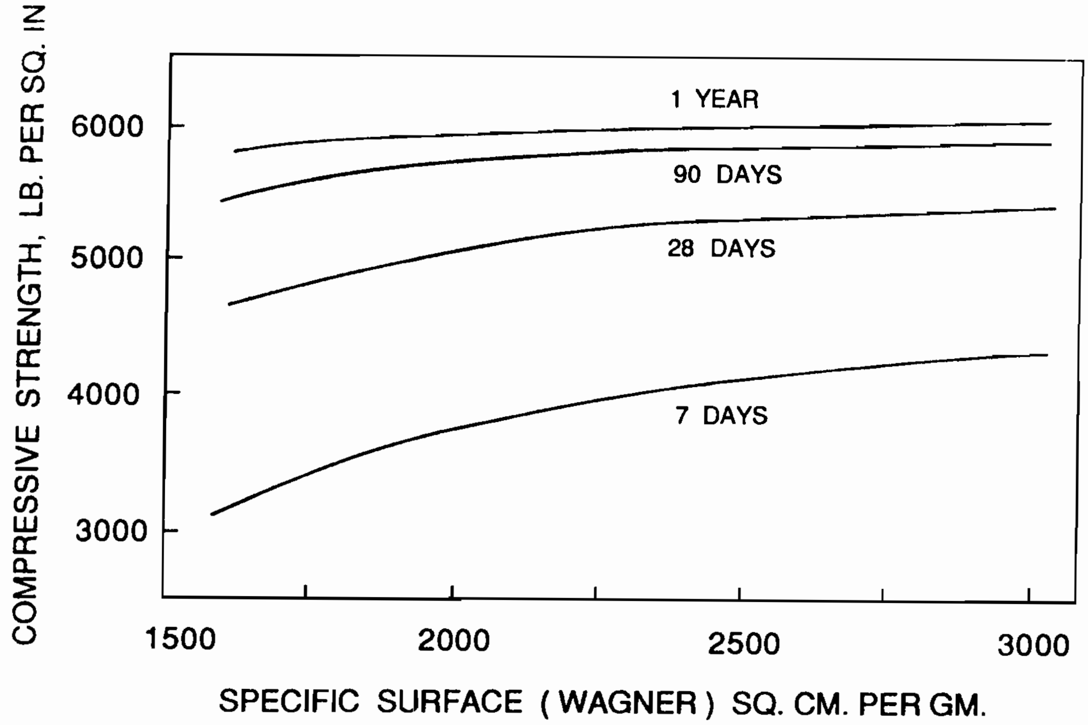


Figure 2.2 Effect of fineness of cement on strength of concrete[10]

There is insufficient data reported in the literature to indicate whether these factors combine to affect adversely or beneficially the AAR in concrete.

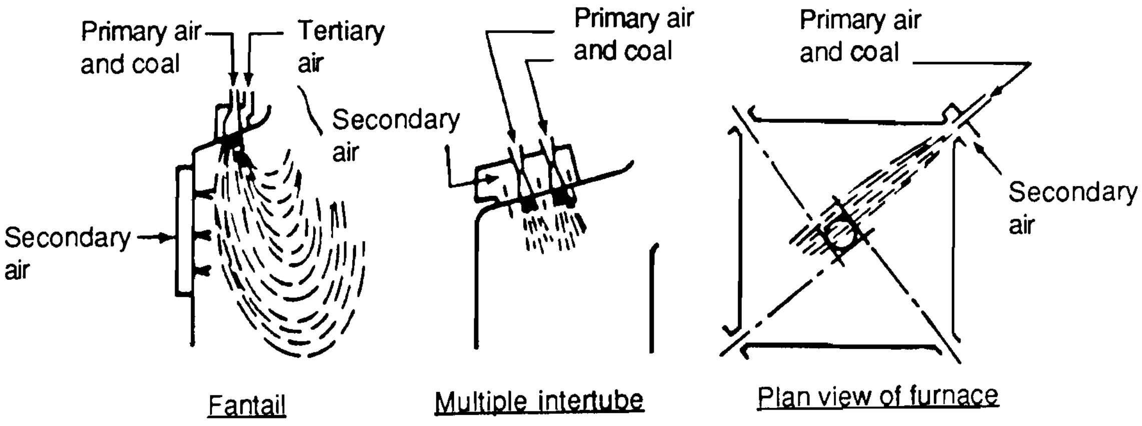
2.3.4 Effect of Fly Ash Fineness on Alkali-Aggregate Reaction. Pozzolanas can be quite coarse in their natural state, but artificial pozzolanas such as fly ash or silica fume are produced in an already finely divided form. Although all burning processes produce ash. the type of ash produced depends on the type of burner used. For example, a cyclone furnace burns at an intense and rapid rate. Coal burned in such a furnace is likely to yield only about 10 percent finely divided ash and 90 percent coarsely divided ash. The fine ash is commonly known as fly ash while the coarser is called bottom ash[4]. The borderline between fly and bottom ashes lies at about 50 fm particle size. Most other burners will produce about 65 percent fly ash and 35 percent bottom ash. Figure 2.3[48] shows several types of furnaces used for burning coal. Figure 2.4[48] shows a diagram of fly ash formation, as suggested by Flagan[49].

Despite the fact that fly ash is composed of fine particle size grains, its fineness is far from consistent. A wide range of variation exist in fineness of fly ashes produced at different power plants. Also, inconsistencies are found, with time, in the fineness of a particular fly ash at one power plant. Several investigations[143,145–148] were conducted trying to find a correlation between fly ash fineness and fly ash mortar and concrete properties. Only water requirement was found to be consistently affected by some fly ash properties. These properties are loss on ignition (LOI) and No. 325 sieve residue (325S). Helmuth[48] states that "a fly ash with a high percentage of +325 material will have a high water requirement in the mortar flow test because the volume of paste is not large enough to avoid particle interference effects".

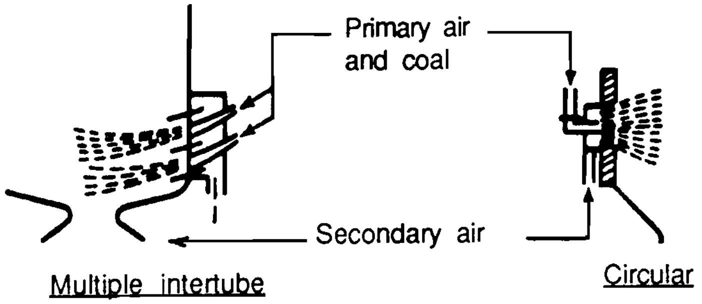
Statistical studies presented by Minnick, Webster, and Purdy[50] show that when the data was restricted to tests results of fly ashes within specified ranges, the resultant deviation of the values was less than 3 percent. The specified ranges were a maximum of 12 percent LOI and a maximum of 20 percent 325S. In light of these facts, the fineness requirement of fly ash contained in ASTM C 618 was changed in 1977: the specific surface area requirement was deleted and fineness was specified by a maximum of 20 percent 325S.

The fineness of pozzolanas affect the rate and intensity of the pozzolanic reaction[48]. This is specially true for natural pozzolanas which can have relatively coarse grain sizes. Table 2.4 gives an example of the influence of fineness on concrete strength.

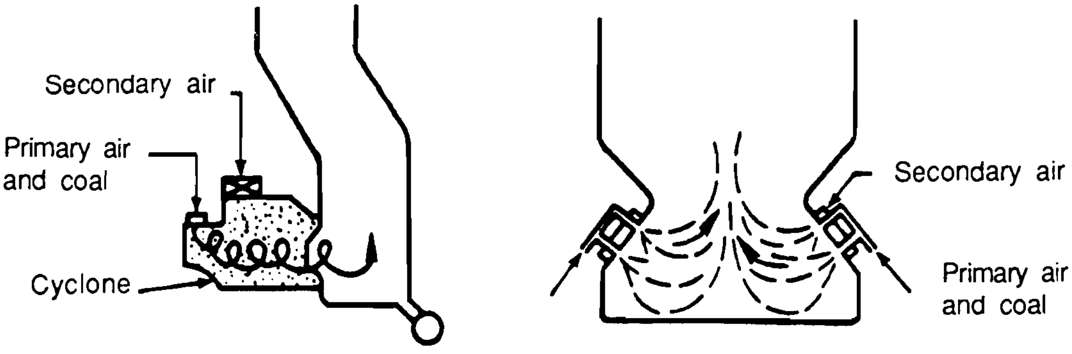
As stated before, the mechanism by which fly ash reduces AAR related expansions involves several possible chemical processes. On one hand, the pozzolanic reaction results in the reduction of "free lime" and, hence, in the reduction



(a) Vertical firing (b) Tangential firing



(c) Horizontal firing



(d) Cyclone firing (a) Opposed- inclined firing

Figure 2.3 Various types of furnaces for firing coal[48]

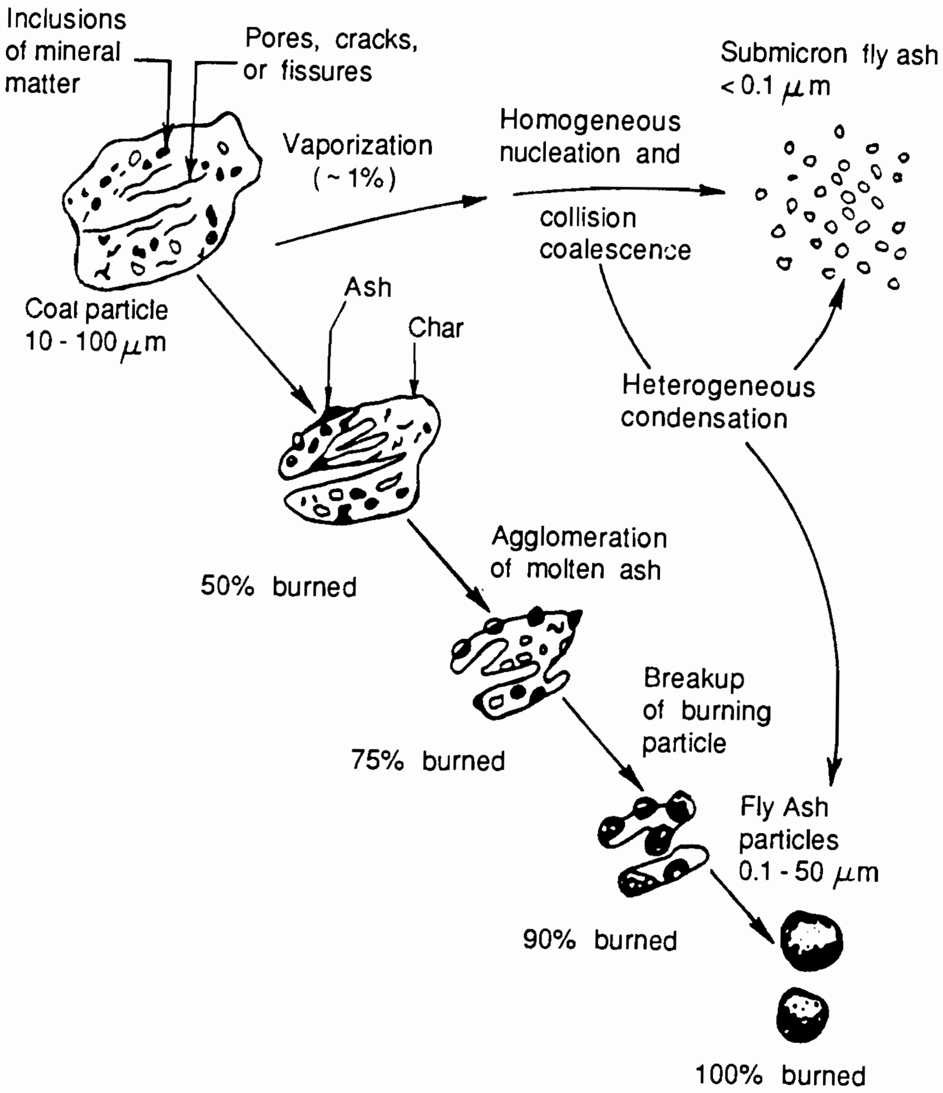


Figure 2.4 Coal combustion and fly ash formation processes[48]

Table 2.4 Effect of fineness pozzolana mortars
(1:4:15 - Lime:Trass:Sand)*

Percentage residue on 170-mesh sieve	Strength(lb/in^2)			
	Bending		Compression	
	28 days	1 year	28 days	1 year
43	183	372	341	1190
14.5	269	475	500	1280
3.0	306	480	690	1460

*Extracted from Reference 10, page 435

of pH of the pore solution, possibly rendering it less susceptible to alkali promoted formation of hydroxide ions and subsequent attack on the aggregate oxygen-silica network. Variations in fly ash fineness cause variations in rate and intensity of pozzolanic reaction. Therefore, the finer the fly ash the greater and more intense the pozzolanic reaction, and, possibly, the more effective the fly ash in reducing AAR related expansions. On the other hand, fly ash acts as mineral water-reducing admixture. According to Helmuth[48], "...the water reduction caused by the fly ash is a result of an adsorption and dispersion process very much like that of the organic water-reducing admixtures". This property, although of very variable effectiveness, contributes to the reduction of the matrix permeability, reducing the amount of "free moisture" within the concrete which plays an important role in AAR.

The incorporation of fly ash to a concrete mixture is generally achieved either by adding the fly ash to the mixture at the time of batching, or by the use of blended cements, known as Type IP cements. There are three main methods for producing Type IP cement:

1. Mechanical mixing of cement and nonground or unclassified fly ash.
2. Separate grinding or classifying of the cement and fly ash and subsequent mechanical mixing, and,
3. Intergrinding or mixing the fly ash with the cement clinker prior to final grinding.

If a fly ash is subjected to a grinding process, an increase in its fineness results. This increase is thought to be the result of the combination of two processes. In the first place, as reported by Osbaeck, grinding of fly ashes reduces the amount of hollow and/or porous particles that it contains; secondly, grinding reduces the amount of agglomerates present in the fly ash.

In both instances, the result is an increase of the fly ash surface area and a reduced 325S, resulting in an increased reactivity, possibly enhancing its ability to reduce the alkali-aggregate reaction related expansions in mortar-bars.

In an earlier study, the behavior of a mixture made with a Type IP cement was compared to the behavior of two mixtures made with the same cement and the same fly ash used in the manufacturing of the Type IP cement. The fly ash was incorporated to these mixtures at the time of batching using two different methods. First, the fly ash was blended with the cement by means of a mechanical mixer which did not provide any grinding, and second, the fly ash and the cement were separately added to the mixing water at the time of batching.

Figure 2.5 shows the results obtained. The mixture containing Type IP cement was significantly more efficient than the other two mixtures in reducing mortar bar expansions. The two cement-fly ash mixtures behaved similarly, indicating that additional mechanical preblending of the cement and fly ash had no effect on the mixture's performance. Thus, the increased fineness of Type IP cement, achieved through the intergrinding process together with the improved dispersion of fly ash particles within the cement matrix, appears to be the reason for its improved performance in inhibiting expansions. This findings motivated the conduction of Phase III of the study reported herein.

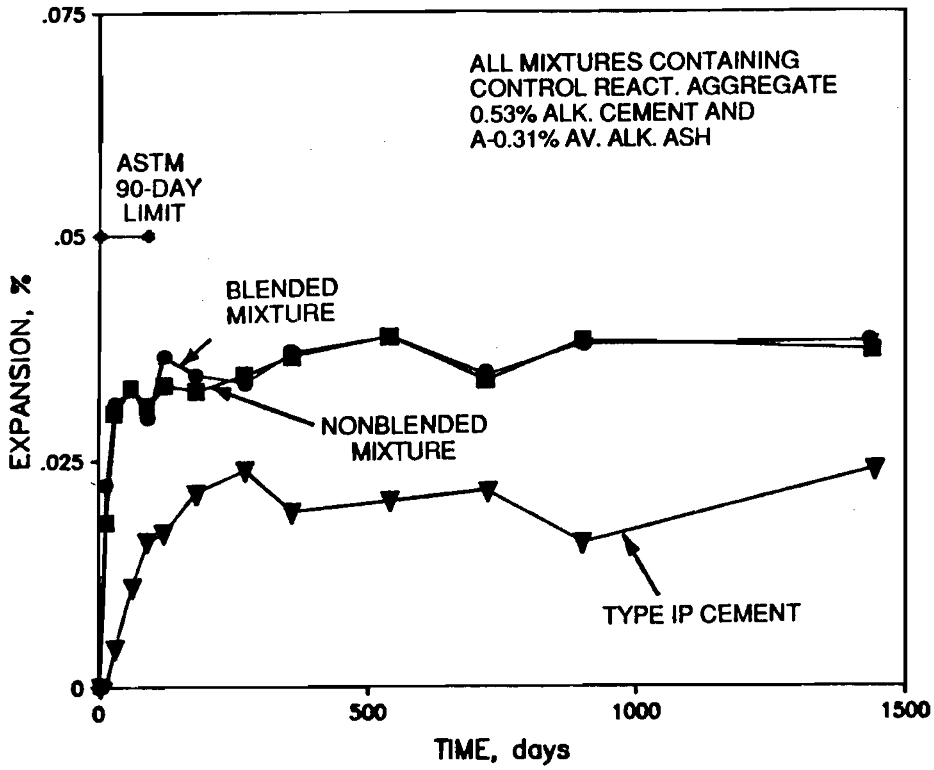


Figure 2.5 Influence of fineness and preblending of fly ash and cement used in Type IP cement

CHAPTER 3
EXPERIMENTAL PROGRAM

3.1 Introduction

ASTM C 227 served as the primary guideline for the testing program described herein, providing specifications for facilities and equipment, test procedures, and interpretation of results. Details on facilities, equipment, and test procedures were presented in Research Report 450-1 of this project[1]. In this chapter, details of the test program will be reviewed.

3.2 Materials.

3.2.1 Aggregate. The four aggregates chosen for use in Phase I were also used in Phase II. One aggregate was considered nonreactive and two were considered reactive based on results of mortar bar tests conducted by the TSDHPT, which are presented in Figure 3.1. The fourth aggregate was Pyrex glass, which served as a control for the tests. To distinguish between the two reactive aggregates, they will be referred to as the "highly reactive" aggregate and the "moderately reactive" aggregate, based on the results shown in Figure 3.1. In Phase III, only the "highly reactive" aggregate was used.

Each of the natural aggregates, which came from sources in Texas, was examined petrographically, as specified in ASTM C 295. The potentially reactive materials present in each aggregate are listed in Table 3.1. No traces of opal, the most reactive of minerals, were observed in either aggregate.

3.2.2 Cement. One objective of this program was to use materials commercially available in Texas in order to provide the TSDHPT with useful information about materials which will actually be used in State projects. The three cements chosen in Phase I were selected from sources within Texas. The two Type I cements reflected the extremes in alkali content of cement produced in Texas (0.43 percent and 0.66 percent), while the Type IP cement utilized local cement and Type A fly ash.

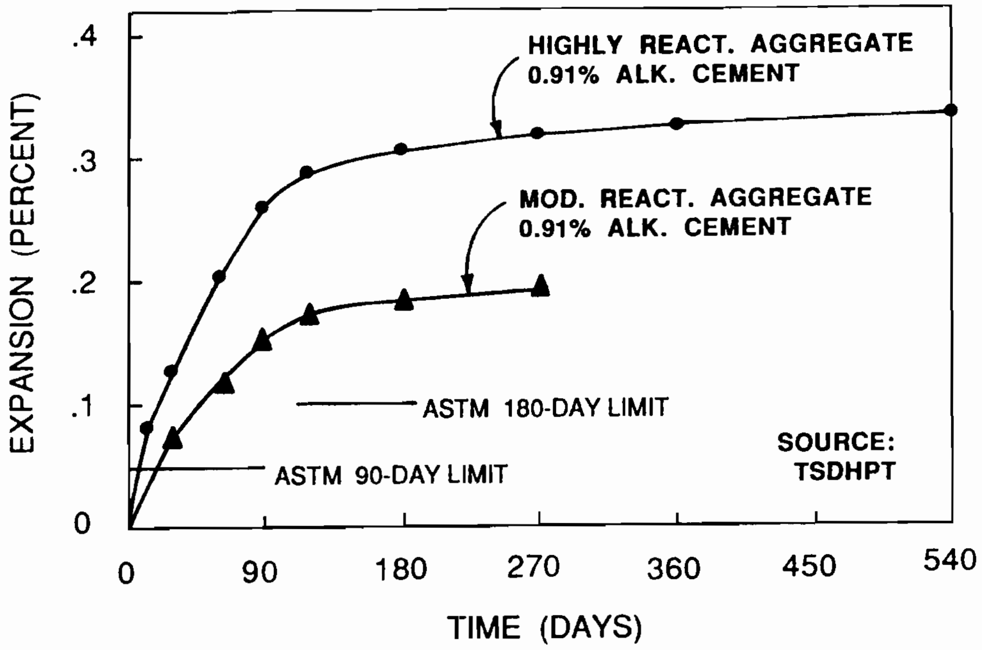


Figure 3.1 Curing tent and humidifier

Table 3.1 Results of petrographic analyses of aggregates used in test program

AGGREGATE	REACTIVE MATERIALS
1. Highly reactive	quartz chert volcanic rocks tuff
2. Moderately reactive	chert rholite chalcedony volcanic rocks
3. Non-reactive	(none)
4. Control	Pyrex glass

In addition to the three cements used in the first phase, two other cements were tested in Phase II. Since alkali contents in cement can rise far above 0.66 percent, a higher alkali cement was desired for testing in Phase II. However, such a cement proved difficult to locate in Texas. A cement with a 1.03 percent total alkali content was found in New York and used in this portion of the program.

Samples of the portland cement and fly ash which were used to manufacture the Type IP cement used in this project were also obtained for study in Phase II. This was done in order to study the effectiveness of adding fly ash to the clinker before grinding as compared to adding fly ash as a mineral admixture for concrete during the batching process. Phase III included only one cement type. The cement containing 1.03 percent available alkalies was used in this Phase. All five cements are described in Table 3.2 and material properties for each are given in the Appendix.

Table 3.2 Cements used in the test program

CEMENTS		
I.D.	ASTM TYPE	TOTAL ALKALI CONTENT (percent)
1	I	0.43
2	I	0.66
3	IP	0.50
4	I	1.03
5	I	0.53

3.2.3 Water. Tap water was used in all Phase I, Phase II, and Phase III mixtures. In order to study the effects of the composition of the water, several mixtures were repeated using distilled water. Table 3.3 contains a chemical analysis of each water. The analyses revealed that while the tap water had a higher pH, the distilled water actually contained more alkalies.

The tap water pH of 8.14 fell just above the recommended pH range of 6 to 8 set by the Corps of Engineers[27] for mixing water. The pH of the distilled water was 5.7, which was below the recommended pH limits.

Table 3.3 Mixing water analyses solubility of silica or other factors.

TAP WATER (pH = 8.14)		DISTILLED WATER (pH = 5.7)	
Impurity	Amount (ppm)	Impurity	Amount (ppm)
Cl	69	Na	82.7
HCO_3	57.6	Ca	55.5
SO_4	51.6	Mg	13.8
Na	40.3	K	13.3
Mg	19.0		
Ca	18.1		
K	3.27		
I	0.35		
Br	<0.35		
Sr	<0.06		
Mn	0.01		
Fe	<0.01		

3.2.4 Fly Ash. The four fly ashes selected for use in Phase I consisted of two Type A and two Type B fly ashes. These were all produced in Texas and were selected to provide the widest range in alkali contents available for each type of fly ash. These fly ashes are listed in Table 3.4. The chemical composition of all fly ashes is presented in the Appendix.

