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16. Abstract

Although aggregates were once thought to be inert, it is now known that all aggregates are chemically reactive. The chemical reactions between the aggregates and the cement paste are responsible for beneficial effects such as enhanced bond, but also of other effects that can be deleterious to the durability of the concrete. Alkali-aggregate reaction is one of such chemical reactions. Its chemistry and mechanism are not yet very well known but several hypotheses have been presented over the years and are reported herein.

The prevention of expansion in concrete due to alkali-aggregate reaction has been widely investigated by many researchers around the world. It is now known that the proper use of mineral admixtures in concrete can reduce the cost of concrete, improve many material properties, and inhibit alkali-silica reaction.

The effect of fly ash and silica fume and a summary of the probable mechanisms in which pozzolans affect the expansion caused by alkali-aggregate reaction in concrete is also reviewed, as well as the different methods of predicting the reactivity of aggregates and a discussion of their relative accuracy and validity.

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by

David C. Schuman
Ramon L. Carrasquillo
and
Josef Farbiarz

Research Report No. 450-2
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

February 1988

PREFACE

This report constitutes a summary of an extensive literature search made to complement the experimental stages of a broad research program studying the effect of fly ash on the expansion caused by alkali- aggregate reaction in concrete.

This study is the Research Project 3-9-85-450, entitled "Alkali-Aggregate Reaction in Concrete Containing Fly Ash," conducted jointly between the Center for Transportation Research, Bureau of Engineering Research, and the Phil M. Ferguson Structural Engineering Laboratory at The University of Texas at Austin. The work was co-sponsored by the Texas State Department of Highways and Public Transportation (TSDHPT) and the Federal Highway Administration. The studies were performed in cooperation with the Texas State Department of Highways and Public Transportation, Materials and Tests Division.

The study was directed and supervised by Dr. Ramón L. Carrasquillo.

SUMMARY

Although aggregates were once thought to be inert, it is now known that all aggregates are chemically reactive. The chemical reactions between the aggregates and the cement paste are responsible for beneficial effects such as enhanced bond, but also other effects than can be deleterious to the durability of the concrete. Alkali- aggregate reaction is one of such chemical reactions. Its chemistry and mechanism are not yet very well known, but several hypotheses have been presented over the years and are reported herein.

The prevention of expansion in concrete due to alkali- aggregate reaction has been widely investigated by many researchers around the world. It is now known that the proper use of mineral admixtures in concrete can reduce the cost of concrete, improve many material properties, and inhibit alkali-silica reaction.

The effect of fly ash and silica fume and a summary of the probable mechanisms in which pozzolans affect the expansion caused by alkali-aggregate reaction in concrete are also reviewed, as well as the different methods of predicting the reactivity of aggregates and a discussion of their relative accuracy and validity.

IMPLEMENTATION

The main objective of the research program of which this report is part, is to provide data for the development of guidelines for proper, economical, and efficient use of fly ash in reducing alkali-aggregate reaction damage in concrete. In doing so, it is of foremost importance to thoroughly understand the chemistry of alkali-aggregate reaction, its mechanisms in deteriorating the concrete matrix, and all the possible means of preventing damage to concrete due to expansions caused by this deleterious reaction.

This report presents the results of a deep and extensive look into the published literature concerning all the aspects of the study of the mechanism in which alkali-aggregate reaction induces expansions in concrete and the different investigations made on the means of preventing damage in concrete due to these expansions.

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CHAPTER 1

INTRODUCTION

1.1 General

As the cost of producing concrete increases and sources of raw materials are depleted, the durability and long-term performance of concrete in service becomes more important. Thus, the need for preventing alkali-silica reaction in concrete also gains importance. The proper use of mineral admixtures in concrete can reduce the cost of concrete, improve many material properties, and inhibit alkali-silica reaction.

This chapter contains background information on alkali-aggregate reactions, including alkali-silica reaction, and on mineral admixtures. The scope of this report is also discussed.

1.2 Background Information

1.2.1 History. Prior to 1940, concrete designers were aware of only two deleterious conditions in concrete which were affected by the composition of the cement: excessive shrinkage in mass concrete and sulfate attack.[25] Most aggregates were considered to be chemically inert and inactive constituents of concrete. Webster's New Collegiate Dictionary, in fact, still defines aggregates as "inert materials."[26]

In the late 1930's, concrete failures occurred in California at several locations where the materials used were considered "sound." A study of over 3000 specimens made from the materials in question was conducted by the California State Division of Highways. Based on the results, Stanton[25] reported a third potentially deleterious condition in concrete which was affected by cement composition: expansive chemical reactions between alkalies in cement and opal or siliceous limestone found in certain aggregates. This reaction was ascertained to be the cause of many concrete failures which had heretofore not been determined.[25,27]

Stanton's comprehensive report[25] established the basis for research which continues today. Among the contributions of this report were:

1. The presentation of many of the factors controlling alkali-aggregate reaction, such as
    - a) nature of reactive silica,

   b) critical percentages of reactive silica present,
   c) particle size of reactive material,
   d) amount of available alkalies, and
   e) amount of available moisture;

2. The introduction of a "mortar bar" test for determining the potential reactivity of cement-aggregate combinations; and
3. The discovery of the effectiveness of pozzolans in reducing expansions.

Sparked by Stanton's report, research interest peaked in the 1940's and 1950's as reactive materials were identified, test methods were developed, and the chemistry of the reaction was studied. In the 1960's and early 1970's, use of nonreactive aggregates and low alkali cements led to a reduction in the incidences of alkali-silica reaction and a corresponding decline of interest in research. With an increase in alkali-silica reaction reports in recent years, interest in the study of this problem has been revived.

1.2.2 Alkali-Aggregate Reactions.

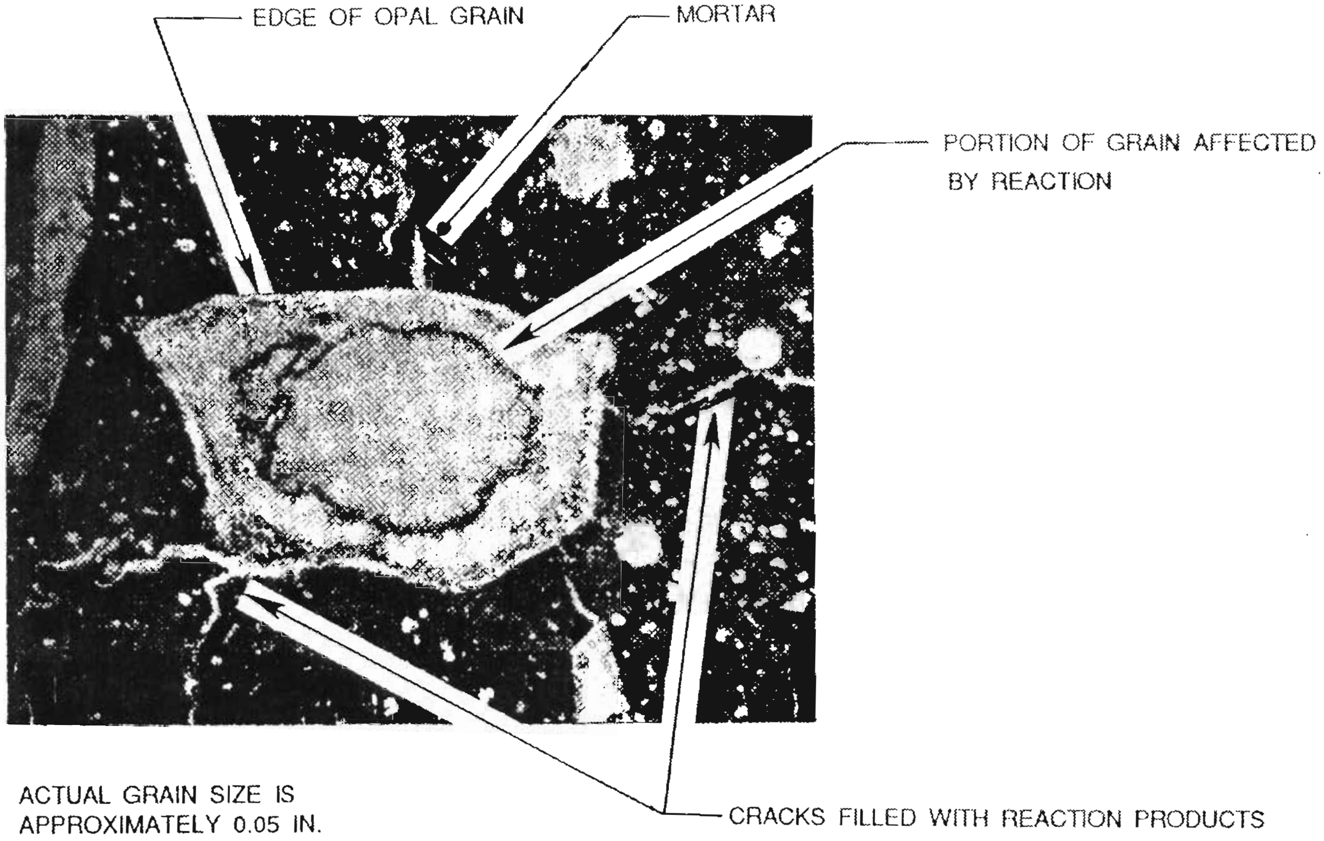
All concrete aggregates chemically react to some extent with cement paste.[1] Some reactions have beneficial effects such as enhancing the bond between aggregates and cement paste.[2] Other reactions cause expansion and cracking of the concrete leading to substantial damage and strength loss.[3]

Alkali-aggregate reaction is a term describing an expansive reaction involving alkalies in cement and certain minerals found in aggregates. The detrimental effects of alkali-aggregate reaction include internal cracks in cement paste around affected aggregate particles, such as the one shown in Fig. 1.1 [2], popouts, and "map" or "pattern" cracking at the concrete surface. Cracking and expansion of concrete, like that shown in Fig. 1.2, can result in the distortion or misalignment of structural elements while reducing the strength of concrete.

Several types of alkali-aggregate reaction are known to occur. These are distinguished by the minerals participating in each reaction. The two predominant forms of reaction are [2]:

1. Alkali-silica reaction involving the silica minerals, and
2. Alkali-carbonate rock reaction involving dolomite.

Table 1.1 lists the minerals and rocks which are known to participate in each reaction.



ACTUAL GRAIN SIZE IS
APPROXIMATELY 0.05 IN.

Figure 1.1 Grain of opal affected by alkali-aggregate reaction [4].

Figure 1.2 Wall exhibiting cracking, expansion, and dislocation due to alkali-aggregate reaction [5].

Table 1.1 Classifications of alkali-aggregate reactivity[3]

Alkali-Reactive Silica Minerals and Rocks

1. Alkali-Reactive Metastable Silica Minerals and Volcanic Glasses

Reactant: Opal, tridymite, cristobalite; acid, intermediate, and basic volcanic glasses: beekite.

Rocks: Opal-bearing rock such as shales, sandstones, silicified carbonate rocks, chert; vitrophyric volcanic rocks: acid, intermediate and basic, such as rhyolites, dacites, latites, andesites, and their tuffs, all varieties with a glassy groundmass, basalts (Iceland).

Expansion: Mainly caused by hydraulic pressure from expansion due to water uptake by alkali-silica gel.

2. Alkali-Reactive Quartzose Rocks

(a) Silica Rocks

(b) Silicate Rocks Rich in Quartz

Reactant: Chalcedony, cryptocrystalline to macrocrystalline and macrogranular quartz with deformed crystal lattice or rich in secondary inclusions; microquartz (0.01 to 0.05 mm in size, i.e., fine to coarse microcrystalline quartz).

Rocks: (a) Rocks normally with about 95% silica, such as chert* without opal but with chalcedony and/or microquartz (some meso- to macroquartz); vein quartz, quartzite, quartzarenite.

(b) Volcanic rocks* as under 1. with devitrified, cryptocrystalline to microcrystalline groundmass; metavolcanics; micro- to macro-granular rocks: argillites, siltstones, greywackes, subgreywackes, arenites, arkoses, slates, phyllites, (quartz-mica) schists, granites, granite and grandorite gneisses, charnockites.

Expansion: Caused by hydraulic pressure from expansion due to water uptake by alkali-silica gel.

Alkali-Reactive Carbonate Rocks

Reactant: Dolomite (metastable; process dedolomitization).

Rocks: Argillaceous dolomitic limestones, argillaceous calcitic dolostones; quartz-bearing argillaceous calcitic dolostones.

Expansion: Due to water uptake by dry clay minerals and other microconstituents, or other physico-chemical causes.

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* Rocks gradational to subgroup 1. depending on composition, and/or texture.

The predominant type of alkali-aggregate reaction which occurs in Texas is the alkali-silica reaction; therefore, only alkali-silica reaction will be discussed in this report.

Several tests have been developed to determine alkali-silica reaction potential. These tests are [7]:

1. ASTM C 227 - "Test for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar Bar Method)",
2. ASTM C 289 - "Test for Potential Reactivity of Aggregates (Chemical Method)", and
3. ASTM C 295 - "Recommended Practice for Petrographic Analysis of Aggregate for Concrete."

As a means of preventing alkali-silica reaction, ASTM C 150 "Specification for Portland Cement" [6] recommends that any cement used in conjunction with potentially reactive aggregates have a total alkali content no greater than 0.60 percent, expressed in terms of equivalent sodium oxide ($Na_2O + 0.658{*}K_2O$).

1.2.3 Mineral Admixtures. Mineral admixtures have traditionally been used to increase the workability of fresh concrete and to increase the durability of hardened concrete.[7]. The use of mineral admixtures dates back to the Greek and Roman eras when certain volcanic ashes were used in mortars to obtain increased strength and resistance to water.

Pozzolans are one type of mineral admixture. A pozzolan is defined as a "siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties" [8]. Calcium hydroxide contributes little to concrete strength on its own. By converting calcium hydroxide to a hydrated cementitious material, pozzolans effectively reduce the permeability of concrete while increasing its strength. Using pozzolans as a partial replacement for cement in concrete often has the additional benefit of reducing expansion due to alkali-aggregate reactions.

Natural pozzolans include diatomite and certain opaline or finely ground volcanic rocks.[9]. Artificial pozzolans occur as byproducts from power plants and metallurgical furnaces. The two most common artificial pozzolans are fly ash and silica fume.[10].

ASTM has defined three classes of pozzolans as shown in Table 1.2. Two classes are comprised of fly ash, the only artificial pozzolan recognized by ASTM, while the third class consists of natural pozzolans.

Fly ash, also known as pulverized fuel ash, is produced during the generation of electricity in coal burning power plants.[10]. When powdered coal is burned in the combustion chamber of a power plant, carbon and other volatile and organic materials are burned off. Most of the impurities such as clays, shales, quartz, and feldspar are fused into small spherical particles during combustion at high temperatures. Many of these spheres are then carried off by the hot flue gas stream. These "fly ash" particles are trapped and collected before they are carried through the stacks and out into the atmosphere.

Many factors affect the composition of fly ash. The most important is the type of coal being burned .[11]. The physical properties and chemical composition of fly ash are also affected by the degree of pulverization, combustion conditions, and collection and processing methods. In addition, chemical precipitating agents, often used during the collection process to enhance the removal of the fly ash, may remain in the fly ash after collection.[12,13].

The net result is a product which exhibits a wide range of properties. Skalny uses the term "fly ashes" since "... each fly ash ... is a different material ... and thus performs differently when used in combination with cements" [14].

ASTM C 618 "Specifications for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture In Portland Cement Concrete" [6] lists the chemical and physical requirements for fly ash intended for use in concrete. It also recommends that a limit of 1.5 percent available alkalies, determined according to ASTM C 311 "Standard Methods of Sampling and Testing Fly Ash or Natural Pozzolans for Use As a Mineral Admixture in Portland Cement Concrete" [7], be specified for fly ash used in concrete containing an alkali reactive cement-aggregate combination.

Silica fume is a byproduct of the fabrication of silicon or silicon alloys.[15]. Quartz, reduced to silicon in the presence of carbon and extreme heat, produces silicon oxide vapor. When this vapor is removed from the furnace and cooled, it oxidizes and condenses into extremely fine silica (silicon dioxide or SiO_2) spheres.

No specification regulating the physical or chemical properties of silica fume for use in concrete exists in the United States.[16]. As with fly ash, the composition of

Table 1.2 ASTM classifications of pozzolans[6]

Class N -	Raw or calcined natural pozzolans, such as some diatomaceous earths; opaline cherts and shales; tuffs and volcanic ashes or pumicites, any of which may or may not be processed by calcination; and various materials requiring calcination to induce satisfactory properties, such as some clays and shales.
Class F -	Fly ash normally produced from burning anthracite or bituminous coal. This fly ash has pozzolanic properties.
Class C -	Fly ash normally produced from lignite or subbituminous coal. This class of fly ash, in addition to having pozzolanic properties, also has some cementitious properties. Some Class C fly ashes may contain lime contents higher than 10 percent.

Source: ASTM C 618

silica fume varies greatly depending on furnace conditions and the raw materials used. The effectiveness of silica fume as a pozzolan depends on its chemical composition and particle size.

1.3 Justification of Report

Alkali-silica reaction is a legitimate concern to concrete users since it is capable of degrading the strength and durability of concrete. The simplest means of avoiding alkali-silica reaction is to use combinations of low alkali (less than 0.60 percent) cement and nonreactive aggregates which have proven histories of service without deterioration. However, this solution is not available to many concrete users. Aggregates of suitable quality and proven performance do not exist in some areas and are being depleted in others. The expense of removing alkalies from cement and environmental concerns regarding their disposal have resulted in cements of higher alkali content. As a result, research to determine alternate methods of inhibiting alkali-silica reaction is urgently needed. For this purpose, a good understanding of the alkali-aggregate mechanisms is of foremost importance.

Diamond has cited additional reasons for studying alkali-silica reaction [17]:

1. Greater use of concrete with increased cement contents and/or lower water contents which leads to higher alkali concentrations in the pore fluids of these concretes,
2. Lack of petrographers trained to recognize reactive aggregates,
3. Test methods which are not always accurate and are not always used, and
4. Discoveries that certain aggregates thought to be nonreactive are, in fact, reactive over long periods of time.

By gaining a more complete understanding of the mechanisms and chemistry of alkali-silica reaction and refining methods of determining potentially reactive constituents, future incidences of damage to concrete can be avoided.

Due to the increased production of fly ash, resulting in increased availability, as well as the lack of alternative uses, fly ash is growing in importance as a constituent of concrete. Using fly ash as a partial replacement for cement in concrete helps reduce a large waste disposal problem, reduces the energy consumed in the production of portland cement, results in lower cost concrete, and often serves to inhibit alkali-silica reaction.[18].

To encourage the use of by-product or waste materials like fly ash, Congress passed the Resource Conservation and Recovery Act in 1976. This act promotes the use of "equivalent concrete" containing fly ash in federally funded projects.[19]. In spite of this legislation, only 11 percent of the fly ash produced in the United States during 1984 was used in concrete, as shown in Fig. 1.3.

A key to increasing the use of fly ash in concrete is to increase the confidence of potential fly ash users. This has been difficult in light of reports that the use of fly ash has aggravated alkali-silica reaction and sulfate attack in some cases.[14]. Research needs related to the use of fly ash in concrete include [20]:

1. Improved characterization of the types of particles found in various fly ashes,
2. Determining the relationships between fly ash particle size and the chemical composition and potential reactivity of the particles,
3. Developing a classification system for fly ashes based on characteristics known to affect their behavior in concrete, and
4. Determining the relationship between the inorganic material found in a particular coal and the properties of the fly ash it produces.

