Analysis of Durability of Advanced Cementitious Materials for Rigid Pavement Construction in California

Report Prepared for

CALIFORNIA DEPARTMENT OF TRANSPORTATION

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April 1999
Pavement Research Center
Institute of Transportation Studies
University of California at Berkeley

Technical Report Documentation Page

1. Report No. FHWA/CA/OR-99/02	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle

Analysis of Durability of Advanced Cementitious Materials for Rigid Pavement Construction in California

5. Report Date

6. Performing Organization Code

7. Authors

Kimberly E. Kurtis and Paulo Monteiro

8. Performing Organization Report No.

9. Performing Organization Name and Address

California Department of Transportation
New Technology and Research, MS-83
P.O. Box 942873
Sacramento, CA 94273-0001

10. Work Unit No.

11. Contract or Grant No.

12. Sponsoring Agency Name and Address

California Department of Transportation
Sacramento, CA 95819

13. Type of Report and Period Covered

14. Sponsoring Agency Code

15. Supplementary Notes

This project was performed in cooperation with the U.S. Department of Transportation, Federal Highway Administration.

16. Abstract

Caltrans specifications for the construction of rigid pavements require rapid setting, high early strength, superior workability concrete with a desired 30+ year service life. These strict specifications provide the motivation for the investigation of advanced cementitious materials for pavement construction. The cementitious materials under consideration by Caltrans may be classified into four categories: Portland cements and blends, calcium aluminate cements and blends, calcium sulfoaluminate cements, and fly ash-based cements. To achieve the desired 30+ year design life, it is essential to select materials that are expected to exhibit long-term durability. Because most of the cementitious materials under consideration have not been extensively used for pavement construction in the United States, it is essential to characterize the long-term durability of each material.

This report provides general information concerning the deleterious reactions that may damage concrete pavements in California. The reactions addressed in this report are sulfate attack, aggregate reactions, corrosion of reinforcing steel, and freeze-thaw action. Specifically, the expected performance of Portland cements and blends, calcium aluminate cements and blends, calcium sulfoaluminate cements, and fly ash-based cements are examined with regard to each of the deleterious reactions listed. Additional consideration is given to any deterioration mechanism that is particular to any of these cement types. Finally, the recommended test program for assessing potential long-term durability with respect to sulfate attack is described.

17. Key Words fast-setting hydraulic cement concrete, concrete cement chemistry, sulfate attack, portland cement concrete, fly-ash cement, calcium sulfoaluminate cement, calcium aluminate cement, alkali-silica reaction, aggregate reaction, corrosion, freeze-thaw effects	18. Distribution Statement No restrictions. This document is available to the public through the National Technical Information Service, Springfield, VA 22161

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 69	22. Price

Form DOT F 1700.7 (8-72)

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.0 EXECUTIVE SUMMARY

The cementitious materials under consideration by Caltrans for rigid pavement construction may be classified into four categories: Portland cements and blends, calcium aluminate cements and blends, calcium sulfoaluminate cements, and fly ash-based cements. With the exception of Portland cements, most of the cementitious materials under consideration have not been extensively used for pavement construction in the United States, and little information about their long-term durability is available. If rigid pavements are to achieve the 30+ year service life defined by Caltrans, it is essential to characterize the long-term resistance of the concrete to sulfate attack, aggregate reactions, corrosion, and freeze-thaw action.

California soils are known to be rich in sulfates. Sulfate resistance of concrete is largely determined by the permeability of the concrete and by the reactivity of the hydration products present. Sulfates may permeate concrete and react with existing hydration products to form ettringite or gypsum. Hydrated cement paste containing larger proportions of monosulfate hydrate, calcium aluminate hydrate, or calcium hydroxide is more vulnerable to damage by sulfate attack. Because they contain greater proportions of these hydration products, certain types of Portland cements are particularly susceptible to sulfate attack.

In general, *low permeability* concrete produced from sulfate-resistant Portland cements, Portland-pozzolan blends, calcium aluminate cements and blends, calcium sulfoaluminate cements, and fly ash-based cements are expected to exhibit improved performance in sulfate-rich environments. However, the chemical composition of several cements submitted for consideration by Caltrans have not been provided by the manufacturers. Thus, ongoing accelerated sulfate testing is being performed to measure the potential long-term durability of each cement in aggressive sulfate environments. A description of the accelerated test program is included in this report.

Two forms of aggregate reactions known to occur in California are addressed: alkali-aggregate reaction and oxidation reactions. The alkali aggregate reaction is greatly dependent upon the alkali content of the cement. Clays used in the manufacture of Portland cements may contribute high alkali concentrations to the pore solution. Low-alkali Portland cements may be specified when needed to provide resistance to alkali-aggregate reactions. Portland-pozzolan blends and calcium aluminate cements and blends are expected to exhibit improved alkali-aggregate reaction resistance in sulfate-rich environments, while the resistance of calcium sulfoaluminate cements is expected to be similar to that of Portland cement. Fly ash-based cements may exhibit improved resistance, but the alkali concentration contributed by the set accelerator should be investigated. The oxidation of sulfide and sulfate minerals, such as pyrite, in aggregate may cause concrete cracking and aggregate pop-outs. Portland-pozzolan blends and fly ash-based cements are expected to exhibit improved resistance to this oxidation reaction because of decreased permeability to water.

Carbonation or chloride attack from $CaCl_2$-containing admixtures, seawater, or de-icing salts may initiate corrosion of steel dowels, which are used to transfer load between pavement slabs. The Building Code limits the maximum chloride ion content for the purpose of corrosion protection of reinforced concrete to 0.15 percent by weight of cement. In addition to low chloride content, low concrete permeability and high pore solution alkalinity are essential for corrosion resistance. Low permeability concrete produced from Portland cement, Portland-pozzolan blends, and calcium sulfoaluminate cements is expected provide resistance to corrosion. The pore solution of the calcium aluminate cement is known to have a lower pH, leading to some concerns about loss of steel passivity. Because information about fly ash-based cement is limited, gauging the performance of this cement type is difficult. The chloride-binding capacity and the pore solution alkalinity of the fly ash-based cement should be investigated.

Freeze-thaw resistance is essentially determined by the physical characteristics of the concrete. When required, air-entraining admixtures may be used to give freeze-thaw resistance. The carbon content of the fly ash-based cement may affect the entrainment of air.

The primary focus of this durability has been expansive reactions that affect concrete, namely sulfate attack, corrosion of reinforcing steel, aggregate reactions, and freeze thaw cycles. While it is essential to characterize resistance to these reactions, damage to concrete is not limited to the reactions discussed. Drying shrinkage and thermal shrinkage can also produce cracking in concrete pavements, affecting pavement performance and service life. Considerable investigation into these forms of cracking is warranted.

2.0 INTRODUCTION

Caltrans specifications for the construction of rigid pavements require rapid setting, high early strength, superior workability concrete with a desired 30 year plus service life. These strict specifications provide the motivation for the investigation of advanced cementitious materials for pavement construction. The cementitious materials under consideration by Caltrans may be classified into four categories: Portland cements and blends, calcium aluminate cements and blends, calcium sulfoaluminate cements, and fly ash-based cements. To achieve the desired 30+ year design life, it is essential to select materials that are expected to exhibit long-term durability. Because most of the cementitious materials under consideration have not been extensively used for pavement construction in the United States, it is essential to characterize the long-term durability of each material.