Five additional fly ashes, also listed in Table 3.4, were tested in Phase II. Two of these fly ashes were produced in Colorado and the other three were produced in Texas. These fly ashes were obtained for testing for a variety of purposes.

Two of these fly ashes were obtained so the effect of the addition of collection additives on fly ash properties and on the control of alkali-aggregate reaction could be studied. Electrostatic precipitators, frequently used to remove fly ash from exhaust gases, operate on the principle of delivering an electrical charge to the fly ash particles and attracting the particles to plates of opposite charge. Chemicals are often added to the fly ash to enhance the effectiveness of the collection process. These chemicals are typically added to the fly ash as a fog just before it reaches the electrostatic precipitator. When such a chemical agent is used, the fly ash may

Table 3.4 Fly ashes used in the test program

No.	Use in Phase	TSDHPT Type	Coal Rank	Available Alkalies	Special Characteristics
1	I and II	A	Lignite	1.38%	
2	I and II	A	Lignite	0.57%	
3	I, II, and IV	B	Subbituminous	4.35%	
4	I, II, and IV	B	Subbituminous	1.67%	
5	II	A	Bituminous	1.76%	
6	II	B	Subbituminous	2.35%	Treated with alkaline precipitating agent
7	II	B	Subbituminous	2.04%	Similar to previous one but not treated with agent
8	II, III, and IV	B	Subbituminous	3.75%	
9	II	A	Lignite	0.31%	Used in Type IP cement tested in this program

contain an objectionable amount of alkalies as well as magnesia, ammonium compounds, or sulfur oxides[36]. One Type B fly ash treated with such an agent (#6 in Table 3.4) was obtained for testing in Phase II, along with another Type B fly ash of similar alkali content (#7 in Table 3.4), which had not been treated. The treated fly ash was unique in that the precipitating agent (sodium carbonate) was added to the coal before burning. Fewer of the alkalies provided by the agent are thought to remain in the fly ash if the agent is also exposed to the combustion process.

Two other fly ashes were chosen on the basis of type and alkali content. One Type A fly ash (#5 in Table 3.4) was selected for use since its alkali content of 1.76 percent was close to that of the low alkali Type B fly ash (#4 in Table 3.4) studied in Phase I. This allowed a comparison between fly ashes of each type having similar alkali contents. One Type B fly ash (#8 in Table 3.4) was selected because its alkali content fell between the alkali contents of the two Type B fly ashes tested in Phase I. This provided an opportunity to further study the effect of available alkalies in fly ash. This fly ash was treated with a calcium sulfate fog prior to collection by an electrostatic precipitator. The remaining fly ash studied in Phase II (#9 in Table 3.4) was used in the production of the Type IP cement used in this program.

Phase III included Type B fly ash from four sources. Two of them used in Phase I and the other two used in Phase II. These fly ashes were chosen because they represented the whole range of available alkalies content of Type B fly ashes used in the program. These fly ashes came from the same sources used in previous phases but were sampled at a different time. Hence, the slight difference in available alkalies contents. Their available alkali contents and the fineness to which they were ground are shown in Table 3.5.

Table 3.5 Available alkalies and percent retained in sieve # 325 for the four fly ashes used in the tests.

Av. Alkali Content (%)	Fineness (Retained in #325 sieve)		
	Original	Intermediate	Fine
0.96	18.3	6.7	0.9
1.90	16.4	7.3	1.2
3.73	11.3	5.9	1.4
4.35	13.3	6.7	0.9

The different level of fineness, expressed in terms of 325S, were obtained by grinding of the fly ash using a laboratory type grinding ball mill.

The fly ash containing 0.96 percent available alkali was from the same source as the fly ash containing 1.67 percent available alkali used in Phase I. Similarly, the ash containing 1.90 percent corresponded to the source of the ash containing 2.35 percent used in Phase II; and, finally, the ash containing 3.73 percent available alkali corresponded to the source of the ash containing 3.75 percent available alkali in Phase II.

3.2.5 Silica Fume. One silica fume was included in the test program. The information on the chemical composition of the silica fume provided by the suppliers is included in the Appendix.

3.3 Mixture Designs

3.3.1 Nomenclature. This report will discuss the exposure testing of specimens representing 239 different mixture designs. In order to simplify the discussion of the test results, the following denominations and abbreviations will be used throughout this report:

1. AGGREGATES:

DESCRIPTION	ABBREVIATION
Highly reactive	Hgh.react.
Moderately reactive	Md.react.
Nonreactive	Nonreact.
Pyrex glass	Ctrl.

2. CEMENTS:

DESCRIPTION	ABBREVIATION
0.43% total alkalies	Low alk.
0.66% total alkalies	Med. alk.
1.03% total alkalies	High alk.
Type IP	IP
Type I used in Type IP	I/IP

3. PERCENTAGE OF CEMENT REPLACED:

DESCRIPTION	ABBREVIATION
No replacement	
17.5, by volume	17.5%, by vol.
15.0, by weight	15%, by wt.
20.0, by weight	20%, by wt.
26.0, by volume	26%, by vol.
34.2, by volume	34.2%, by vol.
28.0, by weight	28%, by wt.
45.0, by volume	45%, by vol.
37.0, by weight	37%, by wt.
62.5, by volume	62.5%, by vol.

4. MINERAL ADMIXTURES:

Fly Ash:

DESCRIPTION	ABBREVIATION
Type A containing 0.31% available alkalies	A/IP
Type A containing 0.57% available alkalies	A-0.57% av. alk.
Type A containing 1.38% available alkalies	A-0.38% av. alk.
Type A containing 1.76% available alkalies	A-1.76% av. alk.
Type B containing 0.96% available alkalies	B-0.96% av. alk.
Type B containing 1.67% available alkalies	B-1.67% av. alk.
Type B containing 1.90% available alkalies	B-1.90% av. alk.
Type B containing 2.04% available alkalies	B-2.04% av. alk.
Type B containing 2.35% available alkalies and chemical additive	B-2.35% av. alk.
Type B containing 3.75% available alkalies	B-3.75% av. alk.
Type B containing 4.35% available alkalies	B-4.35% av. alk.

Silica Fume:

Silica fume abbreviation will be: silica.

3.3.2 Proportioning of Materials. As pointed out in Chapter 2, the reactivity of a cement-aggregate combination depends not only on the materials used, but on the proportions of the materials in the concrete as well. In this test program, ASTM C 227 has been followed as the standard for mixture designs. The designs of the mixtures studied in Phase I have been discussed in detail in a previous report[8].

The designs of the mixtures studied in Phase II and Phase III generally followed the same concept used in Phase I. The ratio of cement to aggregate in mixtures without mineral admixtures was 1:2.25 by weight as specified in ASTM C 227. This ratio was altered when mineral admixtures were used as partial replacements for cement. In Phase I, mineral admixtures replaced cement by weight in three percentages: 15, 28, and 37 percent (17.5, 34.3, and 45 percent, by volume). In Phase II, the replacement of cement with mineral admixtures was done by volume in five percentages: 17.5, 26, 34.3, 45, and 62.5 percent. The volumes of replacement in Phase II were chosen to correspond with the weights of replacement used in Phase I as shown in Table 3.6. The aggregate and cementitious material contents remained constant by weight in all Phase I mixtures and by volume in all Phase II mixtures.

Table 3.6 Percentages of cement replaced with mineral admixtures, by weight and by volume

Replacement Percentages by Weight (used in Phase I)	Equivalent Replacement Percentages by Volume*	Replacement Percentages by Volume (used in Phase II)
15%	17% - 23%	17.5%
28%	31.1% -39.7%	34.3%
37%	40.6% - 49.9%	45%

* Amount is dependent on the specific gravity of the fly ash.
The specific gravities of the fly ashes tested in this program ranged from 1.86 to 2.71.

The volumes of replacement in Phase III were the same as the replacements in Phase I, i.e., 15, 28, and 37 percent, by weight (17.5, 34.3, and 45 percent, by volume).

The amount of water used in each mixture was adjusted so the consistency of the mixture, as measured by the flow table test of ASTM C 230 "Specification for Flow Table for Use in Tests of Hydraulic Cement"[24], fell within the required range specified in ASTM C 109 "Standard Test Method for Compressive Strength of Hydraulic Cement Mortars"[24] and ASTM C 227.

Several mixtures were not designed according to these guidelines. In four mixtures, fly ash was used as a replacement for aggregate rather than cement in an amount equal to 30 percent of the volume of cement in each mixture. Two of these mixtures contained control aggregate and the other two contained moderately reactive aggregate. All of them were low alkali cement mixtures.

Two mixtures contained the same cement (I/IP) and fly ash (A-0.31% av. alk.) used to produce the Type IP cement used in Phases I and II. This Type IP cement contained approximately 20 percent fly ash by weight rather than volume. Therefore, the replacement of cement by fly ash in mixtures containing cement I/IP was done by weight to provide these mixtures with the same proportions of materials used in the mixture containing Type IP cement.

CHAPTER 4
TEST RESULTS

4.1. Introduction

The results of the first 90 days of testing of Phase I specimens have been presented and discussed in a previous report[8]. This chapter contains a presentation of the results obtained from the testing of Phase I specimens from 90 days to 1440 days, results obtained from Phase II specimens up to 1440 days of testing, and results obtained from Phase III during the first 720 days of testing. The first part of this chapter presents the test data obtained from all phases of this study in terms of the ASTM limits for mortar bar expansion. The results obtained during the first 90 days of exposure testing of Phase I specimens will then be updated through 1440 days. Subsequently, the 1440-day Phase II results will be presented in terms of the specific topics studied in that part of the program. This chapter concludes with a presentation of the 720- day Phase III results on the effect of fineness of fly ash in mortar bar expansions.

4.2 Applicability of Limits Specified in ASTM C 227 and ASTM C 33

ASTM C 227 specifies that measurements of mortar bars are to be taken at one and 14 days, and at one, two, three, four, six, nine, and 12 months, and at six-month intervals thereafter, if necessary. The measurements of each specimen of a given material combination at each time period are averaged to provide a representative expansion value for those materials. ASTM C 33 and ASTM C 227 specify that the average expansion of a set of mortar bar specimens is exces- sive if it exceeds 0.05 percent at three months or 0.10 percent at six months. Data for three-month tests are to be considered only when six-month data are not available.

All of the results presented in this chapter and discussed in Chapter 5 will be in terms of the average expansion of all specimens of each material combination, or mixture. This value will simply be referred to as the expansion of each mixture.

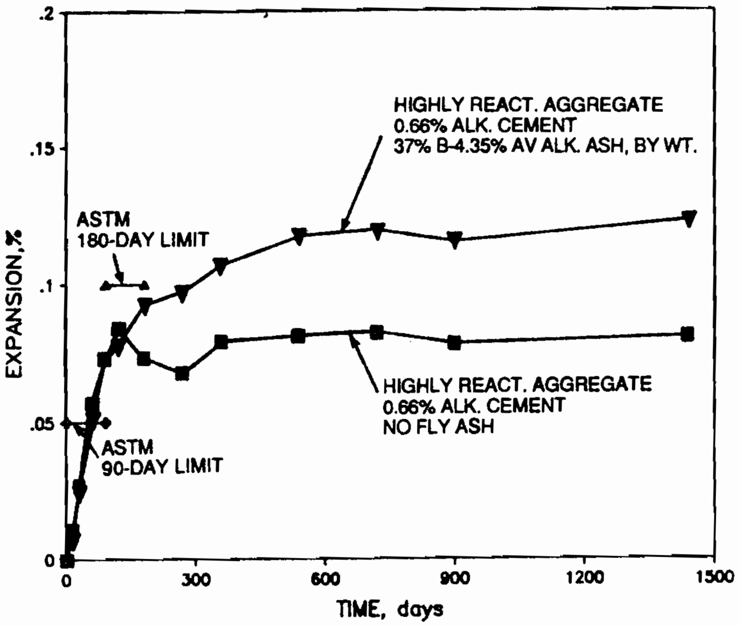
As noted in the Research Report 450-1, 30 of the 108 Phase I mixtures had expansions exceeding the ASTM limit of 0.05 percent at 90 days. Twenty-five of these mixtures had expansions exceeding the 180-day limit of 0.10 percent expansion. No mixtures had expansions exceeding the 180-day limit without having surpassed the 90-day limit as well.

Figure 4.1 illustrates the expansion histories of the five mixtures mentioned above which exceeded the 90-day limit only. The expansions of four of these mixtures were between 0.088 percent and 0.10 percent with two of the four expanding beyond 0.10 percent after 270 days. The remaining mixture showed no expansive tendencies after 90 days.

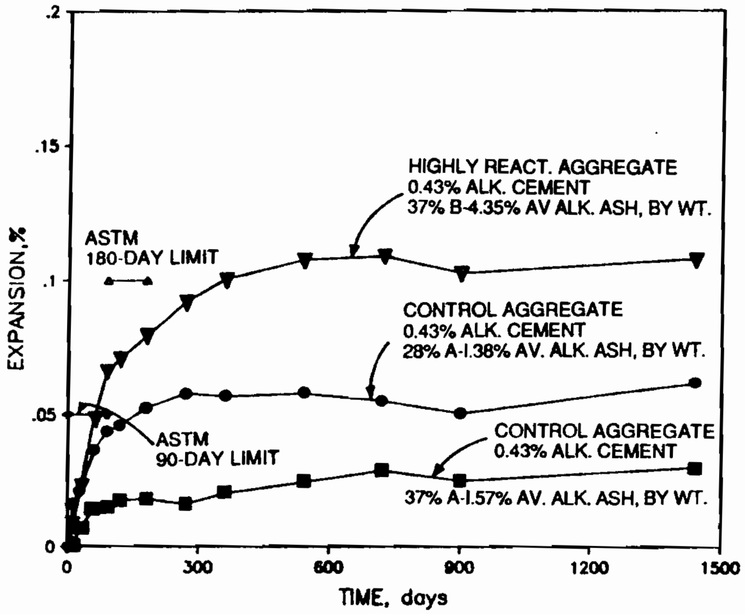
Two mixtures which did not exceed either the 90-day or 180-day expansion limits neared 0.10 percent expansion at 360 days. The expansion histories of these mixtures are shown in Figure 4.2.

In the first phase of this study, the number of mixtures exceeding the ASTM expansion limit at 90 days was greater than the number of mixtures exceeding the 180-day expansion limit. This trend continued for the mixtures in Phase II. Twenty-two of the Phase II mixtures exceeded the expansion limit of 0.05 percent at 90 days. Only 15 of those 22 mixtures also exceeded the 180-day expansion limit of 0.10 percent. Of the seven mixtures not surpassing the 180- day expansion limit, only two mixtures showed expansive tendencies beyond 90 days, with expansions between 0.09 percent and 0.10 percent. The expansion histories of these seven mixtures are shown in Figure 4.3.

In addition to the 15 mixtures mentioned above which exceeded the 180-day expansion limit, one mixture which expanded less than the ASTM 90-day limit also surpassed the 180-day limit. The expansion history of this mixture is shown in Figure 4.4. The specimens containing this combination of materials did not begin to show expansive tendencies until between 60 days and 90 days, but maintained a steady rate of expansion from that time through 360 days, after which the expansion started to curb down; finally, the expansion leveled off after 540 days.



(a)



(b)

Figure 4.1 Phase I mixtures which exceeded the ASTM expansion limit at 90 days only

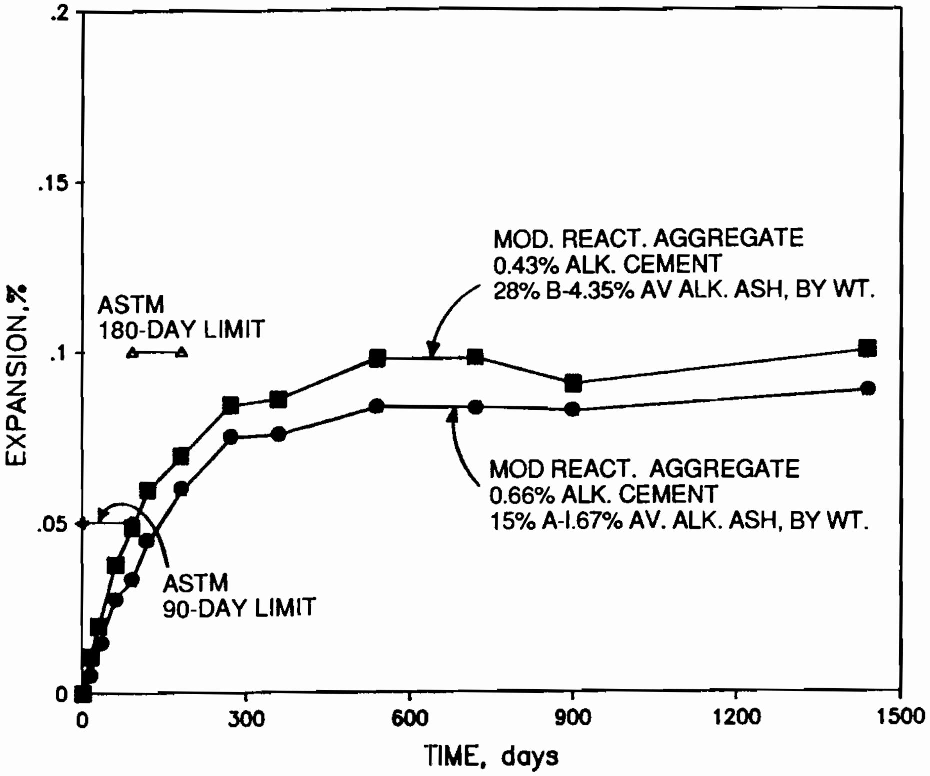


Figure 4.2 Expansion histories of two slowly reactive Phase I mixtures

4.3 Phase I Results

4.3.1 Effect of Aggregate. Three natural aggregates were tested in this program, with Pyrex glass serving as a control aggregate. In the first phase of the program, each aggregate was tested in combination with each of the three cements and the four fly ashes. The results obtained from the first 90 days of exposure testing[53] revealed that the control aggregate was the most reactive, followed by the highly reactive aggregate, the moderately reactive aggregate and the nonreactive aggregate. The results obtained for the two reactive aggregates were in agreement with the results of the tests conducted by the TSDHPT shown in Figure 3.1. At 1440 days, similar results were noted.

Thirty-four of the 108 Phase I mixtures expanded significantly, with values near or exceeding the ASTM limits at 90 days or 180 days. Twenty-two of these mixtures contained the control aggregate, eight contained the "highly" reactive aggregate, while just four contained the "moderately" reactive aggregate.

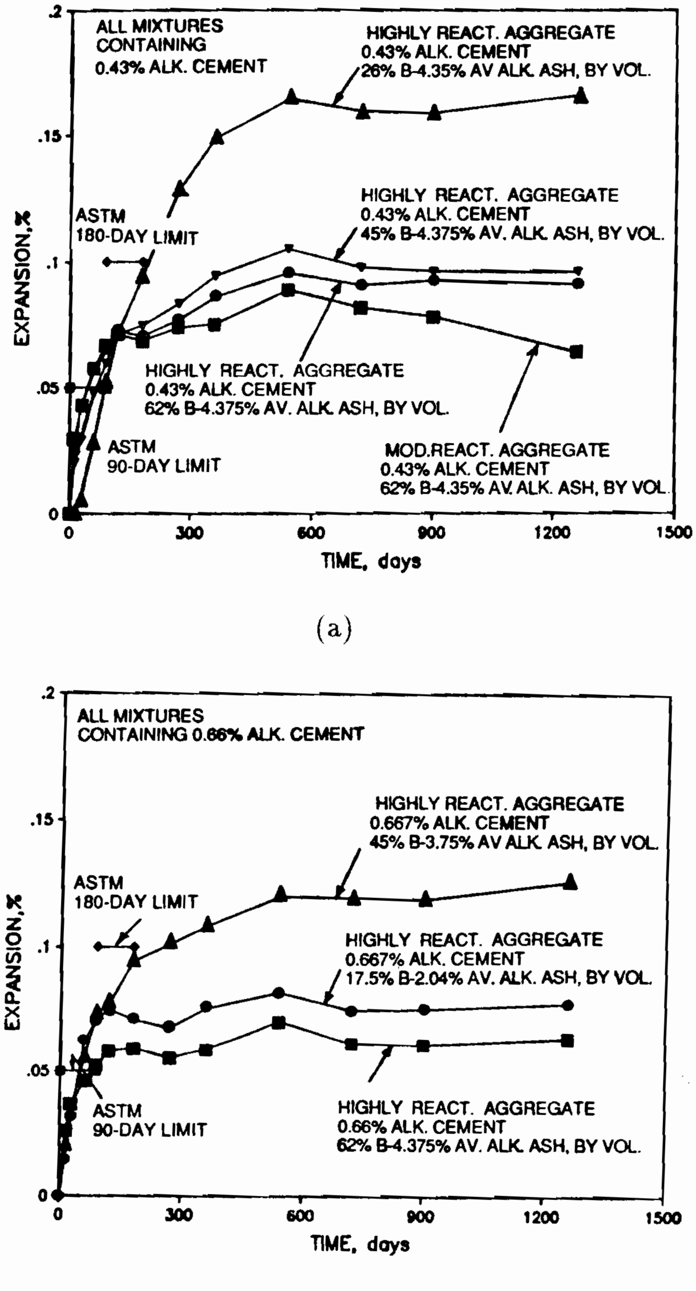


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Figure 4.3 Phase II mixtures which exceeded the ASTM expansion limit at 90 days only

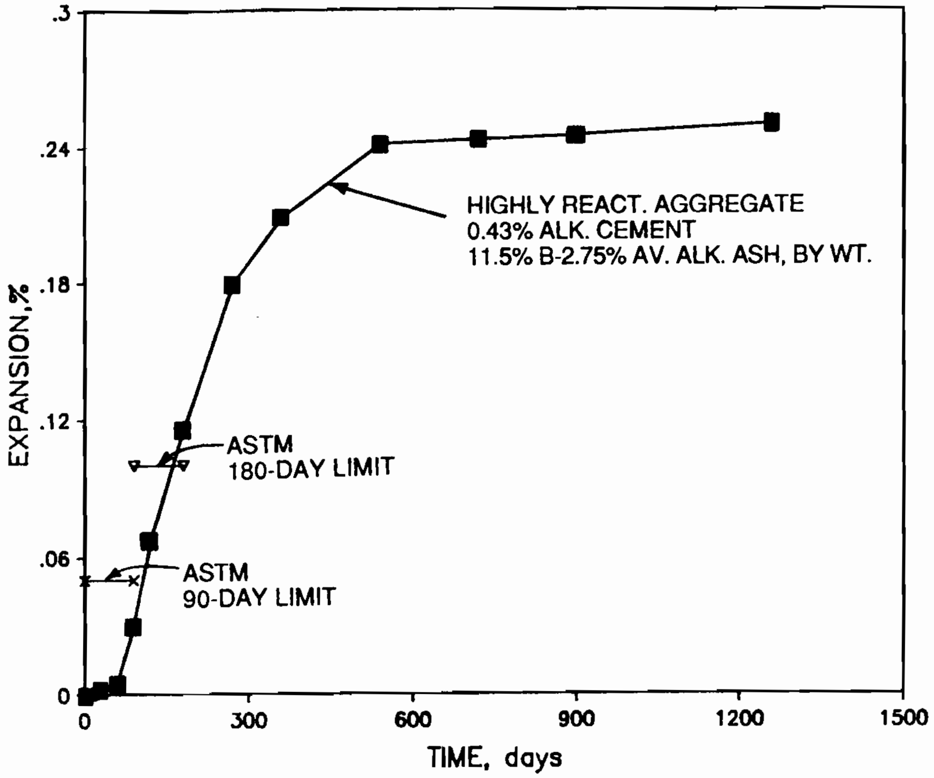


Figure 4.4 Phase II mixture which exceeded the ASTM expansion limit at 180 days only

Figure 4.5 consists of a set of curves comparing the expansions of mixtures containing each aggregate with otherwise identical materials. The same general trend of aggregate reactivity was noted for virtually all other material combinations.