Silica fume is produced in much smaller quantities than fly ash. Of the 1.3 million tons of silica fume produced worldwide annually, only 0.25 million tons are collected and available for use in concrete and other applications.[21]. The current demand for silica fume has affected its cost, which now ranges from 50 percent to 700 percent of the cost of Portland cement. In spite of this, silica fume is still attractive for certain uses. For replacement levels less than 10 percent, one pound of silica fume can replace three to four pounds of cement without affecting the compressive strength of the concrete.[23]. When used with superplasticizers, silica fume concrete has obtained strengths well over 15,000 psi. Also significant is the relatively small amount of silica fume required to inhibit alkali-silica reaction.[21].

Literature on the use of silica fume in concrete is quite limited and has generally treated silica fume as one unique product rather than a class of materials with widely varying chemical compositions.[15]. As with fly ash, much research is needed to establish the effects of the individual constituents of silica fume on concrete properties.

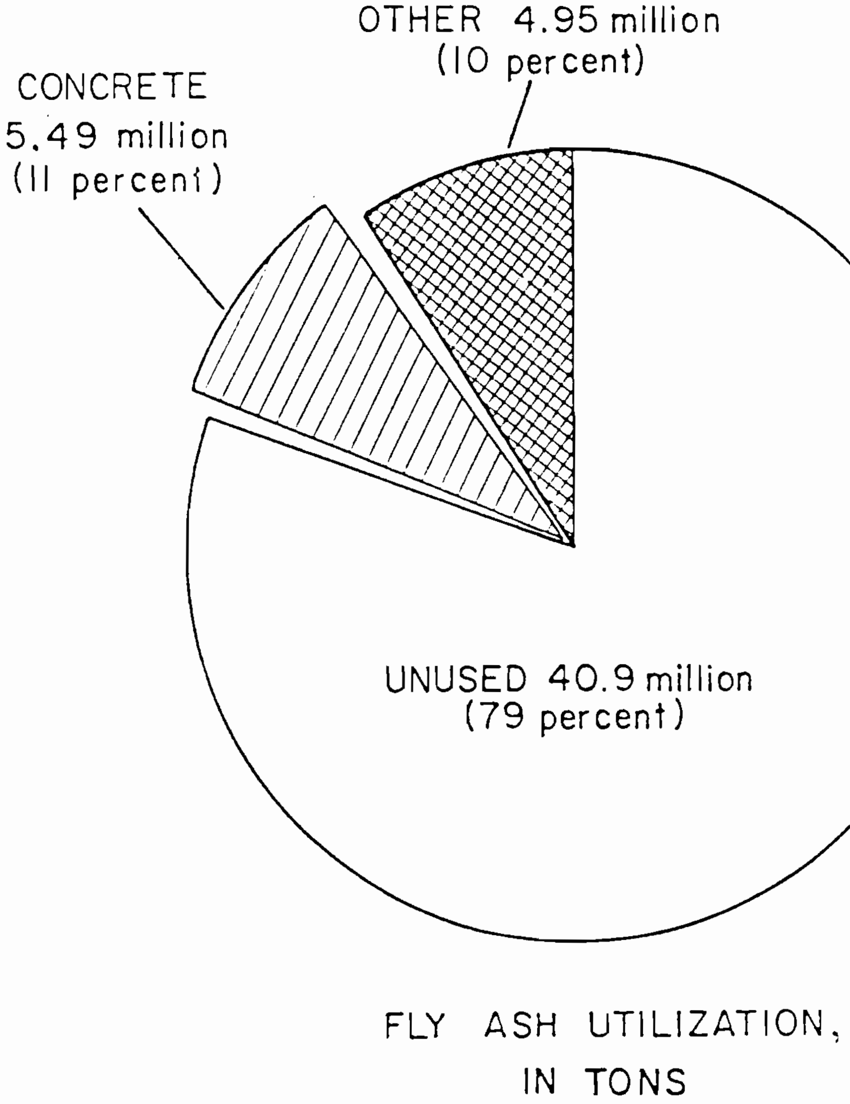


Fig. 1.3 Utilization of fly ash in the United States during 1984 [22]

CHAPTER 2

CHEMISTRY OF ALKALI-SILICA REACTION

2.1 General

The terms "alkali-aggregate reaction" and "alkali-silica reaction" are universally used and accepted. However, these terms offer a somewhat misleading picture of the chemical processes involved. Siliceous aggregates are not directly attacked by alkali ions as might be presumed. Instead, hydroxide ions (OH^-) have been found to initiate damaging reactions with susceptible aggregates.[17] Research has shown that the reaction depends on the formation of high concentrations of hydroxide ions in solution and not on the concentration of alkali ions themselves. This has been demonstrated in tests where hydroxide ions were provided to mortar mixtures containing reactive aggregates and cement with virtually no alkalies.[52] These mixtures displayed all of the symptoms of "typical" alkali-aggregate reactions. 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.

2.2 Decomposition of Silica Particles

The structure of silica consists of a silicon ion (Si^{4+}) surrounded by four oxygen ions (O^{2-}) in the form of a tetrahedron as shown in Fig. 2.1.[28] Since the composition of silica is SiO_2, the tetrahedra at the surface of a silica crystal, shown in Fig. 2.2, cannot be completed. If the silica crystal is poorly formed, uncompleted tetrahedra will also occur in the interior as shown in Fig. 2.3. The oxygen ions of the uncompleted tetrahedra are left with one unsatisfied negative charge and the silicon ions are left with a corresponding unsatisfied positive charge. If water is present (such as pore fluids in cement paste) hydrogen ions (H^+) and hydroxide ions join the "available" ions in the silica crystal to complete the unfinished tetrahedra as shown in Fig. 2.3. Some of these hydrogen ions are later freed into the solution, causing the surfaces of the crystal to be mildly acidic. The finer or more poorly crystallized the silica particle is, the greater the number of hydrogen ions released per mole of silica, and the greater the reactivity of the particle. If strong alkalies are present, silica is peptized in a three-step process [28]:

1. Alkali ions (Na^+, K^+) liberate a corresponding number of hydroxide ions in the cement paste. The hydrogen ions in solution near the surface of the silica join the hydroxide ions to form water. To satisfy the surface charges of the

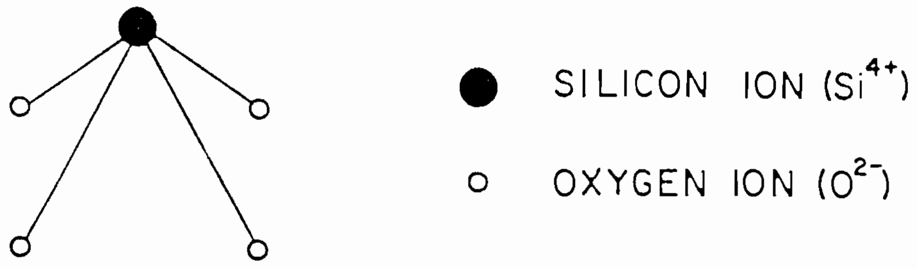


Fig. 2.1 Tetrahedral structure of silica [28]

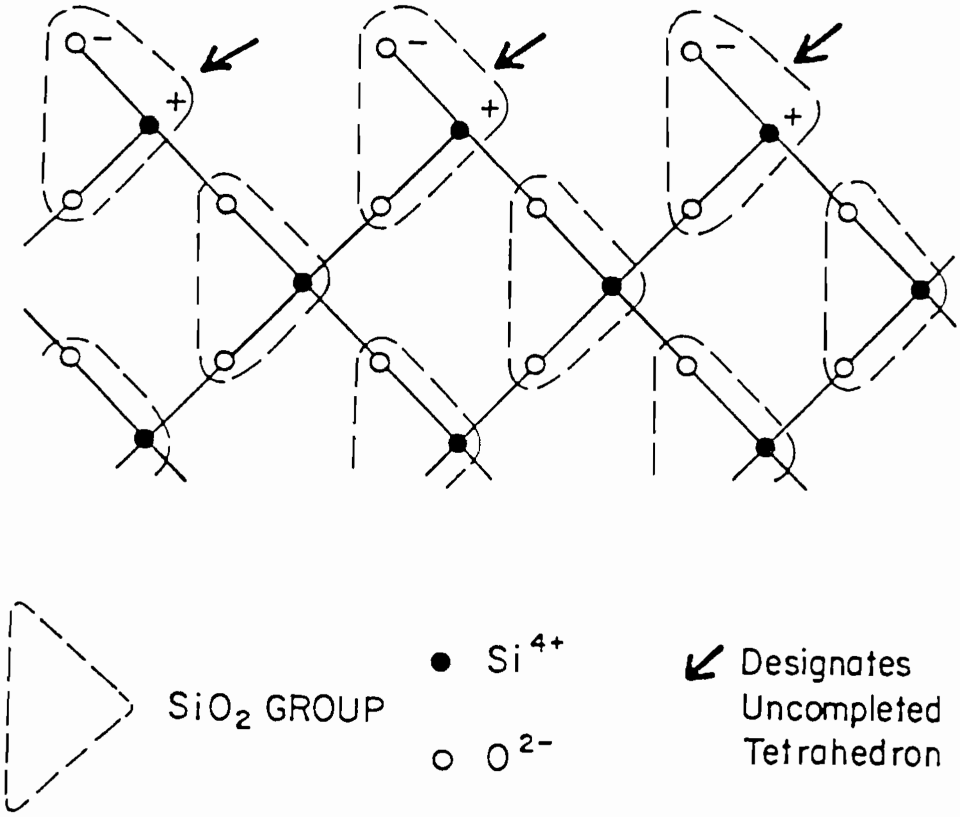


Fig. 2.2 Incomplete tetrahedra and unresolved charges occurring at the surface of a silica crystal to satisfy the SiO$_2$ formulation [28]

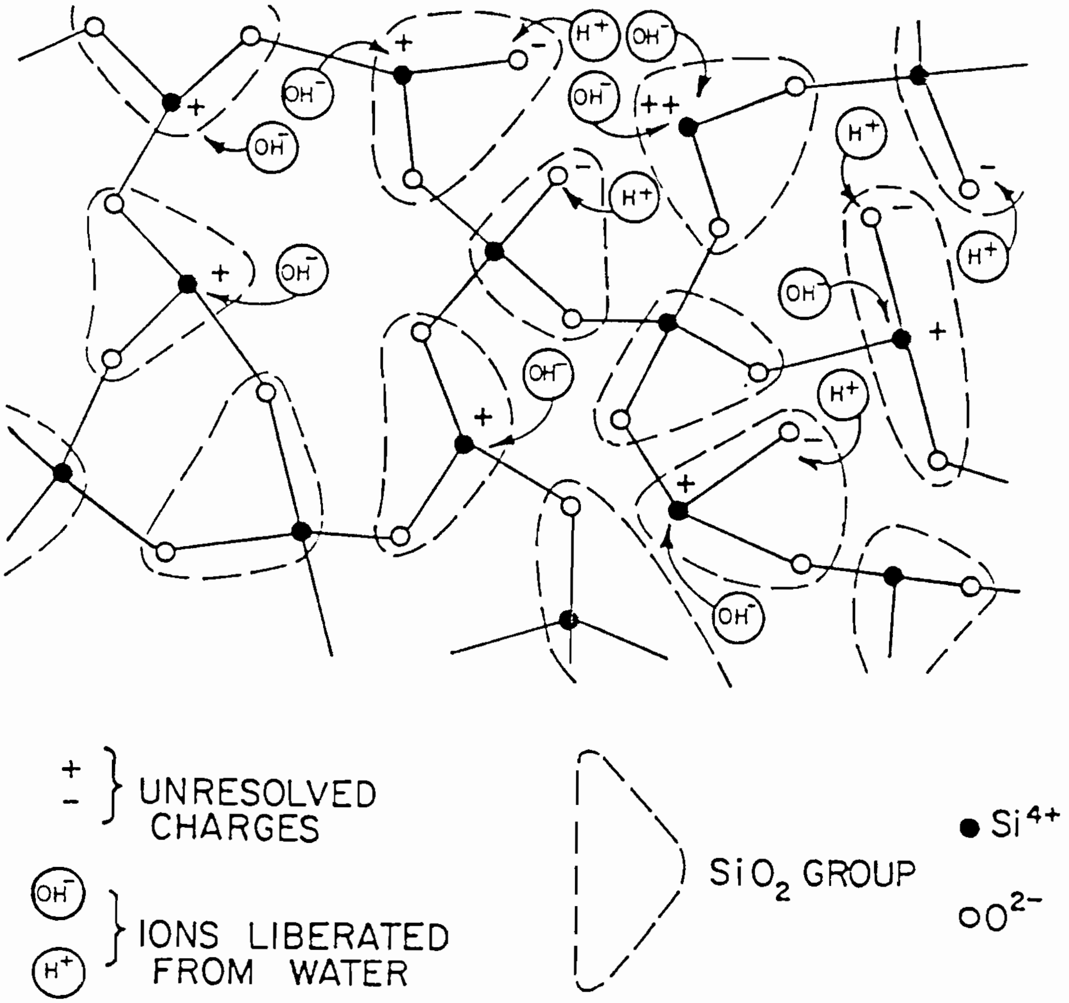


Fig. 2.3 Incomplete tetrahedra on the surface and in the interior of a poorly formed silica crystal. Incomplete tetrahedra and unresolved charges are satisfied by hydrogen and hydroxide ions

silica, alkali ions replace the hydrogen ions as shown in Fig. 2.4. This reaction serves as an acid-base neutralization.

2. If additional hydroxide ions are present after all of the hydrogen ions have been neutralized, the Si-O-Si bonds are attacked as shown in step 1 of Fig. 2.5. A pair of hydroxide ions break a Si-O-Si linkage, freeing the oxygen ion. The hydroxide ions then replace the oxygen ion in the structure, bonding to the silicon ions. No bonding develops between the hydroxide ions, leaving the linkage between the silicon ions broken as shown in step 2 of Fig. 2.5. Table 2.1 shows that the greater the concentration of hydroxide ions (higher pH), the more completely the silica is dissolved.
3. The hydrogen ions separate from the hydroxide ions and are drawn to the displaced oxygen ion to form water. The alkali ions then replace the hydrogen ions as shown in step 3 of Fig. 2.5. Of significance is the fact that the alkali ions play no part in the process until after the Si-O-Si bonds are broken and the oxygen ion has been removed from the silica structure.

Powers and Steinour [28,29] proposed that calcium as well as alkalies could participate in reactions with silica in concrete. They claimed that reaction products consisting of high calcium gels are limited in swelling potential or "safe," while "unsafe" reaction products are those gels containing sodium or potassium which possess great swelling characteristics. Their studies 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. The type of gel formed was thought to be a function of the alkali content of the cement, the amount of reactive material in relation to the amount of alkalies present, and size of the reactive particles. Diamond [17] reported that these hypotheses have been widely accepted although no experimental confirmations have been made. Ming-shu [31], however, has stated that the CaO to Na_2O ratios of some "safe" and "unsafe" reactions are so close that distinction is difficult, rendering the theory unsatisfactory.

2.3 Role Of Alkalies

Lithium, sodium, potassium, rubidium, cesium, and francium are the metallic elements which constitute Group IA of the Periodic Table. These elements are known as the alkali metals, or alkalies. Only sodium and potassium commonly occur in portland

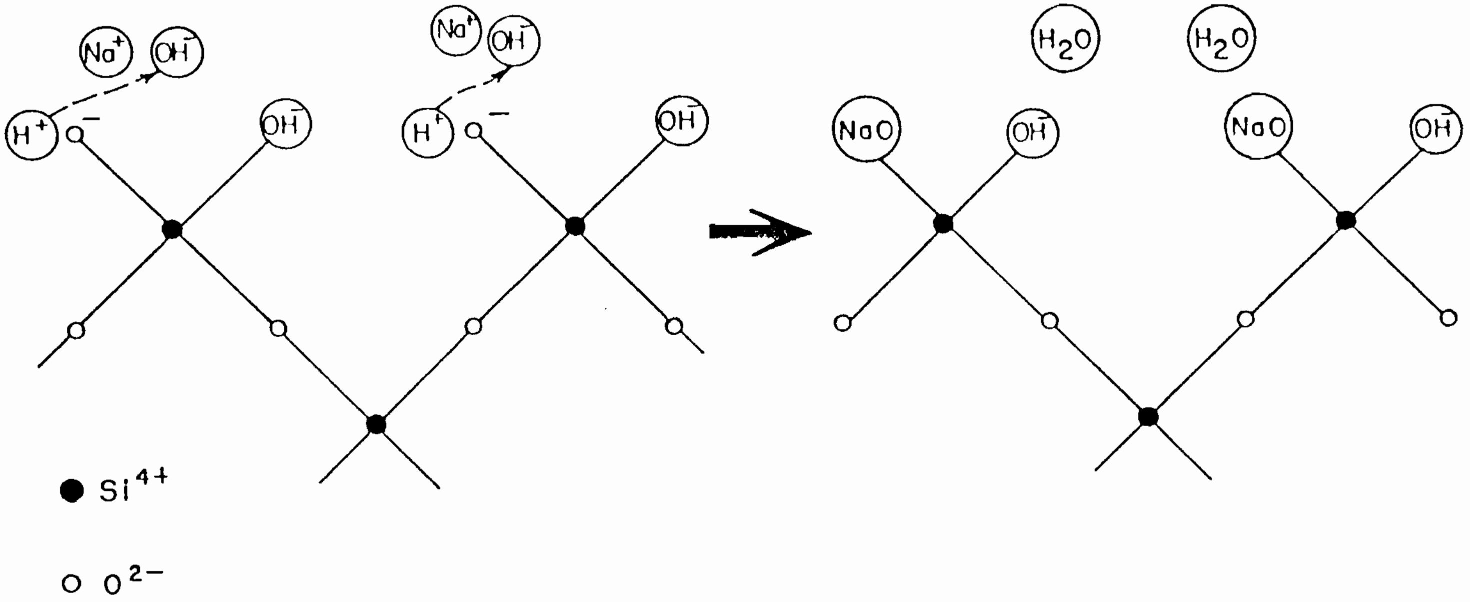


Fig. 2.4 Replacement of hydrogen ions by alkali ions in a silica crystal

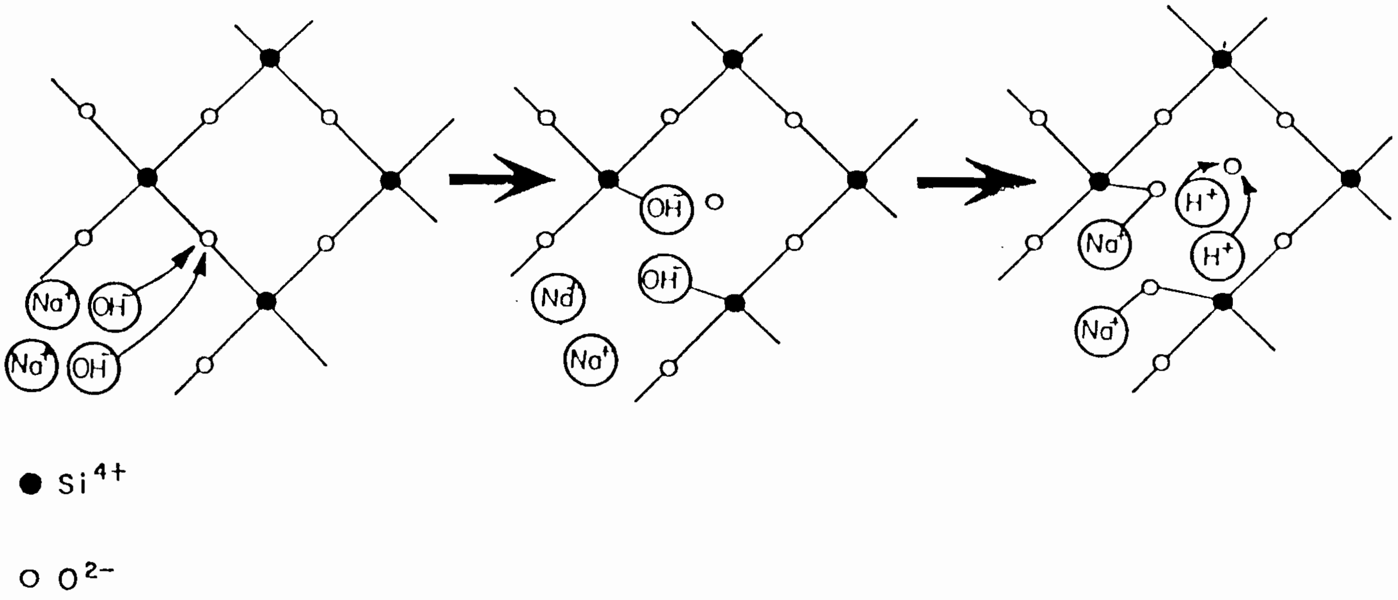


Fig. 2.5 Severing of Si-O-Si bonds by alkali ions

Table 2.1 **Relationship between the solubility of silica and the pH of water** [7]

Medium	pH	Approximate Solubility of SiO_2 (ppm)
Neutral water	7-8	100-150
Moderately alkaline water water	10	<500
Saturated $Ca(OH)_2$	12	90,000
Low-alkali cement paste	12.5	500,000
High-alkali cement paste	>13.50	Infinite

cement.[17] The other alkalies do not comprise a significant portion of cement and are generally ignored.