This report provides general information concerning the deleterious reactions that may damage concrete pavements in California. The reactions addressed in this report are sulfate attack, aggregate reactions, corrosion of reinforcing steel, and freeze-thaw action. Specifically, the expected performance of Portland cements and blends, calcium aluminate cements and blends, calcium sulfoaluminate cements, and fly ash-based cements are examined with regard to each of the deleterious reactions listed. Additional consideration is given to any deterioration mechanism that is particular to any of these cement types. Finally, the recommended test program to for assessing potential long-term durability with respect to sulfate attack is described.

3.0 CONCRETE DURABILITY

When selecting materials for rigid pavements expected to perform for 30+ years in California, material interaction with the environment should be considered. First, the environment to which the pavements will be exposed should be examined. In California, a wide range of environmental conditions exists that may affect concrete durability. It is well documented that California soils are rich in sulfates, which can lead to significant deterioration of concrete structures. For pavements located near the Pacific coast or in regions where de-icing salts are used, precautions should be taken to avoid corrosion of embedded steel dowels, which are used to transfer load across sawed joints. In mountainous areas, the effects of repeated freeze-thaw cycles on the concrete may be significant.

In addition, aggregate, cement, and admixtures should be selected with respect to their long-term durability. Binders may be selected based upon their chemical composition, which may provide additional resistance to corrosion, sulfate attack, or alkali-aggregate reactions. Also, non-reactive aggregates may be required to avoid alkali-silica reactions or oxidization reactions. For regions where freeze-thaw cycles may affect concrete durability, air entraining admixtures or high performance concrete designs may be required. A mix design that will produce concrete of low permeability is essential for resisting most forms of deterioration.

The interaction between the concrete and its environment is described in the following sections. Special consideration is given to reactions that are likely to affect rigid pavements in California, specifically sulfate attack, aggregate reactions, corrosion, and freeze-thaw cycles.

3.1 Sulfate Attack

Sulfates present in soils, groundwater, seawater, decaying organic matter, and industrial effluent surrounding a concrete structure may permeate the concrete and react with existing hydration products. These reactions can cause cracks in the concrete structure. California soils are rich in sulfates, and much attention has been given lately to the sulfate attack on the concrete foundations of hundreds of homes in southern California (1, 2). The Building Code requirements for concrete exposed to sulfate-containing solutions are given in Table 1.

Table 1 Building Code Requirements for Concrete Exposed to Sulfate-Containing Solutions.

Sulfate exposure	Water soluble sulfate in soil (percent by weight)	Sulfate in water (ppm)	Portland Cement type	Maximum water/cementitious materials ratio	Minimum fc (psi)
Negligible	0.0-0.1	0-150	---	---	---
Moderate	0.1-0.2	150-1500	II, IP, IS, P	0.50	4000
Severe	0.2-2.0	1500-10,000	V	0.45	4500
Very severe	Over 2.0	over 10,000	V plus pozzolan	0.45	4500

Essentially, two forms of sulfate attack are known to exist:

- Reaction with monosulfate hydrate and calcium aluminate hydrate to produce ettringite
- Reaction with calcium hydroxide to produce gypsum; results in a decrease in pore solution alkalinity

3.1.1 Ettringite Formation by Sulfate Attack

Depending upon the cement composition (see discussions on cement hydration in Section 4), monosulfate hydrate and calcium aluminate hydrate may form as hydration products. In the presence of calcium hydroxide (CH)[1] (a hydration product of some cements) and water (H), monosulfate hydrate ($C_3A\cdot C\text{þ}\cdot H_{18}$) and calcium aluminate hydrate ($C_3A\cdot H_{13}$) react with the sulfate (þ) to produce ettringite ($C_3A\cdot 3C\text{þ}\cdot H_{32}$):

$$C_3A\cdot C\text{þ}\cdot H_{18} + 2CH + 2\text{þ} + 12H \rightarrow C_3A\cdot 3C\text{þ}\cdot H_{32}$$

$$C_3A\cdot CH\cdot H_{18} + 2CH + 3\text{þ} + 12H \rightarrow C_3A\cdot 3C\text{þ}\cdot H_{32}$$

In hardened concrete, the formation of ettringite by sulfate attack *can*, but does not always, result in expansion and lead to cracking of the concrete. The physical mechanisms by which ettringite causes expansion and cracking is a matter of controversy. Topochemical formation of ettringite with directional crystal growth and swelling of ettringite by water adsorption are among the proposed hypotheses. It is generally accepted that the expansion caused by sulfate attack is the result of a particular mechanisms associated with the ettringite reaction, or is the result of reaction other than the formation of ettringite, such as the formation of gypsum (see Section 3.1.2).

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[1] In cement chemistry the following chemical abbreviations are used:

C: CaO;
S: SiO_2;
A: Al_2O_3;
þ: SO_3;
H: H_2O

When a concrete structure is expected to be exposed to an aggressive sulfate environment, a cement low in C_3A, such as Type II or Type V, is selected to avoid the reaction to form ettringite by sulfate attack as described above. In addition, proper mix design (i.e., low w/c and use of pozzolans) and curing are required to produce concrete less permeable to sulfates.

3.1.2 Gypsum Formation by Sulfate Attack

Gypsum, in addition to ettringite, can be produced during sulfate attack through cation exchange reactions. Loss of stiffness and strength and eventual expansion spalling and cracking are indicative of sulfate attack through gypsum formation. Depending on the cation type present in the sulfate solution (i.e., Na^+ or Mg^{2+}) both calcium hydroxide and C-S-H (the primary strength-giving hydration product) in the cement paste may be converted to gypsum ($CaSO_4$ $2H_2O$) by sulfate attack. For sodium sulfate attack:

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaOH$$

the formation of sodium hydroxide as a byproduct of the reaction ensures that the system will remain highly alkaline, which is an essential condition for the stability of C-S-H. During magnesium sulfate attack:

$$MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + Mg(OH)_2$$

$$3MgSO_4 + 3CaO \cdot 2SiO_2 \cdot 3H_2O + 8H_2O \rightarrow 3(CaSO_4 \cdot 2H_2O) + 3Mg(OH)_2 + 2SiO_2 \cdot H_2O$$

conversion of calcium hydroxide to gypsum is accompanied by formation of magnesium hydroxide which is relatively insoluble and poorly alkaline. Therefore, while both forms of attack will lead to damage by gypsum formation, magnesium sulfate attack is considered to be more severe because it will also compromise the stability of the C-S-H.

Field experience has demonstrated that sulfate attack usually manifests itself in the form of loss of adhesion and strength. It is important to note that the deterioration most often reported in the field is *not* caused by ettringite formation, but is due to the decomposition of CH and C-S-H to gypsum by sulfate ions and conversion of these hydration products to aragonite (presumably due to carbonation).

Proper mix design (i.e., low w/c and use of pozzolans) and curing will produce concrete less permeable to sulfates. The use of pozzolans will also reduce the amount of CH in the hydrated cement paste of Portland cements, calcium sulfoaluminate cements, and fly ash-based cements. Reducing the amount of CH in the hydrated cement paste will limit the effects of this form of sulfate attack.