Two deleteriously expansive mixtures containing highly reactive aggregate, however, were more expansive than the corresponding mixtures containing the control aggregate, as shown in Figure 4.6. These were the two most expansive mixtures observed in the test program.

The mixture containing nonreactive aggregate were used only as a reference level of negligible expansions. Therefore, the focus of this chapter and the discussions contained in the next chapter will be on those mixtures containing the reactive natural aggregates and the control aggregate.

4.3.2 Effect of Cement. Three cements were tested in this part of the program: two ASTM Type I cements with total alkali contents of 0.66 percent and 0.43 percent and an ASTM Type IP cement having a total alkali content of 0.50

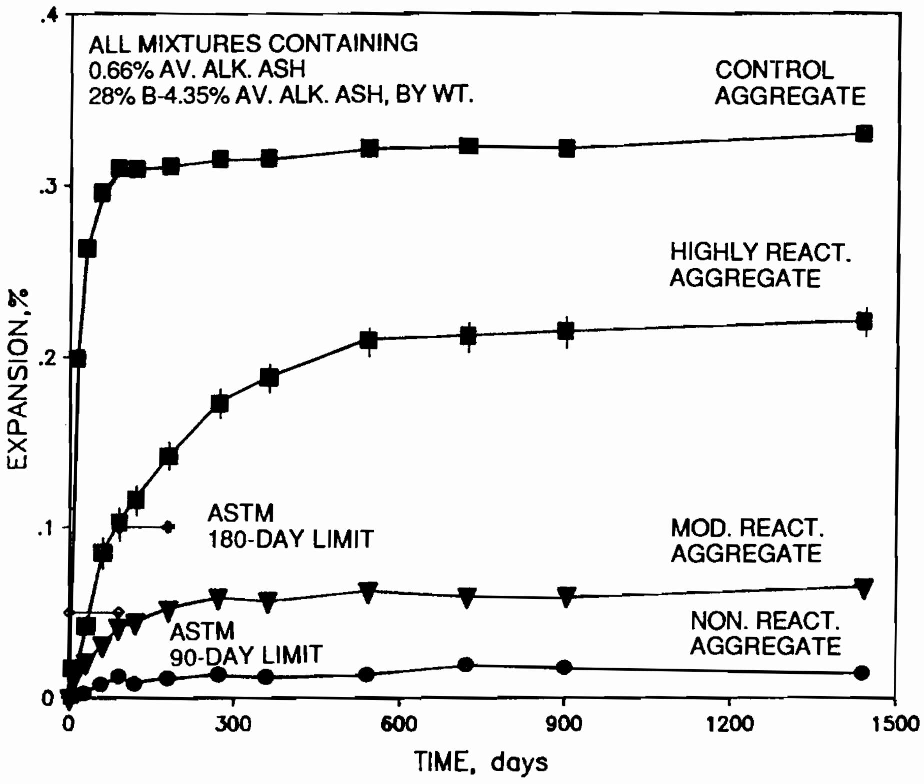


Figure 4.5 Relative reactivity of test aggregates

percent. The two Type I cements were tested in combination with each aggregate and fly ash while the Type IP cement was tested with each aggregate only.

The results obtained during the first 90 days of exposure testing revealed that expansions generally increased with the increase in alkali contents of the Type I cements. Mixtures containing the Type IP cement generally expanded less than similar mixtures containing the low alkali Type I cement. No mixture which contained Type IP cement expanded significantly.

Similar results were noted at 1440 days. Figure 4.7 shows this trend for a typical pair of mixtures containing each Type I cement with otherwise similar materials. Several exceptions to this trend, however, were noted. One deleteriously expansive mixture containing highly reactive aggregate and 17.5%, by vol, B-4.35% av. alk. fly ash in combination with the low alkali cement proved to be more expansive than the corresponding mixture containing the medium alkali cement, as shown in Figure 4.8. This mixture was the most expansive in the test program.

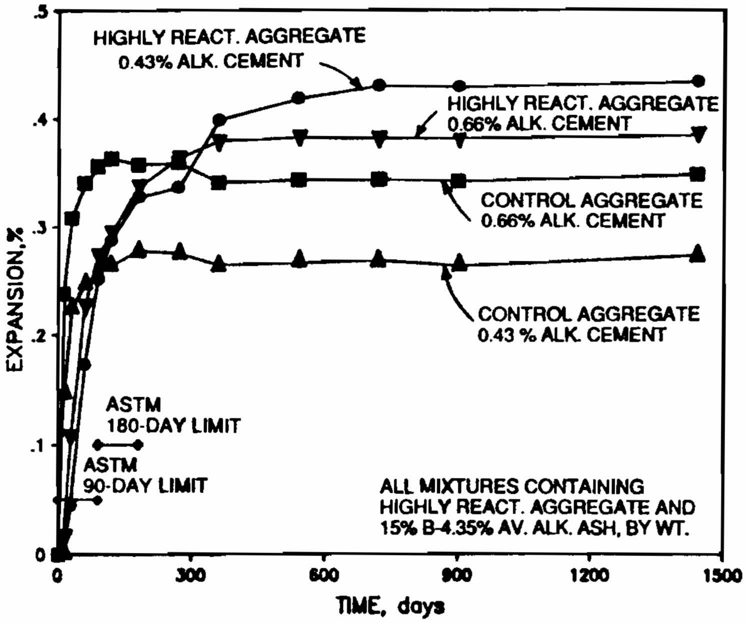


Figure 4.6 Phase I mixtures in which the highly reactive aggregate was more deleterious than the control aggregate

4.3.3 Effect of Fly Ash. Ninety six of the 108 mixtures tested in Phase I contained fly ash added at the time of batching as a partial replacement for cement. Four additional mixtures contained Type IP cement which was produced by adding 20 percent fly ash by weight to the clinker before grinding. The eight remaining mixtures contained no fly ash.

At 90 days, it was observed that mortar bar expansions typically increased as the alkali content of the fly ash increased. However, expansions generally decreased as the amount of fly ash used was increased. This was not the case, however, for mixtures containing the high alkali Type B fly ash. Some percentages of replacement of cement with this fly ash resulted in expansions greater than those experienced by mixtures without fly ash. In several instances, the use of the low alkali Type B fly ash also resulted in increased expansions.

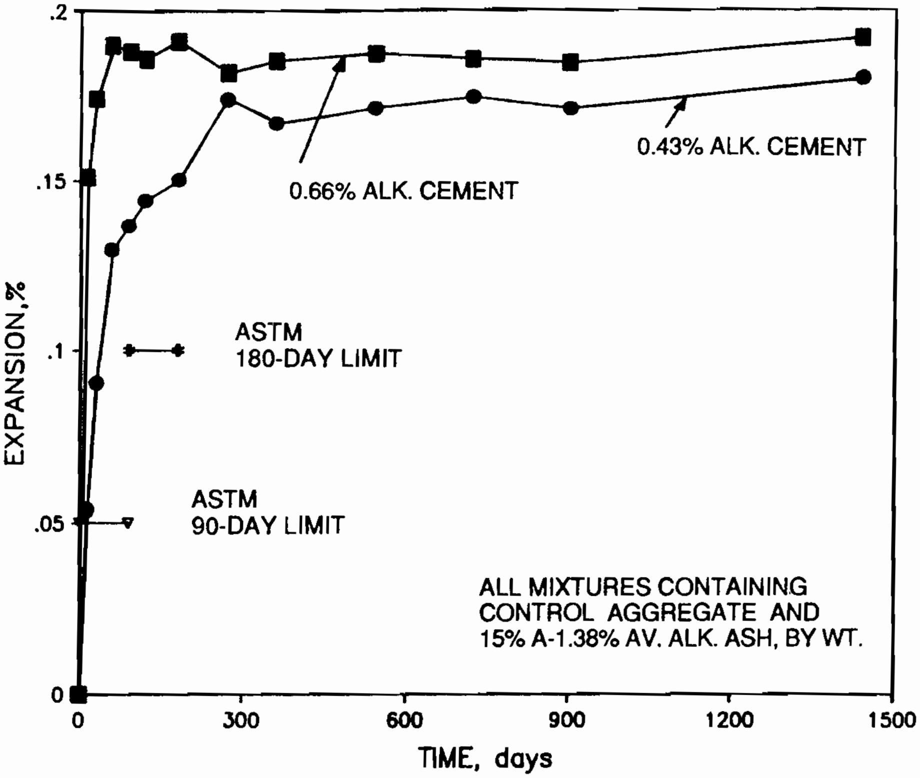


Figure 4.7 Relative reactivity of test cements

The results obtained at 1440 days were quite similar. Figure 4.9 shows the increase in mortar bar expansions resulting from the use of fly ashes containing increasing amounts of available alkalies.

Figure 4.10 illustrates, for typical mixtures containing the Type A fly ashes and the low alkali Type B fly ash, the beneficial effects derived by increasing the amount of cement replaced by these fly ashes. The high alkali Type B fly ash, and in certain instances the low alkali Type B fly ash, however, had a detrimental effect on expansions as can be seen in Figure 4.11.

4.4 Phase II Results

4.4.1 Fly Ash Treated with a Chemical Precipitating Agent. To assess the effect of the use of an alkaline precipitating agent (sodium carbonate) on the behavior of fly ash with respect to alkali-silica reaction, 24 mixtures were studied. Twelve mixtures contained fly ash treated with such an agent, while twelve similar mixtures contained an untreated fly ash. These fly ashes were both classified as

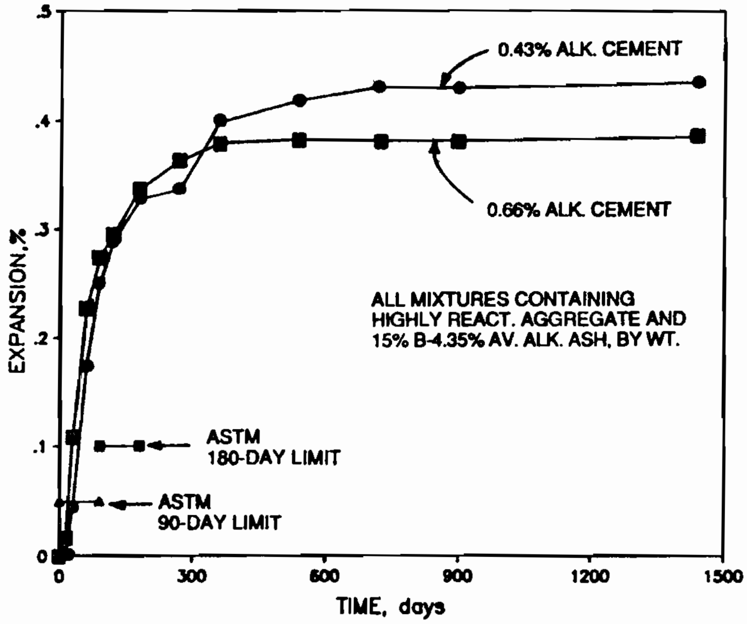


Figure 4.8 Mixture in which the low alkali cement was more deleterious than the high alkali cement

Type B and had similar alkali contents. The treated fly ash contained 2.35 percent available alkalies and the untreated fly ash contained 2.04 percent available alkalies. Only the four mixtures containing the highly reactive aggregate and either fly ash at a 17.5 percent replacement level, by volume, showed significant expansions. Figure 4.12. shows the expansions of these mixtures at 1440 days. Of these, the two mixtures containing the treated fly ash exhibited much greater expansions than the corresponding mixtures with untreated fly ash. These expansions show the same trend observed at 180 days, with the exception of the expansion corresponding to 28 percent by weight which at 900 days exceeded 0.1 percent but which was under this limit at 180 days.

4.4.2 pH of Mixing Water. Since the solubility of silica increases as the pH of the solution increases, the effect of the pH of mixing water on mortar bar expansions was studied. Four Phase I mixtures made with tap water were repeated using distilled water. The pH of the tap water was 8.14 while the distilled water had

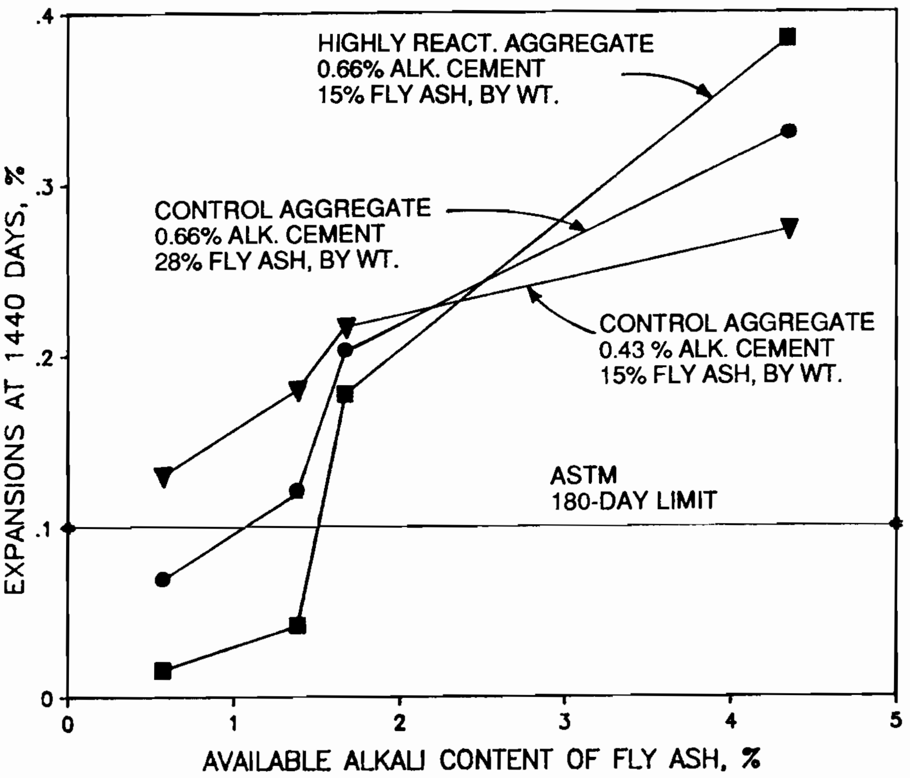


Figure 4.9 Relationship between the alkali content of fly ash and expansions

a pH of 5.7. The 1440-day results shown in Figure 4.13 reveal that in two cases, the use of distilled water significantly reduced expansions.

4.4.3 Available Alkali Content and Classification of Fly Ashes. The effect of the available alkali content of fly ash on expansions due to alkali- silica reaction was studied in Phase I with the use of four fly ashes. In Phase II, two additional fly ashes were studied to allow further observation of the effect of alkalies in fly ash.

One of these fly ashes was a Type A fly ash with a higher alkali content than either of the Type A fly ashes used in Phase I. This fly ash contained 1.76 percent available alkalies in comparison to the high-alkali Type A fly ash used in Phase I, which had an available alkali content of 1.38 percent. The alkali content of the new fly ash was also quite close to that of the low alkali Type B fly ash, which contained 1.67 percent available alkalies. Thus, a comparison of Type A and Type B fly ashes of similar alkali contents was also possible.

Mixtures containing these fly ashes generally exhibited similar behavior as illustrated in Figure 4.14. Only in mixtures containing medium alkali cement and

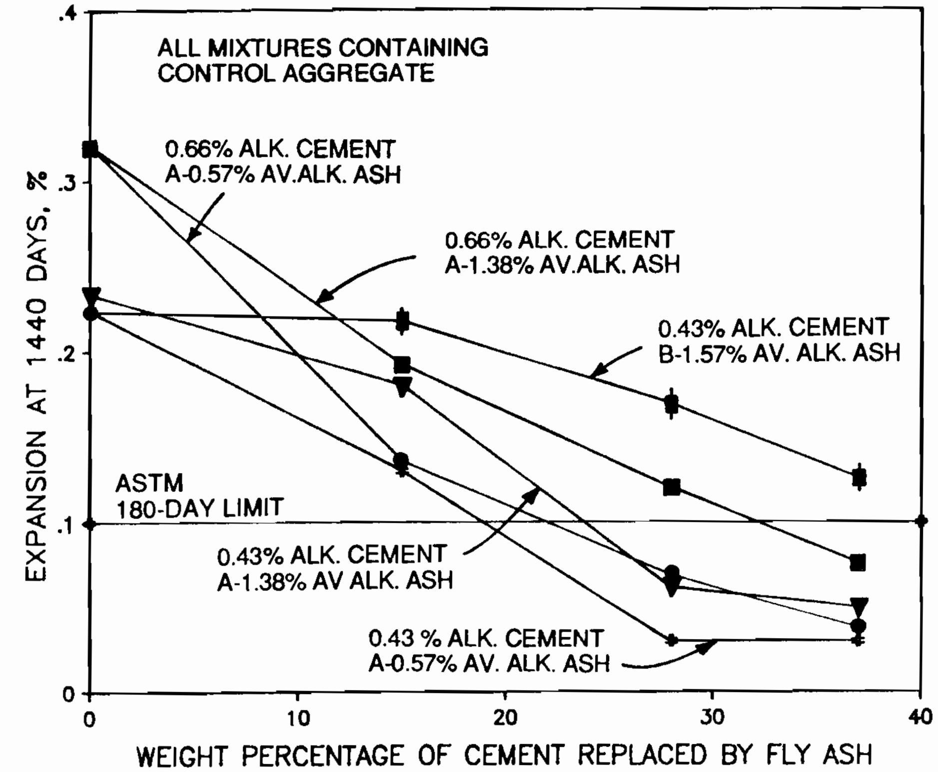


Figure 4.10 Relationship between the amount of cement replaced by fly ash and expansions

highly reactive aggregate did significant differences in expansion occur. The Type B fly ash exhibited significantly different behavior as compared to the two Type A fly ashes in these cases as shown in Figure 4.15.

The other new fly ash was a Type B fly ash with an alkali content of 3.75 percent, which fell between the alkali contents of the two Type B fly ashes tested in Phase I which had available alkali contents of 1.67 percent and 4.35 percent. The mixtures containing the new fly ash (3.75 percent available alkalies) were significantly more expansive at all replacement levels than corresponding mixtures containing the lower alkali fly ash (1.67 percent available alkalies) as can be seen in Figure 4.16 and Figure 4.17. However, mixtures containing the higher alkali fly ash (4.35 percent available alkalies) were more expansive than corresponding mixtures containing the new fly ash only at a replacement level of 17.5 percent.

4.4.4 Total Alkali Content of Cement. The medium alkali cement used in Phase I had a total alkali content of 0.66 percent which was barely above the ASTM limit of 0.60 percent. In Phase II, a cement containing a much higher alkali content

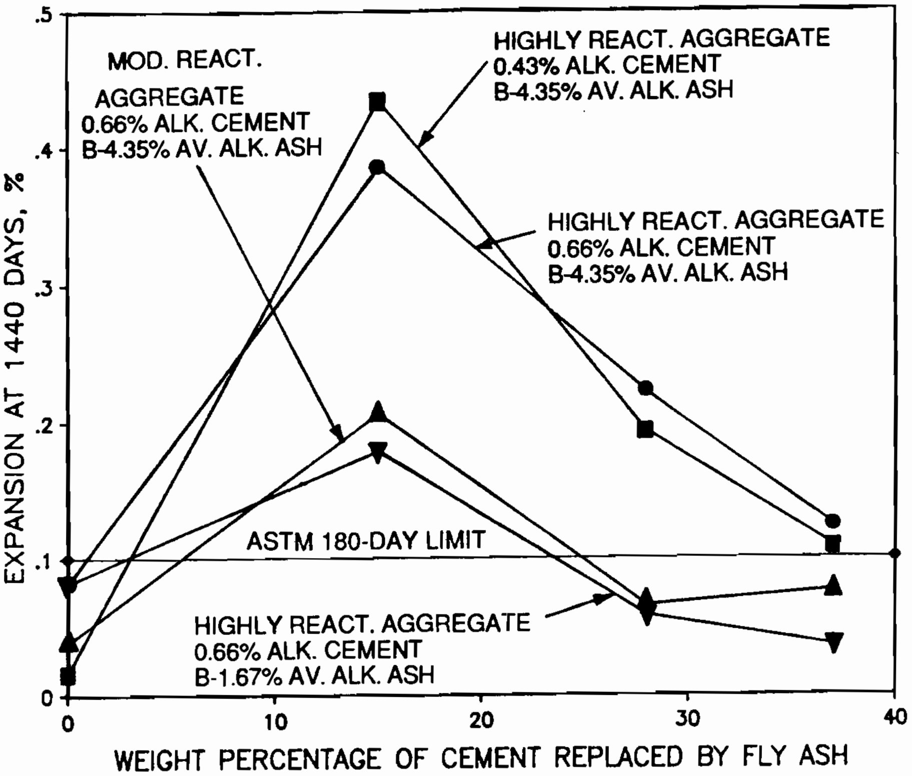
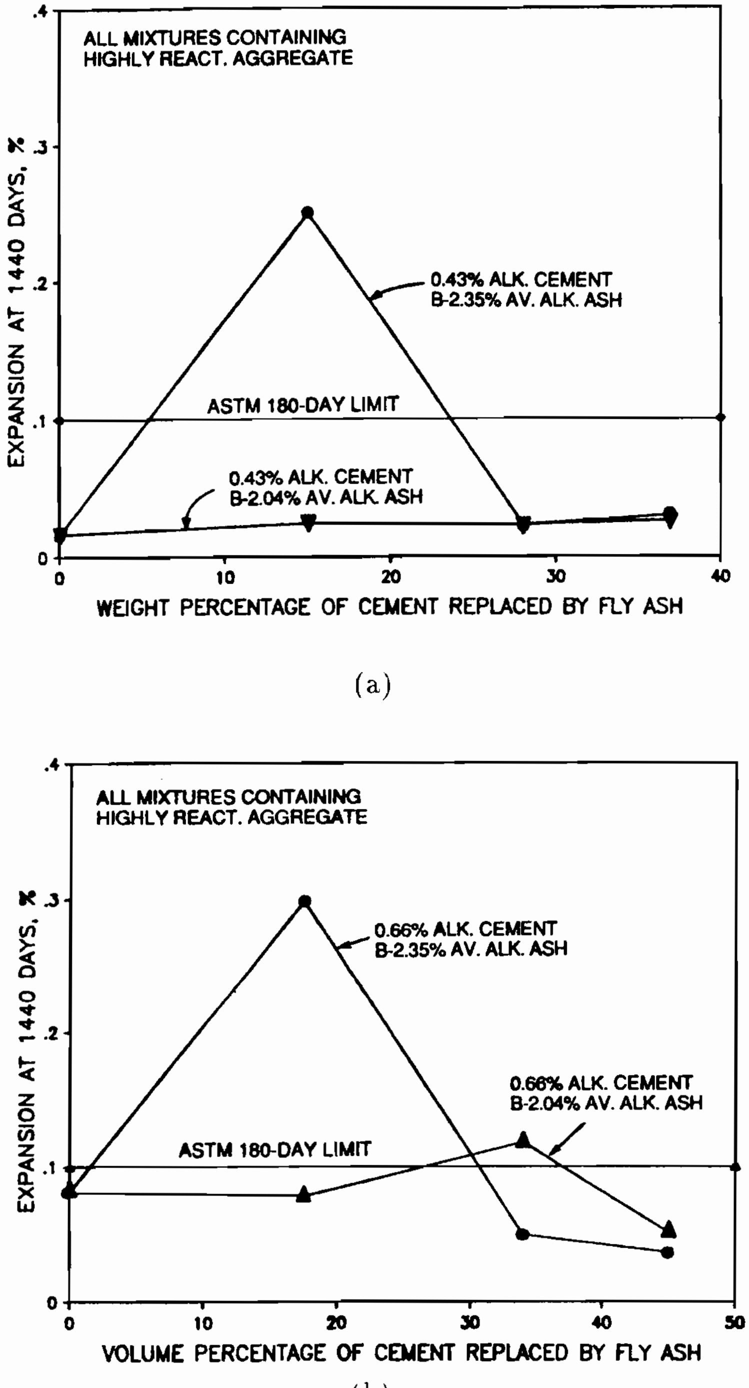


Figure 4.11 Relationship between the amount of cement replaced by Type B fly ash and expansions

was used in eight mixtures. The use of this cement having an alkali content of 1.03 percent resulted in significant increases in expansions, as can be seen in Figure 4.18. This cement is referred to as "high alkali" cement throughout this report.