Sodium and potassium occur in both "water- soluble" and "water- insoluble" forms in cement. The percentage of alkalies in cement which are soluble varies widely with cements.[32,17] A test of a large number of cements produced in the United States revealed that from as little as 10 percent to as much as 60 percent of the total alkalies in cement are readily water-soluble.[17]

Virtually all of the soluble alkalies occur as sulfates which are derived more often from impurities in kiln fuel than from cement raw materials.[17] Potassium sulfates are more common than sodium sulfates. Insoluble alkalies are usually present in solid solution in the dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and calcium aluminoferrite (C_4AF) constituents of clinker.

Little information exists pertaining to the rates at which alkali ions in cement enter the pore solutions of concrete. The highly soluble alkali sulfates can be assumed to dissolve quickly in the concrete mixture water.[17] The time required for the alkali in the C_2S, C_3A, and C_4AF phases of cement to reach solution would seemingly depend on the rates of hydration of the particular phases.

Most cement pastes are saturated or supersaturated with calcium hydroxide ($Ca(OH)_2$).[17]. 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.

Alkalies released during hydration by C_2S, C_3A, and C_4AF are in the form of alkali aluminates or silicates, which are salts of a strong base and a weak acid. Although these salts are released slowly during hydration, they readily dissolve in water, liberating hydroxide ions. Alkali sulfates, however, are essentially neutral salts and the balance of hydroxide ions and hydrogen ions in water remains unchanged when they are dissolved.

The production of hydroxide ions by alkali sulfates is apparently related to the formation of ettringite.[17] The initial source of the sulfates required for ettringite to develop is gypsum in the cement. Once the gypsum is depleted, the sulfate ions from alkali sulfate in the cement are free to participate in the formation of ettringite. The alkali ions, which remain in solution, are then balanced by hydroxide ions obtained from $Ca(OH)_2$ produced during cement hydration. As hydroxide ions are liberated to balance the alkali ions, calcium is freed to be included in the formation of ettringite. Meanwhile, the alkali ions and hydroxide ions are free to begin the peptization of silica. Thus, evidence suggests that sulfate attack may promote alkali-silica reaction in concrete.[33]

Although alkali ions are generally released into solution before hydroxide ions, the number of hydroxide ions generated eventually becomes proportional to the number of alkali ions. Those alkali ions which do reach solution tend to remain in solution indefinitely, as few alkalies are incorporated into the hydration products of cement.[17] 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.

A complete report of the chemical composition of cement includes the total quantity of alkalies present, including soluble and insoluble forms, determined according to ASTM C 114 "Standard Methods for Chemical Analysis of Hydraulic Cement".[6] The rationale for reporting the quantity of the soluble and the insoluble alkalies is apparently based on the observations that both soluble and insoluble forms of alkalies may eventually be released into the pore solutions of concrete, as noted above.

2.4 Role of Calcium Hydroxide

Chatterji [34] has studied the role of $Ca(OH)_2$ in alkali- silica reactions. This research revealed that little evidence of expansion or reaction occurs in specimens made with reactive material combinations when no $Ca(OH)_2$ is present. The $Ca(OH)_2$ had been leached out of these test specimens by means of submersion in a calcium chloride solution.

Chatterji et al. [35] stated that in the presence of free $Ca(OH)_2$, sodium ions released from alkali salts, hydroxide ions from $Ca(OH)_2$, and water molecules all penetrate reactive aggregate particles. Si-O-Si bonds are broken by the action of the hydroxide ions and the alkali ions, opening the particles to further attack. Silicon ions tend to diffuse out of the disrupted zones of the particles. $Ca(OH)_2$ in the surrounding paste tends to restrict the diffusion of the silicon ions, but not the sodium ions, hydroxide ions, or water molecules. If the amount of ions and molecules drawn into a particle is greater than the amount of silicon ions diffusing out, expansion occurs.

Chatterji [34] suggested two methods for removing $Ca(OH)_2$ from concrete:

1. utilization of high C_2S cement with reactive aggregates, maintaining as low a cement content as possible, and
2. use of enough pozzolanic material to completely convert all $Ca(OH)_2$ to C-S-H.

Understanding the first suggestion requires some knowledge of the hydration reactions of Portland cement. C_2S and C_3S are the two main constituents of Portland cement, comprising roughly three- fourths of a typical cement.[7] Both C_2S and C_3S react with water to form C-S-H and $Ca(OH)_2$ as follows:

$$2C_3S + 6H \rightarrow C - S - H + 3Ca(OH)_2 \qquad (2.1)$$

$$2C_2S + 4H \rightarrow C - S - H + Ca(OH)_2 \qquad (2.2)$$

As indicated by the equations, C_3S produces three times as much $Ca(OH)_2$ as an equal amount of C_2S. For the purpose of comparison, Table 2.2 lists the five types of portland cement recognized by ASTM and their typical C_2S and C_3S contents.

The second suggestion serves as an explanation for the well documented beneficial effect pozzolans have on alkali-silica reaction expansions. Bhatty [36] indicated that pozzolans reduce or eliminate alkali-silica reaction by:

1. converting $Ca(OH)_2$ to C-S-H, and
2. reacting with high calcium to silica ratio C-S-H to produce low calcium to silica ratio C-S-H which can incorporate large amounts of alkalies into its structure. These alkalies are prevented from initiating attack on susceptible aggregates.

C-S-H has no specific chemical composition.[7] The calcium to silica ratio in C-S-H varies from 1.5 to 2.0 or higher, depending on factors like the age of the paste, hydration temperature, water to cement ratio, and impurities in the paste.

According to Bhatty [36], for a pozzolan to be effective in inhibiting alkali-silica reaction, a sufficient amount must be added to lower the calcium to silica ratio below 1.5. Replacement of 25 percent to 30 percent of cement with low calcium fly ash

Table 2.2 Typical C_2S and C_3 contents of ASTM Types I, II, III, IV, and V portland cement [7]

ASTM Cement Type	C_2S Content*	C_3S Content*
I	25	50
II	30	45
III	15	60
IV	50	25
V	40	40

could generally be expected to curtail expansions. In addition, Bhatty stated that if enough silica is contributed by the aggregate, as little as 20 percent replacement might be sufficient.

CHAPTER 3
MECHANISM OF ALKALI-SILICA REACTION

Several hypotheses exist regarding the mechanism by which alkali-silica reaction causes internal expansion in concrete. The first, an osmotic pressure theory, was proposed by Hansen in 1944.[37] This theory states that expansion due to alkali-silica reaction involves the following steps which are illustrated in Fig. 3.1.

1. Alkali hydroxides in the cement paste (NaOH, KOH) react with silica particles (SiO_2) to form alkali silicates.
2. The alkali-silicates are confined to the same volume as the silica which participated in the reaction. Since the alkali silicates formed require more volume than did the silica, pressure is exerted on the surrounding cement paste.
3. The alkali-silicates are dissolved by water from the immediately surrounding cement paste. The silicate ions in the alkali silicate solution associate into complex ions.
4. The cement paste acts like a semi-permeable membrane, allowing water to pass through, but not the large, complex silicate ions. Since water molecules tend to diffuse away from water rather than from a solution, more water is drawn into the pocket of alkali silicate solution than escapes from it. An osmotic pressure cell is thus formed. Increasing hydrostatic pressure is exerted on the surrounding cement paste.
5. Alkali hydroxides are brought into the pocket of solution by the water. Additional reactions with the silica occur and further pressure is exerted against the cement paste.

The hydraulic pressure exerted by the confined reaction products causes expansion of the surrounding mortar. This continues until sufficient pressure is generated to crack the mortar. Studies by McConnell et al. [4] and Parsons and Insley [38] have supported the osmotic pressure theory. McConnell et al. showed that pressures exceeding 550 psi could be developed in an osmotic cell model simulating mortar conditions. Pike and Hubbard [39] have measured pressures greater than 2000 psi attributable to expansions caused by alkali-silica reaction. Diamond and Thaulow [30] have observed expansions reaching 2 percent without significant cracking, indicating that elastic expansions due to hydraulic pressure can be quite significant.

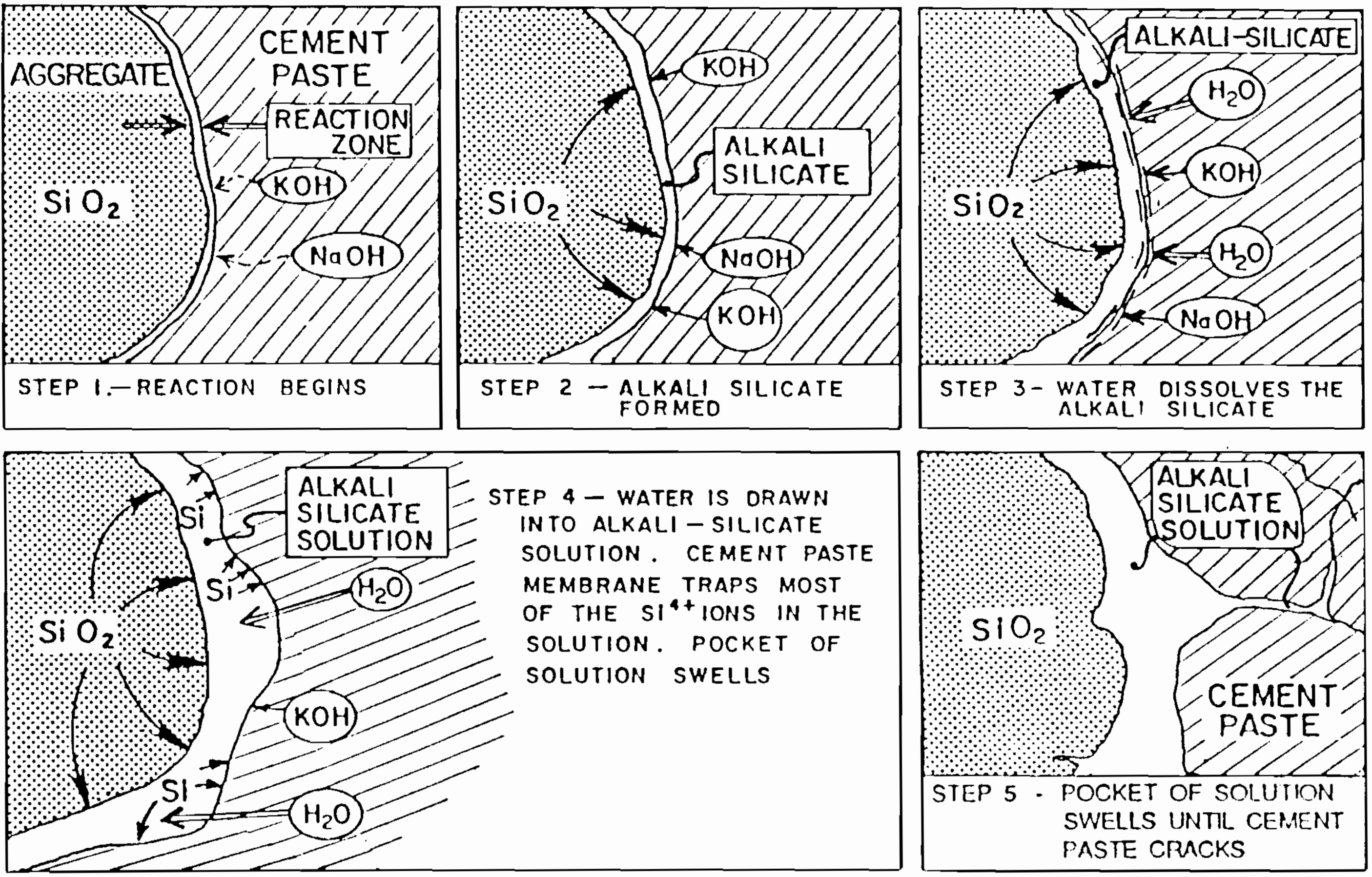


Fig. 3.1 Illustration of osmotic pressure theory [37]

Studies by Nielsen [40], however, suggested that alkali-silica reaction is, in fact, incapable of initiating cracks in concrete, but leads to concrete damage when reaction products intrude into existing cracks (formed by vibration, bleeding, thermal stresses, etc.) and cause these cracks to widen.

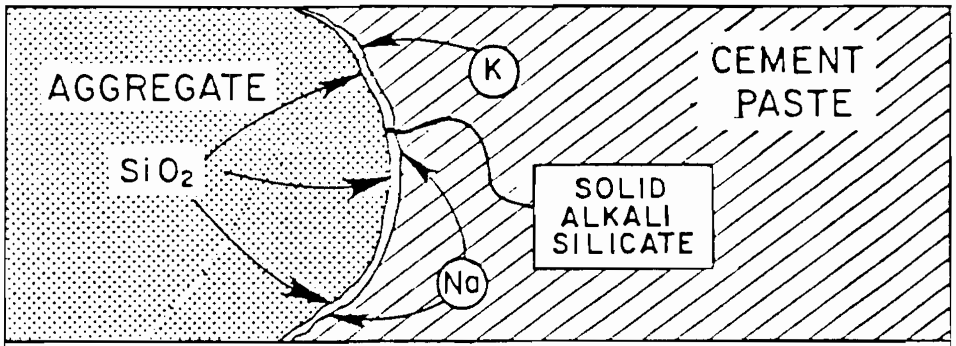
Studies by several researchers have contradicted the osmotic pressure theory.[17,41] Their evidence indicated that cracks form in cement paste during the early stages of alkali-silica reaction, thereby allowing circumvention of the semi-permeable cement paste membrane. Under such conditions, a "true" osmotic pressure cell could not exist. Instead, expansion was suggested to be a result of the swelling of aggregate particles which absorb water upon reacting with alkalies. This mechanism is described below and illustrated in Fig. 3.2:

1. A siliceous aggregate particle reacts with alkalies in the cement paste to form a solid alkali silicate complex as the reaction product.
2. The alkali silicate "gel" (colloidal, particles dispersed throughout a medium of soft to firm rigidity) begins to absorb water and swell. Shortly thereafter, the mortar surrounding the concrete cracks.
3. Inelastic expansion of the mortar occurs as the gel continues to swell, widening and extending the cracks in the mortar. This expansion continues until the gel has imbibed so much water it becomes a solution and loses its rigidity. By the time a sodium silicate gel becomes a solution, its volume will have increased by as much as 130 percent.

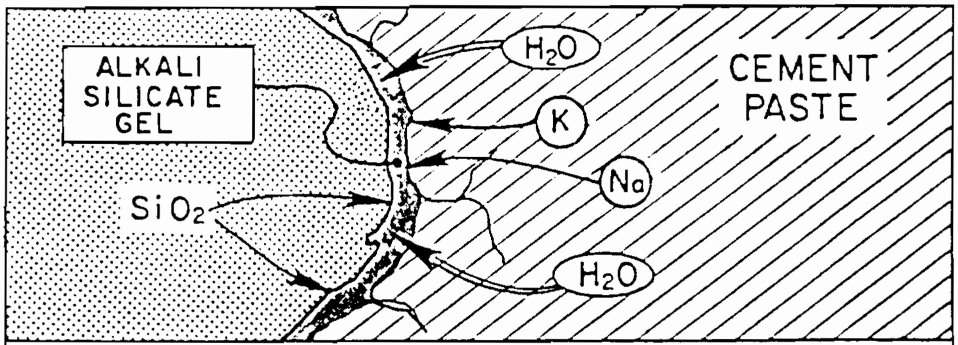
McGowan and Vivian [41] reported that a "positive correlation" existed between measured expansions of mortar specimens and expansions estimated from the mean number and width of cracks in the mortar specimens. They concluded that expansion due to alkali-silica reaction was primarily a result of widening of cracks.

Ming-shu [31] agreed with this expansion theory and suggested that expansion is related to the following factors:

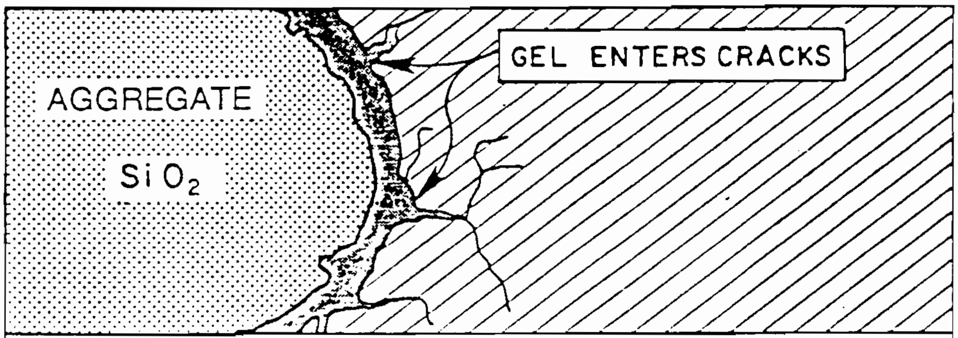
1. the number of reactive particles in a unit volume of mortar,
2. the amount of alkalies available per unit surface area of reactive particles,
3. the expansive force generated by each particle due to alkali-silica reaction, and
4. the tensile strength of the cement paste.



STEP 1 — SOLID ALKALI SILICATE FORMED ON PARTICLE SURFACE



STEP 2 — ALKALI SILICATE ABSORBS WATER, BECOMES GEL, AND SWELLS. CEMENT PASTE CRACKS.



STEP 3 — GEL CONTINUES TO SWELL, WIDENING AND EXTENDING CRACKS.

Fig. 3.2 Illustration of mechanical expansion theory [17,41]

Hansen [42] and Diamond [43], on the other hand, have stated that "virtual" osmotic cells could exist in cement paste which has cracked if chemical or electrical forces, rather than physical mem- branes, restricted the flow of ions.