3.2 Reactive Aggregate

Certain aggregate deposits in California are known to be reactive. Concrete produced from these aggregates may, as a result, exhibit poor durability. Two forms of aggregate reactions are addressed in this section: alkali-aggregate reactions and sulfur and sulfide mineral reactions.

3.2.1 Alkali-Aggregate Reactions

In concrete, alkali metal ions and hydroxyl ions, contributed principally by the cement and reactive aggregate, can participate in a destructive alkali-aggregate reaction (AAR). Three forms of AAR are believed to exist: alkali-carbonate reaction, alkali-silicate reaction, and alkali-silica reaction.

The alkali-carbonate reaction occurs between alkalis in the concrete pore solution and certain dolomitic limestones. The dedolomitization reaction exposes the surfaces of clays present in the dolomites. In the presence of water, the clays expand. Reactive dolomites are very fine-grained, dense, and frequently contain illite and chlorite clay minerals (3). In Ontario, concrete pavements have experienced expansions of up to one percent by the alkali-carbonate reaction.

The alkali-silicate reaction occurs between the alkalis present in the pore solution and interlayer precipitate in phyllosilicates, such as phyllites, agrillites, and greywackes. The interlayer precipitate is dissolved during this reaction, and repulsive forces are induced between the remaining phyllosilicate layers (3). The expansive pressures generated are large enough to cause cracking and expansion of the affected concrete member.

Alkali-silica reaction is initiated at aggregate surfaces exposed to the alkaline pore solution in concrete. As a result, a crystalline, densely structured silica network, such as quartz, is comparatively more resistant to attack than an open-structured silicate, such as opal. Mehta and Monteiro (4) have listed silicates in a decreasing order of reactivity as: opal, obsidian, cristobalite, tridymite, chalcedony, cherts, cryptocrystalline volcanic rocks (andesites and rhyolites), and strained or metamorphic quartz. The product of this reaction is an alkali-silicate reaction (ASR) gel that tends to imbibe water found in the concrete pores, leading to swelling of the gel and eventual cracking of the affected concrete member.

Alkali-aggregate reactions may be controlled through careful material selection and design. When possible, non-reactive aggregates and low-alkali cement and should be selected. Because swelling is the mechanism of expansion, reducing the permeability of the concrete will reduce the amount of water available for swelling, thereby reducing the amount of damage caused by alkali-aggregate reactions. Partial replacement of cement with pozzolans will reduce the amount of alkalis contributed to the concrete by the cement and will reduce the permeability of the concrete. In addition, chemical additives have been found to reduce expansion by alkali-silica reaction (5). Lithium salts, one such additive, have been the focus of much ongoing research (6). However, the mechanism by which these additives reduce expansion is unknown, and the long-term implications to the environment and to the concrete are uncertain.

3.2.2 Oxidation of Sulfide and Sulfate Minerals

The sulfides of iron (e.g., pyrite, marcasite, and pyrrohotite) are frequently found in natural aggregates. In California, aggregate containing pyrite (FeS_2) is particularly common. Marcasite, which is found mainly in sedimentary rocks, readily oxidizes to form sulfuric acid and hydroxides of iron (4). The formation of acid is undesirable, especially from the standpoint of the potential corrosion of steel in prestressed and reinforced concrete. In addition, the sulfates formed during oxidation of the minerals are free to react with calcium hydroxide in the cement paste to form gypsum, or may react with monosulfate hydrate or calcium aluminate hydrate to form ettringite (7). Marcasite and certain forms of pyrite and pyrrohotite are suspected of being responsible for expansive volume changes in concrete, causing cracks and pop-outs.

3.3 Corrosion

Corrosion of embedded steel in concrete is a destructive electrochemical process that ultimately weakens reinforced concrete structures. While rigid pavements are not as heavily reinforced as bridges or buildings, some embedded steel is used. In particular, steels dowels are used to transfer load between concrete slabs. Chloride ingress or carbonation of the concrete may initiate corrosion of the dowels.

3.3.1 Effects of Corrosion

Corrosion of embedded steel may undermine the strength of a reinforced concrete member in several ways. Because corrosion products have a greater volume than the original steel, internal tensile stresses will develop in the cement mortar at the steel/mortar interface. As a result, the surrounding concrete will crack and eventually spall away as corrosion of the internal steel advances. In addition, under tensile stress developed during corrosion, existing fine cracks and microcracks in the surrounding concrete will enlarge and coalesce into a few wide cracks, providing increased ionic transport between the surface of the concrete and the surface of the reinforcing steel. This ionic transport effectively promotes the corrosion process and allows the ingress of other aggressive species (e.g., sulfates, carbon dioxide). Formation of such fine cracks decreases concrete stiffness and tensile strength, while the formation of larger, wider cracks increases concrete permeability. Thus, the structural integrity of the reinforced concrete member is increasingly compromised as cracking progresses. With the steel corroding away, the reinforcing bar cross-section is reduced, and the member's tensile strength is decreased. Furthermore, as corrosion advances, the bond between the steel and surrounding concrete is weakened, which adversely affects the load transfer between the two materials. To ensure that reinforced concrete members performs according to their design capacity and design service life, it is important to prevent or delay the occurrence of corrosion.

3.3.2 The Corrosion Process in Concrete

When steel is exposed to a highly alkaline environment, such as concrete pore solution, a submicroscopic oxide film forms on the steel surface. For steel embedded in concrete, the formation of this oxide film, also called a passive film, is a function of environmental pH. Any metal or alloy is said to be in a “passive” state when it resists corrosion in an environment where corrosion is thermodynamically favorable (8). Passivity is not a characteristic of a metal or alloy, rather it is characteristic of a material with respect to a given environment. Thus, in the alkaline pore solution, when the passive film is intact, the steel resists corrosion. Corrosion will only be initiated when the passive layer is removed or damaged, such as by chloride attack or carbonation (see Sections 3.3.2.1 and 3.3.2.2).

Corrosion is an electrochemical process involving the transfer of ions. In reinforced concrete, electrons are produced at the anodic site by the oxidation of the steel. That is, the metal goes into solution as metal ions at the anode, and the loss of metal indicates the site of corrosion. The rate of steel corrosion in concrete is dependent on the rate of the anodic reaction. These anodic reactions are (9):

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e^-$$

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 6e^-$$

$$Fe + 2H_2O \rightarrow FeO_2^- + 3H^+ + 2e^-$$

$$Fe \rightarrow Fe^{++} + 2e^-$$

These reaction equations demonstrate that oxides will form on the surface of the steel during corrosion. Magnetite, Fe_3O_4, has a gray-black appearance and hematite, Fe_2O_3, is red-brown.

Electrons released at the anodic site are consumed at the cathodic site. Typically, at the cathode, oxygen or hydrogen will be reduced. The thermodynamic driving force for the reduction of oxygen is much greater than that for hydrogen. As a result, the oxygen reaction is more likely to occur, and the reduction of hydrogen during corrosion in concrete is rarely a factor. The cathodic reactions are (9):

$$2\,H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

$$2H^+ + 2e^- \rightarrow H_2$$

The previously discussed reactions at the anode and cathode result in corrosion of reinforcing steel. Ferrous ions (Fe^{++}) produced in the anodic reaction combine with the hydroxyl ions produced in the cathodic reaction to form the corrosion product ferrous hydroxide ($Fe(OH)_2$).