4.4.5 Percentage of Cement Replaced by Fly Ash. It was noted in the previous report that the replacement of 17.5 percent of the volume (15 percent, by weight) of cement with either Type B fly ash caused expansions much greater than those of corresponding mixtures without fly ash. The existence of such a "pessimum" proportion of replacement has been acknowledged by some researchers[40]. Replacement of 34.3 percent of the cement typically resulted in much lower expansions, nearing those of the mixtures without fly ash. In this phase of the study, it was desired to observe the effect of replacing a volume of cement between 17.5 percent and 34.3 percent with fly ash. A replacement level of 26 percent was chosen for this test.



(a)

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Figure 4.12 Effect of fly ash treated with a precipitating agent on expansions

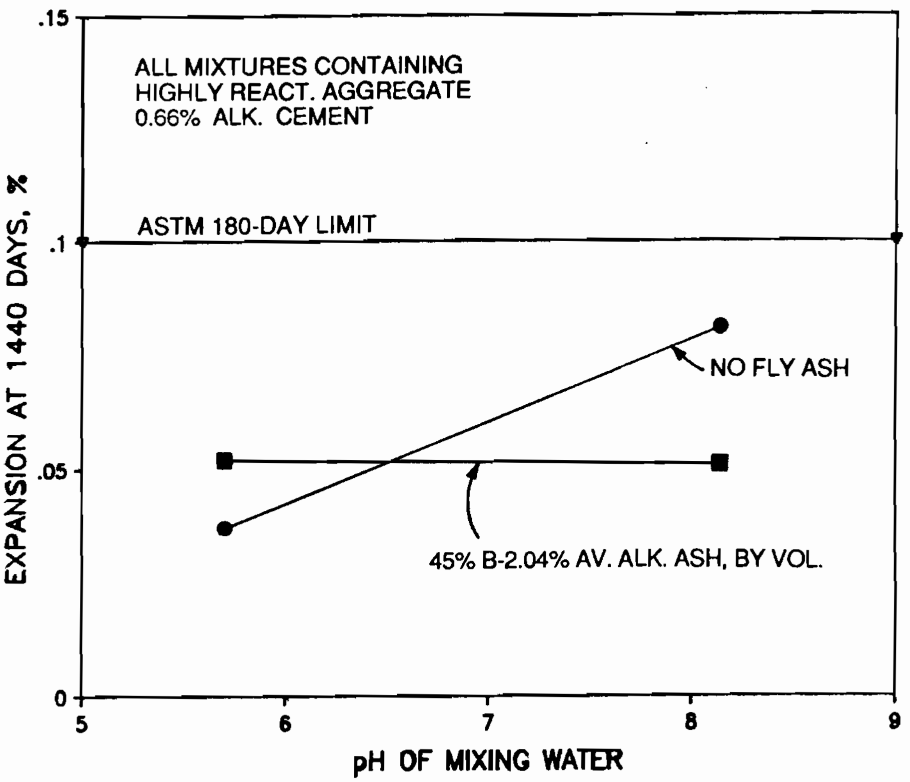


Figure 4.13 Effect of low pH distilled water on expansions

It was also noted that while replacement levels of 34.3 percent resulted in lower expansions than replacement levels of 17.5 percent, in some instances expansions increased slightly when 45 percent of the cement, by volume, was replaced with fly ash. To determine if this trend would continue for replacement levels greater than 45 percent, four mixtures were prepared with fly ash as a replacement for 62.5 percent of the volume of cement.

Figure 4.19 presents 1440-day expansion data for mixtures representing four cement-aggregate combinations with all six percentages of cement replacement. Those mixtures containing 26 percent fly ash expanded significantly less than the mixtures containing 17.5 percent fly ash and had nearly the same magnitude of expansions as those mixtures which contained fly ash at the 34.3 percent replacement level. The mixtures containing 62.5 percent replacement resulted in slightly smaller expansions than those of mixtures containing 45 percent replacement, in almost all of the mixtures.

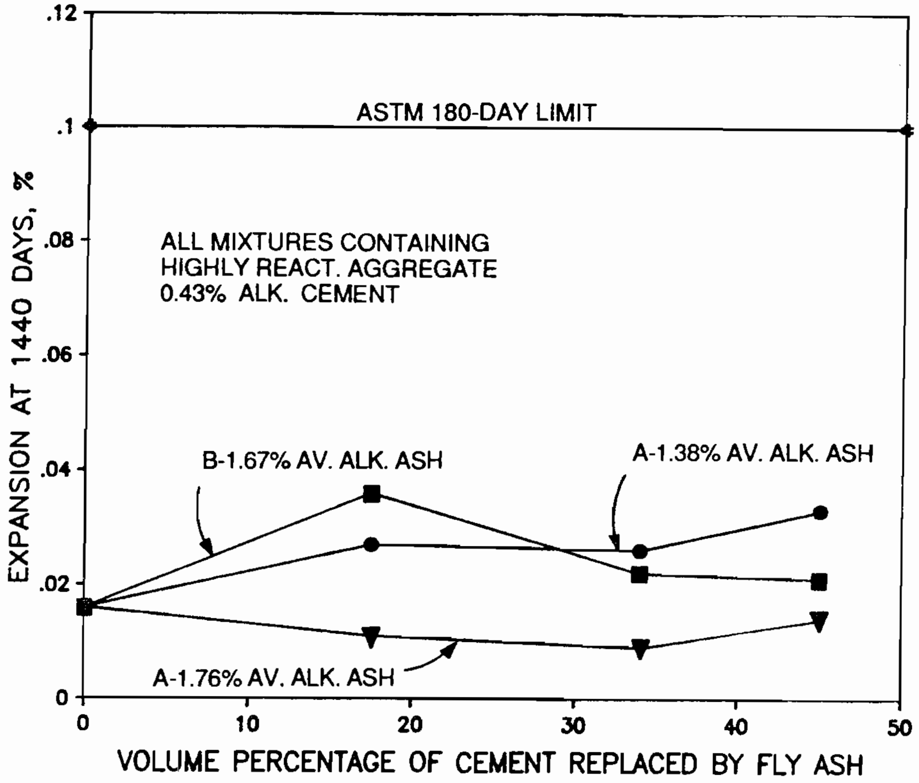


Figure 4.14 Effect of Type A and Type B fly ashes of similar alkali content when used with low alkali cement

4.4.6 Partial Replacement of Aggregate with Fly Ash. In four Phase II mixtures, a volume of aggregate equal to 30 percent of the total volume of cement was replaced by fly ash. Replacing a portion of the aggregate with fly ash served to increase the alkali content of these mortars while decreasing the amount of reactive silica present. As a result, the ratio of alkalies to silica in these mixtures was substantially increased without replacing any of the cement with fly ash.

The 1440-day expansions of these mixtures are compared to the expansions of mixtures containing a similar amount of the same fly ash (34.3 percent by volume) as a replacement for cement in Figure 4.20. The mixtures containing fly ash as an aggregate substitute, which had a substantially lower total cementitious material content, showed greater expansions than those containing fly ash as a cement substitute in three of the four test cases.

4.4.7 Influence of Fineness and Preblending of Cement and Fly Ash on Behavior of Type IP Cement. The 90-day results of Phase I indicated that mixtures

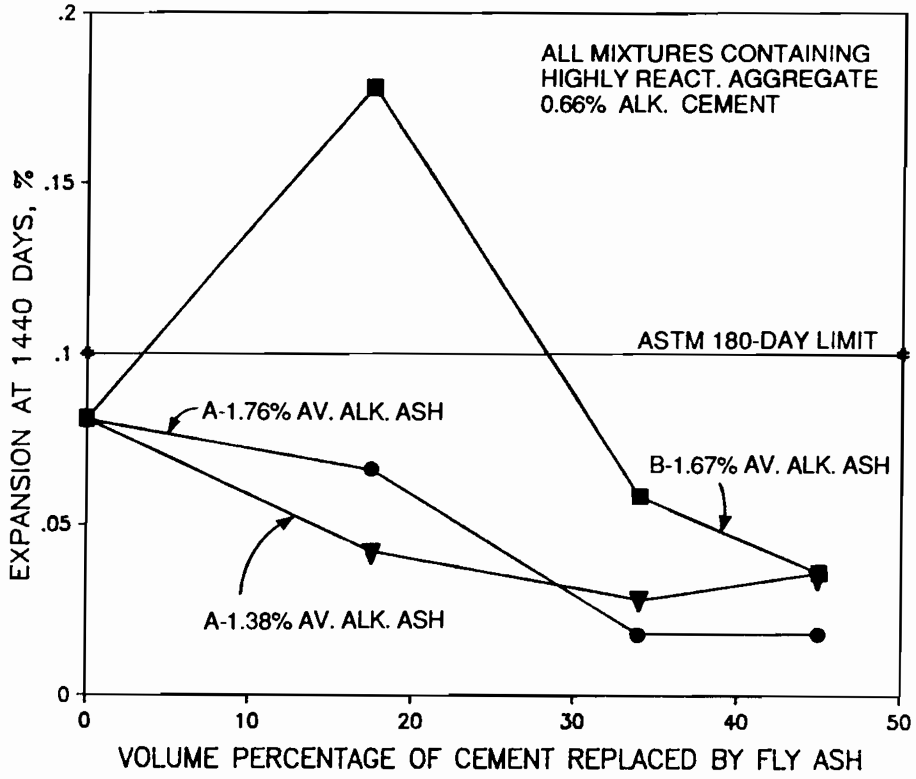


Figure 4.15 Effect of Type A and Type B fly ashes of similar alkali content when used with med. alkali cement

containing Type IP cement experienced much smaller expansions than mixtures containing the Type I cements tested. This was attributed to the fact that the fly ash in Type IP cement was added to the clinker before grinding, presumably resulting in a greater dispersion of the fly ash in the cement than would be obtained by adding fly ash to the cement during batching.

To determine if either the fineness or the preblending of Type IP cement was responsible for its effectiveness in inhibiting alkali-silica reaction, several test mixtures were studied in Phase II. Two mixtures were made using the same Type I cement (I/IP) and fly ash (A/IP) used to manufacture the Type IP cement. In the first mixture, the fly ash and cement were combined during batching as was done in all other mixtures in this program. The fly ash and cement used in the second mixture were mechanically blended before batching to simulate the blending presumed to occur during the intergrinding of the fly ash and clinker of the Type IP cement. These two mixtures were compared with the mixture containing Type IP cement. From this comparison the influence of the fineness and the blending of Type IP cement can be observed. The expansion history of these mixtures is presented

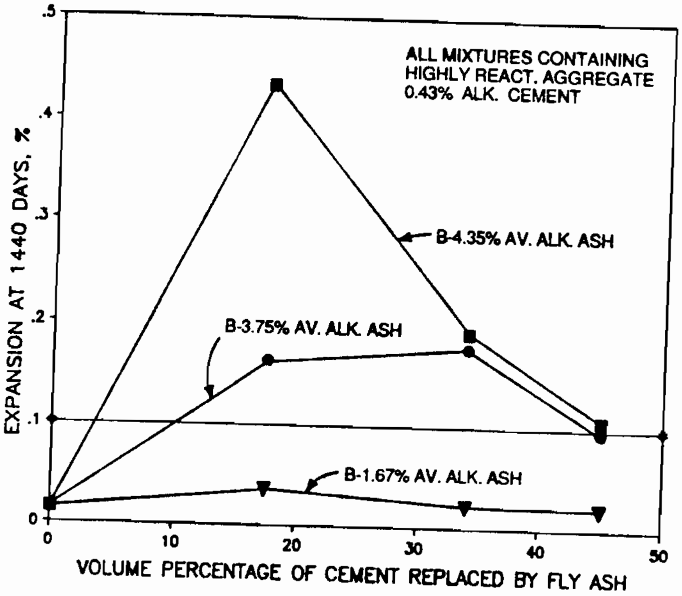


Figure 4.16 Effect of Type B fly ashes used with low alkali cement

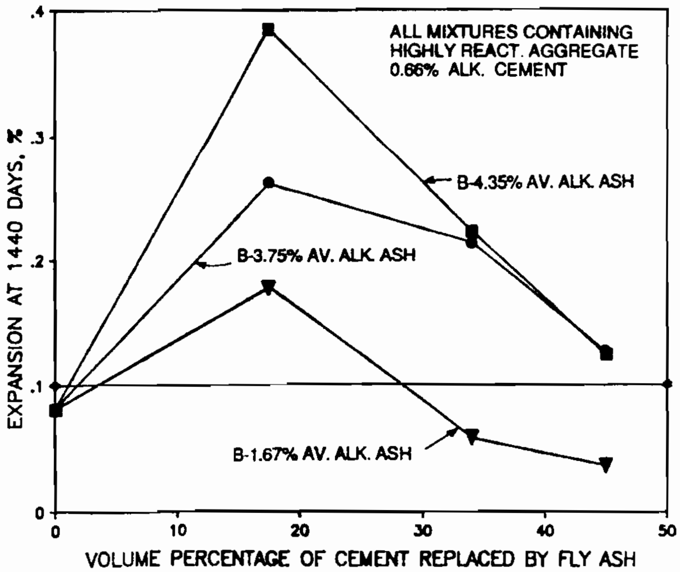


Figure 4.17 Effect of Type B fly ashes used with med. alkali cement

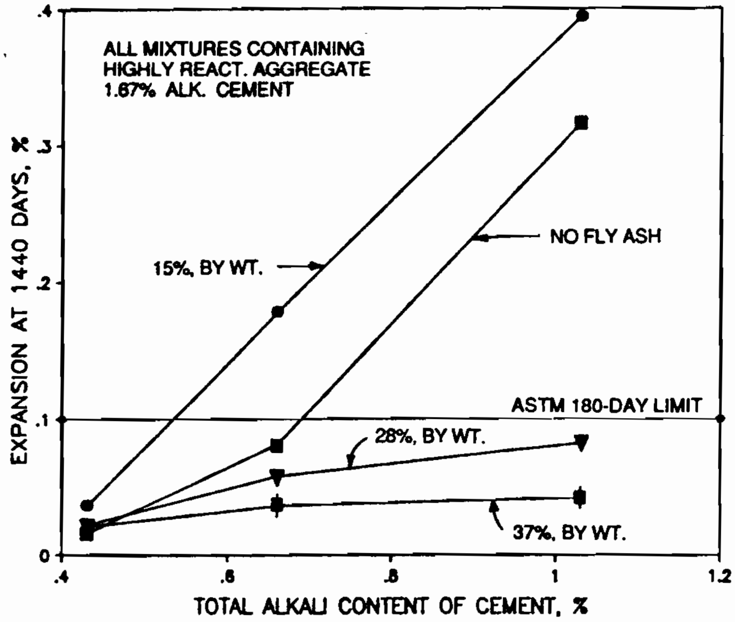


Figure 4.18 Influence of alkali content of cement on expansions

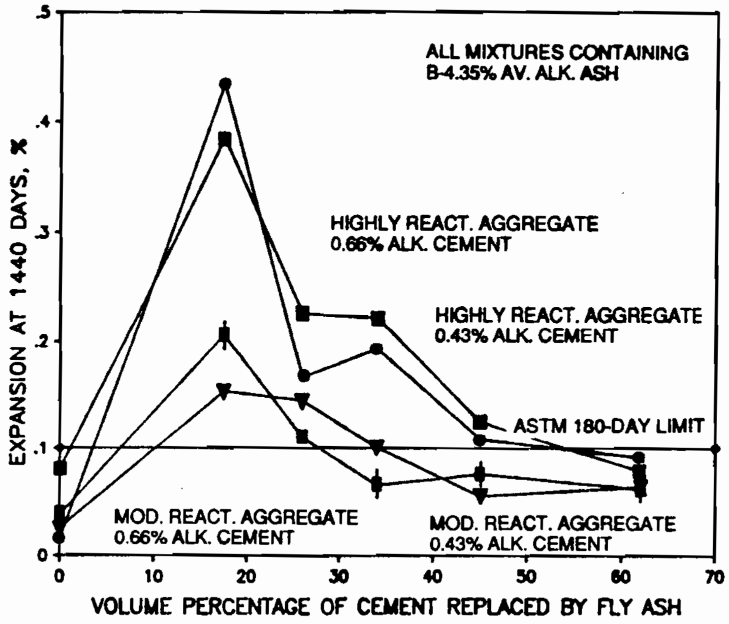


Figure 4.19 Influence of the amount of cement replaced by fly ash on expansions

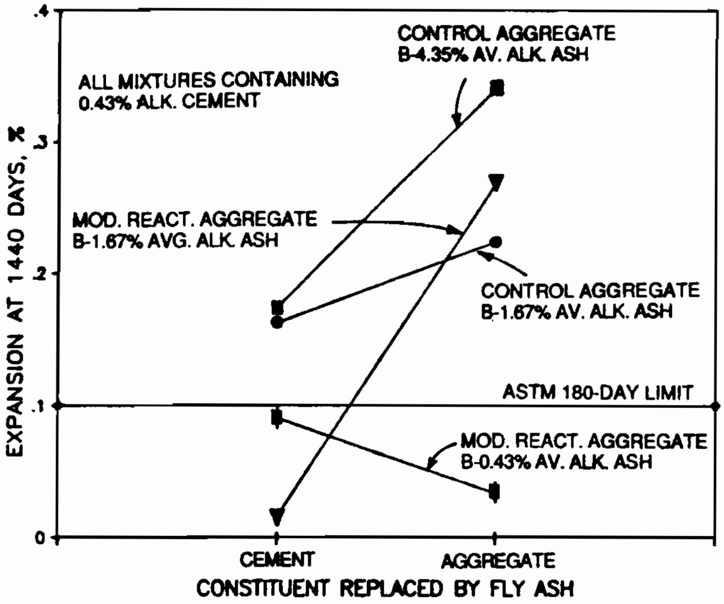


Figure 4.20 Effect of the partial replacement of aggregate with fly ash

in Figure 4.21. The I/IP and A/IP mixture that was mechanically blended had similar expansions to the I/IP and A/IP mixture that was not blended. Both of these mixtures expanded more than the mixtures containing Type IP cement.

4.4.8 Silica Fume. To compare the effectiveness of silica fume with that of the fly ashes tested, 15 mixtures were prepared in Phase II using one silica fume as a partial replacement for cement. The three replacement percentages used, 17.5 percent, 34.3 percent and 45 percent by volume, allowed direct comparisons with corresponding mixtures containing fly ash. Figure 4.22 contains expansion data for a series of mixtures containing silica fume and corresponding mixtures containing Type A and Type B fly ashes having available alkali contents ranging from 0.57 percent to 4.35 percent.

4.5 Phase III Results

In this Phase of the project, four Type B fly ashes were ground down to two fineness levels. The first level was at about 50 percent of the original fineness, measured as the percent retained in the 325S. The second level was at about two

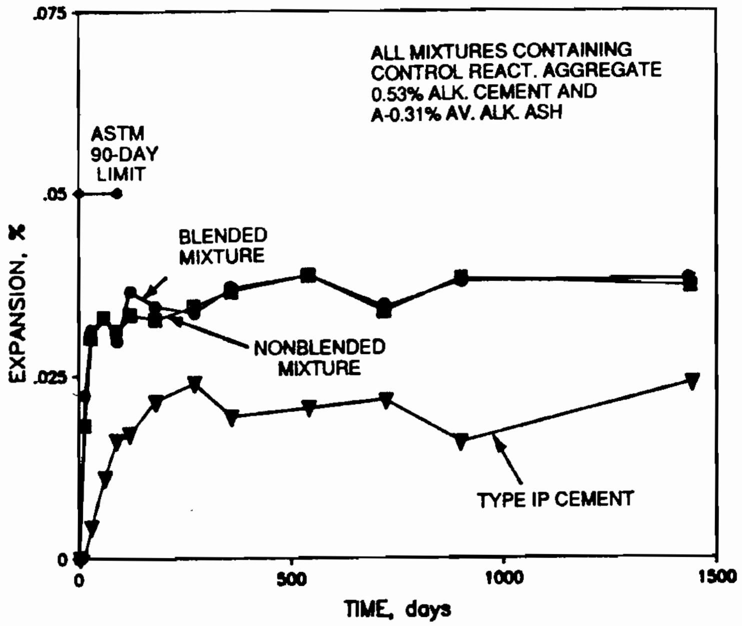


Figure 4.21 Influence of fineness and preblending of fly ash and cement used in Type IP cement

percent 325S. All mixtures contained the highly reactive aggregate used in Phases I and II, and the high alkali cement of Phase II. The available alkali contents and the fineness of the fly ashes were presented in Table 3.5.

Figure 4.23 shows the test results for the mixtures made with the fly ash containing 0.96 percent available alkalies. It can be observed that no relation can be found between and expansions.

Figure 4.24 shows the test results for the mixtures made with the fly ash containing 1.90 percent available alkalies. No relationship was observed between the expansions and the 325S for this fly ash. While the mixtures containing 37 percent fly ash replacement exhibited as slight increase in expansions as the 325S increased, the mixtures containing 15 and 28 did not exhibited a similar relationship with the 325S.