Powers and Steinour [28,29] 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 Fig. 3.3

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. This agrees with the second theory.

Powers and Steinour agreed with Vivian [44] that no semi-permeable membrane is required for expansion to occur. They did, however, suggest that in mass concrete, alkali-silica gel could fill cracks in the cement paste, allowing the cement paste to act as a membrane and permitting an osmotic cell to develop.

All of these hypotheses have received general acceptance [17], although none have been confirmed by experimental evidence.

Studies by Struble and Diamond [45] have revealed some unusual behavior by "synthetic" silica gels, prepared as models of the gels formed in concrete. Some gels swelled little when exposed to water in an unloaded state, but exerted great expansive forces when placed under load. They suggested that this could explain why localized regions affected by alkali-silica reaction may expand, in spite of being surrounded by large masses of concrete (such as in dams).

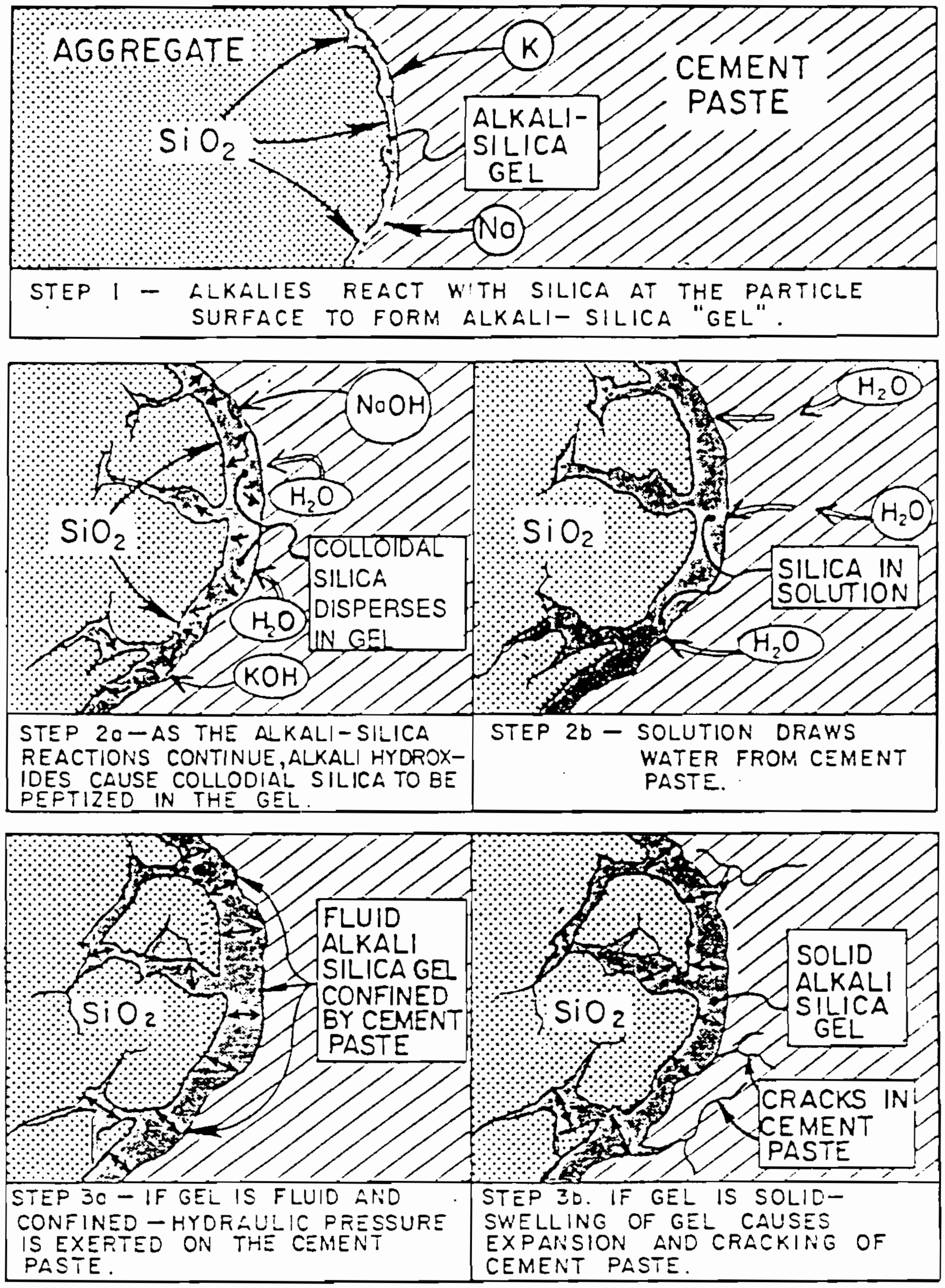


Fig. 3.3 Illustration of expansion theory of Powers and Steinour [28,29]

Other gels were observed to expand greatly until loading, whereupon they rapidly liquified. The behavior of these gels was thought to explain the appearance of fluid reaction products on the surface of the affected concrete. It was also thought to be related to the appearance of alkali-silica reaction products in concrete which has exhibited little expansion, such as the cases reported by Vivian.[17]

CHAPTER 4
ROLE OF CONCRETE CONSTITUENTS IN ALKALI-SILICA REACTION

4.1 Role of Aggregate

4.1.1 Reactive Minerals And Rocks. A mineral is a naturally occurring solid element or compound with a unique chemical composition and orderly atomic arrangement, possessing unique properties including the tendency to form crystals.[46] Rocks are aggregations of one or more kinds of minerals.

Silicates, which are compounds of silicon, oxygen, plus one or more metals, comprise over 90 percent of the rock-forming minerals.[46] The structure of all silicates is comprised of some arrangement of the silicon-oxygen tetrahedra shown in Fig. 2.1. Silicates are classified by the ratios of silicon to oxygen in their structures. A silicate with a 1:2 silicon to oxygen ratio is known as quartz.

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. Quartz grains may be freed from igneous rocks by weathering and incorporated into sediments. Silica in solution or colloidal sized particles is also produced by the weathering of igneous rocks. These products are precipitated or deposited as quartz or in other forms such as opal.

Quartz is the only thermodynamically stable form of silica.[47] Although once considered nonreactive, recent evidence indicates that quartz crystals of all sizes are susceptible to attack. The susceptibility of quartz to reactions depends on factors like deformations and disruptions of the crystal structure, surface irregularities, grain size and shape, and the presence of pores and inclusions.[2] All of these factors result in openings in the crystal structure, increasing the surface area exposed to alkali-silica reactions. Expansive reactions involving quartz tend to be very slow.

Opal is a hydrous silica (SiO_2*nH_2O) which is often defined as a "mineraloid" because it has no true crystalline structure and no definite chemical formula. Opal is commonly found in rocks used as concrete aggregates.[47] In comparison to quartz, the amorphous to nearly amorphous structure and well-connected systems of voids found in opal result in a much greater surface area exposed to alkali-silica reaction. Not surprisingly, opal is extremely reactive.

Cristobalite and tridymite, similar in nature to opal, are considered minerals due to their better-defined crystalline structures.[47] Since their crystalline structures are very open in nature [2], these minerals are only metastable in behavior and are known to be reactive.[48] Neither of these minerals are common in rocks used as concrete aggregates.

Cryptocrystalline is a term describing a crystal structure so fine it cannot be seen under an ordinary microscope.[46] Chalcedony, a mineral, is a cryptocrystalline form of silica which has a complex, fibrous structure.[47] Chalcedony often occurs in chert and flint, as well as in a few other rocks. Chert and flint are granular cryptocrystalline rocks which are quite similar, but vary in their degrees of reactivity.[2,47] Many attempts have been made to correlate the properties of these rocks with susceptibility to alkali attack but little success has been achieved. Chert is also susceptible to frost damage.[2]

Certain volcanic rocks are comprised partly or entirely of volcanic glasses.[2] A glass is defined as a solid with a disorderly structural arrangement. The structure of volcanic glasses, similar to that of opal, consists of small random clusters of silica tetrahedra with other materials incorporated around the clusters. Volcanic glass is unstable and reactive. The degree of reactivity depends on the exact composition and texture of the glass. Artificial glasses such as "Pyrex" are also reactive.[47] Pyrex glass contains about 80 percent silica. Due to the constant composition and high silica content of Pyrex glass, it 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" [6]

Tuff is a rock composed of volcanic ash.[46] The reactivity of tuff can be traced to the silica found in the magma serving as the source of the ash and to the fineness of the particles.

4.1.2 Amount, Type, and Size of Reactive Particles. The degree and rate of reactions involving an aggregate are influenced by many factors including [25]:

1. types of reactive materials present,
2. amounts of reactive materials, and
3. sizes of reactive particles.

The relationship between amount, size, and reactivity of a material is complex. McConnell et al. [4] have stated that the extreme variations in expansion of concrete due to the size and amount of reactive particles present defy description by a single hypothesis. The highly variable chemical and physical conditions in concrete and mortar result in a nonproportional relationship between the rate or amount of reaction and the expansion actually experienced. For example, a highly reactive combination of cement and aggregate may yield little expansion if either the aggregate or mortar is excessively porous and able to accommodate the expansive reaction products.

The amount of reactive material in an aggregate which results in the maximum expansion is known as the "pessimum" proportion.[49] Figure 4.1 illustrates the pessimum proportions for several reactive materials. The pessimum proportion and resulting expansion also vary with the alkali content of the cement used as shown in Fig. 4.2.

The Corps of Engineers considers an aggregate to be "potentially deleteriously reactive" if it contains [1]

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 [48]

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.

Figures 4.3, 4.4, and 4.5 illustrate the rate and degree of reactivity for a number of materials by comparing expansions of specimens containing pessimum proportions of these materials in otherwise nonreactive aggregates. Uniform gradations of particles of each material were used to eliminate the effects of particle size on the observed reactions.

For some materials such as chert, expansion of concrete decreases markedly as the percentage of reactive material increases beyond the pessimum proportion. Mather[51], for example, reports that certain gravels in Mississippi and Louisiana contain chert in amounts far in excess of the pessimum proportion. Expansion of concrete containing these gravels has been found to be so low that the materials could be considered safe.

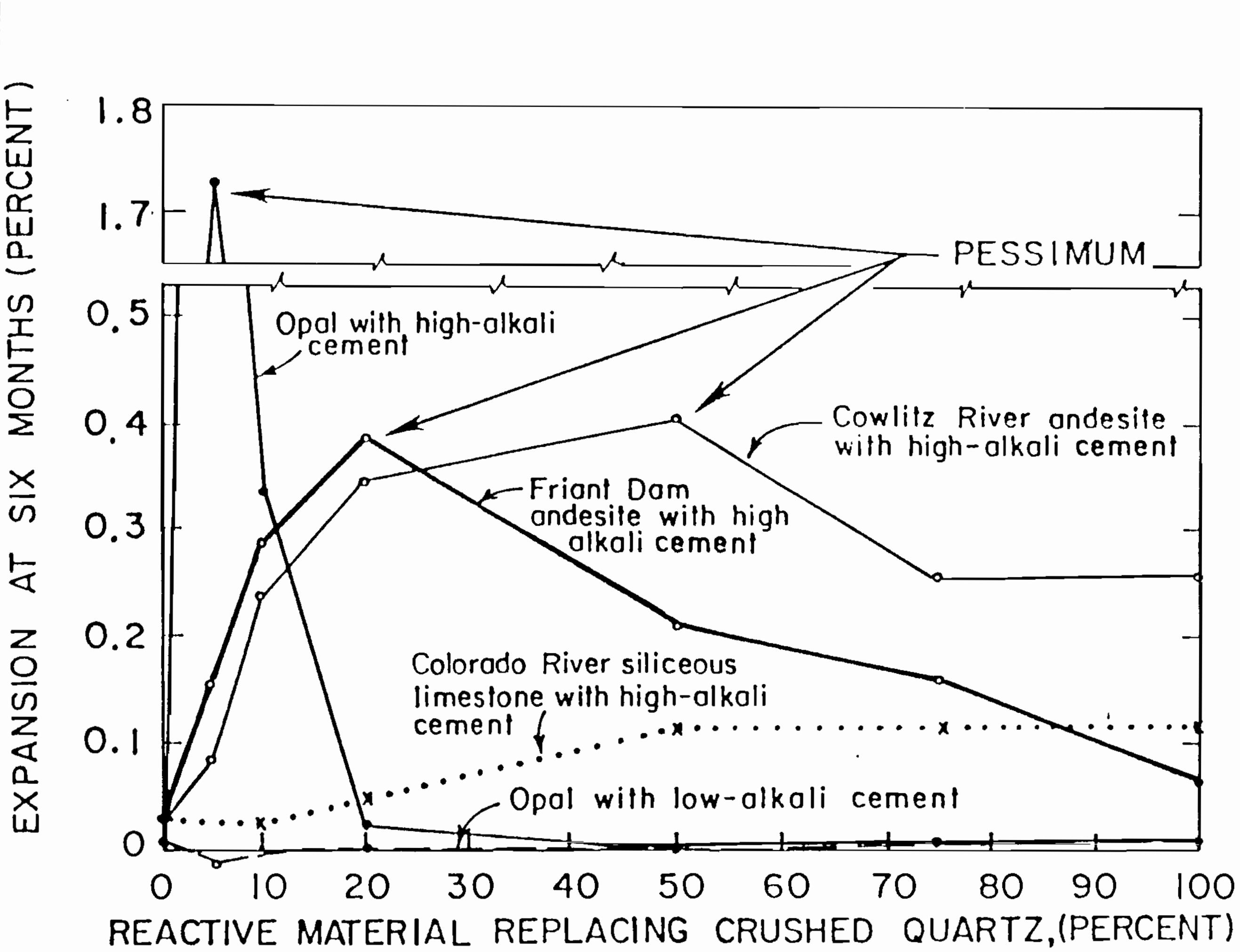


Fig. 4.1 Relationship between the proportion of reactive material in a crushed quartz control aggregate and expansion of test specimens [4]

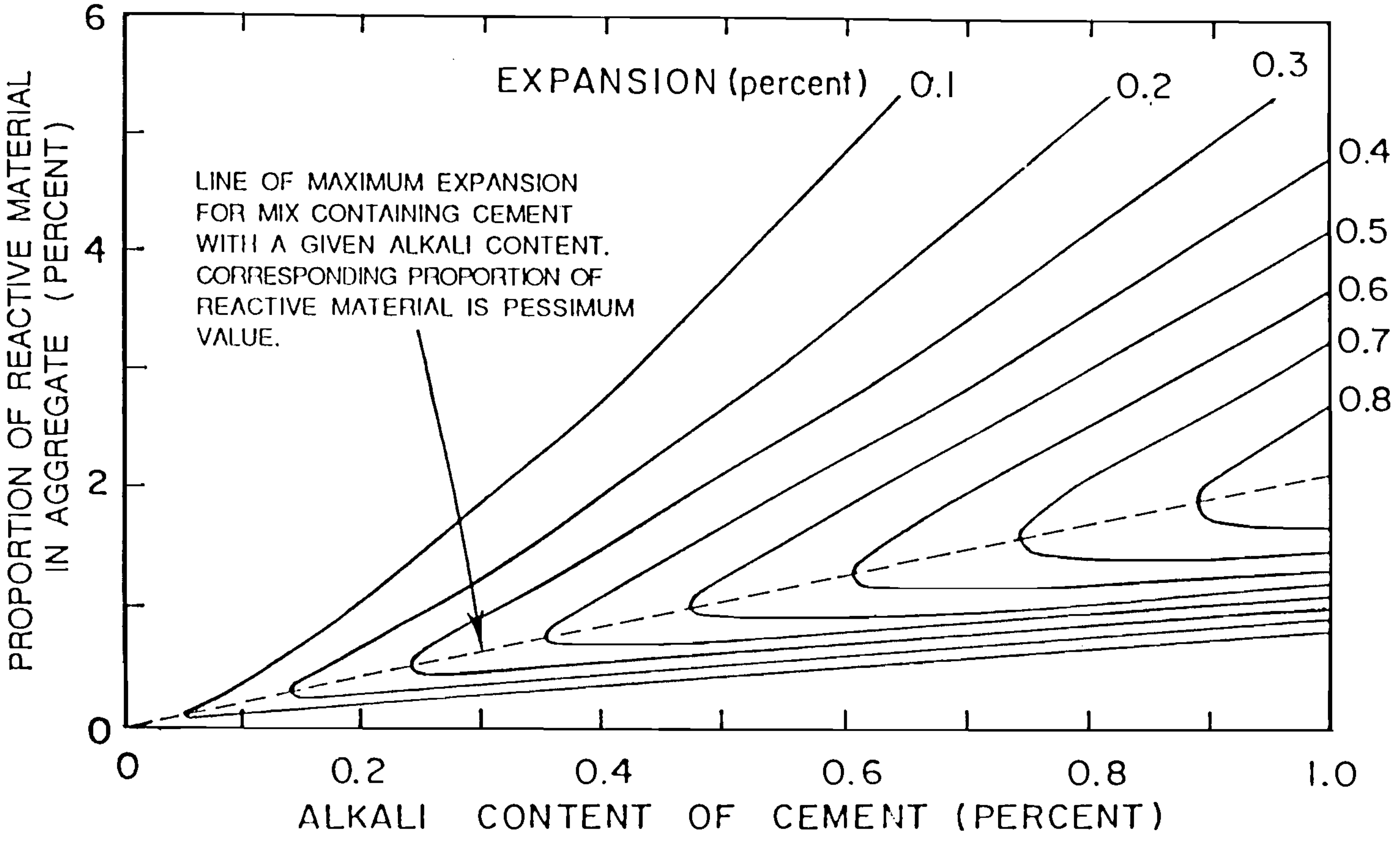
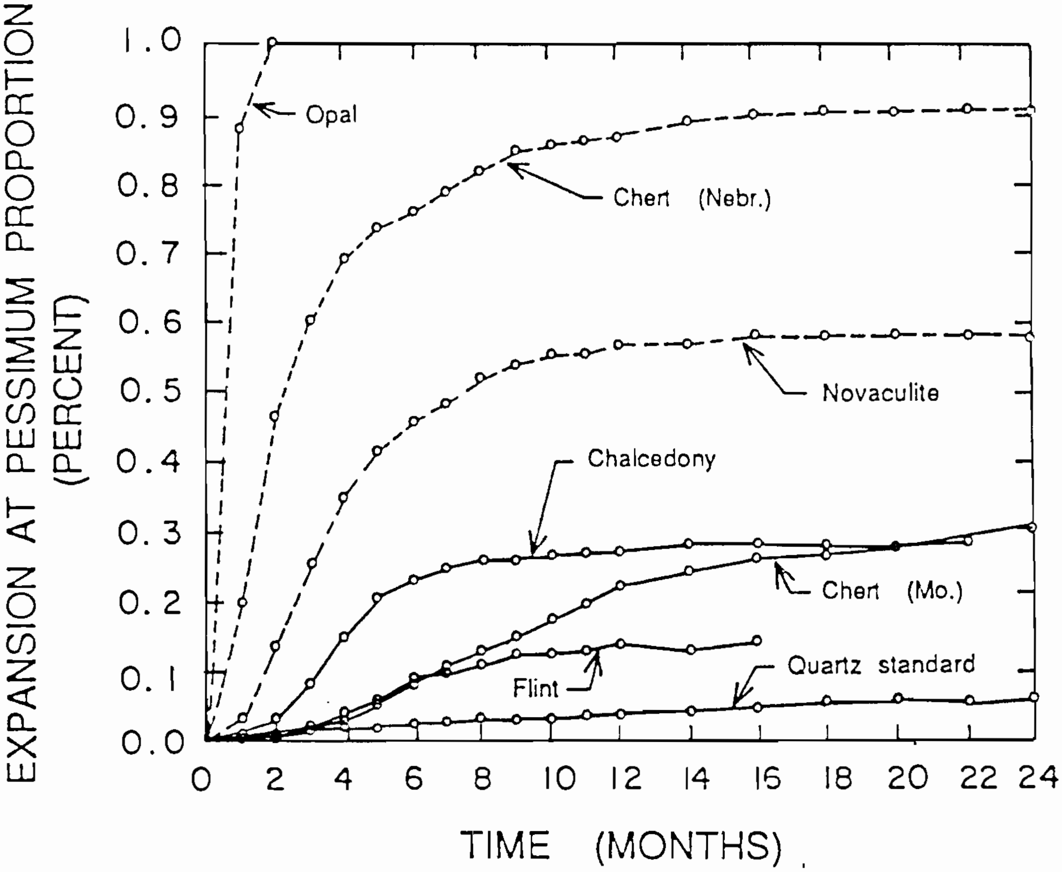