The corrosion rate can be increased by the presence of other ions in the concrete. According to Hime and Erlin (10), the reaction of ferrous ions and hydroxyl ions in the presence of chloride ions can also result in the formation of the corrosion product $Fe(OH)_2$. Chloride ions are produced by this process, increasing the corrosion rate of the steel reinforcement:

$$Fe^{++} + 6Cl^- \rightarrow FeCl_6^{-4}$$

$$Fe^{+3} + 6Cl^- \rightarrow FeCl_6^{-3}$$

$$FeCl_6^{-3} + 2OH^- \rightarrow Fe(OH)_2 + 6Cl^-$$

The process of corrosion for steel reinforcement bars embedded in concrete is illustrated in Figure 1. The diagram shows that the electrons are released at the anodic site and travel through the steel to the cathodic site, where they are consumed. The reduction of oxygen at the cathode produces hydroxyl ions (OH^-). The production of hydrogen gas, caused by the reduction of hydrogen, is less likely, but possible. The corrosion process may be limited by the rate of diffusion of the hydroxyl ions, as well as by the availability of oxygen (O_2), water (H_2O), or other aggressive ions (Cl^- in Figure 1).

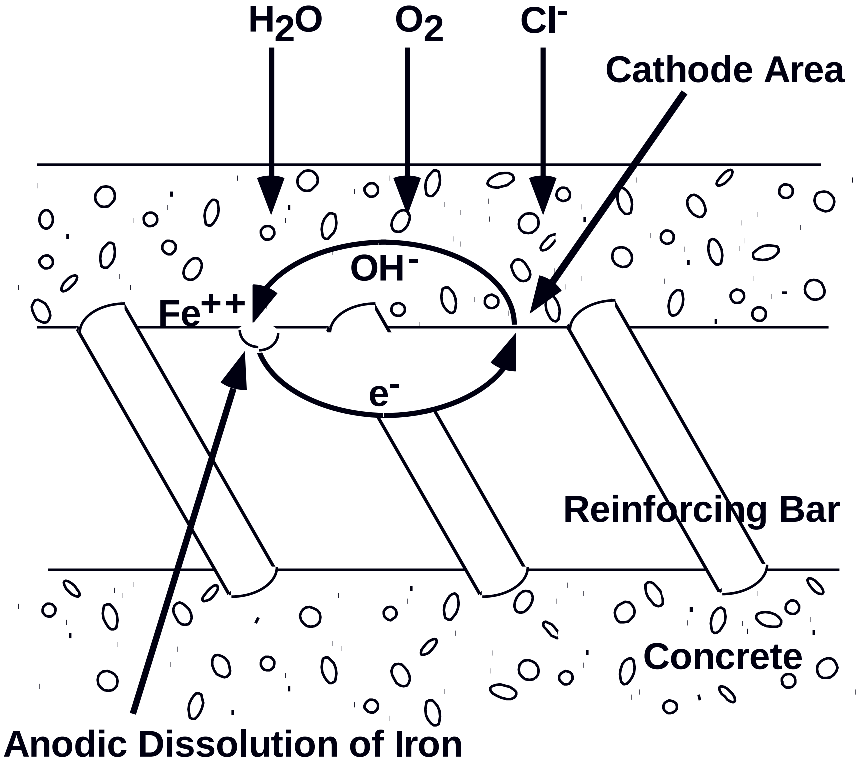

Figure 1: Schematic illustration of the corrosion process of reinforcing steel in concrete (Adapted from Hansson, 1984 [11]).

3.3.2.1 Depassivation by Chlorides

Chloride ions can be introduced into the concrete during its manufacture. The Building Code sets limits on the maximum chloride ion content for corrosion protection of reinforcement. For reinforced concrete exposed to chloride in service, the maximum water-soluble chloride ion content in concrete is 0.15 percent by weight of cement.

Chlorides may be introduced when seawater or water with a high chloride concentration is used as mixing water, when chloride contaminated coarse or fine aggregates are used, or when chloride containing admixtures such as calcium chloride are used. In addition, chloride present in the surrounding environment may penetrate the concrete. Deicing salts, seawater, and chloride-contaminated soils are the primary sources of external chlorides. When concrete is dry, chlorides can penetrate several millimeters in a few hours by the capillary draw of salt water into the concrete (12). Diffusion of chlorides through the pore solution of wet concrete occurs more slowly. Typical diffusion rates for fully saturated cement paste are on the order of 10^{-8} cm2/s (13).

While it has been determined that chloride ions act as catalysts for the loss of the protection offered by the passive film, the exact mechanisms of this process are not well understood. However, attack on the passive film by chloride ions is generally accepted to be a localized phenomenon. This form of attack causes microgalvanic cells to form on the reinforcing steel. In regions where the depassivation has occurred, iron will be lost by oxidation. The areas that remain protected by the passive film will become cathodic and, thus, sites of oxygen reduction.

Chloride ions exist in concrete in two forms: bound and free. Only the free chloride ions — those dissolved in the pore solution — participate in the corrosion process. Many factors have been found to influence the chloride binding capacity of concrete. For instance, because chloride ions combine with tricalcium aluminate (C_3A) present in the cement paste to form Friedel's salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$), concrete made from cement with a high C_3A content will have a greater potential for binding chloride ions. Hussain *et al.* (14) demonstrated the beneficial effects of such cement. By raising the C_3A content of cement from 2.43 percent to 14 percent, with all other factors remaining constant, the chloride threshold (the chloride ion content below which corrosion will not occur in concrete) was increased by a factor of 2.85. Kayyali and Haque (15) found that the use of superplasticizing admixtures increased the levels of free chlorides in concrete, but that the addition of fly ash resulted in an increase in chloride binding capacity. Hussain *et al.* (14) also reported moderate increases in the threshold with higher levels of concrete alkalinity and that the presence of sulfates moderately increased or decreased the threshold depending on the cement composition.

3.3.2.2 Depassivation by Carbonation

When the pH of the surrounding environment is higher than 11.5, the passive film will remain intact and will provide protection against corrosion (4). When the pH falls below this level, the film becomes unstable and the protection of steel will be lost. Carbonation of concrete is the most common mechanism for the loss of alkalinity in concrete.

Because of contact with decaying organic matter, significant concentrations of dissolved carbon dioxide (CO_2) are often contained in mineral waters, groundwater, and seawater (4). This gas and its solution in water, carbonic acid (H_2CO_3), react with the calcium hydroxide cement paste — a process termed “carbonation.” Nitrous and sulfurous oxides can also react in this way. Carbonation of calcium hydroxide ($Ca(OH)_2$) present in the hydrated cement paste is shown by the reactions below:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

or alternatively:

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O$$

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

From these equations, it can been seen that calcium hydroxide in the hydrated cement paste is consumed through reaction with carbon dioxide or carbonic acid. This results in a gradual loss of the buffer, which is essential for maintaining alkalinity.

The kinetics of the carbonation reaction in concrete have been widely studied, and a parabolic model has been generally accepted as the best way to describe the depth of carbonation expected over a period of time. According to this model, the depth of carbonation can be predicted by

$$x = k\, t^{1/2}$$

where x is the thickness of the carbonation layer, t is exposure time, and k is a constant dependent on cover permeability. In good quality concrete, the rate of carbonation is on the order of 1mm/year, indicating that carbonation should not present a problem during the design service life of a reinforced concrete structure which has more than 50mm concrete cover over the reinforcement (16).