Figure 4.25 shows the test results for the mixtures made with the fly ash containing 3.73 percent available alkalies. As in the previous case, no clear trend

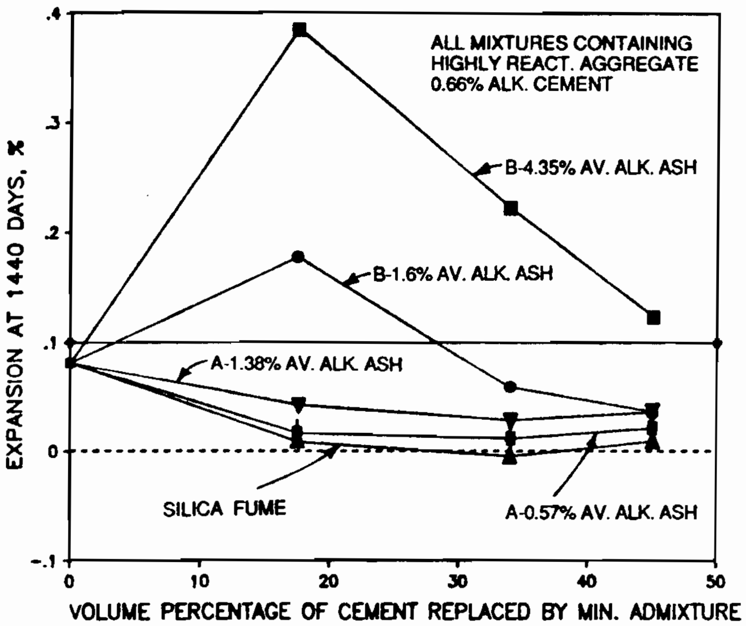


Figure 4.22 Comparison of the behavior of silica fume with that of several fly ashes

was observed between amount of fly ash retained in sieve #325 and expansions for a given cement replacement.

Figure 4.26 shows the test results for the mixtures made with the fly ash containing 4.35 percent available alkalies. As before, no clear trend was observed between amount of fly ash retained in sieve #325 and expansions for a given cement replacement.

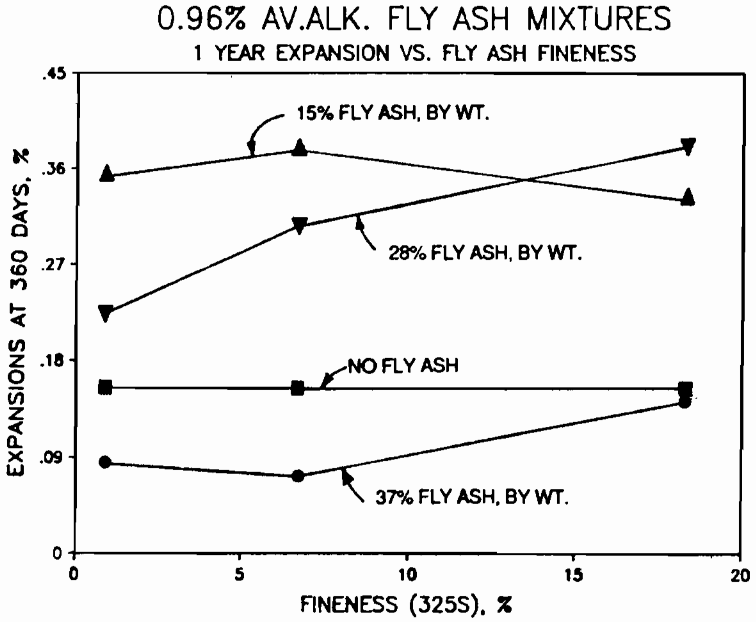


Figure 4.23 Effect of fineness of the fly ash containing 0.96 percent available alkalies on the alkali-aggregate reaction in concrete

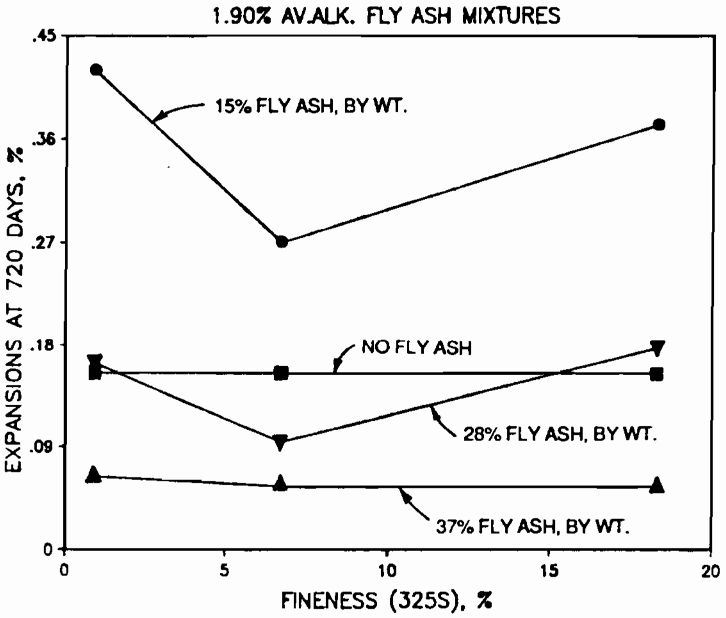


Figure 4.24 Effect of fineness of the fly ash containing 1.90 percent available alkalies on the alkali-aggregate reaction in concrete

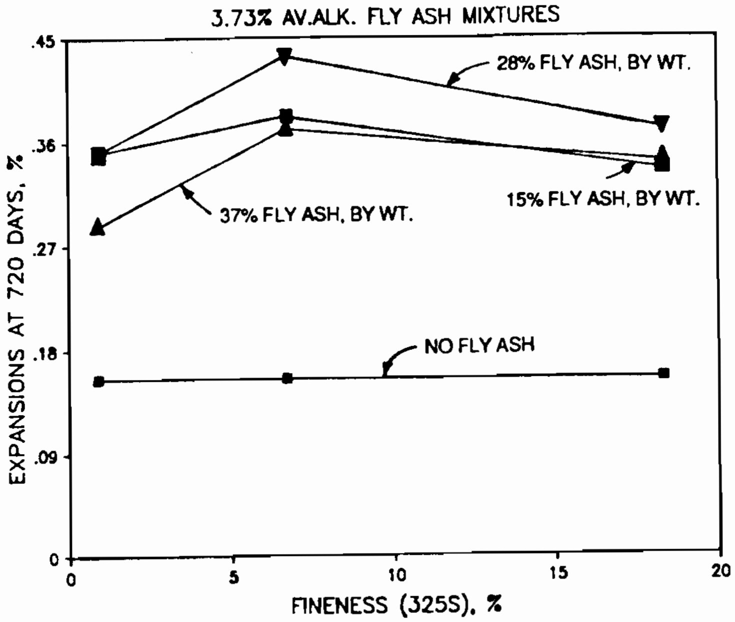


Figure 4.25 Effect of fineness of the fly ash containing 3.73 percent available alkalies on the alkali-aggregate reaction in concrete

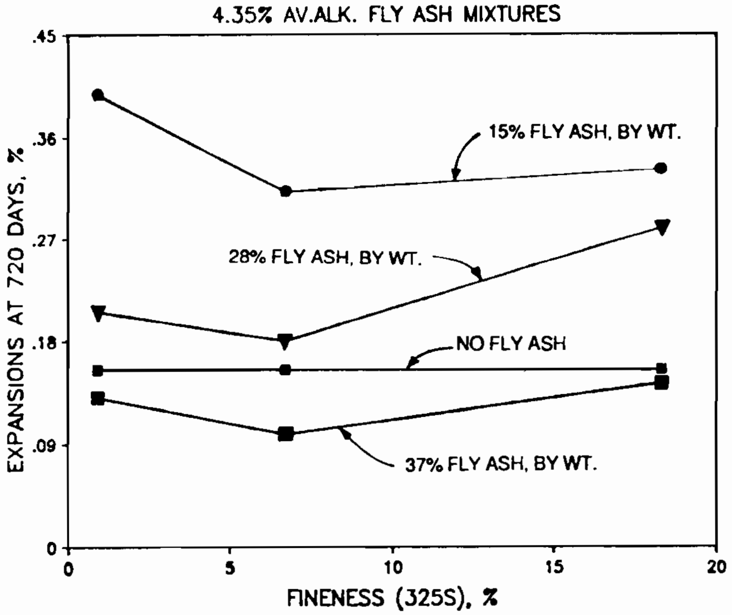


Figure 4.26 Effect of fineness of the fly ash containing 4.35 percent available alkalies on the alkali-aggregate reaction in concrete

CHAPTER 5
DISCUSSION OF TEST RESULTS

5.1 Introduction

The test results presented in Chapter 4 will be discussed in this chapter. The format of this chapter will be the same as that of the previous chapter. The first portion contains a discussion of the results of this test program in terms of ASTM C 227 and ASTM C 33, which contain guidelines for the interpretation of results obtained from mortar bar tests. The discussion will include several proposed revisions to the standards and their potential effects on the interpretation of the results of this study. The results obtained during the first 90 days of exposure testing of Phase I specimens will then be compared with results obtained through 1440 days. The conclusions based on 90-day data [53] will be reviewed with respect to the later data. Then, a discussion of the results obtained from the tests conducted during Phase II will be presented. This chapter will conclude with the discussion on the results of Phase III on the effect of fineness on mortar-bar expansions.

5.2 Applicability of Limits Specified in ASTM C 227 and ASTM C 33

ASTM C 227 specifies that material combinations are potentially reactive if mortar bars fabricated from these materials expand in excess of 0.05 percent at 90 days and/or 0.10 percent at 180 days. Fifty-two of the 202 mixtures studied in both phases of this program exceeded the 90-day limit. Forty of these mixtures also exceeded the 180-day limit. Only one mixture exceeded the 180-day limit without surpassing the 90-day limit. ASTM C 33 states that results obtained after 180 days of exposure testing of mortar bars are preferable to results obtained after 90 days of testing. The wording of this statement appears to imply that results obtained at 90 days have been found to be less reliable. It follows that expansion limits at this date would need to be more conservative to ensure that all deleterious combinations of materials would be detected. Hence, the number of mixtures with expansions greater than 0.05 percent at 90 days would be expected to be greater than the number of mixtures with expansions exceeding 0.10 percent at 180 days. The results of this study support the above assumption. Based on these results, the 90-day expansion limit can be justified as an early, but conservative guideline, having a slight risk of overlooking late-expanding material combinations as was the case for a highly reactive aggregate mixture in this study, containing low alkali cement partially replaced by 17.5%, by vol, B-2.35% av.alk. fly ash.

A number of researchers do not consider ASTM C 227 to be a reliable and accurate test. Several have proposed changes to ASTM C 227, including modifications of the expansion limits and the length of the exposure testing period. The implications of some of these variations on the results of this study are discussed below.

A study of several material combinations by Heck[1] revealed a strong correlation between indications of potential reactivity as determined by the results of the ASTM C 289 Chemical Test and the ASTM C 227 Mortar Bar Method at 90 days. Heck did not, however, observe any correlation between these results and 180-day results obtained from ASTM C 227 tests since the 180-day results indicated that none of the material combinations tested were potentially reactive. Although the 180-day data obtained from mortar bar tests is considered by ASTM to be preferred to 90-day data, the strong corroboration of the 90-day data by the ASTM C 289 results led Heck to propose a revision of the ASTM 180-day expansion limit. By reducing the 180-day limit to 0.075 percent, he was able to achieve good agreement between the 90-day results, the 180-day results, and results from ASTM C 289 tests.

In contrast to the results observed by Heck, 77 percent of the mixtures in this program which exceeded the 90-day expansion limit also exceeded the 180-day expansion limits. If the proposed limit of 0.075 percent is applied to the data from this program, the correlation between the 90-day and 180-day results would improve to 92 percent. ASTM C 289 was not conducted for any of the aggregates tested in this program, either by the TSDHPT or as part of this research program. Therefore, no comparison can be made between the two test methods.

Several factors must be considered when evaluating the revision to ASTM C 227 proposed by Heck.

1. Of the two expansion limits contained in this specification, the limit found to be preferable by ASTM is the one which is being considered for revision. Although the origins of the ASTM limits are uncertain, they appear to have

been based, at least in part, on the comparison of mortar bar test results with observations of concrete in service[2,3]. The results observed by Heck were not verified in the field.

2. ASTM C 289 is known to provide misleading results in some cases. Sims[46,47] reported that certain types of siliceous aggregates known to perform satisfactorily in service and in mortar bar tests may be identified as "deleterious" or "potentially deleterious" by the ASTM C 289 test method.
3. ASTM C 289 is intended only to indicate the potential reactivity of aggregates. It does not serve to predict the behavior of cement-aggregate or cement-aggregate-mineral admixture combinations. The use of the results of ASTM C 289 to establish the criteria for ASTM C 227 disregards the effects of constituents other than aggregates on the results of mortar bar tests.

As a result, the evidence presented by Heck does not seem sufficient to warrant the alteration of ASTM C 227.

Stark[4], on the other hand, has presented stronger evidence for revisions. He cites instances of concrete in service which has deteriorated due to alkali-silica reaction, even when mortar bars containing the same materials have not surpassed the 90-day or 180-day expansion limits. In order for the reactive potential of these aggregates to be determined, Stark and other researchers[5], have recommended that the ASTM C 227 test procedure be extended so the limit of 0.05 percent expansion would apply to 6-month results and the limit of 0.10 percent would apply to 12-month results. A limit of 0.10 percent expansion at 12 months is currently being evaluated in Iceland[6].

This proposed revision would have a minor effect on the interpretation of the results of Phase I. While 30 mixtures exceeded 0.05 percent expansion at 90 days, 36 surpassed that mark at 180 days. However, just two of the 108 test mixtures exceeded 0.10 percent expansion between 180 days and 1440 days, increasing the number of material combinations which would be considered potentially deleterious from 25 to 27. The expansions of these two mixtures were so close to the 180-day limit that their use in the field would have been questionable, even without the extension of the testing period. Only one additional mixture approached the 0.10

percent limit between 180 days and 1440 days, expanding from 0.068 percent to 0.091 percent, as illustrated in Figure 4.2.

The Bureau of Reclamation[7] also utilizes a 12-month testing program for its mortar bar specimens. In their specifications, expansions between 0.10 percent and 0.20 percent are considered "marginal" with greater expansions considered "deleterious". By these standards, 16 of the Phase I mixtures would be considered "marginal" while only 11 would be considered "deleterious". The relative leniency of these limits is apparent and has been commented upon by researchers[8]. The Bureau of Reclamation, however, has continued to maintain this standard.

As the preceding discussion has indicated, increasing the length of the test program would have had little effect on the evaluation of these materials for alkali-silica reactivity. Changing the expansion limits at either 180 or 360 days, however, would have had a significant bearing on the number of material combinations considered to be deleterious. The effects of these proposals are summarized in Figure 5.1.

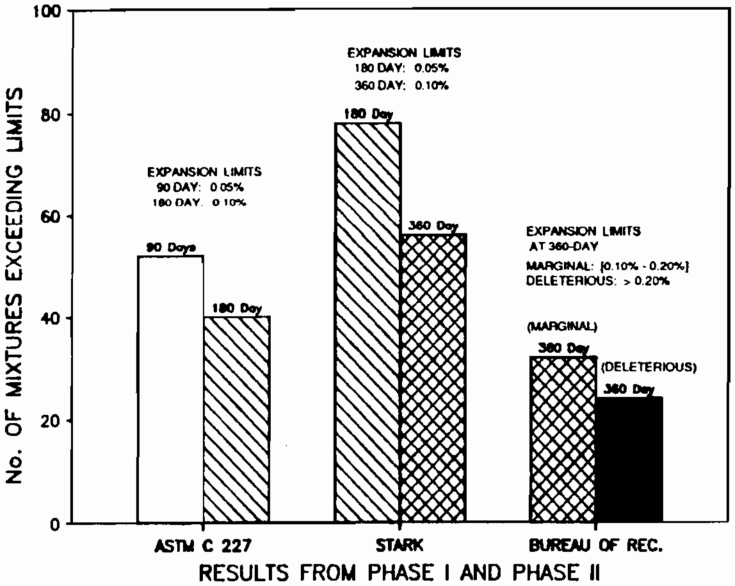


Figure 5.1 Effects of proposed revisions to ASTM C 227 on interpretation of test results

The reliability of these proposed revisions to ASTM C 227 has not been verified by conclusive tests. However, they do serve to point out possible concerns in the ASTM C 227 testing procedure. ASTM C 227, as the prevailing standard, was accepted for use in this program for determining alkali-silica reactivity. Since only three of the 108 Phase I mixtures approached or exceeded the 0.10 percent expansion limit between 180 days and 1440 days, there is no reason to believe that the use of the three-month and six-month limits of ASTM C 227 provided less than accurate results.

5.3 Phase I Results

5.3.1 Effect of Aggregate. The two reactive aggregates used in this program were identified by the TSDHPT using the procedures described in ASTM C 33. These tests, conducted with a cement having a total alkali content of 0.91 percent, revealed that one aggregate was distinctly more reactive than the other, as was shown in Figure 3.1.

Phase I of this program included a similar set of mixtures, using a cement with an alkali content of 0.66 percent. The results, shown in Figure 5.2, support those of the TSDHPT tests. However, at 90 days test age, the moderately reactive aggregate was not determined to be potentially deleterious while at 180 days neither reactive aggregate was indicated to be potentially deleterious based on the measured expansion at each test age.

ASTM C 33 states that the cement used to test the reactivity of aggregates should have an alkali content substantially in excess of 0.60 percent, preferably exceeding 0.80 percent. These results indicate that an alkali content of 0.66 percent is not enough in excess of 0.60 percent to produce a reliable indication of the reactivity of these aggregates.

Based on the results obtained during this phase of the program, ASTM C 33 appears to be a suitable procedure to follow to determine the potential reactivity of aggregates if the recommendations regarding the alkali content of the test cement are followed.

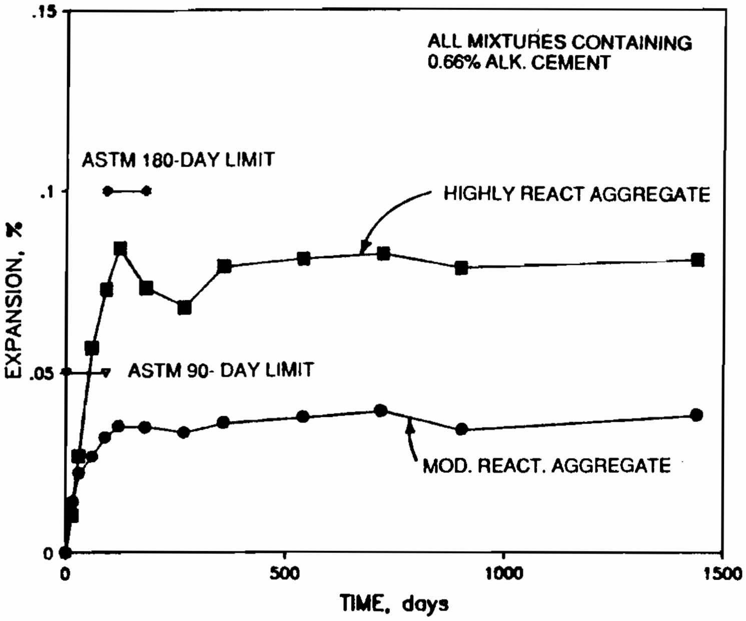


Figure 5.2 Potential reactivity of siliceous aggregates tested with med. alkali cement as per ASTM C 33

The 90-day results obtained for all Phase I mixtures indicated that Pyrex glass was the most reactive aggregate tested, followed by the highly reactive aggregate, the moderately reactive aggregate, and the nonreactive aggregate. As stated in the previous chapter, results at later ages continued to support these observations.

Figure 5.3 shows the 180-day expansions of the mixtures containing each natural aggregate in combination with each cement tested in Phase I. Based on the results presented in this figure, all three aggregates were determined to be adequate for use with the low alkali cement and the Type IP cement. The moderately-reactive and nonreactive aggregates were also found to be adequate for use with the high alkali cement. Even the highly-reactive aggregate did not appear to be strongly deleterious when used with the high alkali cement. With the proper choice of cement, the test results seem to indicate that any of these aggregates could be used safely in the field without the use of mineral admixtures.

At 1440 days, only two exceptions to the hierarchy of reactivity occurred among the significantly expansive mixtures of Phase I. The two mixtures containing

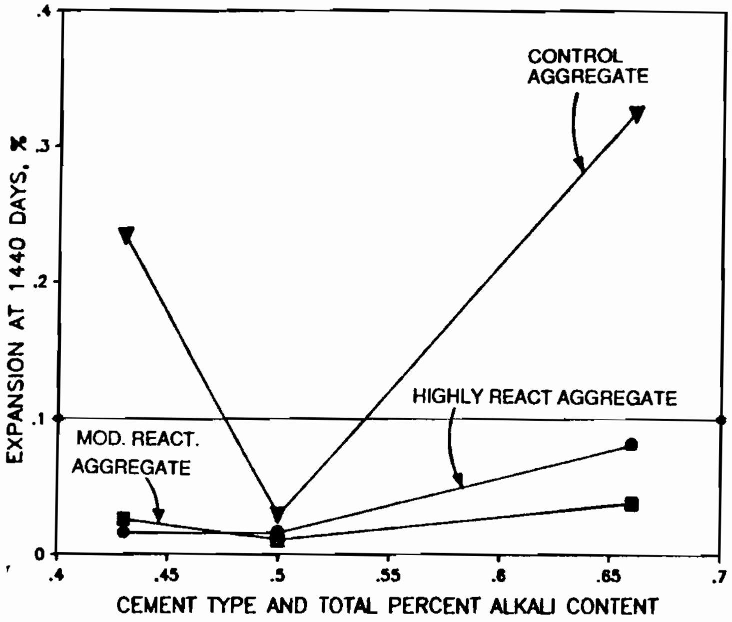


Figure 5.3 Comparison of expansions of mixtures containing each cement-aggregate combination

the highly reactive aggregate and a 17.5%-by vol. of B-4.35% av.alk. fly ash replacement of both low and high alkali cements, expanded more than the corresponding mixtures containing control aggregate. These mixtures were the most expansive mixtures in the entire program.

These factors all point to the possibility that the amount of alkalies contributed by the cement and fly ash to these mixtures was closer to the pessimum amount for the highly reactive aggregate than for the control aggregate.

These results illustrate how, in certain instances, the use of less reactive aggregates actually serves to aggravate rather than alleviate the potential for alkali-silica reaction. Due to the existence of the pessimum phenomenon, the concrete designer must know more than just the potential reactivity of each individual constituent to be used in a batch of concrete. The materials must be tested in the lab in the same proportions to be used in the field if an accurate assessment of the risk of deleterious behavior is to be made.

5.3.2 Effect of Cement. Three cements were tested in Phase I of the project: two Type I cements and a Type IP cement. At 90 days, it was reported[53] that expansions of the test specimens were generally greater in mixtures containing the high alkali Type I cement than in corresponding mixtures containing the low alkali Type I cement. This conclusion was verified at 1440 days. Mixtures containing the Type IP cement continued to be less expansive than corresponding mixtures containing the other two cements. This occurred even though the Type IP cement had a total alkali content of 0.50 percent compared to the low alkali cement which had a total alkali content of 0.43 percent.

Results obtained during this program indicate that the 0.60 percent limit on alkalies suggested in ASTM C 150 is not a reliable guideline. The mixtures containing the two reactive aggregates and the high alkali cement, with no fly ash replacement, did not exceed the 180-day expansion limit, not even after 1440 days of exposure testing, as shown in Figure 5.3. This suggests that for some reactive aggregates, the 0.60 percent limit on total alkalies is too low. On the other hand, the mixture containing the control aggregate and low alkali cement, with no fly ash replacement, exceeded both expansion limits, indicating that for some strongly reactive aggregates, a limit of 0.60 percent alkalies in cement is too high. The latter observation is supported by the studies conducted by Stark[57] which were discussed in Section 5.2 of Research Report 450-2 of this program[16].