Fig. 4.2 Variation of the pessimum proportion of one reactive material in a control aggregate with the alkali content of cement [50]



4.3 Expansion of test specimens containing a high alkali cement and pessimum proportions of siliceous rocks and minerals [4]

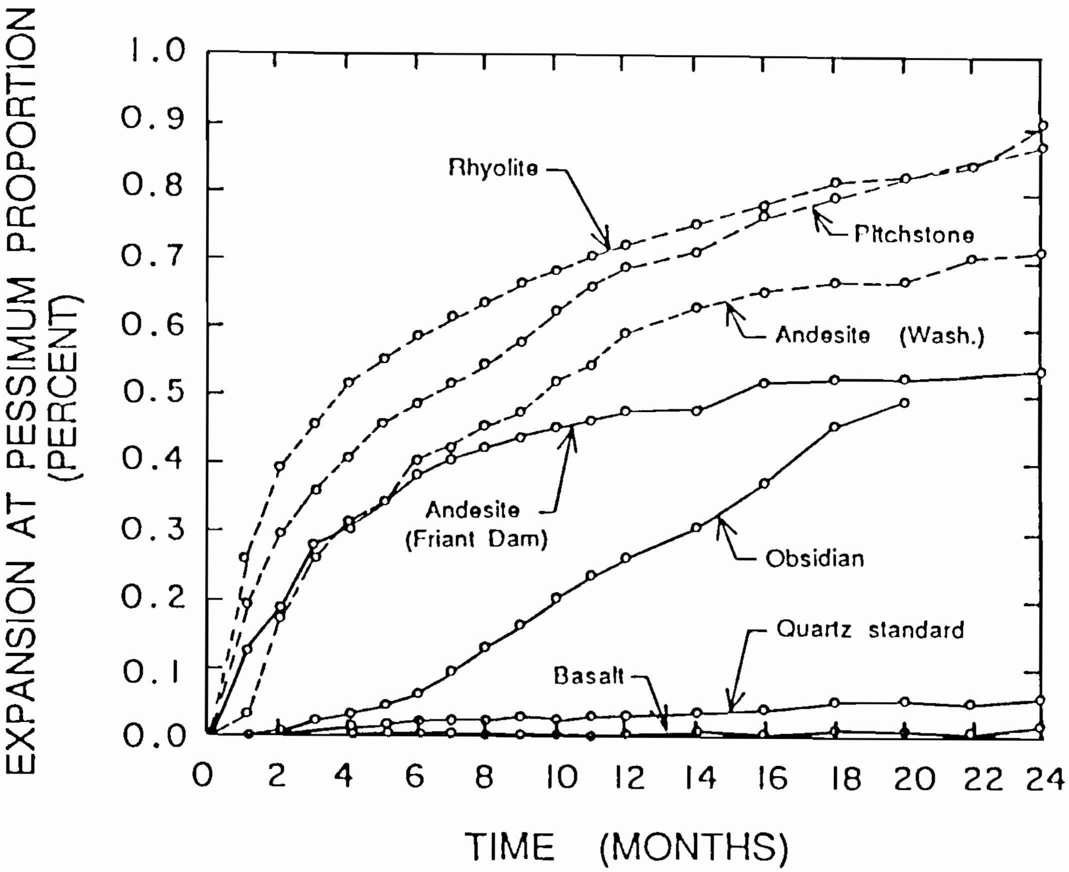


Fig. 4.4 Expansion of test specimens containing a high alkali cement and pessimum proportions of rock types selected from gravel [4]

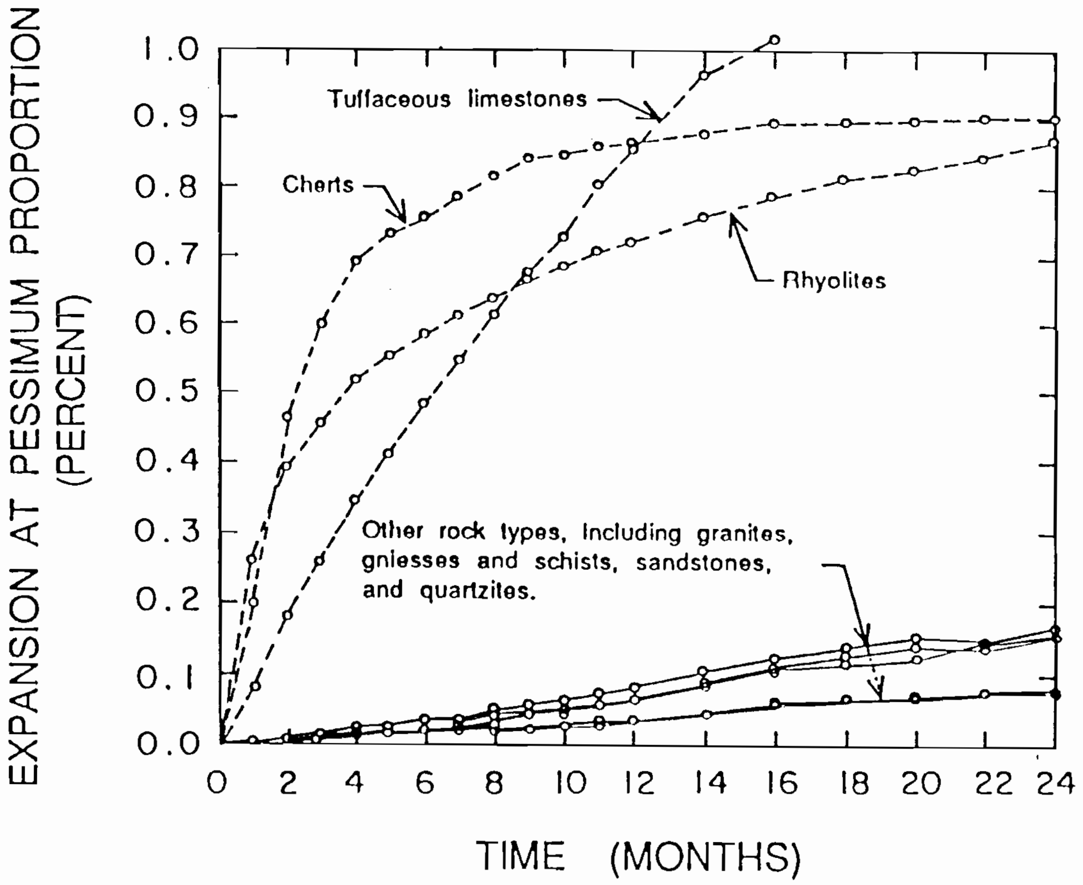


Fig. 4.5 Expansion of test specimens containing a high alkali cement and pessimum proportions of volcanic rocks [4]

The size of reactive particles in an aggregate also affects expansion of concrete in various ways. Studies of very reactive materials have indicated that for a fixed percentage of reactive material in an aggregate, reactivity increases as particle size decreases. For less reactive material, however, the opposite appears true.[25] These observations hold for particles retained on a #325 sieve (greater than 44 microns or 0.0017 in. diameter).

Behavior of materials passing a #325 sieve is apparently not as predictable. Some studies have indicated that reactive materials of this degree of fineness inhibit expansions.[1,52] Other studies revealed that, at least in certain proportions, very reactive particles as fine as 20 to 30 microns or 0.0008 to 0.0012 in. actually lead to expansions as great as, if not greater than, those involving larger materials.[30]

Additionally, the pessimum proportion for a given material in an aggregate has been found to vary with particle size.[53]

4.2 Role of Cement.

4.2.1 Alkali Content. Alkalies are considered to be "minor" constituents of portland cement, typically comprising from 0.2 percent to 1.3 percent of the total cement weight.[54] The influence of alkalies on the properties of concrete, however, is not minor. Expansions due to alkali-silica reaction increase as the alkali content of cement and the weight of alkalies per unit volume of concrete increase as shown in Figs. 4.6 and 4.7.

The total alkali content of cement, calculated as alkali oxides, is typically expressed in terms of equivalent sodium oxide. Some evidence indicates that potassium accelerates expansions of concrete due to alkali-silica reaction more than sodium, but causes lower ultimate expansions.[55,56] However, other evidence shows that expansions appear to be more related to total alkali content than to the individual amounts of sodium and potassium.[17]

Alkalies also affect many other properties including [57,58,54]:

1. drying shrinkage (increases as alkali content increases),
2. setting time,
3. response to admixtures (accelerators, set retarders),
4. staining or discoloration of surfaces,
5. reactions of C_2S and C_3S with water, and
6. strength:

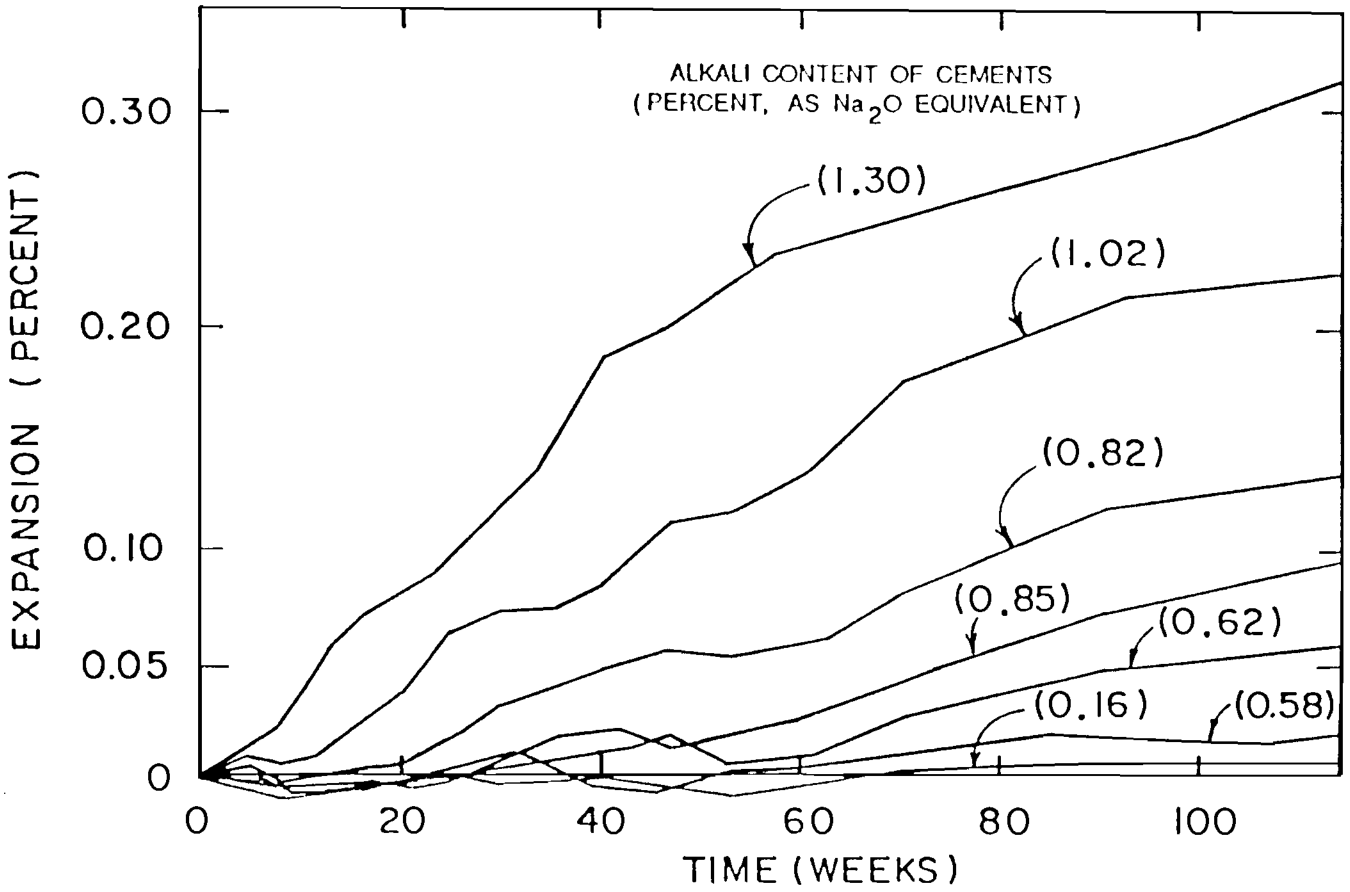


Fig. 4.6 Relationship between the alkali content of cement and expansion of test specimens [59]

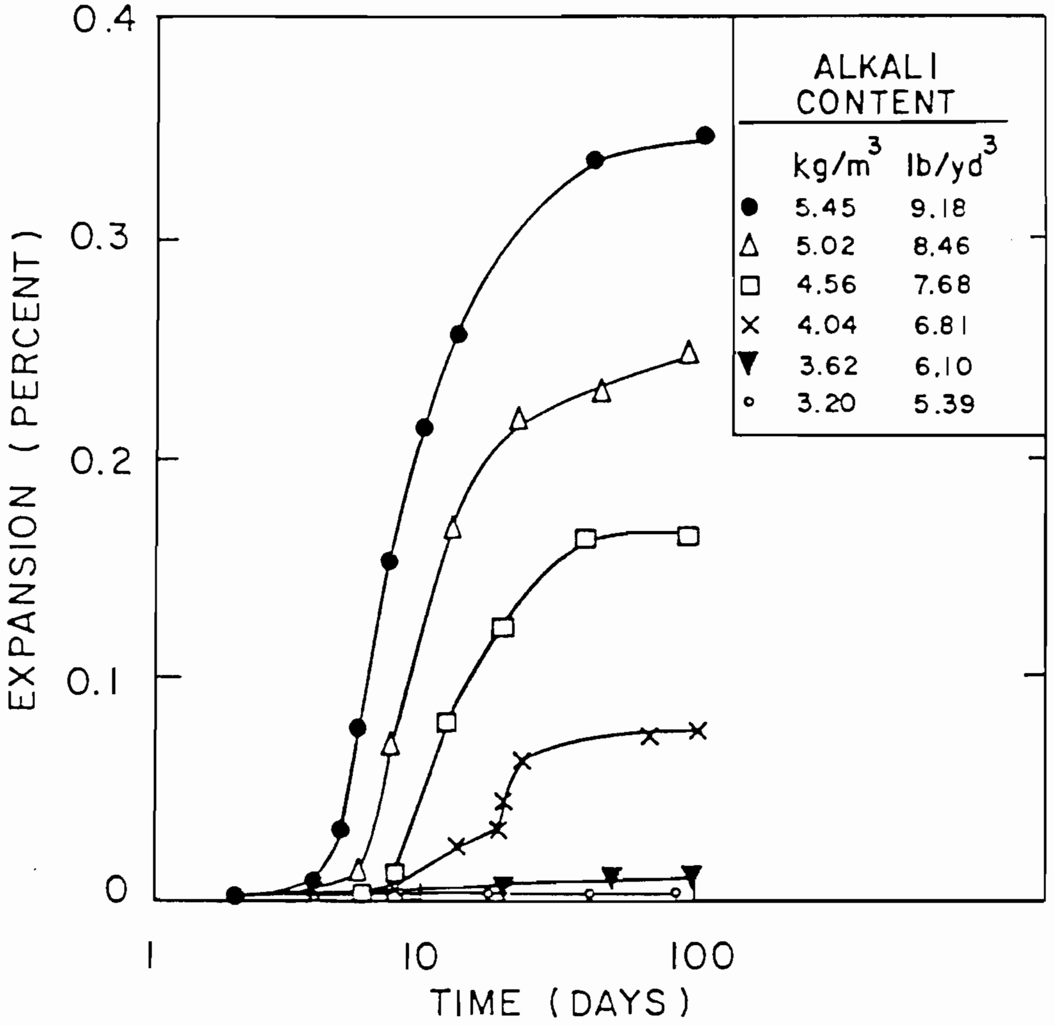


Fig. 4.7 Relationship between the alkali content of concrete and expansion of test specimens [27]

a) cements containing no alkalies experience abnormally slow strength gains;

b) for cements containing 0 percent to 0.4 percent Na_2O: as sodium oxide content increases, strength increases;

c) from 3 days to 28 days: K_2O is responsible for poor strength gain; and

d) from 28 days on: increasing alkali content causes decreased rate of strength gain.

The alkali content of cement also appears to affect the strength and durability of concrete containing fly ash .[60]

Stanton observed that alkali-silica reaction was negligible when the alkali content of the cement used was less than 0.60 percent.[25] Subsequent studies [29,61,62] verified this observation. ASTM adopted this value as a recommended limit for total alkalies in cement used with reactive aggregates and included it in ASTM C 150.

In recent years, some criticism of this standard has arisen. Mather [1] has stated that the ASTM approach is insufficient because:

1. in some cases where the 0.60 percent limit was specified, a higher limit would have been safe, and
2. in other cases, significant cracking occurred with nonreactive aggregates and cements exceeding the 0.60 percent limit.

Oberholster et al. [59] claimed that the 0.60 percent limit ignores two facts:

1. not all of the alkalies in a cement may be available for reaction with aggregates since solubility of alkalies varies between cements, and
2. the alkali content of concrete depends on the alkali content of cement plus the cement content of the concrete.

The latter aspect is illustrated in Fig. 4.8, which shows the decrease in expansion for mixtures containing a given cement as cement content decreases. The above two factors have been incorporated by Oberholster et al. [59] into a diagram, presented in Fig. 4.9, which relates the active alkali content of a cement (alkalies released in solution), cement content of the concrete, alkali content of the concrete, and potential for deleterious reaction.