Carbonation and the resulting loss in alkalinity will typically begin at the concrete surface and will move in the form of a "carbonation front" toward the center of the concrete section. The carbonated concrete will have pH of less than 8, but the uncarbonated concrete will maintain its high alkalinity. Thus, the uncarbonated concrete will continue to provide a protective cover for the embedded steel. In permeable concrete, concrete with low cover depth, or in concrete containing microcracks connected to surface cracks, the carbonation front may reach the reinforcing steel and will thus lead to the onset of corrosion (17). Therefore, concrete with low permeability, adequate cover depth, and low potential for microcracking is crucial for the protection of concrete from corrosion.

3.4 Freeze-Thaw Effects

Freeze-thaw effects on concrete should be considered when constructing rigid pavements in the Sierras or other mountainous regions in California. Freezing and thawing cycles can damage rigid pavements through damage of the hydrated cement paste or damage to the aggregate.

3.4.1 Frost Damage to Hydrated Cement Paste

A saturated cement paste containing no entrained air will expand upon freezing due to the generation of hydraulic pressure. With increasing air entrainment, the tendency to expand decreases because the entrained air voids provide escape boundaries for the hydraulic pressure.

Progressive expansion of non-air entrained cement paste by repeated freeze-thaw cycles leads to deterioration of the concrete by cracking and spalling. Scaling may also be caused by freeze-thaw cycles. Most scaling is caused by inadequate entrained air content, application of calcium and sodium chloride de-icing salts, the performance of finishing operations when bleed water is still on the surface, and insufficient curing before exposure to frost action.

To avoid damage by freeze-thaw action in the hydrated cement paste, air-entraining admixtures are generally recommended. However, for concrete with very low water to cement ratio ($w/c < 0.30$), air entrainment may not be necessary or desirable (18). Concern about loss of strength associated with larger air volumes has initiated the investigation of freeze-thaw resistance of "high performance" concrete. Mixtures with very low w/c that have been properly cured and exhibit very low permeability contain very little freezable water. As a result, research is focused on the determination of a minimum w/c below which air entrainment will not be necessary to impart adequate resistance to freeze-thaw cycles.

3.4.2 Frost Damage to Aggregate

Verbeck and Landgren (19) proposed three classes of aggregate based upon permeability: low, intermediate, and high. The permeability of the aggregate plays a dual role in determining frost resistance. First, it determines the degree of saturation or the rate at which water will be absorbed in a given period of time. Second, aggregate permeability determines the rate at which water will be expelled from the aggregate on freezing, and, thus, the hydraulic pressure developed.

Low permeability aggregate with high strength can accommodate the elastic strain caused by freezing of water without exhibiting aggregate fracture.

Aggregates of intermediate permeability have a significant proportion of the total porosity represented by small pores of approximately 500nm and smaller. Capillary forces in such small pores cause the aggregate to be easily saturated and to hold water. On freezing, the magnitude of the pressure developed depends primarily on the rate of the temperature drop and the distance that the water under pressure must travel to find an escape boundary and relieve pressure. Pressure relief may be available either in the form of any empty pore within the aggregate or at the aggregate surface. The critical distance for pressure relief in the hydrated cement paste is approximately 0.2mm; it is much greater for most aggregate because of their higher permeability relative to cement paste.

Aggregates of high permeability, which generally contain a large number of large pores, permit easy entry and egress of water. However, they may cause durability problems because the transition zone between the aggregate surface and the cement paste matrix may be damaged when water under pressure is expelled from an aggregate particle. In such cases, the aggregate is not damaged. This illustrates why the results of freeze-thaw and soundness tests on aggregate alone may not be reliable for the prediction of concrete behavior.

These considerations have given rise to the concept of a critical aggregate size with respect to frost damage. With a given pore size distribution, permeability, degree of saturation, and freezing rate, large aggregate may cause damage, but smaller particles of the same aggregate would not. However, no single critical size for a general aggregate type may be defined because the size depends on the freezing rate, degree of saturation, and permeability of the aggregate.

4.0 PERFORMANCE ISSUES

The cements submitted to Caltrans for durability testing can be classified into four groups. Table 2 provides description of the chemical composition (if supplied by the manufacturer) and the designation for each of the cements under consideration. Many of the manufacturers have requested that the cement tradenames be concealed. Hence, the cements will be referred to in all reports by a designation based upon their classification, as shown in Table 2. An analysis of the expected durability of each of the four classes — Portland cements and blends, calcium aluminate cements and blends, calcium sulfoaluminate cements, and fly ash-based cements — is presented. Resistance to sulfate attack, aggregate reactions, corrosion, freeze-thaw action is addressed. In addition, durability issues particular to each cement type are discussed.

Table 2 Designation, Classification, and Description of Cements Tested for Sulfate Resistance.

Designation	Classification	Description
PC1	Portland-Pozzolan Blend	Primarily Type III cement with proportions of Class F fly ash and silica fume
CA1	Calcium Aluminate Blend	Primarily CA
CA2	Calcium Aluminate Blend	No information provided
CA3	Calcium Aluminate Blend	No information provided
CSA1	Calcium Sulfoaluminate	C_2S, C_3S, C_4AF, C_3A, $C\text{þ}$, and $C_4A_3\text{þ}$
CSA2	Calcium Sulfoaluminate	Primarily C_2S and $C_4A_3\text{þ}$
FA1	Fly Ash-Based Cement	Primarily Class C fly ash

4.1 Portland Cements and Blends

Portland cement clinker is produced from calcium-containing materials, such as limestone, chalk, and marl, and from silica-containing materials, such as clay and shale. In addition to silica, clays may also contain alumina (Al_2O_3), iron oxide (Fe_2O_3), and alkalis (Na_2O, K_2O). After manufacture, Portland cement is typically composed of 45-60 percent tricalcium silicate (C_3S), 15-30 percent dicalcium silicate (C_2S), 6-12 percent tricalcium aluminate (C_3A), 6-8 percent ferrite (C_4AF), and 5 percent calcium sulfate. For a particular mix design and environment, the specific proportions of these compounds in the cement and the fineness of the cement determine the setting, hardening (or strength development), and durability of the Portland cement concrete.

Because rapid set times and strength gain are desired by Caltrans for rigid pavements, a Type III Portland cement blend is recommended. To improve resistance to sulfate attack, pozzolanic material will be blended with the Type III cement. Currently, the durability of several different Portland cement blends is being evaluated. In general, the blends may be described as approximately 80 percent Type III cement, approximately 10 percent Class F fly ash, and 6-10 percent silica fume. For mix designs with w/c=0.29, compressive strength measured approximately 55 MPa at 24 hours and approximately 110 MPa at 28 days with ambient curing (20). It should be noted that the development of high performance concrete mixtures should be specific to the intended application. These mix designs have not been specifically designed for pavements. Should the durability of these mixtures prove to be inadequate for environmental conditions in California, it may be necessary to further adjust the amount of pozzolan or the cement type to attain the desired early strength and to retain the necessary workability for paving.