Revisions to the alkali limit in ASTM C 150 will be required to improve the ability of concrete mixture designers to prevent alkali-silica reaction in concrete, without restricting the use of materials. Such a revision would need to take into account such factors as the alkali content of the cement, the cement content of the concrete, the reactivity of the aggregates, and the use of mineral admixtures containing alkalies.

The behavior of the mixtures containing the Type IP cement indicates that the alkalies in blended cements are not equivalent in reactivity to the alkalies in Type I cements. This is not surprising in light of the fact that the alkalies in Type IP cement come not only from the portland cement, but from the fly ash, as well. Only the available alkalies in fly ashes are considered to be free to participate in reactions with aggregates[9]. However, the total quantity of alkalies in the fly ash are included in the reported alkali content of a blended cement. Thus, the reactivity of a Type IP cement is likely to be less than indicated by the total alkali content. Furthermore, the deleterious activity of the alkalies in a blended cement could be offset, in part, by the pozzolanic behavior of the fly ash. In order to more effectively use this type of cement, separate guidelines governing its use will have to be developed.

5.3.3 Effect of Fly Ash. ASTM C 618 includes a suggested limit of 1.5 percent available alkalies for fly ashes to be used with reactive cement-aggregate combinations. Of the four fly ashes tested in Phase I, the two Type A fly ashes met this criterion while the two Type B fly ashes did not.

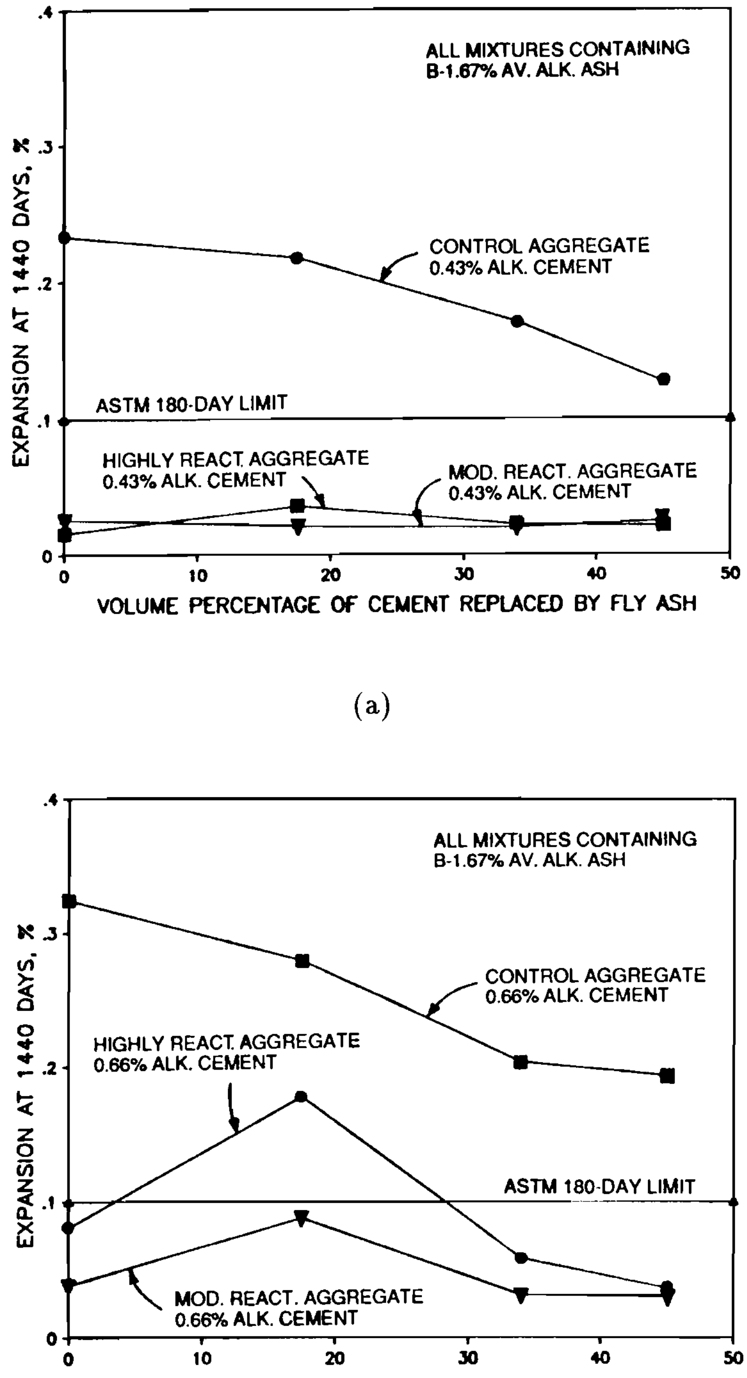
The two Type A fly ashes reduced expansions when used at any percentage of replacement for cement. When sufficient amounts were used, expansions were reduced below the ASTM limits at 180 days for all cement-aggregate combinations.

The low alkali Type B fly ash had an available alkali content of 1.67 percent, which was slightly in excess of the ASTM limit. However, when sufficient quantities of this fly ash were used expansions were reduced for all cement-aggregate combinations, as shown in Figure 5.4. Except for mixtures containing Pyrex glass, the expansions were reduced below the 180-day ASTM limit even through 1440 days of exposure testing.

Based on these results, the limit of 1.5 percent available alkalies in fly ashes suggested by ASTM does not appear to be an adequate guideline. These results indicate that the amount of cement replaced by a fly ash, as well as the alkali content of the fly ash, influence its effect on alkali-silica reaction.

The behavior of the Type B fly ash containing 4.35 percent available alkalies shown in Figure 5.5., however, demonstrates that certain fly ashes are not adequate for use with reactive cement-aggregate combinations, regardless of the amount used. It should be noted that this fly ash did not cause adverse effects when used with nonreactive aggregates. The effects of alkali content of fly ashes and percentages of cement replacement with fly ash were studied further in Phase II of this program, and will be discussed in greater detail later in this chapter.

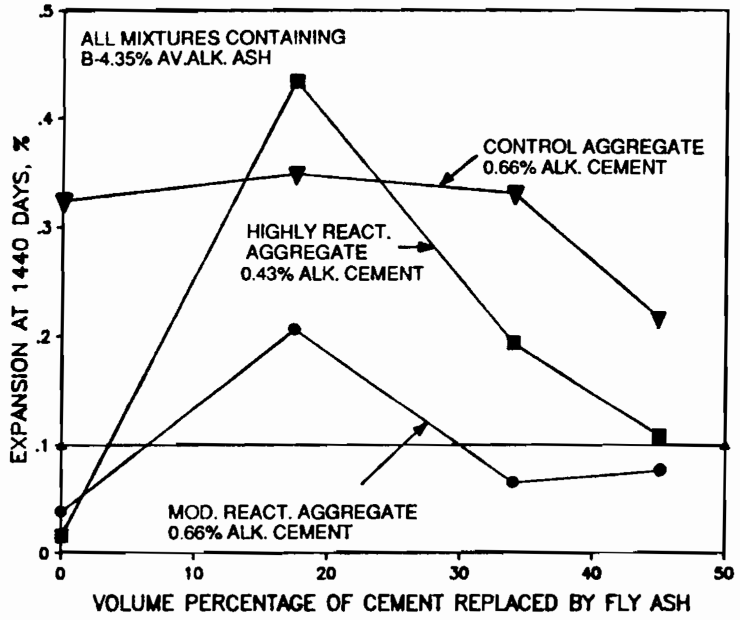
The fly ash incorporated into the production of Type IP cement served to inhibit alkali-silica reaction more effectively than fly ash added to concrete at the time of batching. Mixtures containing Type IP cement experienced negligible expansions between 90 days and 1440 days.



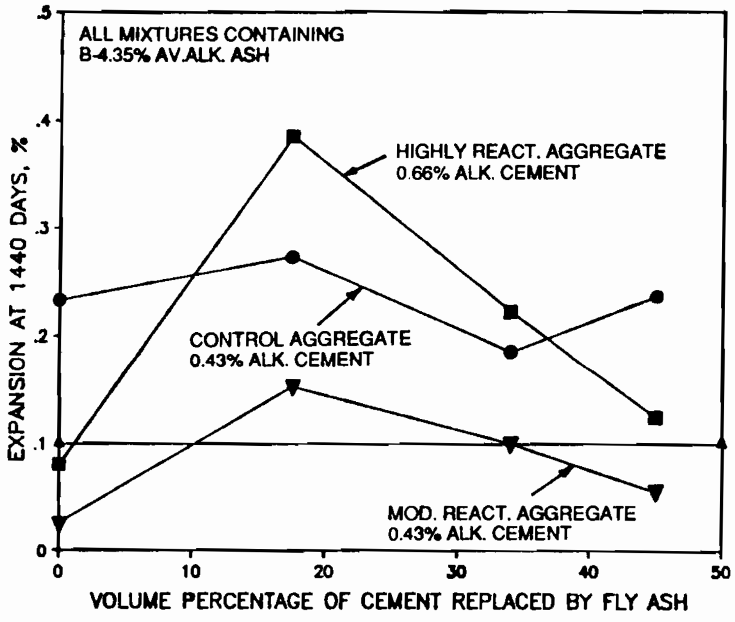
(a)

(b)

Figure 5.4 Effect of the amount of cement replaced by low alkali Type B fly ash



(a)



(b)

Figure 5.5 Effect of the amount of cement replaced by high alkali Type B fly ash

The desirable properties of this blended cement may have been due, at least in part, to the very low alkali contents of the fly ash and portland cement used. The available alkali content of the fly ash was only 0.31 percent, while the total alkali content of the cement was 0.53 percent. The increased fineness and blending of the cement and fly ash resulting from the intergrinding of the fly ash with the clinker could be another factor influencing the behavior of the Type IP cement. These characteristics of the blended cement were studied further in Phase II of this program and will be discussed again later in this chapter.

5.4 Phase II Results

5.4.1 Fly Ash Treated With a Chemical Precipitating Agent. This portion of the program was comprised of 24 mixtures, 12 containing a Type B fly ash treated with a chemical precipitating agent (sodium carbonate) and the other 12 containing a similar, but untreated, Type B fly ash. Twelve mixtures were fabricated with nonreactive aggregate and exhibited no expansive behavior. Of the 12 remaining mixtures which contained highly reactive aggregate, only those mixtures containing either fly ash as a replacement of 17.5 percent of the cement by volume expanded significantly. In these two cases, the mixtures containing the fly ash treated with the chemical precipitating agent expanded much more than the mixtures containing the untreated fly ash, as shown in Figure 4.12.

The difficulty in analyzing these results lies in the fact that there is no way to determine the amount of alkalies added to the fly ash by the precipitating agent or the availability of these alkalies to participate in deleterious reactions. The greater expansions of the mixtures containing the treated fly ash could have been due to the chemical agent or the 0.31 percent higher alkali content of the treated fly ash.

Only one mixture in this test program exceeded the ASTM 180-day expansion without exceeding the 90-day limit as well. This was a hgh. react. aggregate mixture, and contained the treated fly ash as a replacement for 17.5 percent of the low alkali cement by volume. However, this delayed reactivity did not appear to be related to the precipitating agent. Other mixtures containing this treated fly ash or

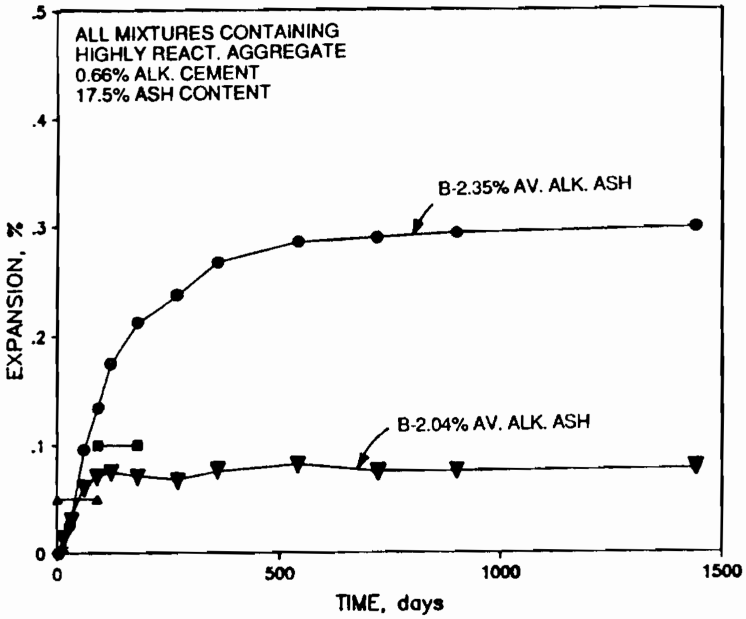


Figure 5.6 Expansion rates of mixtures containing fly ashes treated with precipitating agents

the medium-alkali fly ash used in Phase II, which was treated with a sodium sulfate fog, expanded much earlier, as shown in Figure 5.6.

The effect of these agents on the behavior of the two treated fly ashes cannot be discerned from these test results. Research is needed to determine the quantity of alkalies added to fly ash by these agents and their effect of the behavior of fly ash. With such knowledge, it can be determined if the benefits gained by using these agents outweigh the detrimental effects of the additional alkalies.

5.4.2 pH of Mixing Water. Four Phase I mixtures prepared with tap water were repeated in Phase II using a low pH distilled water. Mixtures containing highly reactive or nonreactive aggregate and high alkali cement without fly ash were much less expansive when prepared with distilled water instead of tap water, as indicated in Figure 4.13. The behavior of the other two pairs of mixtures indicated the water had very little effect.

The beneficial effect of the distilled water on the behavior of the mixture containing the highly reactive aggregate and high alkali cement was quite substantial, as was shown in Figure 4.13. According to the results of this test, the use of the low pH water would allow this potentially deleterious material combination to be used safely in the field, presumably by reducing the solubility of the silica in the aggregate.

Additional research could further delineate the role that the pH of mixing water has on alkali-silica reaction. Even without additional study, it would seem to be prudent for the concrete mixture designer to avoid using strongly basic water (pH ¿ 9) in conjunction with reactive siliceous aggregates whenever possible.

5.4.3 Available Alkali Content and Classification of Fly Ashes. One additional Type A fly ash was obtained for testing in Phase II. This fly ash had an available alkali content of 1.76 percent, which provided the opportunity to compare two Type A fly ashes having less than 1.5 percent alkalies with one having in excess of 1.5 percent alkalies.

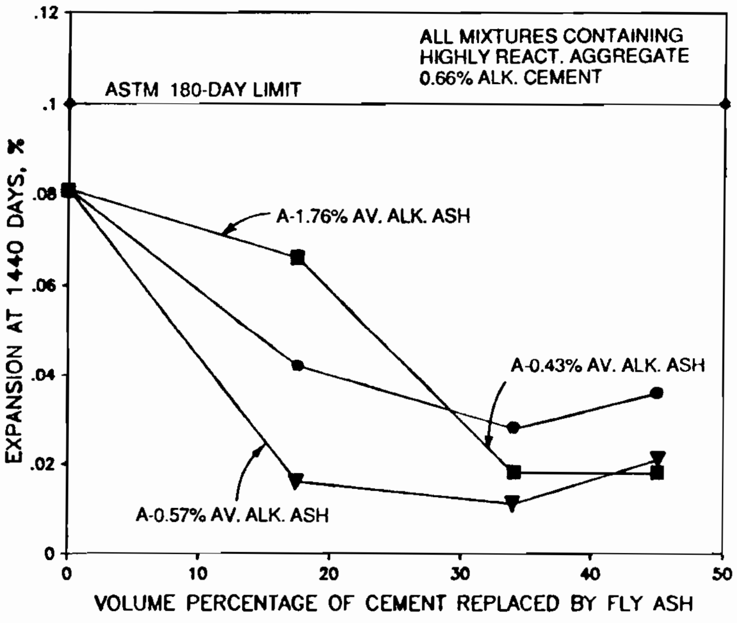


Figure 5.7 Effect of the alkali content of Type A fly ashes

The results, summarized in Figure 5.7, indicate that each fly ash was very effective in inhibiting expansions in mixtures containing the highly reactive aggregate and high alkali cement. The differences in the alkali contents of these fly ashes did not have a significant effect on the magnitude of the expansions. From these results, it appears that the ASTM limit of 1.5 percent available alkalies is not applicable.

The addition of the third Type A fly ash to the testing program also allowed the comparison of Type A and Type B fly ashes with similar alkali contents. The Type A fly ashes had alkali contents of 1.38 percent and 1.76 percent and the Type B fly ash contained 1.67 percent alkalies. The results, which were summarized in Figures 4.14 and 4.15, indicated that these fly ashes, in general, were equally effective. However, the Type B fly ash was significantly deleterious when used at a 17.5 percent replacement level in mixtures with highly reactive aggregate. From these results it becomes apparent that factors other than the alkali content of a fly ash influence its behavior with respect to alkali-silica reaction.

Also studied in this portion of the project were three Type B fly ashes having different alkali contents. A fly ash containing 3.75 percent available alkalies was tested in Phase II to correspond with Phase I mixtures containing Type B fly ashes with available alkali contents of 1.67 percent and 4.35 percent. The medium alkali fly ash behaved quite similarly to the high alkali fly ash except at a 17.5 percent replacement percentage. When used at that proportion, the high alkali fly ash resulted in much greater expansions.

In all, eight different fly ashes were tested in mixtures containing highly reactive aggregate and low alkali or high alkali cement. Figure 5.8 illustrates the effect that the alkali content of these fly ashes had on the expansions of these mixtures. These graphs show that expansions generally became greater as the alkali content of the fly ash increased. Expansions tended to increase sharply for alkali contents exceeding 2.0 percent.

Several studies which were discussed in Chapter 2 dealt with the effect of calcium on alkali-silica reaction. Bhatty[10] reported that pozzolanas reduce or eliminate alkali-silica reaction by converting $Ca(OH)_2$ to C-S-H and reducing the ratio of calcium to silica in existing C-S-H, which allows it to incorporate more

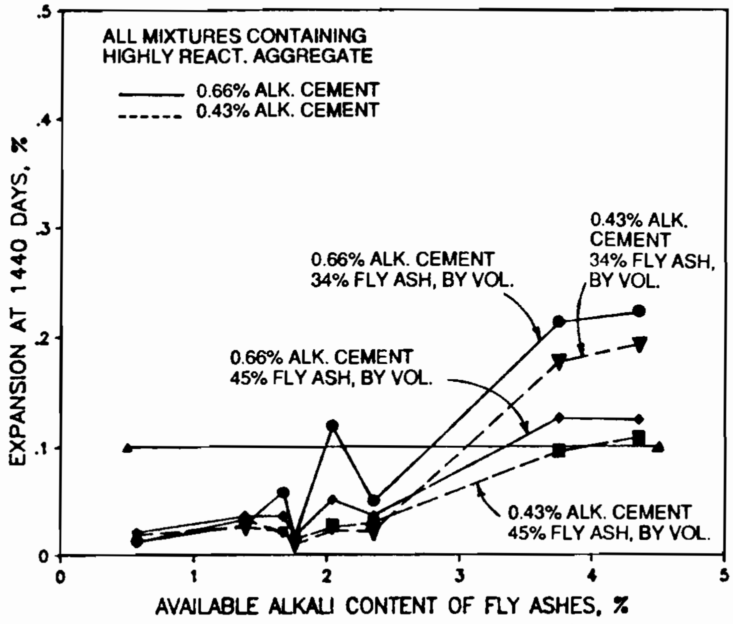


Figure 5.8 Effect of the alkali content of fly ashes

alkalies into its structure. The lower the calcium content of the fly ash, the more effective it will be in inhibiting expansions.

Figure 5.9 shows the CaO content of each of the eight fly ashes whose behavior was illustrated in Figure 5.8. From this graph it can be seen that the CaO content of these fly ashes is independent of the alkali content. From the comparison of Figures 5.8 and 5.9, the available alkali content appears to have more influence on the behavior of a fly ash than the calcium oxide content. However, of the five fly ashes with alkali contents clustered in the range of 1.38 percent to 2.35 percent, those with the higher calcium oxide contents tended to promote greater expansions.

5.4.4 Total Alkali Content of Cement. To further study the effect of alkalies in cement on mortar bar expansions, a cement with a total alkali content of 1.03 percent was obtained for testing in this phase of the program. A comparison of the expansions of the eight mixtures containing this cement with corresponding mixtures containing the high alkali cement used throughout this program was presented in Figure 4.18. Not surprisingly, the mixtures containing the "very high" alkali cement expanded more.

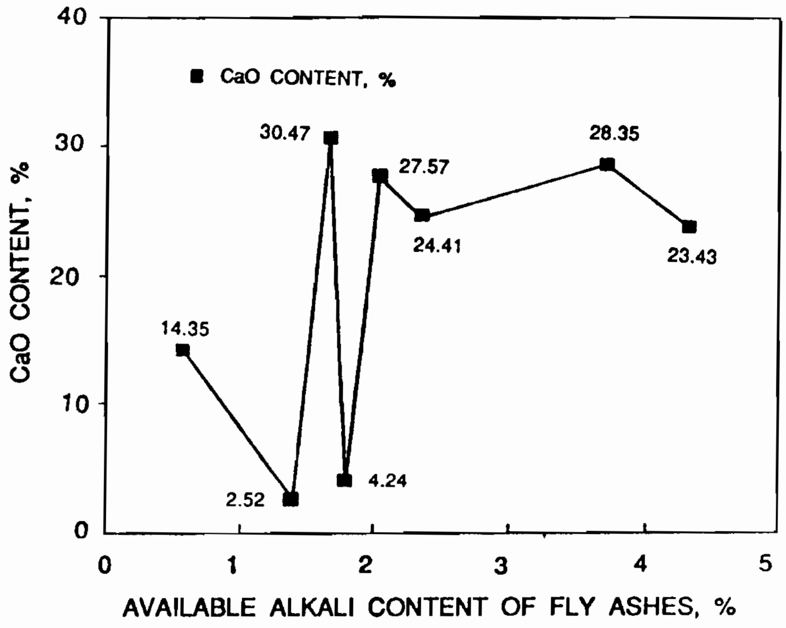


Figure 5.9 Relationship between the alkali content and calcium oxide content of the test fly ashes

While the cement containing 0.66 percent total alkalies was determined to be adequate for use with the moderately reactive aggregate and only questionably deleterious when used with the highly reactive aggregate, the cement containing 1.03 percent total alkalies proved to be unacceptable for use with the highly reactive aggregate. However, this cement-aggregate combination could be used if at least 34.3 percent of the cement, by volume is replaced with the Type B fly ash having 1.67 percent available alkalies as shown in Figure 5.100. These results indicate again that reactive materials can be combined in concrete if careful attention is given to the selection and proportions of the materials used.

Earlier in this chapter the ASTM standards for alkalies in cement and fly ash were discussed in terms of the results of this test program. The alkali contents of the materials were related to the behavior of the test specimens without regard to the proportion of each alkali-bearing material used in the mortar or the combinations of alkali-bearing materials in the mixture.