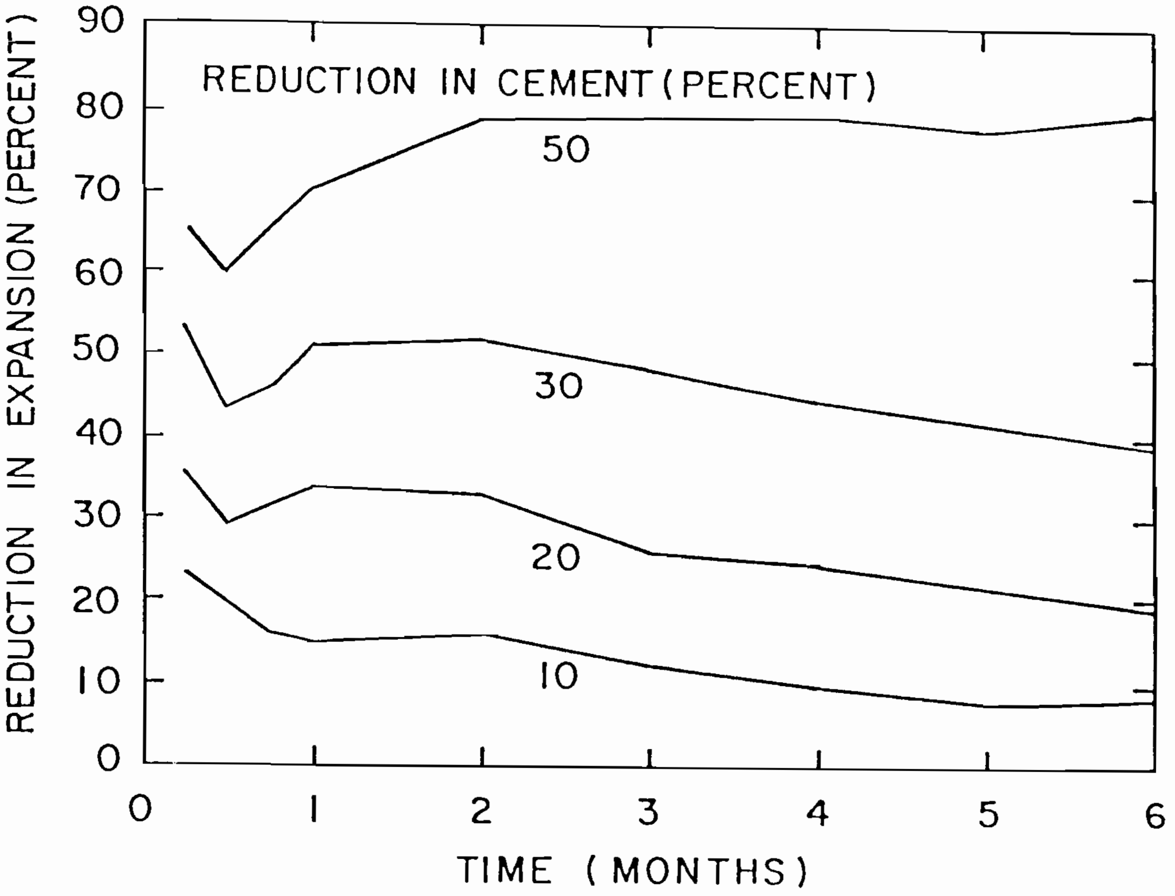


Fig. 4.8 Reduction of expansion of test specimens in relation to reduction of cement content of concrete [63]

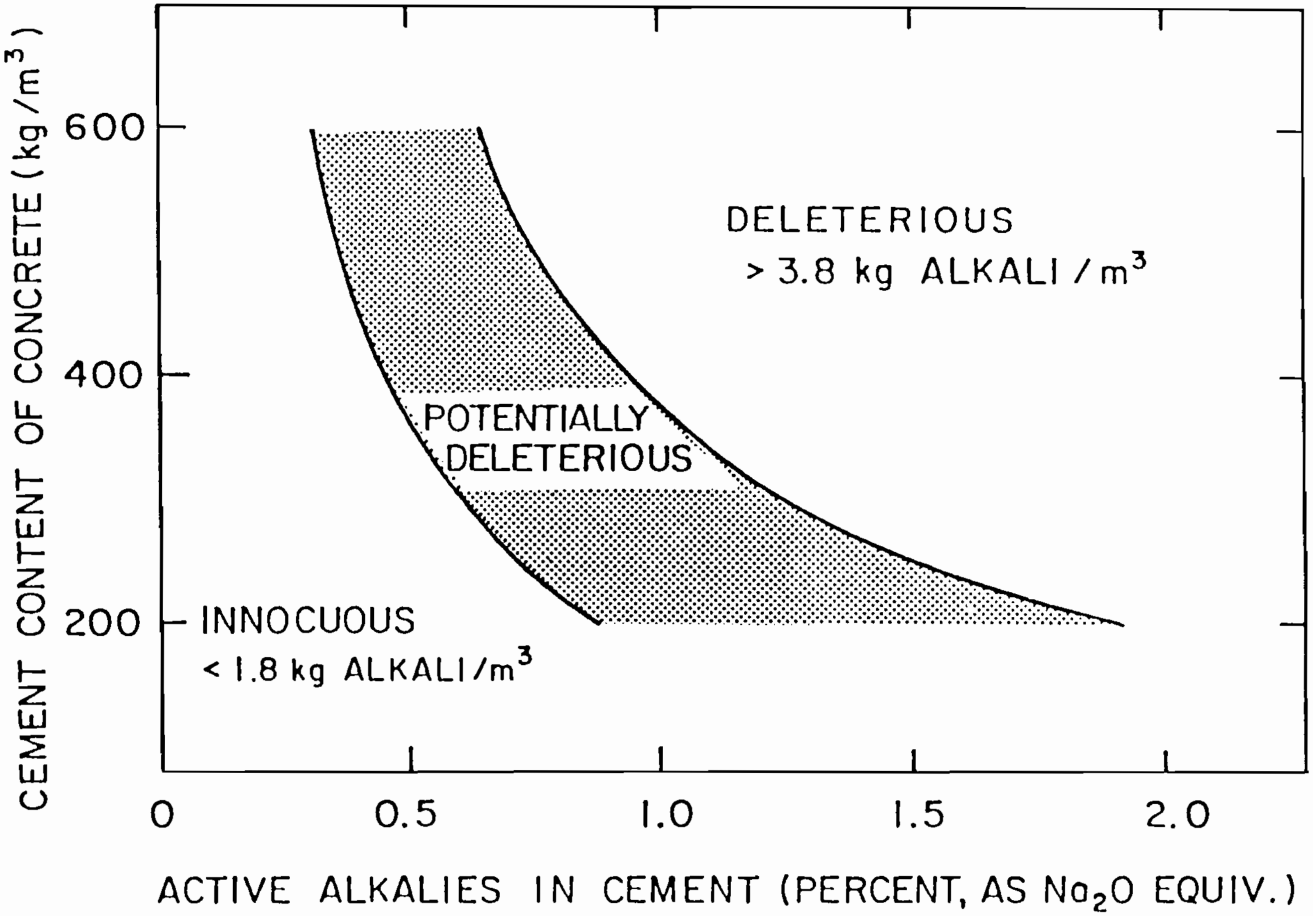


Fig. 4.9 Relationship between "active" alkalies in cement, cement content of concrete, and potential for alkali-silica reaction [59]

While research in West Germany has indicated that the 0.60 percent total alkali limit provides adequate security against deleterious reactions, more flexible standards have been developed.[58] A limit is placed on total alkalies per unit volume of concrete, based on the reactivity of the aggregate. Thus, the lowest alkali cement is required only for the "worst case" of rich mixtures containing the most reactive aggregates. As a result, more responsibility is given to the concrete mixture designer, who must select a cement while considering the reactivity of the aggregate and the allowable alkali content per unit volume. This approach has also been studied in Denmark [58] and in Great Britain, New Zealand, and Australia [27] and has been promoted for use in the United States.[1] The effect of mineral admixtures and their alkalies has not been addressed by these studies.

Although a value for total alkalies per unit volume of concrete can be calculated, the actual distribution of alkalies in a concrete mass is not necessarily constant. Studies by Nixon et al. [64] indicated that evaporation of moisture from the top surface of concrete causes water to be drawn upward to the surface. Soluble alkalies are carried by the migrating moisture. Consequently, these alkalies are concentrated near the top of the concrete at levels far greater than would be expected. Such conditions might be involved in cases where reactions are observed in concrete containing low alkali cement or aggregate thought to be nonreactive.

4.2.2 Fineness. One of the final steps of the production of portland cement is grinding a blend of clinker and gypsum into a fine powder.[54] The rate of hydration of a cement depends on its total surface area which, in turn, depends on the degree to which the cement is ground. For rapid strength development, high fineness of the particles is required. Increasing the fineness of a cement, however, greatly increases its cost. Other effects of increased fineness are:

1. more rapid deterioration of the cement on exposure to the atmosphere,
2. increased amounts of gypsum required for set retardation,
3. increased water content of the concrete required for a given consistency,
4. slightly improved workability for a given consistency, and
5. intensifying alkali-aggregate reactions.

Several investigations into the effects of cement fineness on alkali-silica reaction have been conducted.[61,65] Figure 4.10 demonstrates the marked effect fineness has on expansion of test specimens. Alkalies are thought to be released more rapidly from a fine cement than from a coarse cement and are therefore more readily available to participate in reactions with aggregates.[61]

4.2.3 Type. ASTM recognizes five types of portland cement (I-V) plus cement/fly ash (IP), and cement/blast furnace slag (IS) blends, as shown in Table 4.1. Virtually all studies of alkali-silica reaction have involved Type I cement as it is the type used most frequently.

The effect of fly ash on the characteristics of concrete has been found to be practically the same whether it is added as an admixture while making concrete or blended with clinker before or after grinding to form Type IP cement.[60] The advantage of blending the fly ash with the clinker lies in the ability to control the uniformity of the product.

No standards exist regarding the use of blended cements with reactive aggregates. Research by Mehta et al. [58] indicated that not all Type IP cements can be used safely with reactive aggregates. Based on the results of this study, guidelines restricting the alkali content of blended cements appear to be necessary, although a 0.60 percent limit, similar to that for portland cement, could be too restrictive for blended cements.

This study also included mixtures containing Types I, III, and V cement. For specimens containing each type of cement, expansions generally increased as alkali contents increased, with few exceptions. Typically, specimens containing Type III cement expanded similarly to those containing Type I cement with a like amount of alkalies. Type V cement specimens generally expanded more than the Type I and Type III cement specimens with similar alkali contents.

Based on the work of Chatterji [34] and studies of cement fineness[65], the high C_3S content and increased fineness of a typical Type III cement would seem to indicate that this cement would promote greater expansions than would Type I or Type V cement. Mixes containing Type I or Type V cement would be expected to be closer in behavior, while those containing Type IV cement would be expected to expand least of all.

Lerch and Ford [66] studied the behavior of cement Types I, II, III, IV, and V in mixtures with nonreactive and reactive aggregates. The alkali contents of these cements varied widely, preventing valid comparisons, but it was observed that the cement of lowest alkali content which produced 0.075 percent expansion in specimens after five years of exposure testing was a Type III cement.

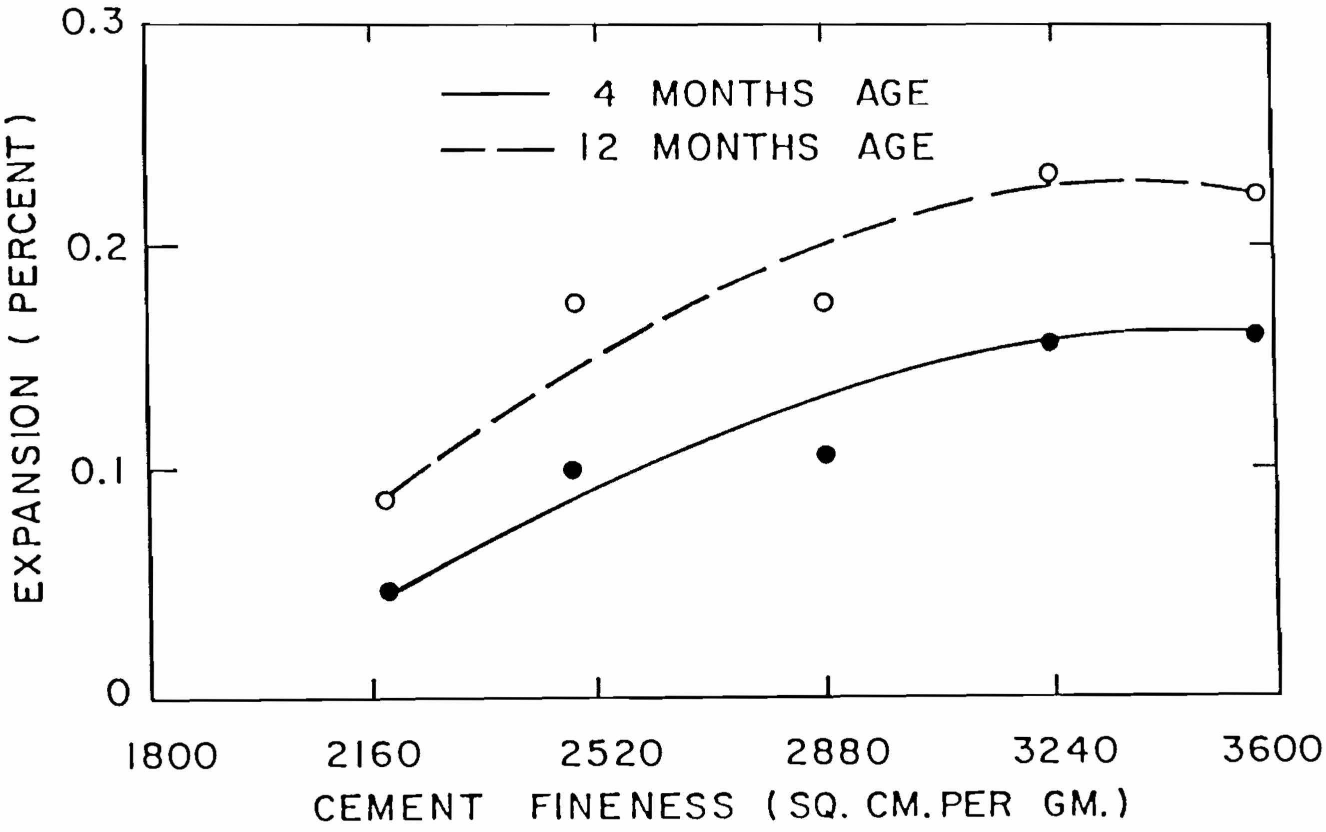


Fig. 4.10 Effect of cement fineness on expansion of test specimens [27]

Table 4.1 ASTM classification of cement[7]

ASTM Type	Description
I	General purpose
II	Moderate heat, moderate C_3S and C_3A content
III	High early strength, high C_3S content, very fine
IV	Low heat, low C_3S and C_3A content, coarse
V	Sulfate resistant, low C_3A content
IP	Fly ash blended with portland cement in amounts of 15% to 40%, by weight. Behavior similar to Type IV cement
IS	Blast furnace slag blended with portland cement in amounts of 25% and 65% by weight. Behavior similar to Type IV cement

4.3 Role of Water

Unlike the cement and aggregate components of concrete, little attention is usually given to the mixing water used. Often, the old adage "if you can drink it, you can make concrete with it" is followed .[7,67] Despite the lack of attention given to it, the presence of water is not only necessary for the hydration of cement, it is a critical factor in the occurrence of alkali-silica reaction. Water serves as a vehicle for alkalies and hydroxide ions to reach the surfaces of siliceous aggregates and is also necessary for expansion to occur.

The effect of alkali ions in mixing water can be judged by determining the amount of ions supplied by the water as a percentage of the weight of cement in a mixture.[68] 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, as shown in Table 4.2.

Since the solubility of silica increases as pH increases, as shown in Table 2.1, the pH of the mixing water could be expected to have a bearing on the degree and rate of alkali-silica reaction. Steinour [68] discussed the effects of the pH level of mixing water, but only from the aspect of potential for causing quick-set or lower strength. The Corps of Engineers [69] states that water having a pH ranging from 6.0 to 8.0 is safe for use in concrete, but does not provide the rationale for such a limit.

Relatively pure water can be obtained by the distillation of tap water.[70] The general effect of the impurities found in tap water can be seen by comparing mixtures containing tap water with mixtures containing distilled tap water. Mather [71] reported, however, that specimens containing tap water behaved no differently than those containing distilled water.

4.4 Role of Mineral Admixtures

The beneficial effects of mineral admixtures on expansions due to alkali-silica reaction were discovered by Stanton early in his research.[25] Natural pozzolans, particularly finely ground portions of reactive aggregates, received much of the initial attention.[25,72] Later studies included artificial pozzolans, as well.[73]

Table 4.2 Typical chemical compositions of city water [68]

TYPICAL ANALYSES OF CITY WATER SUPPLIES (parts per million					
Analysis No.	1	3	5	6	7
Silica (SiO_2)	2.4	12.0	10.0	9.4	22.0
Iron (Fe)	0.14	0.02	0.09	0.2	0.08
Calcium (Ca)	5.8	36.0	92.0	96.0	3.0
Magnesium (Mg)	1.4	8.1	34.0	27.0	2.4
Sodium (Na)	1.7	6.5	8.2	183.0	215.0
Potassium (K)	0.7	1.2	1.4	18.0	9.8
Bicarbonate (HCO_3)	14.0	119.0	339.0	334.0	549.0
Sulfate (SO_4)	9.7	22.0	84.0	121.0	11.0
Chloride (Cl)	2.0	13.0	9.6	280.0	22.0
Nitrate (NO_3)	0.54	0.1	13.0	0.2	0.52
Total Dissolved Solids	31.0	165.0	434.0	983.0	564.0

Silica fume and rice husk ash, two extremely fine, highly siliceous by-products, have proven to be the most effective inhibitors of expansion.[74] Natural pozzolans tend to be moderately effective.[75] 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.

4.4.1 Fly Ash. Use of "coal ash" in concrete occurred as early as 1914.[76] Interest in the use of this by-product in concrete arose with the realization that the conditions under which coal ash is produced are similar to those under which volcanic ash is produced. It was anticipated that a low carbon coal ash of sufficient fineness might prove to be equal to volcanic ash as a pozzolan. The term "fly ash" was coined by Davis et al..[58,77] in the first comprehensive report on the properties of concrete containing fly ash. This report led to much wider acceptance of the use of fly ash, particularly in mass concrete. The use of fly ash became even more widespread as its ability to inhibit alkali-silica reaction in some situations became known.

Coal is a sedimentary and metamorphic rock composed of combustible matter derived from ancient swamps.[46] Coal starts as organic material composed primarily of carbon, hydrogen, and oxygen. Deep burial of the material over time results in increased heat and pressure, driving off the oxygen and hydrogen. Differences in coal type are primarily a function of maximum temperature. Pressure and the nature of the original plant material play much less significant roles. Figure 4.11 illustrates the ranking of coals according to carbon content.

Coal contains from 3 percent to 30 percent inorganic residues, with the amount decreasing as rank increases.[78] When coal is pulverized and burned, these impurities are not volatilized. In a typical combustion chamber, the larger particles of impurities collect at the bottom of the boiler, while smaller particles are carried off by the hot flue gases. These particles are known as "bottom ash" and "fly ash" respectively.

Fly ash comprises 10 percent to 85 percent of the residue.[78] The distribution between bottom ash and fly ash is a function of the burner type, the temperature at which the particles of coal may become fused together, and the type of boiler.