4.1.1 Hydration and Strength Development: Portland Cements and Blends

After manufacture, Portland cement is typically composed of 45-60 percent tricalcium silicate (C_3S), 15-30 percent dicalcium silicate (C_2S), 6-12 percent tricalcium aluminate (C_3A), 6-8 percent ferrite (C_4AF), and 5 percent calcium sulfate. When Portland cement is dispersed in water, the calcium sulfate and the high-temperature compounds of calcium go into solution, and the liquid phase is rapidly saturated with various ionic species. Within a few minutes, the first needle-shaped crystals of ettringite ($C_3A\cdot 3C\text{þ}\cdot H_{32}$) form. A few hours later, large prismatic crystals of calcium hydroxide (CH) and small fibrous crystals of calcium silicate hydrates (C-S-H) begin to fill the empty space formerly occupied by water and the dissolving cement particles. After some days, depending on the aluminate-to-sulfate ratio of the Portland cement (see Section 4.1.2), ettringite may become unstable and decompose to form monosulfate hydrate ($C_3A\cdot C\text{þ}\cdot H_{12\text{-}18}$). The solid volume of hydrated cement paste of Portland cements is composed primarily of C-S-H (50-60 percent), CH (20-25 percent), and calcium sulfoaluminate compounds (15-20 percent) (4).

The setting time of Portland cement is dependent upon the rate of ettringite formation, which in turn is dependent upon the proportions of C_3A and $C\text{þ}$ in the cement. Typical initial setting times range from 1.5 to 2.5 hours, and final setting times may range from 2.5 to 3.5 hours (21).

The rate of strength gain is dependent upon ambient temperature, cement fineness, and cement composition. Higher temperatures and more finely ground cements accelerate hydration and, hence, strength development. Of the major constituents in Portland cement, the hydration of the C_3A and C_3S compounds occurs most rapidly. Cements with greater proportions of these compounds will produce higher early strengths. It should be noted that the heat of hydration associated with C_3A is quite high. In addition, high amounts of C_3A decrease the sulfate resistance of the cement paste. Therefore, high early strength cements such as Type III cement, have a maximum amount of C_3A allowed. Such cements are finely ground and contain a larger amount of C_3S than regular Portland cement. The hydration of C_3S produces C-S-H, the primary strength-giving compound in the hydrated Portland cement paste.

Pozzolanic materials, such as fly ash, silica fume, and slag, are often used as a partial replacement for cement or fine aggregate in concrete mixtures. A pozzolan is defined as a siliceous or siliceous and aluminous material which in itself possesses little or no cementing property, but which will, in a finely divided form and in the presence of moisture, chemically react with CH at ordinary temperatures to form compounds possessing cementitious properties (4). The reaction can be described as:

$$\text{POZZ} + \text{CH} + \text{H} \rightarrow \text{C-S-H}$$

Pozzolanic materials are often industrial by-products and are generally less expensive than cement. Their use in concrete is beneficial from an economic standpoint and from an environmental one, as the material will not be landfilled. In addition, the use of pozzolans as a partial replacement for cement improves the durability characteristics of the concrete. This is accomplished through an overall pore size refinement and a densification of the transition zone between the cement paste and the coarse aggregate. This results in less microcracking and a less permeable concrete. In addition, a reduction in the amount of CH in the hydrated cement paste improves the concrete’s resistance to sulfate attack.

4.1.2 Sulfate Resistance: Portland Cements and Blends

The chemical processes involved in sulfate attack are rather straightforward, and are reviewed in several publications (7, 4, 22). The principal solid phases in well-hydrated Portland cement paste are calcium silicate hydrate (C-S-H), calcium hydroxide (CH), and the aluminabearing hydration products. When the amount of reactive alumina in Portland cement is low, for example, corresponding to 5 percent or less tricalcium aluminate (C_3A), the amount of gypsum (5-6 percent) normally present in the industrial Portland cements is sufficient to convert all the reactive alumina from C_3A to ettringite ($C_3A \cdot 3C\text{þ} \cdot H_{32}$), which is the stable sulfoaluminate phase in a sulfate environment with pH greater than 11.5 (Table 3). However, ordinary Portland cements usually contain more than 5 percent C_3A. When the reactive alumina in cement corresponds to approximately 8 percent C_3A, calculations show that the monosulfate hydrate ($C_3A \cdot C\text{þ} \cdot H_{12\text{-}18}$) would then be the eventual product of hydration with a Portland cement containing 5 percent gypsum. Hydration of Portland cements with more than 8 percent C_3A would result in the formation of calcium aluminate hydrate ($C_3A \cdot CH \cdot H_{12\text{-}18}$) in addition to monosulfate hydrate. These reactions are represented in Table 3.

Table 3 Relationship between Calcium Aluminate, Gypsum, and Cement Hydration Products.

Percent C_3A	**Percent Gypsum**	**Hydration Product**
5 percent or less	5-6 percent	$C_3A \cdot 3C\text{þ} \cdot H_{32}$
8 percent	5 percent	$C_3A \cdot C\text{þ} \cdot H_{12\text{-}18}$
8 percent or more	5 percent	$C_3A \cdot CH \cdot H_{12\text{-}18}$ and $C_3A \cdot C\text{þ} \cdot H_{12\text{-}18}$

From the discussion of sulfate attack (Section 3.1), it may be summarized that the amount of monosulfate hydrate, calcium aluminate hydrate, and calcium hydroxide present in the hydrated cement paste, coupled with the permeability of the concrete, control the sulfate resistance of the concrete. Type II Portland cement is moderately sulfate resistant. This type of cement contains no more than 8 percent C_3A which limits the formation of monosulfate hydrate and calcium aluminate hydrate during hydration. Type V Portland cement is more sulfate resistant and contains no more than 5 percent C_3A. It is important to note the C_3A content of Type V cement may be too low for adequate corrosion resistance in some environments (Section 4.1.4). Type III cement may contain up to 15 percent C_3A, which, depending upon the permeability of the concrete and the sulfate exposure conditions, may exhibit low resistance to sulfate attack. Pozzolanic materials may be blended with any Portland cement to reduce permeability and to reduce the amount of CH present in the hydrated cement paste.

4.1.3 Resistance to Alkali-Silica Reaction: Portland Cements and Blends

Clays and shales used in the manufacture of Portland cement may contribute alkalis to the cement and eventually to the pore solution in Portland cement concrete. Typically, where the alkali-silica reaction (ASR) is active, the pH of the pore solution measures 13.5-13.9. Accelerated tests may be performed to determine whether the combination of a particular cement and aggregate may be reactive. Low alkali cements are available if a reactive aggregate must be used. In addition, pozzolans may be used as a partial replacement for cement to reduce the alkali concentration in the pore solution and to reduce the permeability of the concrete to water. Reducing the amount of water available will reduce the swelling of ASR gel.

4.1.4 Resistance to Corrosion: Portland Cement and Blends

In Portland cement concrete, the high alkalinity of the pore solution affords protection to embedded reinforcing steel by the formation of a protective passive layer (Section 3.3). In addition, calcium hydroxide, a hydration product of Portland cement, acts as a buffer maintaining high alkalinity in the pore solution, maintaining passivation of the steel.

Low permeability of the concrete restricts chloride ingress and carbonation, either of which will depassify embedded steel and lead to corrosion. Because chloride ions combine with tricalcium aluminate (C_3A) present in the cement paste to form Friedel's salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$), concrete made from Portland cement with a high C_3A content will have a greater potential for binding chloride ions. Bound chloride ions are not free to attack the passive layer. Corrosion of some reinforced concrete structures produced with Type V cement has been attributed to the low (<5 percent) C_3A content of the cement.