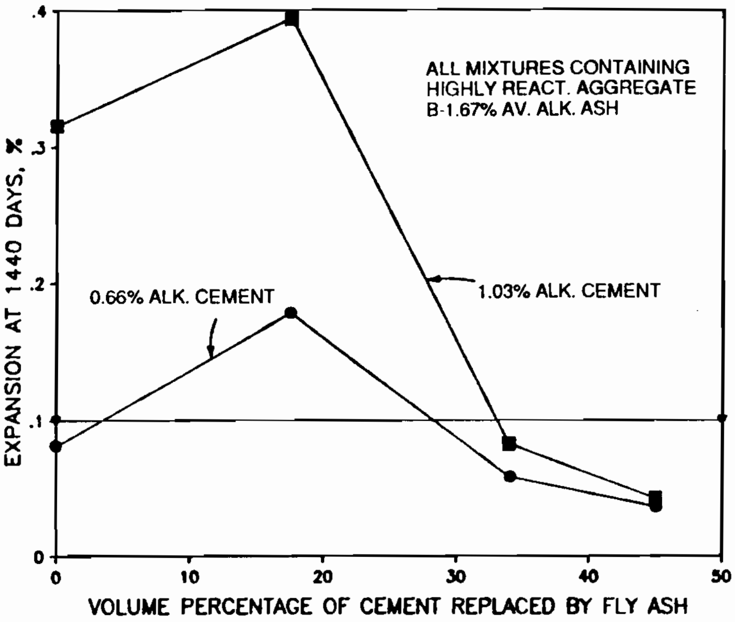


Figure 5.10 Effect of the alkali content of cement

The current practice in Denmark and West Germany[11] involves limiting the weight of total alkalies per unit volume of concrete, based on the reactivity of the aggregate. The quantity of alkalies in the concrete is considered to be a function of the alkali content of the cement and the cement content of the concrete. Neither the presence of mineral admixtures nor the effect of their alkalies are addressed in this method.

To determine the effect of alkalies from fly ash and water, as well as cement, the combined weight of the total alkalies in the cement and water and the available alkalies in the fly ash has been calculated for each batch of mortar prepared for this program. The contributions of alkalies from the tap water and distilled water used in this program were negligible. Figure 5.11 contains a series of graphs comparing the weight of alkalies per unit volume of mortar to expansions.

These graphs reveal that mixtures containing similar quantities of alkalies did not experience similar degrees of expansions. Since each of these mixtures would have contained different proportions of alkalies from the cement, water, and fly ash, the results indicate that the alkalies from each source vary in their effects on

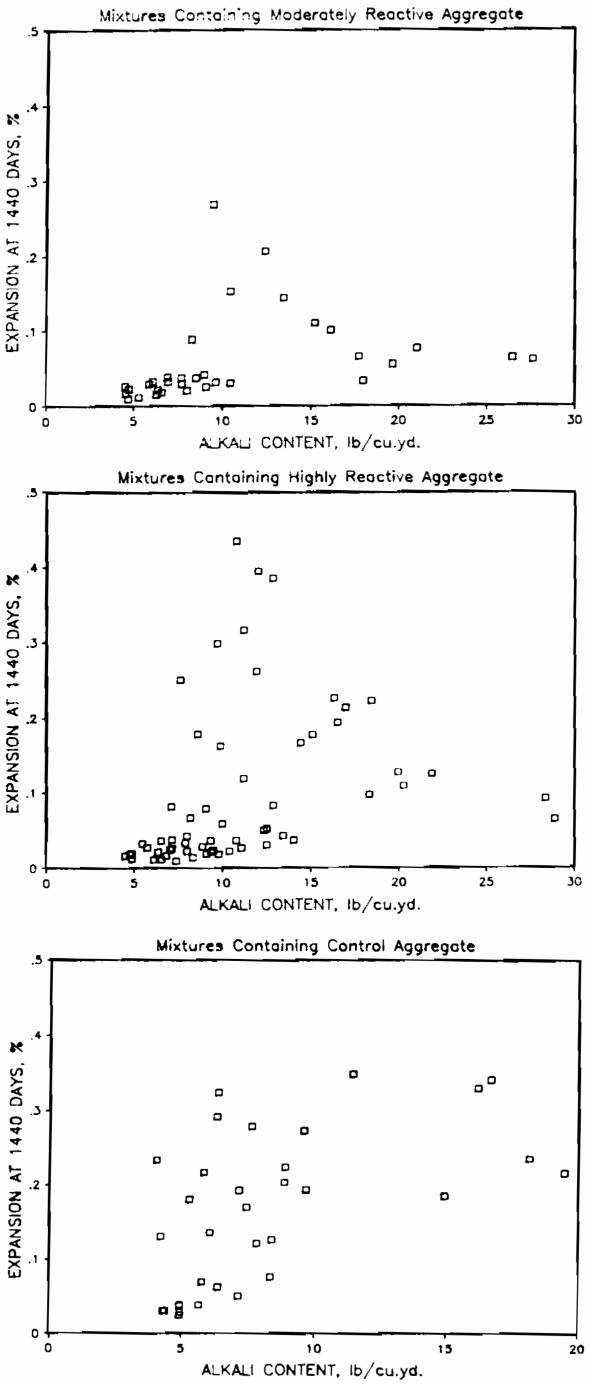


Figure 5.11 Expansions vs. quantity of alkalies provided to mortar by cement and fly ash

expansions. Attempts to derive some sort of relationship between the relative effects of the alkalies from each source needs to be studied further.

Several factors complicate this relationship. As the amount of fly ash in a mixture increases, the effect of the alkali contributed by the fly ash is increasingly offset by the ability of the fly ash to produce C-S-H which can incorporate alkalies into its structure. Another factor is the pessimum propor- tions of the aggregates. As the alkali content fluctuates, the pessimum proportion, likewise varies. Thus, increases in the alkali content of the concrete could, in some instances, result in decreases in expansion. Another factor is the degree of availability of the alkalies derived from each source. Soluble and insoluble alkalies in cement may not be equally effective. Alkalies present in cement may not be equally active in comparison to alkalies contained in fly ash. Other factors, such as the fineness of the materials and the quantity of CaO in the fly ash, may have a bearing on these results.

It is interesting to note that the maximum expansions occurred in mixtures containing from roughly 7 to 15 pounds of alkalies per cubic yard of mortar, or from 4.2 to 8.9 kg/m^3. This range appears to encompass the pessimum limit of alkalies for these aggregates. Studies in Europe and Australia[12] have indicated that damaging expansions in concrete are likely to occur when alkalies are present in amounts greater than 4 kg/m^3. This relates well to the results presented in Figure 5.11, even though the quantities of alkalies shown in the figure are the combined totals from the cement, fly ash, and water.

Alkalies are not the only constituents of cement which participate in reactions with siliceous aggregates. $Ca(OH)_2$ has been found to contribute to alkali-silica reaction by providing hydroxide ions, which break silicon- oxygen bonds in siliceous aggregates. The amount of $Ca(OH)_2$ produced during cement hydration is dependent on the amounts of C_2S and C_3S present in the cement. The reaction of C_3S with water produces three times more $Ca(OH)_2$ than is produced by an equal amount of C_2S. It follows that high C_2S cement is preferable for use with reactive aggregates.

Table 5.1 shows the C_2S and C_3S contents of the Type I cements used in this project and the relative amounts of $Ca(OH)_2$ produced by equivalent amounts of each cement. The three Type I cements with the lowest total alkali contents contained more C_3S and less C_2S than the typical cements listed, suggesting that these cements might be more deleterious than other cements of equal alkali contents. The very high alkali cement, on the other hand, contained a smaller quantity of C_3S, but more C_2S, than the typical cements. The actual effect of the C_2S and C_3S contents of these cements cannot be determined since cements of equal alkali contents would have to be compared.

Table 5.1 C_2S and C_3S contents of cements used in test program

Alkali Content, percent	C_2S Content, percent	C_3S Content, percent	Relative Amount of $Ca(OH)_2$ Produced
1.03	21.43	47.95	1.00
0.66	13.68	56.86	1.11
0.50	15.57	58.31	1.16
0.43	11.54	61.14	1.18
Typical Cement Reported by Mindess & Young[4]	25.00	50.00	1.06
Reported by Neville[29]	16.60	54.10	1.08

5.4.5 Percentage of Cement Replaced with Fly Ash. Two additional percentages of cement replacement were studied in this portion of the program. Mixtures containing fly ash as a replacement, by volume, for 26 percent and 62.5 percent of the cement, were found to have several trends and were noted in the initial phase of the program.

Mixtures containing Type B fly ash at a 17.5 percent replacement level were typically much more expansive than corresponding mixtures containing no fly ash or fly ash at a 34.3 percent replacement level. A replacement level of 26 percent was studied to observe the trend of expansions for replacements between 17.5 and 34.3 percent. The results, which were presented in Figure 4.19 revealed the 26 to be comparable to the 34.3 percent replacement level in effectiveness. Subsequent increases in replacement beyond 34.3 percent had much less effect on expansions.

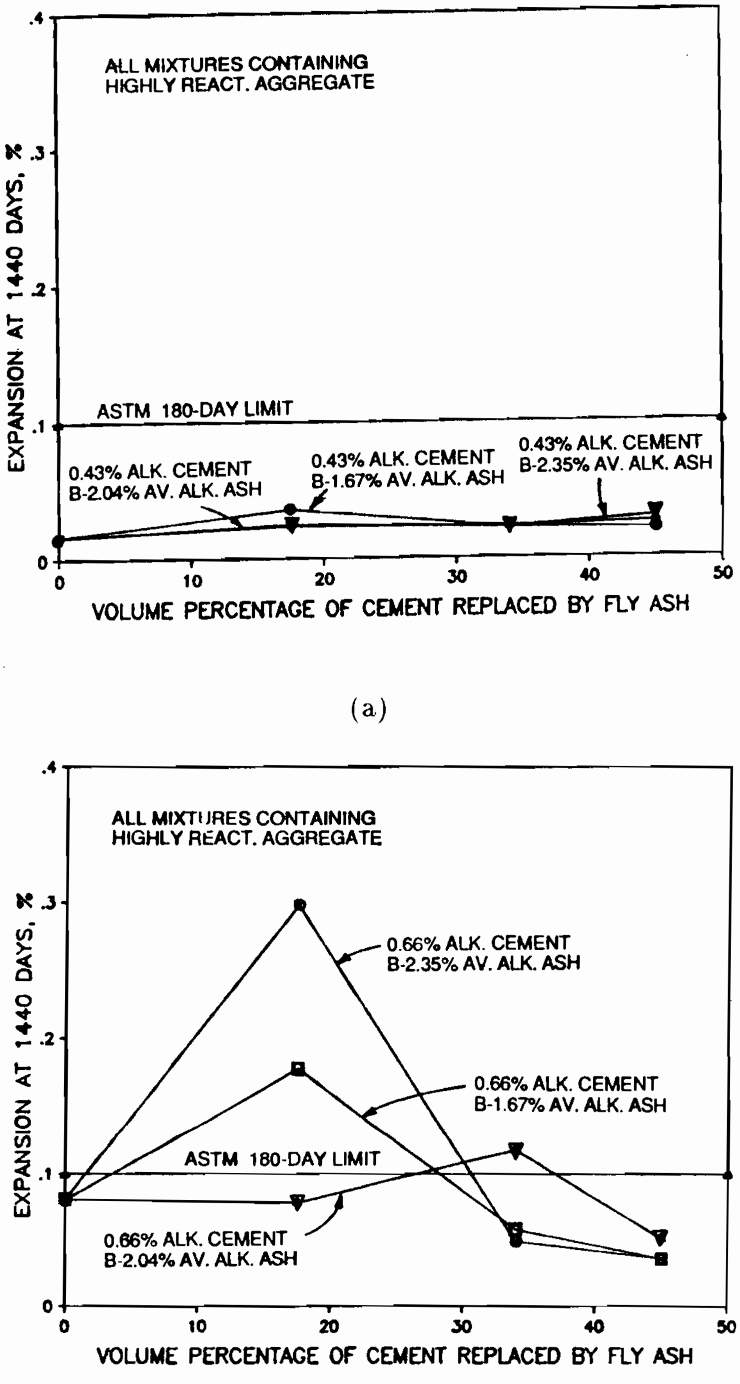
Based on these results, it appears that increasing the percentage of replacement as little as 10 percent beyond the pessimum value is sufficient to obtain satisfactory results. Increasing the proportion of fly ash beyond this level provides diminishing benefits.

Of the four groups of mixtures studied in this part of the program, one exhibited the trend of slightly greater expansions with 45 percent replacement than with 34.3 percent replacement. At 180-days exposure testing, the results shown in Figure 4.19, indicated that this group of mixtures containing moderately reactive aggregates and high alkali cement, along with another group of mixtures containing the same aggregate and low alkali cement, experienced increased expansions with 62.5 percent replacement. The amount of the increase however, was not significant enough to warrant concern about a second pessimum proportion of replacement. Moreover, as observed in Figure 4.19, these increased expansions were completely negligible after 1440 days exposure testing. Based on theses results, a limit on the maximum amount of cement replaced by fly ash would not be necessary.

The replacement level of 17.5 percent was also a pessimum value for mixtures containing two of the three Type B fly ashes, which had alkali contents at or below 2.35 percent. As seen in Figure 5.12, increasing the proportion of replacement to 34.3 percent reduced expansions below those of the corresponding mixtures without fly ash.

5.4.6 Replacement of a Portion of Aggregate with Fly Ash. In an attempt to achieve a very high amount of alkalies in a mortar mixture, an amount of aggregate equal to 30 percent of the volume of cement was replaced by fly ash in four Phase II mixtures. This not only provided an increased amount of alkalies to each mixture, but also reduced the amount of silica, greatly increasing the alkali to silica ratios of these mixtures.

These mixtures can be compared to four similar Phase I mixtures in which 28 percent of the cement, by weight, was replaced by the same fly ash. In three of four cases, the mixture in which the aggregate was replaced was much more expansive than the corresponding mixture in which the cement was replaced. In the other instance, the mixture in which the aggregate was replaced expanded much less.



(a)

(b)

Figure 5.12 Pessimum effect of several Type B fly ashes at a 17.5 percent replacement level

To gain insight into the behavior of these mixtures, knowledge of the alkali-silica ratios of these mixtures would be needed. The exact ratio for each mixture could not be determined due to several factors:

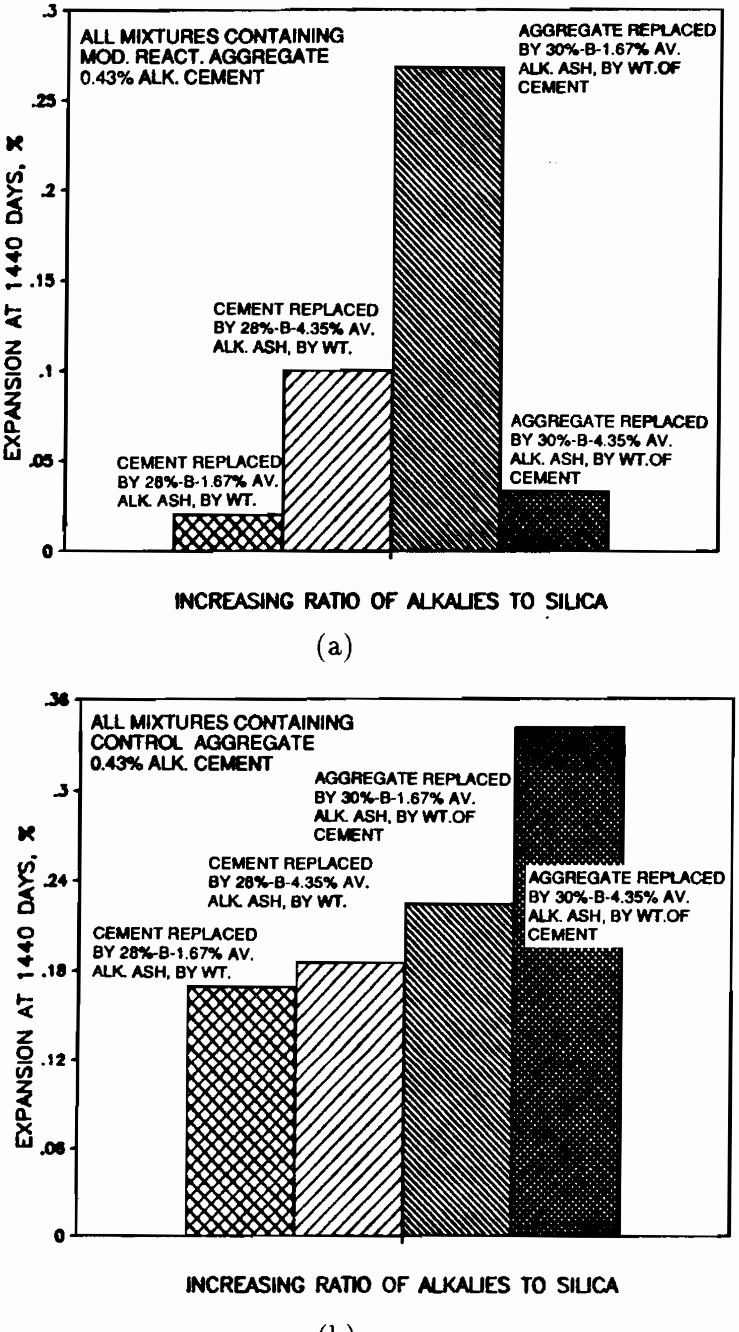
1. the exact quantity of silica in the aggregates was not known,
2. the relative effect of the alkalies provided by the cement and fly ash could not be compared, and
3. the effect of the fly ash on the incorporation of alkalies into the structure of the C-S-H could not be determined.

The relative ratios of alkalies to silica could, however, be estimated for mixtures containing the same aggregate.

The mixture in which cement was replaced with the low alkali Type B fly ash would have the lowest quantity of alkalies and the greatest quantity of silica, resulting in the lowest alkali-silica ratio. Because the alkalies in fly ash do not appear to be equal in reactivity to those found in cement, and since only 28 percent of the cement, by weight, was replaced in these mixtures, it can be assumed that the alkali-silica ratios of these mixtures were increased only slightly by the use of the high alkali, rather than low alkali Type B fly ash. A much greater increase in the alkali-silica ratio was likely to be afforded by the replacement of 30 percent of the aggregate with the low alkali Type B fly ash. The largest ratio would result from replacing the aggregate with the high alkali Type B fly ash.

Figure 5.13 shows the expansions for mixtures containing the same aggregate in order of the estimated alkali-silica ratios. For the mixtures containing moderately reactive aggregate, expansions increased the higher the alkali-silica ratio except for the mixture having the highest ratio, which experienced the smallest expansion. This seems to indicate that the second highest alkali-silica ratio was near the pessimum value. Increasing or decreasing the alkali-silica ratio from this value would result in smaller expansions.

For mixtures containing the control aggregate, expansions remained constant or increased as the alkali-silica ratio increased. The pessimum alkali- silica ratio for this aggregate was apparently higher than the ratios of any of these mixtures.



(a)

(b)

Figure 5.13 Influence of the ratio of alkalies to silica in mortar bars on expansions

From these results it can be seen that replacing 30 percent of an aggregate, by weight, with fly ash could aggravate alkali-silica reaction by adversely affecting the ratio of alkalies to silica in the concrete. This would particularly be true in mixtures containing highly-reactive aggregates and low alkali cements. In these cases, the alkali-silica ratio could be boosted from a safe to a deleterious level. On the other hand, expansion could be reduced if the alkali-silica ratio was raised sufficiently beyond the pessimum value.

This portion of the study highlights the critical nature of the ratio of alkalies to silica in concrete, which is reflected in the ratio of cement to aggregate used. The standard ratio of cement to aggregate of 1:2.25 by weight specified in ASTM C 227, allows valid comparisons to be made between results obtained from any performance of this test. However, this standard ratio may not accurately represent the proportions of materials used in the field, meaning results from the mortar bar test may not be indicative of the behavior of concrete in the field.

5.4.7 Effect of Fineness and Preblending of Type IP Cement. As mentioned in the discussion of the Phase I results, the Type IP cement used in this project proved to be much more effective in inhibiting expansions than the other cement-fly ash combinations tested. Two mixtures were made in this part of the project using the same cement and fly ash used to produce the Type IP cement. The intent was to determine if the materials used in the Type IP cement, or its fineness or preblending were responsible for its superior performance.

The superior performance of the Type IP cement was shown in Figure 4.21. Two mixtures containing the cement and fly ash used in the IP cement were prepared during Phase II. The cement and fly ash used in one mixture were mechanically blended before batching to simulate the blending received by the Type IP cement during the grinding of the fly ash and clinker. The results shown in Figure 4.21 indicate that the Type IP cement was more effective than the cement-fly ash mixtures. The two cement-fly ash mixtures behaved similarly, indicating that additional preblending of the cement and fly ash such as that received by the Type IP cement had no effect on its performance. Since both cement-fly ash mixtures expanded more than the Type IP mixtures, the increased fineness of the fly ash in

Type IP cement, due to fly ash-clinker intergrinding, appears to be the factor enhancing its effectiveness in inhibiting expansions. This was investigated in Phase III of this project and will be discussed later.

5.4.8 Effect of Silica Fume. Silica fume has been used successfully in a number of cases as an inhibitor of alkali-silica reaction in concrete. One silica fume was used as a partial replacement for cement in 15 Phase II mixtures.

Complete information on the composition of this silica fume was not received. The data provided by the producer was only sufficient to determine that this silica fume could have belonged in five of the seven categories of silica fume presented in Table 2.2. Obtaining detailed information on the composition of silica fume is important, as some contain a substantial amount of alkalies or possess unusual characteristics such as those described in Table 2.3.

In each mixture tested, the silica fume reduced expansions to a greater degree than any of the fly ashes tested, and far below the ASTM limits of expansion. The beneficial effect of the silica fume was particularly noticeable in the mixtures containing the control aggregate and high alkali cement, as shown in Figure 5.14.

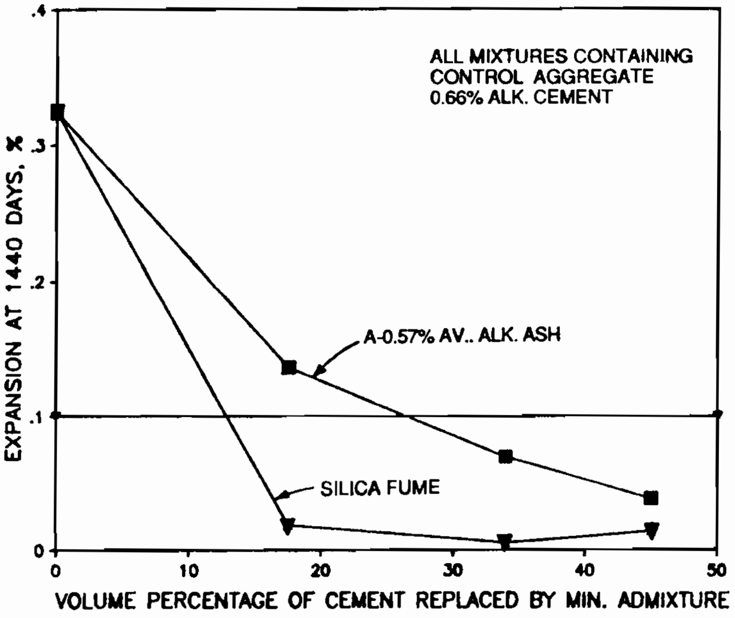


Figure 5.14 Comparison of silica fume and fly ash as a partial replacement for cement

Other studies[45] have shown that the replacement of as little as 7 percent of cement with silica fume is sufficient to inhibit deleterious expansions. Since the use of silica fume at a 17.5 percent replacement level allowed almost no expansions of any magnitude, it is possible that the use of a smaller proportion of silica fume with these materials would have produced satisfactory results, as well.