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.[78] Silica, iron, aluminum, and calcium constitute 95 percent to 99 percent

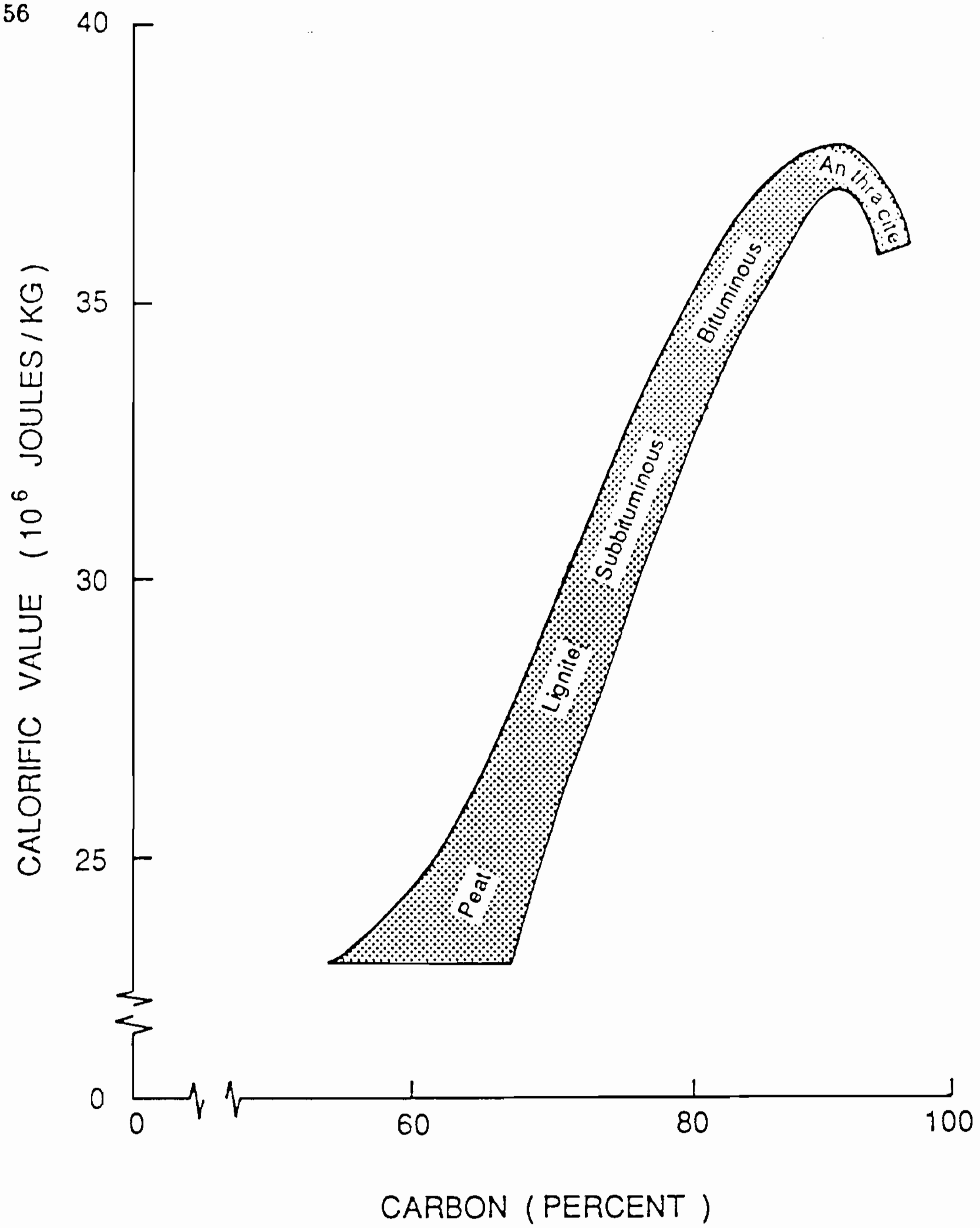


Fig. 4.11 Ranking of coals by carbon content [46]

of fly ash. Magnesium, titanium, sodium, potassium, sulfur, and phosphorus account for 0.5 percent to 3.5 percent while up to 50 other elements may occur in trace amounts.

Fly ash generally consists of particles ranging from 1 micron to 100 microns or 0.00004 to 0.004 in. in diameter, as shown in Fig. 4.12.[75] The majority of particles is fine enough to pass a #325 sieve (less than 44 microns or 0.0017 in. diameter). The range of particle sizes is affected by the dust collection equipment used.[79] The particles retained by mechanical collectors are coarser than those retained by electrostatic systems.

Fineness is considered to be the single most important physical characteristic influencing the chemical activity of fly ash.[78] The rate at which fly ash participates in reactions increases as particle size decreases.[80] Coarser particles are "distinctly deleterious" and their removal is recommended. The fineness of fly ash is frequently expressed in terms of the amount passing a #325 sieve or in terms of surface area per unit mass.

Fly ash is predominantly glassy due to rapid cooling during the collection process.[80] The finer the particles present, the greater the amount of glass.[78] These glassy particles may either be solid or hollow, and range from rounded to spherical in shape. The hollow empty spheres are known as cenospheres while hollow spheres filled with smaller particles are called plerospheres. The remainder of the particles are porous in nature and vary from rounded to elongated in shape.

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 as was shown in Table 1.2. The chemical and physical requirements for each class of fly ash are presented in Table 4.3. Of interest is the difference in the minimum $SiO_2 + Al_2O_3 + Fe_2O_3$ required for each class. The presence of these constituents is considered indicative of the pozzolanic potential of the fly ash. The requirement for the presence of these three oxides is to ensure that sufficient glassy particles are present in the fly ash to participate in pozzolanic reactions. A smaller amount of these constituents is required for Class C fly ashes since they typically contain large amounts of calcium, which provides these fly ashes with cementitious properties of their own. Early studies attempted to relate each of these individual oxides to fly ash performance in concrete, but met with little success.[80]

The classification of fly ash by coal source has not received total acceptance.[82] The TSDHPT recognizes two types of fly ash, known as Type A and Type B, based on chemical composition.[81] The requirements for these two classifications are also presented in Table 2.5. These types vary in calcium content, which is indicated indirectly by the

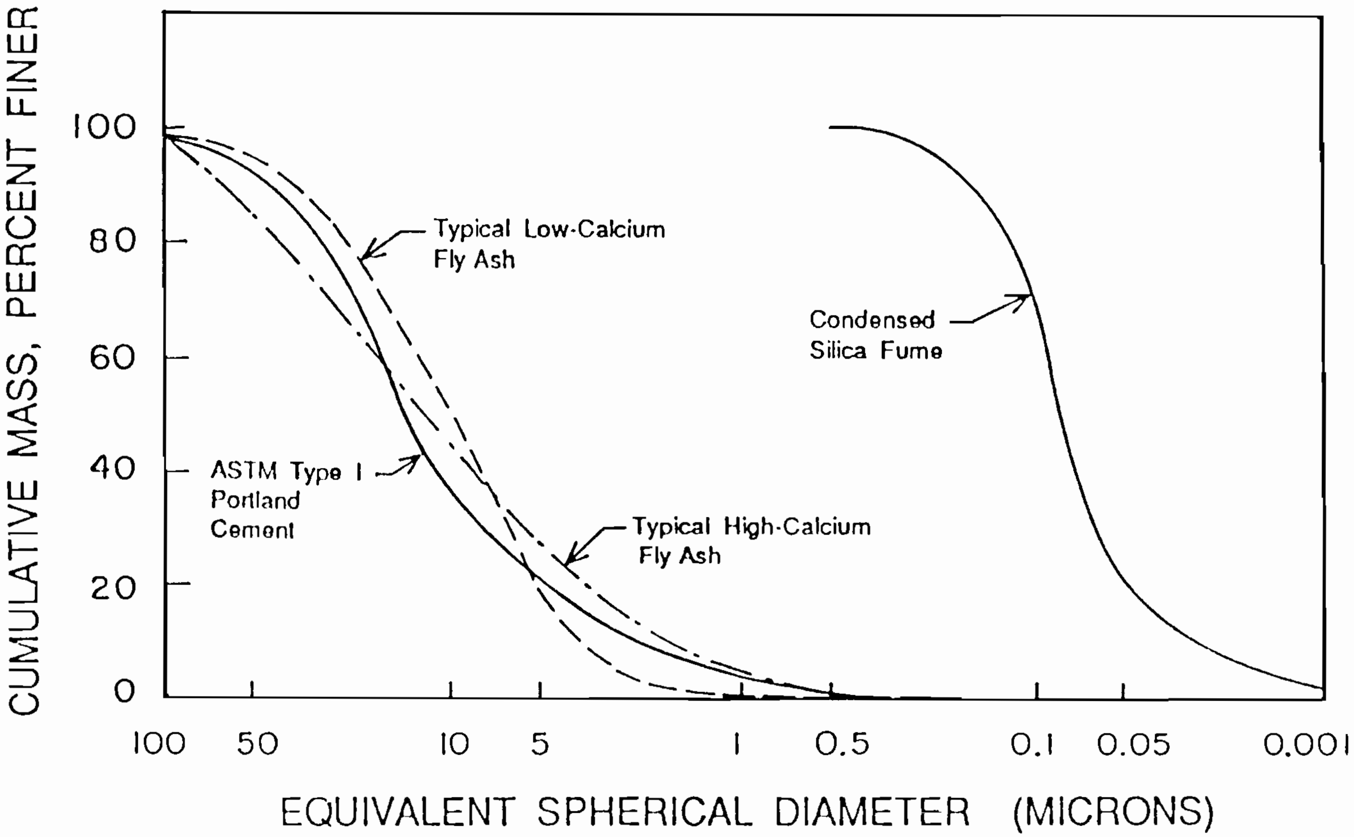


Fig. 4.12 Typical particle size distributions for mineral admixtures and portland cement [75]

Table 4.3 **ASTM and TSDHPT specifications for fly ash composition**[6,81]

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	5.0	5.0
Available alkalies (expressed as Na_2O) maximum %	1.5	1.5	1.5	1.5
Loss on ignition	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

amount of SiO_2 + Al_2O_3 + Fe_2O_3. Type A fly ash is typically low calcium (high Si+Al+Fe oxide content) while Type B fly ash is typically high calcium (low Si+Al+Fe oxide content). Type A usually corresponds to ASTM Class F while Type B usually corresponds to Class C fly ash. The TSDHPT classification will be used throughout this report.

The ASTM specifications have also received criticism regarding the requirements for the presence of minimum amounts of SiO_2, Al_2O_3, and Fe_2O_3 in fly ash. Mehta [75] stated that this requirement is arbitrary and has no direct relationship to the properties of the material. He has suggested a new classification system which is presented in Table 4.4. This system is based on minerological and particle characteristics and includes mineral admixtures such as silica fume, which are not currently covered by ASTM specifications.

Butler [82] has stated that the practical significance of the measurement of the sum of silica, aluminum, and iron oxides in fly ash is not great. Instead, he suggested that a rapid determination of the chemical uniformity and the presence of alkalies would provide more insight into fly ash quality. These characteristics could be determined rapidly by measuring the amounts of acid-soluble and water-soluble material in the pozzolan. Butler has proposed a new set of chemical and physical requirements for ASTM C 618 based on such tests. In addition, the three classes of pozzolans defined in ASTM C 618 would be revised to accommodate new materials like silica fume as shown in Table 4.5.

Kokubu [60] reported that requirements for silica content alone are logical since pozzolanic activity varies greatly with changes in this parameter. Japan and the Soviet Union currently have requirements for SiO_2 content, rather than combined SiO_2, Al_2O_3, and Fe_2O_3 content.

Diamond [20] has proposed that "sensible groupings" of fly ash based on specific measurable characteristics affecting concrete be established. The two most important criteria are the amounts of carbon residue and analytical CaO present. Other proposed criteria include particle size, alkali sulfate content, total sulfate content, and percentage of cenospheres.

Dhir et al. [83] have observed that fineness is the best physical parameter for classifying fly ash. The fineness of fly ash was found to relate well to other characteristics of the ash as well as having influence on the design properties of concrete. They have proposed a system of classification based on fineness as shown in Table 4.6.

Table 4.4 System of classification of mineral admixtures for concrete proposed by Mehta[75]

CLASSIFICATION	CHEMICAL AND MINERALOGICAL COMPOSITION	PARTICLE CHARACTERISTICS
I. Cementitious and Pozzolanic		
a. Granulated Blast Furnace Slag	Mostly silicate glass containing mainly calcium, magnesium, aluminum, and silica. Crystalline compounds of melilite group may be present in small quantity.	Unprocessed material is of sand size and contains 10% to 15% moisture. Before use it is dried and ground to to particles less than 45 microns (usually about 500m^2/kg Blaine). Particles have rough texture
b. High-calcium fly ash	Mostly silicate glass containing mainly calcium, magnesium, aluminum, and alkalies. The small quantity of crystalline matter present generally consists of quartz and C_3A; free lime and periclase may be present; $C\bar{S}$ and $C_4A_3\bar{S}$ may be present in the case of high-sulfur coals. Unburnt carbon is usually less than 2%.	Powder corresponding to 10% to 15% particles larger than 45 microns (usually 300-400 m^2/kg Blaine). Most particles are solid spheres of less than 20 microns diameter. Particle surface is generally smooth but not as clean as in low- calcium fly ashes
II. Highly Active Pozzolans		
a. Condensed silica fume	Consists essentially of pure silica in noncrystalline form. diameter (about 20 m^2/kg surface area by nitrogen adsorption).	Extremely fine powder consisting of solid spheres of 0.1 micron average
b. Rice husk ash: (Mehta-Pitt process)	Consists essentially of pure silica in noncrystalline form. (about 60 m^2 surface area by nitrogen absorption).	Particles are generally less than 45 microns but they are highly cellular
III. Normal Pozzolans		
a. Low-calcium fly ash	Mostly silicate glass containing aluminum, iron, and alkalies. The small quantity of crystalline matter present consists generally of quartz, mullite, sillimanite, hematite, magnetite.	Powder corresponding to 15% to 30% particles larger than 45 microns (usually 200-300 m^2/kg Blaine). Most particles are solid spheres of average 20 micron diameter. Cenospheres and plerospheres may be present
b. Natural materials	Besides aluminosilicate glass, natural pozzolans contain quartz, feldspar, mica.	Particles are ground to mostly under 45 micron and have rough texture

Table 4.5 System of pozzolan classification proposed by Butler[82]

CLASS	CURRENT ASTM REQUIREMENT BASED ON SOURCE OF FLY ASH (ASTM C 618)	PROPOSED REQUIREMENT BASED ON MINERAL ADMIXTURE PROPERTIES
N	Natural pozzolans	Materials that increase water demand*
F	Anthracite or bituminous fly ash	Water reducing, cementitious materials
C	Lignite or subbituminous fly ash	Water reducing, nonsetting materials

* Water demand determined according to Section 33 of ASTM C 311

Table 4.6 System of fly ash classification proposed by Dhir et al.[83]

CLASS	FINENESS*	OBSERVATIONS
Premium	<5	Excellent properties; not widely available
1	5 to 20	Good properties; relatively widely available
2	20 to 35	Good to adequate properties; widely available
3	>35	Doubtful economic viability

* The mass proportion of fly ash retained on a 45 micron sieve determined according to British Standard BS 3892: Part 1: 1984 [89]

The use of fly ash in proper amounts has been found to reduce expansion in concrete due to alkali-silica reac- tion.[73,84,85,86,87] The mechanism by which this occurs is not known [75], and has been the subject of much research and some controversy. Hobbs [88] has reported that fly ash merely dilutes the alkalies present in cement, proportionately reducing the effect of the reaction between alkalies and silica. Other studies [73,85] have indicated that the effect of fly ash on alkali-silica reaction is more extensive than could be expected from a diluting agent, meaning that fly ash also is chemically involved.

A number of studies have focused on the interaction between calcium and fly ash with regard to alkali-silica reaction. Research by Chatterji [34] showed that the presence of free $Ca(OH)_2$ is required for the development of alkali-silica reaction. The use of a sufficient quantity of fly ash, or other pozzolans, results in the conversion of all of the free $Ca(OH)_2$ to C-S-H. According to Bhatty [36], the reaction of a low calcium fly ash with $Ca(OH)_2$ yields C-S-H with a low molar ratio of calcium to silica. This type of C-S-H readily incorporates alkalies into its structure, preventing them from participation in reactions with silica particles. A sufficient quantity of fly ash is necessary to bind all of the alkalies in the cement and eliminate the danger of alkali-silica reaction. Higher calcium to silica mole ratio C-S-H is not able to incorporate alkalies, and cannot prevent their reaction with silica. These findings corroborate earlier work done by Rayment.[90]

Ming-shu et al. [91] have taken a different approach to this research, but have come up with similar conclusions. Their work indicated that the greater the acidity of a pozzolan, the more effective it will be. Thus, the greater the amount of silica (acid) and the smaller the amount of CaO (base), the more effective the pozzolan will be in preventing alkali-silica reaction. The effect of the pozzolan is to lower the basicity of the hydration products in the concrete. The more basic the products, (the smaller the proportion of calcium to silica) the greater the amount of alkalies which can be retained. Dunstan [86], in a study of mortar bar specimens, also reported that as the CaO content of a fly ash increases, the amount required to control expansions increases as well.

The effect of alkalies contained in fly ash on alkali-silica reaction is also uncertain. According to Dunstan [86], alkalies in fly ash do not participate in reactions with aggregates, nor do alkalies added to the fly ash by precipitating agents used during the collection process. A study of two fly ashes by Diamond [92] revealed that the use of these fly ashes maintained or slightly reduced the level of alkalies present in the pore solutions of concrete. Alkalies in other fly ashes, it was cautioned, could be more mobile and available for reactions. Diamond also suggested that the use of alkaline precipitating agents in the collection process be banned as their contribution of alkalies to concrete was not desirable.

Smith [93] reported that alkalies in fly ash, although often present in greater quantities than in cement, are trapped in a glassy matrix and released into solution more slowly. Hence, these alkalies would not be free to contribute significantly to the alkali concentration in pore solutions.

High calcium (low silica) fly ashes have been found to contain larger amounts of soluble alkalies, particularly sodium.[75,93] 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. Smith [93] reported that this maximum limit was based on test results using a Class F fly ash, in which potassium was the main source of alkalies. Since the sodium based alkalies which are predominant in Class C fly ashes may be more soluble, it was suggested that the limit of 1.5 percent available alkalies may not be adequate.

The specification for available alkalies in fly ashes contrasts with the specification for cement, which is in terms of total alkalies. Research has indicated that only the soluble, or available, alkalies in fly ashes are released into the pore solutions of concrete to participate in alkali-silica reactions.[20]

The ability of fly ash to lower the pH of pore solutions in concrete is of interest due to the increased solubility of silica in water as the pH rises, as was shown in Table 2.1. Mehta and Polska [87] reported that the pH of mortar decreases significantly as the amount of pozzolan increases. Others, however, have found the pH of fly ash concrete to be only slightly reduced.[86]

The use of fly ash in concrete significantly decreases its permeability.[7,78] 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.

4.4.2 Silica Fume. Silica fume is a recent addition to the category of mineral admixtures for concrete.[94] The earliest documented use of silica fume as a pozzolanic admixture to prevent alkali-silica reactions came in 1972 in Iceland although research began in the 1950's.[95] Technically, most silica fumes do not meet the requirements of ASTM C 618 for pozzolans, since mortars containing silica fume tend to require more water to achieve a suitable workability than is allowed by this specification. Silica fume does, however, meet the pozzolanic definition of a "siliceous material in finely divided form" and is considered the most effective pozzolan in controlling alkali-silica reaction.[74] Studies conducted in Iceland [21] have demonstrated that alkali-silica reaction can be suppressed by replacing as little as 7 percent of the cement in concrete with silica fume as shown in Fig. 4.13.

Silica fume particles are spherical in shape and extremely small in size as illustrated in Table 4.7. As a result, silica fume can cause problems for those handling it. While some concern exists regarding the potential for it to cause silicosis or other health problems, no significant problems are known to have occurred.[16]

Depending on the silicon alloy produced and furnace design, different types of silica fume are produced. Aitcin et al. [15] recognize seven types of silica fume which are presented in Table 4.8. Due to the purity of the materials used in silicon alloys, silica fume from a given source is very constant in composition.