Pozzolans may be used to decrease the permeability of the concrete without compromising pore solution alkalinity.

4.1.5 Resistance to Freeze-Thaw: Portland Cement and Blends

Freeze-thaw resistance is essentially determined by the physical characteristics of the concrete. For concrete with very low w/c, very little freezable water may be present. Because of the loss in strength associated with using air entraining admixtures, it may be undesirable to entrain air for freeze/thaw resistance. It has been suggested that a maximum w/c below which freezing and thawing effects may be negligible exists. This w/c may lie between 0.25 and 0.30 (18). However, experience in concrete paving with a w/c this low is limited.

For concrete with a higher w/c air entraining admixtures may be used to protect from the effects of freezing and thawing. Air contents between 3.5 percent and 7.5 percent are specified by ACI Building Code 318, depending on the maximum aggregate size and the exposure conditions. As a guideline, in medium- and high-strength concretes, each percent increase in air content results in a 5 percent decrease in strength.

4.1.6 Thaumasite Formation: Portland Cements and Blends

Thaumasite ($Ca_3Si(OH)_6(SO_4)(CO_3)\cdot 12H_2O$) formation may be considered to be combination of carbonation and sulfate attack. While the presence of ettringite is essential for the reaction to occur, the reaction mechanisms by which thaumasite is produced are not clearly understood. Taylor (23) has suggested that the ettringite acts as a nucleating agent for thaumasite formation. The reaction may occur between the ettringite, C-S-H, and calcium carbonate (produced by the carbonation of CH). Assuming ettringite and atmospheric carbon dioxide are readily available, the reaction is only limited by the amount of calcium and silicate present in the hydrated cement paste. The reaction may result in expansion and C-S-H decomposition. It should be noted that damage to concrete structures by thaumasite formation has rarely been reported. However, the reaction should be considered when selecting a Portland cement that will produce a significant amount of ettringite. The reaction may be best avoided by producing concrete with low permeability.

4.2 Calcium Aluminate Cements and Blends

Calcium aluminate cements (CAC) are composed primarily of alumina (approximately 40 percent) and lime (approximately 40 percent), but also contain ferric or ferrous oxides (approximately 15 percent), fused silica (approximately 5 percent), and small amounts titanium dioxide, silica and magnesia.

Typically, bauxite and limestone are the raw materials used in the manufacture of CAC, which may also be known as high-alumina cements or cement fondu. Costs of the raw materials and the difficulty in processing the CAC clinker, which is much harder than Portland cement clinker, cause the price of CAC to be higher than Portland cements. However, for some construction projects, properties imparted to the concrete by CAC may justify the increased cost.

According to information provided by the manufacturers, three cements being investigated may be classified within the calcium aluminate cements and blends group. Information provided by the manufacturers is limited, but it appears that two cements are blends of CAC and PC while one is CAC (primarily composed of calcium aluminate). An analysis of the potential durability of CAC and CAC blends for the construction of rigid pavements in California is examined in this section.

4.2.1 Hydration and Strength Evolution of CAC and Blends

The properties of CAC and blends are dependent on the hydration characteristics of the cement and the microstructure of the hydrated cement paste. CAC is composed principally of monocalcium aluminate (CA) which usually amounts to 50 to 60 percent of the cement by weight. The hydration of CA produces CAH_{10}, small quantities of C_2AH_8, and alumina gel (AH_3). $C_{12}A_7$ is the other major component of CAC and is believed to hydrate to C_2AH_8. With time, at both normal and elevated temperatures, both CAH_{10} and C_2AH_8 transform (or convert) to C_3AH_6 and alumina gel. Higher temperatures, higher concentrations of lime, or a rise in alkalinity encourage this transformation. Details concerning the implications of this transformation can be found in Section 4.2.2.

$C_{12}A_7$ sets within a few minutes, but CA sets more slowly. Thus, CAC with a higher C:A ratio sets or solidifies more rapidly. In addition, larger proportions of $C_{12}A_7$ may result in early loss of workability of the concrete mixture due to rapid setting.

Although CAC products have setting times comparable to ordinary Portland cement (2-3 hours), the rate of strength gain (or hardening) at early ages is quite high, achieving 80 percent of the total strength at 24 hours (4). The rapid hardening characteristics are linked to the hydration of the CA component of the cement. Within 24 hours of hydration, the strength of normally cured CAC concretes can attain values equal to or exceeding the7-day strength of ordinary Portland cement. A high rate of heat evolution is associated with this rapid strength development. The rate of heat liberation from a freshly hydrated CAC can be as high as 9 cal/g per hour, which is about three times as high as the rate for high-early strength Portland cement (4). However, the total heat of hydration is about the same for both types of cement.

For applications where rapid setting and hardening is desirable, blends of calcium aluminate cements with Portland cements may be used. An almost instantaneous set or "flash set" may be induced by blending CAC and PC where either cement type makes up 20-80 percent of the mixture (24). The decrease in setting time is often accompanied by a loss in long-term strength. Generally, the early strength of CAC/PC blends may be higher than for calcium aluminate cement alone, but later strengths will be lower (25).

4.2.2 Conversion

The principal CAC hydration products, CAH_{10} and C_2AH_8, are thermodynamically unstable and will convert over time to C_3AH_6. Because the reaction involves dissolution and reprecipitation, moisture must be available. Thus, the porosity of the concrete and the w/c will have an effect on the rate of conversion. However, with cement paste thicker than 25mm, the interior relative humidity is 100 percent, indicating that conversion may take place even when the porosity and environmental humidity are low (26). In addition, temperature has a significant influence on the rate of this reaction. The reaction proceeds more slowly at lower temperatures and more rapidly at higher temperatures. Table 4 shows the average amount of conversion to be expected over time as a function of w/c and temperature.

The original hydration products have a lower density than the products of conversion. Thus, conversion will increase the porosity of the concrete, which may result in significantly lower strength and increased permeability. Table 5 shows the effect of conversion on the strength of 3-inch (7.62 cm) concrete cubes (27). It has been suggested that post-conversion strengths of CAC concrete with w/c less than 0.40 may be adequate for some structural applications. Caution should be used however, as even a slight increase in w/c (Table 5), which may occur during construction, will produce concrete of much lower strength than anticipated.

An additional effect of the increase of porosity resulting from conversion is the increased risk for ingress of aggressive ions, such as sulfate and chloride. These issues are discussed in subsequent sections concerning sulfate resistance (Section 4.2.3) and corrosion resistance (Section 4.2.5).

Because of conversion, calcium aluminate cements were not considered in the Strategic Highway Research Program. In addition, British Standards do not allow the use of calcium aluminate cements. However, after much research into CAC performance, current French regulations for calcium aluminate cements require a maximum w/c of 0.40 and a minimum cement content of 400 kg/m3. It is believed that converted CAC concrete produced by the French guidelines and designed based upon the converted strength will exhibit satisfactory strength and durability.

Table 4 Development of Conversion with Age (from Teychennén, 1975 [28]).

Range of w/c	Temperature (C)	Average Degree (percent) of Conversion				
		28 days	3 months	1 year	5 years	8 years
0.27-0.40	18	20	20	25	30	45
	38	55	85	80	85	90
0.42-0.50	18	20	20	25	40	50
	38	60	80	80	80	90
0.52-0.67	18	20	20	25	50	65
	38	65	80	80	85	90

Table 5 Effect of Conversion on Strength of 3-inch (7.62 cm) Cubes (adapted from Neville, 1963 [27]).