The use of silica fume in this program may, in fact, have been too successful as a majority of the mixtures experienced net shrinkages at 180 days of as much as 0.022 percent as shown in Figure 5.15. Although no correlation between mortar bar shrinkage and damage to structures has been developed, it is conceivable that shrinkage of this magnitude could be indicative of the potential for damage to structures resulting from subsequent contraction and cracking of members.

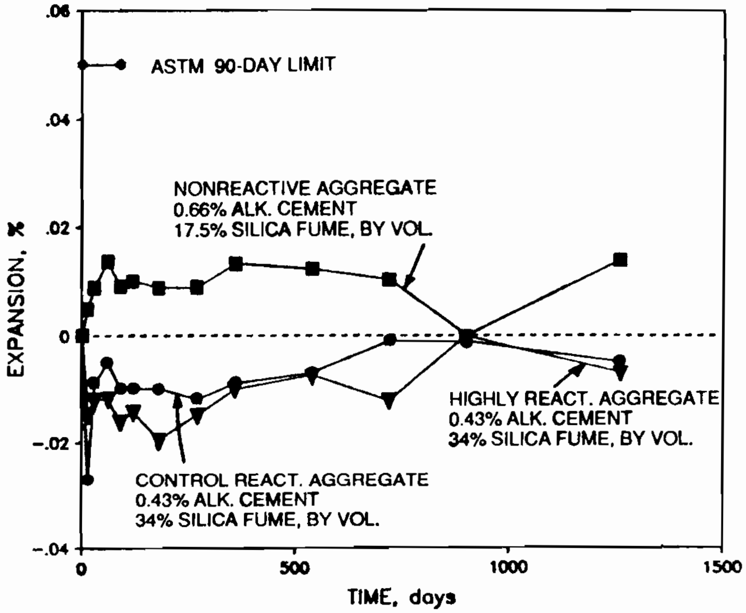


Figure 5.15 Shrinkage of mixtures containing silica fume

Another area of concern in this study was the high water demand of mixtures containing silica fume. The water to binder (cement plus mineral admixtures) ratio for mixtures containing silica fume ranged from 0.53 to 1.07. The amount of water required for silica fume mixtures could be reduced by using the least amount of silica fume required to control expansions and by using superplasticizers.

5.5 Phase III Results

As discussed in section 5.4.7, the superior performance of Type IP cement was believed to be a consequence of the increased fineness of both fly ash and cement as a result of the clinker-fly ash intergrinding during the Type IP manufacturing process. However, the test results of this Phase failed to substantiate the claim that the finer the fly ash, the more effective it is in reducing alkali-aggregate reaction related expansions for three out of the four fly ashes tested.

The test results for the B-0.96% av. alk. fly ash were illustrated in Figure 4.23. This figure showed that expansions increased as the 325S increased, regardless of the amount of cement replaced; i.e., the finer the fly ash, the more effective it is in reducing alkali-aggregate reaction related expansions.

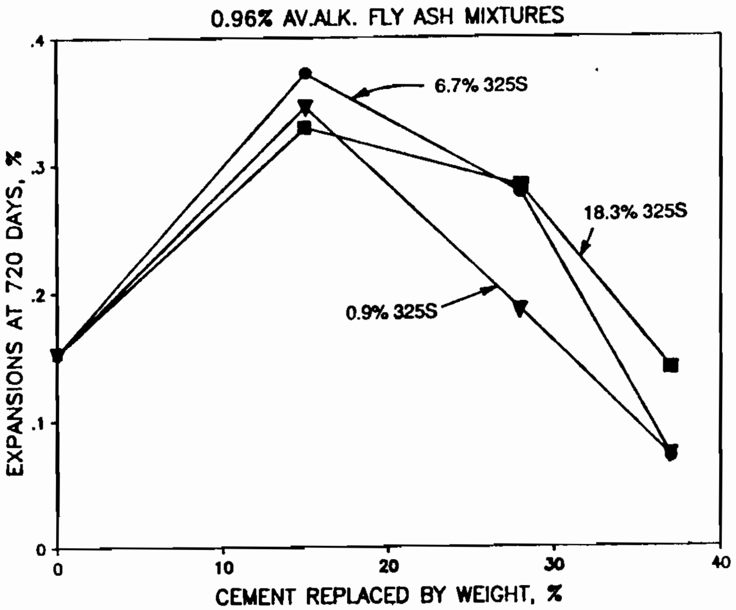


Figure 5.16 Effect of the amount of cement replaced by the fly ash containing 0.96 percent available alkalies on expansions

In Figure 5.16, these results are plotted in terms of the amount of cement replaced by weight. During Phase I, fly ash from this same source exhibited a "pessimum limit" in mixtures containing the 0.66 percent total alkalies cement. It is not surprising then to see that this fly ash exhibits a "pessimum range", with its peak also at about 15 percent fly ash replacement by weight, when combined with the 1.03 percent total alkalies cement. Moreover, regardless of the fineness level, the fly ash replacement causes increases in expansions with respect to the mixture containing no fly ash for both 15 and 28 percent replacement. It is only when 37 percent of the cement weight is replaced by fly ash that the expansions are reduced below those of the reference mixture. It is also clear from this graph, that the behavior of the fly ash, in terms of the different fineness levels, become distinct only when replacing cement at a rate of 28 percent or more.

Test results for the second fly ash tested were presented in Figure 4.24. No correlation was found from this data between expansions and fineness of fly ash. While the finer fly ash caused the greater expansions when replacing 15 percent of the cement weight, it caused the smaller expansions at a 37 percent replacement rate, and an intermediate expansion at a 28 percent replacement rate. Only at 37 percent replacement rates did the expansions consistently decreased by an increase in fineness. Figure 5.17 shows these test results in terms of the amount of cement being replaced. A "pessimum range" is also observed for this fly ash. In this case, the "pessimum limit" lies at about 28 percent fly ash replacement.

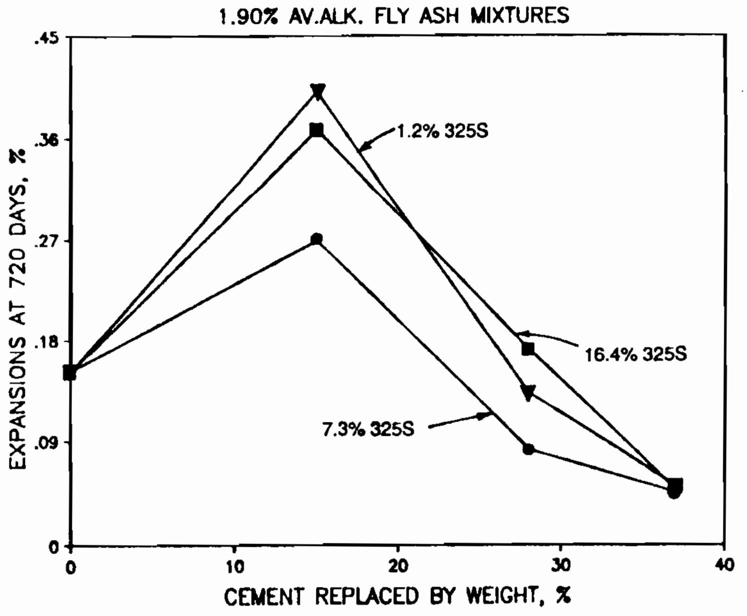


Figure 5.17 Effect of the amount of cement replaced by the fly ash containing 1.90 percent available alkalies on expansions

The third fly ash, B-3.73% av. alk., exhibited similar trends as the second fly ash but at higher expansion levels, as illustrated in Figure 4.25. Again, only at a 37 percent replacement rate was it observed that the finer the fly ash, the smaller the mortar bar expansions. Figure 5.18 shows that all of the fly ash percentage of replacement resulted in increased expansions with respect to the reference mixture containing no fly ash.

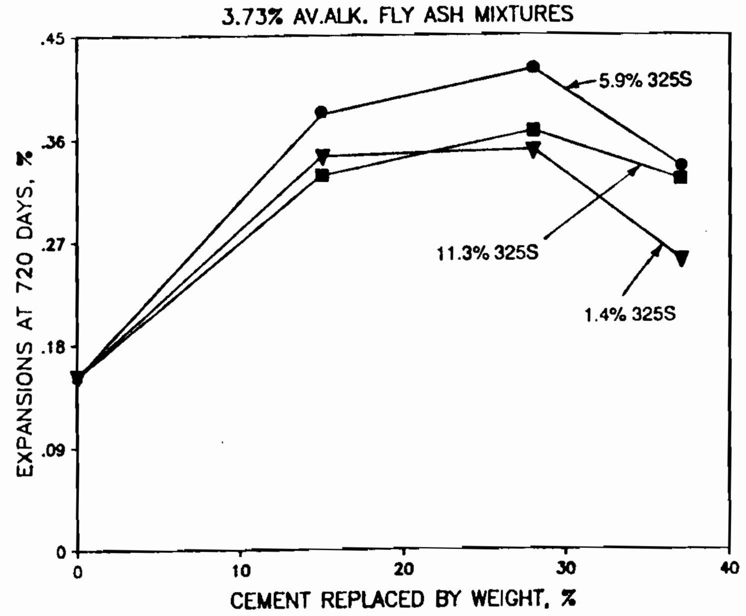


Figure 5.18 Effect of the amount of cement replaced by the fly ash containing 3.73 percent available alkalies on expansions

Finally, the B-4.35% av.alk. fly ash test results, which were presented in Figure 4.26, also show inconsistencies between fineness level and degree of expansions. Only the 28 percent replacement rate showed reduced expansions as the fineness of the fly ash was increased. Figure 5.19 shows that for this case a "pessimum limit" occurs at about 28 percent fly ash replacement.

In light of these results, the assumptions presented in section 2.3.4 pertaining to the effect that fly ash fineness might have on alkali-aggregate reaction were reviewed. In the first place, the literature reports that "...the resultant deviation of the values was less than 3 percent for specified ranges of a maximum of 12 percent LOI and a maximum of 20 percent 325S" for properties such as water

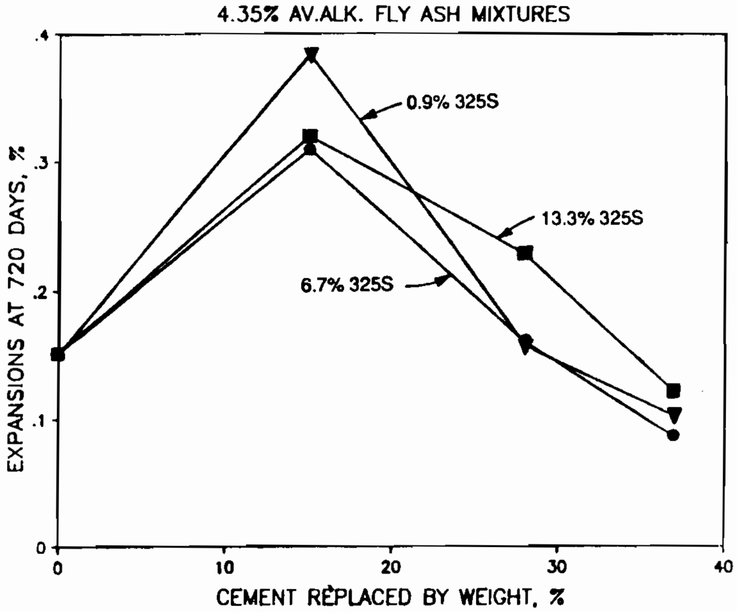


Figure 5.19 Effect of the amount of cement replaced by the fly ash containing 4.35 percent available alkalies on expansions

requirement. The fly ash tested in this Phase had an original fineness of less than 20 percent 325S which could partially explain the differences in results and, therefore, the inconsistencies observed.

On the other hand, while it is true that a finer fly ash reacts more rapidly and more thoroughly possibly enhancing the beneficial effects of the pozzolanic reaction, it is also true that a finer fly ash possibly releases alkalies in a faster, more complete manner. In the case of a Type IP cement, in which the cement and fly ash have a low content of alkalies, 0.50 and 0.31 percent, respectively, the effect of a more rapid release of these low alkali content was probably outweighed by the beneficial effects of the increased pozzolanic reaction. In the case of the mixtures tested in this Phase of the study, the cement had a very high content of alkalies of 1.03 percent, and the fly ashes, all Type B, had alkali contents of as much as 4.35 percent. The effect of these alkalies probably outweigh any possible beneficial effect coming from the pozzolanic reaction.

CHAPTER 6
SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

6.1 Summary

The objective of this study was to determine the influences of the constituents of portland cement, aggregates, and mineral admixtures on alkali- silica reaction.

This testing program has included:

- 3 natural aggregates and Pyrex glass (control),
- 3 Type I and 1 Type IP cements,
- 4 Type A and 5 Type B fly ashes,
- Tap and Distilled (low pH) Water, and
- 1 Silica Fume.

ASTM C 227 was the primary guideline for the evaluation and comparison of these materials, most of which are available for use in highway projects in the state of Texas.

The results of this testing program demonstrated that:

1. each of the natural aggregates studied can be used safely in concrete without mineral admixtures, if the cement is chosen carefully with respect to alkali content,
2. each of the cements tested can be used in concrete with any of the aggregates tested, if a suitable mineral admixture is used as a partial replacement for cement in the proper proportion,
3. the silica fume and seven of the nine fly ashes tested reduced expansions significantly when used in proper proportions as partial replacements for cement, and
4. fineness of Type B fly ash does not affect significantly its effectiveness in reducing alkali-aggregate related mortar bar expansions.

6.2 Conclusions

Of the conclusions drawn from the 90-day results of the first phase of this study[53], the following were found to be valid on the basis of the 1440-day test results described herein:

1. The 0.6 percent limit set up by ASTM C 150 for the alkali content of cement cannot be used as the only measure to prevent damage to concrete due to alkali- aggregate reaction.
2. The main variable affecting alkali- aggregate reaction in concrete containing no fly ash is the amount of alkalies contained in the cement.
3. The degree of alkali-aggregate reactivity of concrete mixtures increases when the alkali content of the cement increases.
4. The replacement of a portion of cement with fly ash is an effective measure to reduce the expansion in concrete due to alkali-aggregate reaction.
5. The available alkalies contained in the fly ash do participate in the alkali-aggregate reaction in concrete, regardless of fly ash type.
6. When the available alkali content of fly ash is less than 1.7 percent, its beneficial effect in preventing expansion due to alkali-aggregate reaction increases as the percentage of cement replaced increases, regardless of fly ash type. Consideration must be given to other factors such as proportions.
7. As the available alkali content of fly ash increases, there is a minimum percentage of cement replaced below which the fly ash causes expansions larger than those of a mixture without fly ash, and above which the fly ash causes smaller expansions. This minimum is known as the pessimum limit.
8. For fly ash mixtures which exhibit a pessimum limit, the lower the available alkali content of the cement the higher the pessimum limit, and vice-versa.
9. Minimum percentage of replacement, rather than the 1.5 percent maximum available content specified by both ASTM and TSDHPT, is the factor defining the effectiveness of fly ash replacement to prevent deleterious expansions in concrete due to alkali-aggregate reaction.

10. The minimum period of time to conduct the ASTM C 227 to provide accurate information is 90 days.

From the results of Phase I updated through 1440 days and the 1440-day results obtained from the second phase of the program, these additional conclusions have been drawn:

1. The ASTM 90-day expansion limit for mortar bars of 0.05 percent has merit as a quick and conservative guideline, possessing just a slight risk of overlooking deleterious material combinations.
2. The limit of 0.60 percent total alkalies in cement used with reactive aggregates stated in ASTM C 150 is not reliable, as it is too low in some circumstances and too high in others.
3. Substituting a less reactive aggregate for one that is more reactive may cause greater, rather than smaller expansions. The concrete designer should not only consider the properties of each material used in concrete, but also how the materials will respond when used in combination.
4. The recommended limit of 1.5 percent available alkalies in fly ash used with reactive cement-aggregate combinations stated in ASTM C 618 does not accurately reflect the behavior of fly ash with respect to alkali-silica reaction. The calcium content of a fly ash and the percentage of cement replaced by that fly ash, as well as its available alkali content, influence its behavior.
5. The ratio of alkalies to silica in concrete seems to play a critical role in the degree of expansion of concrete due to alkali-silica reaction. The ratio of cement to aggregates, by weight, specified in ASTM C 227 for mortar bars could lead to misleading test results if different proportions of cement and aggregate are used in the field.
6. The calculation of the total quantity of alkalies per unit volume of concrete is not a useful and realiable tool for use in concrete containing fly ash, since the alkalies contained in cement and fly ash are not equally reactive and the proportion of fly ash used influences the magnitude of expansions.

7. The greater fineness and dispersion of the fly ash in Type IP cement and not the additional blending of the cement and fly ash, appears to be the factor enhancing its inhibiting effect on alkali-silica reactions.
8. The silica fume tested in this program was more effective in inhibiting expansions than any of the fly ashes which were tested.

Test results from Phase III lead to the conclusion that there is not a consistent correlation between the variability of Type B fly ash fineness, within the ASTM limits, and mortar bar expansions. Hence, conclusion seven of Phase II remains to be substantiated by experimental data. Test results from Phase III confirmed the existence of a "pessimum range" of values for Type B fly ashes, when combined with reactive aggregates and high alkali cements.

As a result of this study, the following guidelines are recommended for the selection of materials and their proportions in order to ensure a reduction in potential alkali-aggregate reaction.

1. If the fly ash is a TSDHPT Type A fly ash containing less than 1.7 percent available alkalies and less than 10 percent CaO, it can be used at any cement replacement level in cement.
2. For all other fly ashes, the fly ash should not be used in concrete at cement replacement levels of less than 25 percent by volume. Preferably, ASTM C 227 mortar bar expansion tests should be conducted using the proposed materials and proportion for a job in order to determine the adequacy of the 25 percent minimum replacement lower limit.

6.3 Recommendations for Future Research

Alkali-silica reaction is a complex, challenging problem facing concrete designers. This report has addressed several of the topics related to this phenomenon. Related topics which would be of interest for further study are presented below.

1. To address the concerns of many researchers regarding the validity of ASTM C 227, further tests involving mortar bars and larger specimens should be conducted. The results obtained should be compared with the results obtained from full scale specimens in the field.

2. Many proposed tests for the determination of the alkali-silica reaction potential require much less time to conduct than ASTM C 227. Studies to determine if any of these tests are valid and easily adaptable to general usage are needed.

3. Guidelines regulating the alkali contents of Type I cement and fly ash used in concrete containing reactive aggregates are not effective. Further research could include the development of improved methods of determining the reactivity of alkalies in these materials. Improved guidelines should also take into account the proportions of these materials used and the effects of other constituents besides alkalies.

4. Currently there are no guidelines regulating the use of Type IP cement or silica fume. Guidelines similar to those for type I cement or fly ash need to be developed and tested.

5. No guidelines have been established to regulate the quality of water used in concrete. Additional research into the deleterious effect of high pH mixing water on alkali-silica reaction is needed to determine if a limit on pH is necessary.

6. To understand the effects of alkalies added to fly ash by chemical precipitating agents, further investigation will be necessary to determine the quantity of alkalies added and their reactivity, and the effect of the method of applying such agents.

7. Further test are necessary to explain the superior performance of Type IP cement and to determine wether the fineness of Type A fly ashes affects differently the alkali-aggregate reaction expansions as compared to the Type B fly ashes.

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APPENDIX

Table A.1 Cement Properties

Cement Code						
ASTM Type		I	I	IP	I	I
Chemical Constituents						
(by weight, in percent)						
Alkali Oxides:	Na_2O	0.07	0.07	0.24	0.27	0.24
	K_2O	0.54	0.90	0.40	1.16	0.44
Total Alkalies:						
$[Na_2O + 0.658 * K_2O]$		0.43	0.66	0.50	1.03	0.53
Metal Oxides:	CaO	64.41	63.54	53.58	62.51	65.15
	AL_2O_3	5.50	5.92	8.46	6.02	5.31
	Fe_2O_3	1.90	2.56	2.73	2.11	3.24
	SiO_2	20.11	19.73	28.84	20.09	20.85
	SO_3	3.01	2.97	3.06	3.65	2.77
	MgO	1.31	1.25	1.10	2.36	1.04
Phase Analysis:	C_3S	61.14	56.86	n/a	47.95	58.31
	C_2S	11.54	13.68	n/a	21.43	15.57
	C_3A	11.35	11.35	n/a	12.37	8.58
	C_4AF	5.78	7.78	n/a	6.41	9.85
Physical Properties						
Specific Gravity:	(assumed)	3.15	3.15	3.15	3.15	3.15
Specific Surface:	(cm^2/gr - Wagner)	1825	1750	3690	n/a	1900

Table A.2 Fly Ash Properties

Fly Ash Code TSDHPT Classification		A	A	B	B
Chemical Constituents (by weight, in percent)					
Available Alkalies: $[Na_2O + 0.658 * K_2O]$		1.38	0.57	4.35	1.67
Oxides:	SiO_2	60.82	46.33	32.64	34.63
	Al_2O_3	18.00	21.42	23.39	22.45
	Fe_2O_3	3.35	6.43	6.46	5.83
	$SiO_2 + Al_2O_3 + Fe_2O_3$	82.17	74.18	62.49	62.90
	CaO	2.52	14.35	23.43	30.47
	MgO	0.48	1.00	2.59	1.89
	SO_3	0.00	2.56	4.30	4.61
Physical Properties					
Specific Gravity:		1.86	2.46	2.71	2.63
Specific Surface: (cm^2/gr - Blaine)		2877	3189	4560	3762
Percent Retained on #325 (44 micron) Sieve		46.70	9.00	14.32	18.00

Fly Ash Code TSDHPT Classification						
Chemical Constituents		A	B	B	B	A
Available Alkalies: $[Na_2O + 0.658 * K_2O]$		1.76	2.35	2.04	3.75	0.31
Oxides:	SiO_2	47.33	38.28	37.56	30.40	63.48
	Al_2O_3	24.44	21.48	19.76	21.68	19.10
	Fe_2O_3	5.56	5.77	4.39	4.47	2.89
	$SiO_2+Al_2O_3+Fe_2O_3$	77.33	65.53	61.71	56.55	85.47
	CaO	4.24	24.41	27.57	28.35	9.22
	MgO	0.39	1.71	2.05	5.60	1.88
	SO_3	0.08	4.25	4.57	4.29	0.25
Physical Properties						
Specific Gravity:		2.02	2.62	2.55	2.62	n/a
Specific Surface:	(cm^2/gr - Blaine)	3095	3508	3642	3940	26.13
Percent Retained on #325 (44 microns) Sieve		46.70	9.00	14.32	18.00	35.70

Table A.3 Silica Fume Properties

Chemical Constitutents: (by weight, in percent)	
SiO_2	75 - 98
C	2 - 5
Other Constitutents	not determined
Physical Properties:	
Specific Gravity: (approximate)	2.3