Most literature dealing with the use of silica fume in concrete makes no mention of the composition of the silica fume used.[15] The information which has been published shows that the silica fume in use typically falls in the "Si" and both "SiFe-75 percent" categories of Table 2.10. These three products are nearly identical in composition.

No published data exists regarding the use of the other four classes of silica fume in concrete.[15] These four are quite different in composition than the other three and possess qualities that could make their use in concrete undesirable. Some of these unusual qualities are presented in Table 4.9.

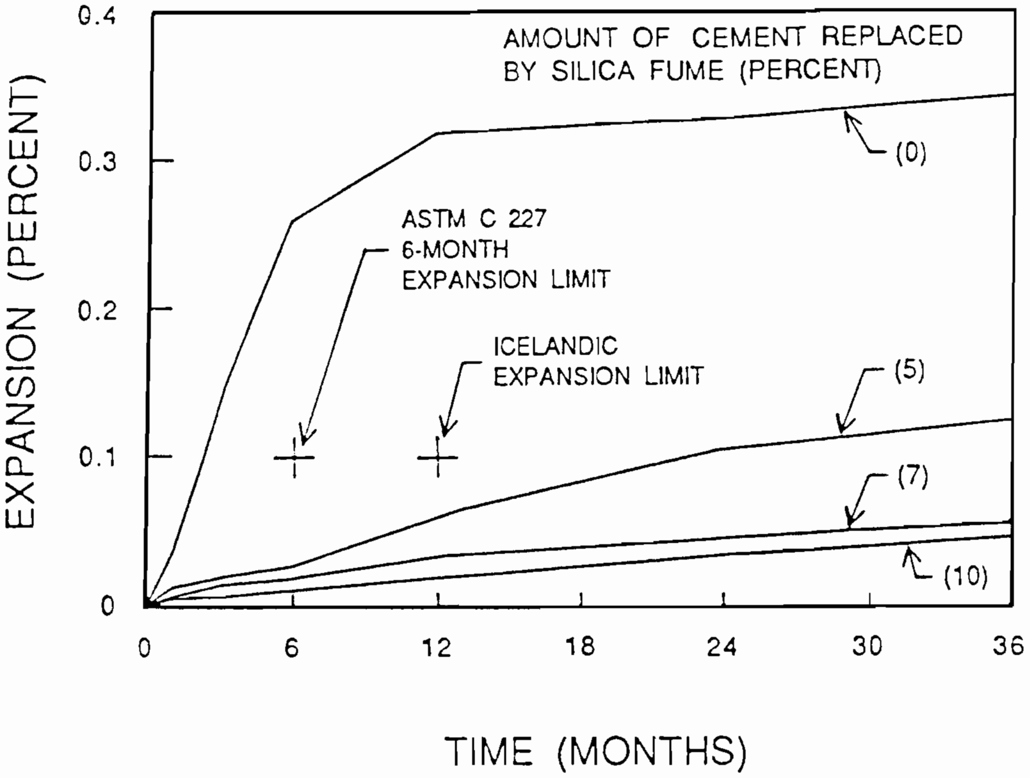


Fig. 4.13 Effectiveness of one Icelandic silica fume in reducing expansion of test specimens [21]

Table 4.7 Fineness of silica fume in comparison to other materials[23]

MATERIAL	FINENESS (surface area per unit mass) m^2/kg
Silica fume	20,000
Tobacco smoke	10,000
Fly Ash	400-700
Typical portland cement	300-400

Table 4.8 Proposed classification of silica fumes by chemical composition [15]

	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

Table 4.9 Unusual characteristics of several classes of silica fumes[15]

CLASS	CHARACTERISTICS
CaSi	The calcium carbide in this type of silica fume reacts with water in a cement mixer 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 percent	This silica fume has also been 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.

CHAPTER 5
TESTS FOR DETERMINING POTENTIAL REACTIVITY OF MATERIALS

5.1 ASTM Standards

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 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 criterion is for use only when six-month data are not available.

ASTM C 227 was developed from the mortar bar tests developed by Stanton in his initial work.[25] At first, correlation of mortar bar expansions with field reports of deterioration were qualitative in nature.[96,97] By 1946, enough data were available to allow Blanks and Meissner[61] to relate the degree of mortar bar expansion to the occurrence of deterioration in actual structures. Aggregates causing mortar bar expansions exceeding 0.1 percent in one year were regarded as deleterious while those causing expansions between 0.04 percent and 0.1 percent were considered suspicious.

Based on these and other test results, ASTM C 33 "Standard Specification for Concrete Aggregates"[6] was amended to indicate that aggregates causing mortar bar expansions of 0.05 percent at six months and/or 0.1 percent at 12 months should be considered "potentially reactive."[71] These limits were pushed forward to three months and six months, based on the results of further testing in the 1950's.

A skilled petrographer can use ASTM C 295 to determine the potentially reactive materials present in a particular aggregate.[93] If suspect materials are found, a chemical test may also be run to further define the potential for reaction. This chemical test, ASTM C 289, classifies 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. Finally, the results of ASTM C 227 would corroborate whether an aggregate is potentially reactive.

Should these tests provide strong indications that the aggregate is reactive, one of three remedies can be selected:

1. use of another, less reactive aggregate;
2. use of a cement containing less than 0.6 percent total alkalies as recommended by ASTM C 150; or
3. use of a mineral admixture (optionally meeting the requirements of ASTM C 618).

In case of inconclusive or contradictory test results, it is left to the judgement of the engineer whether or not the aggregate should be approved or rejected for use.

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. ASTM C 441 differs, however, in several respects. One variation is the requirement of three different mixtures for each test. In the control mixture, a cement with a total alkali content of at least 1.0 percent is preferred. In the test mixture, 25 percent of the cement is replaced by the mineral admixture. The job mixture consists of the actual cement intended to be used on the job plus the intended replacement volume of mineral admixture. 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.

In order to eliminate one variable from the test results, Pyrex glass is used as a control aggregate in all mixtures. Both ASTM C 441 and ASTM C 227 currently specify the gradation of aggregates shown in Table 5.1.

One additional difference between the two test methods is the procedure specified to measure the consistency of the mortar. ASTM C 441 requires the determination of the consistency of the mortar measuring its flow by means of the flow test as specified in ASTM C109 (Test for Compressive Strength of Hydraulic Cement Mortars). This specification calls for a flow of 110 to 115 obtained with 25-+“ drops of the flow table in 15 seconds. ASTM C 227 requires the mortar to have a flow of 105 to 120 obtained with ten +” drops of the flow table in 6 seconds.

The ASTM tests have been subjected to some criticism. While Heck [98] observed good correlation between mortar bar expansion at three months and test results from ASTM C 289, poor correlation existed with six-month data. Poor correlation was also found between the amounts of reactive materials determined by ASTM C 295 and mortar bar expansions. Heck concluded that these three tests were not effective if used

Table 5.1 Gradations of aggregates specified in ASTM C 227 and ASTM C 441[6]

SIEVE SIZE		
PASSING	RETAINED ON	WEIGHT PERCENT
No. 4 (4.75mm)	No. 8 (2.36mm)	10
No. 8 (2.36mm)	No. 16 (1.19mm)	25
No. 26 (1.18mm)	No. 30 (600 microns)	25
No. 30 (600 microns)	No. 50 (300 microns)	25
No. 50 (300 microns)	No. 100 (150 microns)	15

individually and the six-month expansion limit needed to be reduced to 0.075 percent to be useful. Tuthill[99] has stated that the advancement of the ASTM expansion limits from six and 12 months to three and six months was a "dubious" effort to allow concrete producers to obtain faster test results.

Oberholster et al.[59] reported instances of certain materials which did not exceed the three or six-month expansion limits when used in mortar bars but proved excessively deleterious in the field. Reference was made to Tuthill's comments[99] regarding the compression of the length of the ASTM C 227 test procedure, and a return to the original limits at six and 12 months was endorsed. Stark[100] has reported similar cases. Mortar bar expansions for several of these cases are presented in Fig. 5.1.

Iceland has adopted the six and 12-month limits for the purpose of evaluating the effectiveness of longer test periods. [95] The Bureau of Reclamation has always used a 12-month test period considering expansions of 0.10 percent to 0.20 percent as "marginal" with greater expansions being "deleterious."[101] While no concern has been voiced about the length of this test procedure, some researchers have stated that the expansion limits may be too high to detect many deleterious material combinations.[102]

Another aspect studied by Stark[100] is the theory that cement containing less than 0.60 percent total alkalies is "safe." Some mixtures containing cement with as little as 0.35 percent total alkalies have been found to be unacceptably expansive in the field as well as in mortar bar tests as shown in Fig. 5.2.

Sims[103,104] believes that the intent of these tests has been misunderstood. Frequently, test results are seen as being definitive and are used on 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...."

5.2 Correlation of Test Data with the Behavior of Concrete in Service

While the ASTM limits on mortar bar expansion were established on the basis of observed degradation of concrete, little effort has been made to quantify the degree of degradation or expansion of concrete in the field and relate that to the degree of expansion of mortar bars [102]

Stanton [25] observed no correlation between mortar bar expansions and the dynamic modulus of elasticity of concrete. While compressive strengths of concrete

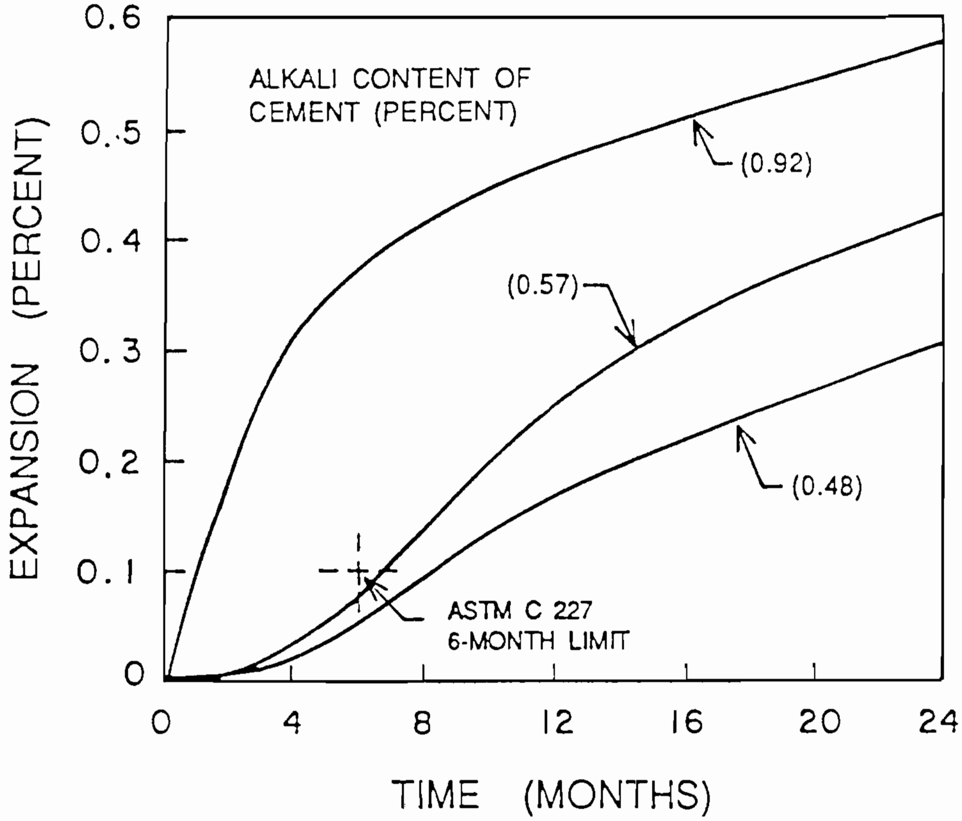


Fig. 5.1 Expansion behavior of several concrete mixtures containing low alkali cement which were indicated to be safe by the criteria of ASTM C 227 but were deleteriously expansive in the field [100]

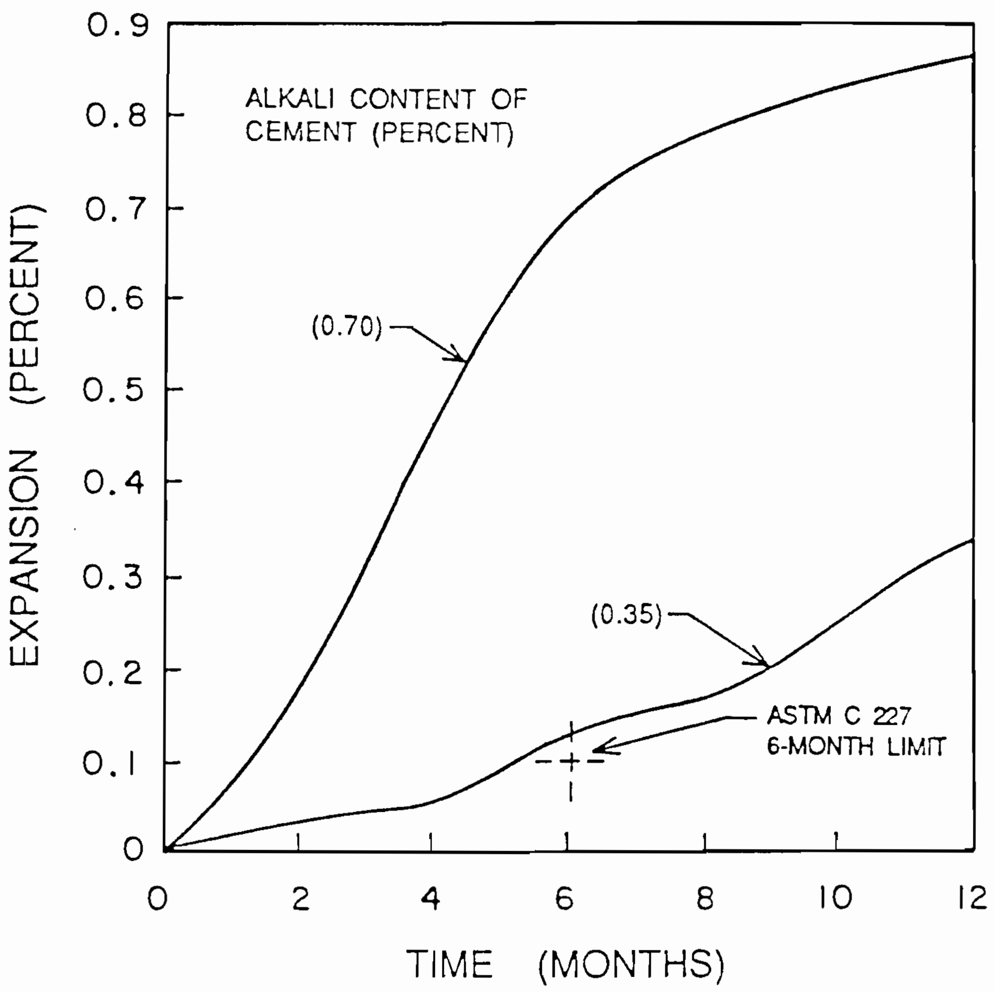


Fig. 5.2 Expansion behavior of one concrete mixtuure containing slow alkali cement which did not meet the expansion criteria of ASTM C 227 and was deleteriously expansive in the field [100]

cylinders were generally found to decrease as expansion of mortar bars increased, this information has not been fully developed. Vivian [44] has reported that the tensile strength of mortar is reduced by as much as 75 percent by cracking related to alkali-silica reaction.

Several slabs with reference points embedded in the corners were cast outdoors in Nebraska in the 1940's.[5] After six and one-half years of exposure, the slabs exhibited pronounced cracking and had expanded over 0.8 percent linearly. Concrete reference beams, 3 in. x 3 in. x 15 in., stored in sealed containers, expanded only one-third as much as the slabs. This study ably demonstrated techniques for quantifying the degree of expansion which can be caused by reactive cement-aggregate combinations.

One failure of current tests, according to Grattan-Bellew,[102] is that cracking is not considered. Cracks, not expansion, cause damage to concrete, and formation of microcracks could be used as an indicator of deleterious reaction in concrete. Oberholster et al.[59] reported that 300-mm cubes exposed to an outdoor environment experienced significant cracking when the linear expansion of the cubes exceeded 0.05 percent. Heck [98] and Stark [100] reported development of significant microcracking in mortar bars as expansions exceeded 0.05 percent. These observations add significance to the ASTM three-month expansion limit of 0.05 percent.

Grattan-Bellew [102] also indicated that correlation between laboratory data and the deterioration of similar concrete in service may be complicated by reinforcing steel and concrete strength.

5.3 Alternative Test Methods

Numerous tests have been proposed as alternatives to ASTM C 227. While most of these tests have never received widespread acceptance,[105] several are in use today.

The prism test of the Canadian Standards Association (CSA A23.2-14),[106,107] a method for evaluating alkali-carbonate reactive aggregates, has been endorsed by some researchers for use in evaluating alkali-silica reactive aggregates. Since the specimens are larger, the same size of aggregates used in the field can also be tested in the laboratory.[59] Other tests in existence, listed in Table 5.2, utilize mortar bars, but vary from the ASTM standards in the interpretation of results and the duration of testing.

A common criticism of ASTM C 227 is the length of time required for obtaining results. A number of tests have been proposed as much quicker alternatives.[108,109,110,111,112] These proposals generally make use of chemical tests of

Table 5.2 Methods of testing for potential of alkali-silica reaction currently proposed or in use[102]

TEST METHOD	EXPANSION LIMITS (%)	TIME (months)
MORTAR BAR METHOD (ASTM C 227)[6]	0.05 0.10	3 6
Canadian Standards Association CAN3 A23.1-M77, App. B3.4[106,107]	"Linear expansions of 0.04 percent or more indicate potentially deleterious reactivity."	"Determined from comparative test data."
Corps of Engineers EM 1110-2-2000 (Mortar bar test)[13]*	0.05 0.10 "Slope and trend of expansion to be taken into consideration."	6 12
Bureau of Reclamation (Mortar bar test)[101]*	deleterious: ≥ 0.20 marginal: 0.10-0.20	12 12
Rate method[114] *, **	***	any age

* procedure follows ASTM C 227

** proposed test

*** no fixed limit on expansion - analysis based on interpretation of slop of mortar bar expansion vs. time curve the materials or involve the exposure of specimens to increased heat and alkaline solutions to increase the rate and degree of reactions. In all of these cases, the researchers have reported good results. These proposals, however, have elicited little response in the literature and no results of repeat tests have been published.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Alkali-silica reaction will continue to become more prevalent as alkali contents of cements continue to increase and sources of non- reactive aggregates are depleted. At the same time, the use of mineral admixtures to partially replace cement in concrete will increase since their proper use can result in improvements of the physical properties of concrete while providing environmental and economic benefits.

ASTM C 227 has been 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.

6.2. Recommendations for Future Research

Alkali-silica reaction is a complex and 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, companion tests involving mortar bars and full-size concrete specimens should be conducted. The results will provide valuable information needed to correlate the test results obtained in the laboratory with the expected damage in the field.
2. Many proposed tests for the detection of 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. 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.
4. The existing guidelines regulating the quality of water used in concrete are very limited. 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.
5. To understand the effects of alkalies added to fly ash by chemical precipitating agents, an investigation will be necessary to determine the quantity of alkalies added and their reactivity, and the effect of the method of incorporating such agents.

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