Cement	w/c	Aggregate*/ Cement	1-Day Strength at 18C (MPa)	Strength after Conversion (MPa)
A	0.29	2.0	91.0	56.4
	0.35	3.0	84.4	51.5
	0.45	4.0	72.1	18.7
	0.65	6.2	42.8	5.1
B	0.30	2.1	92.4	58.2
	0.35	3.0	80.7	48.4
	0.45	4.0	68.6	29.5
	0.65	6.2	37.2	11.2
	0.75	7.2	24.5	7.1

*Maximum Size Aggregate = 9.5mm (3.8in.)

4.2.3 Resistance to Sulfate Attack: CAC and Blends

CACs were originally developed as sulfate-resistant cements. It is important to note in the discussion of the hydration of CAC above (Section 4.1.) that calcium hydroxide (CH) is not a hydration product. This feature distinguishes CAC from Portland cement and is responsible for the excellent sulfate attack resistance of unconverted CAC (Section 3.2). However, lean mixtures and concretes that have experienced conversion are less resistant to sulfate attack. Conversion results in an increased porosity in the cement paste, allowing the ingress of sulfates into the concrete. Reaction of sulfates with C_3AH_6, the product of conversion, is expansive (29). Cracking of the concrete may result from this reaction.

4.2.4 Resistance to Alkali-Silica Reaction: CAC and Blends

Calcium aluminate cements are produced from limestone and bauxite, while Portland cements are produced from limestone, clays, and shales. Clays and shales contribute alkalis to the cement and eventually to the pore solution in Portland cement concrete. Typically, where ASR is active, the pH of the pore solution measures 13.5-13.9. The pore solution of CAC concrete is usually much less alkaline, measuring 11.4-12.5 (30). Thus, alkali attack of reactive aggregate in concrete produced from CAC is unlikely. However, where CAC/PC blends are used, depending upon the alkali content of the Portland cement and the proportions of the blend, sufficient alkali concentration may be present in the pore solution to induce an alkali-silica reaction with a reactive aggregate.

4.2.5 Resistance to Corrosion: CAC and Blends

In Portland cement concrete, the high alkalinity of the pore solution affords protection to embedded reinforcing steel by the formation of a protective passive layer (Sec. 3.3.2). In addition, calcium hydroxide, a hydration product of Portland cement, acts as a buffer maintaining high alkalinity in the pore solution, and maintaining passivation of the steel.

With calcium aluminate cement concrete, the pH of the pore solution measures 11.4-12.5, and no calcium hydroxide is produced during hydration. In addition, conversion causes an increase in porosity of the concrete and may allow ingress of chloride ions from external sources. As a result, some concerns exist as to the corrosion resistance of reinforced CAC concrete. While widespread durability problems have not been reported and field evidence shows no quantifiable difference between PC and CAC reinforced concrete, BRE Digest 392 states, "The lower initial alkalinity has led to a view that reinforcement in high-alumina cement may be more susceptible to corrosion compared with OPC concrete." (31)

4.2.6 Resistance to Freeze-Thaw: CAC and Blends

Freeze-thaw resistance is essentially determined by the physical characteristics of the concrete. With little published data concerning freeze-thaw resistance of CAC concrete, it may be assumed that the behavior will be similar to that of Portland cement concrete. In order to satisfactorily resist damage by freeze-cycles, Campas and George (32) recommend a minimum strength of 50MPa and a maximum porosity of 13 percent, as measured by vacuum-assisted water absorption. These recommendations should be met even if the concrete has converted in order to adequately ensure durability to freeze-thaw cycles.

4.2.7 Resistance to Alkalis: CAC and Blends

When concrete produced with CAC is in contact with highly alkaline ($pH > 12$) environment, deterioration of aluminate hydrates may occur by two mechanisms. First, aluminate hydrates may be directly dissolved by alkaline solutions. Second, in a process termed "alkaline hydrolysis," aluminate hydrates decompose through a reaction with carbon dioxide and alkalis to form alkali aluminate and calcium hydroxide (24). Reaction of these products with carbon dioxide produces calcium carbonate and hydrated alumina, releasing alkalis to continue to degradation of aluminate hydrates. This second series of reactions is insufficiently understood, and only a few structures have reportedly experienced distress by alkaline hydrolysis.

Construction in such highly alkaline environments is not common. However, because of the direct dissolution of aluminate hydrates in alkaline environments, concerns have been raised about construction of CAC concrete abutting PC concrete or on top of a cement treated base. Potentially, alkalis from the Portland cement or lime from the CTB may be leached and in turn dissolve the aluminate hydrates in the calcium aluminate cement concrete. Such a reaction could only occur in a porous CAC concrete during wetting and drying cycles.

4.3 Calcium Sulfoaluminate Cements

In general, calcium sulfoaluminate cements are used where shrinkage compensation, early strength, or rapid setting is desired. Typically, such cements are composed primarily of Portland cement, but also contain calculated proportions of C_4A_3þ and Cþ which can be adjusted to provide early strength, rapid setting, or shrinkage compensation.

Two of the cements being investigated may be classified within the calcium sulfoaluminate cement group. Information provided by the manufacturers gives the approximate chemical composition of CSA2 as:

C_3S	0-2 percent
C_2S	48-52 percent

C_3A	0-3 percent
C_4AF	9-11 percent
C_4A_3þ	33-36 percent
Cþ	4-6 percent

The manufacturer of CSA1 has not provided the chemical composition.

An analysis of the potential durability of calcium sulfoaluminate blends for the construction of rigid pavements in California is examined in this section.

4.3.1 Hydration and Strength Evolution of Calcium Sulfoaluminate Cements

Portland cement is composed primarily of calcium silicates (C_2S and C_3S) which hydrate to form calcium-silicate hydrate (C-S-H) and calcium hydroxide (CH). The hydration of tricalcium silicate (C_3S) begins within an hour of mixing and produces about 60 percent C-S-H and 40 percent calcium hydroxide (CH). Hydration of dicalcium silicate (C_2S) occurs more slowly and produces a larger proportion (82 percent) of calcium silicate hydrate (C-S-H) than calcium hydroxide (18 percent) (4). In general, cements containing larger amounts of C_2S than C_3S produce less permeable concretes that exhibit greater resistance to chemical attack and smaller drying shrinkage (see Section 4.1.1 for more details on hydration of Portland cement).

While large proportions of C_2S are desirable from a durability standpoint, the slower rate of strength evolution and later setting point are restrictive. Proportions of calcium sulfoaluminate (C_4A_3þ) and calcium sulfate (Cþ) may be used to compensate for these characteristics. The hydration of calcium silicates is accelerated in the presence of sulfate ions in solution. In addition, $C_4A_3\text{þ}$ hydrates rapidly in the presence of lime (C) and $C\text{þ}$ to form ettringite ($C_3A{\cdot}3C\text{þ}{\cdot}H_{32}$):

$$C_4A_3\text{þ} + 8C\text{þ} + 6C + 96H \rightarrow 3(C_3A{\cdot}3C\text{þ}{\cdot}H_{32})$$

Ettringite produced by this reaction is believed to be expansive, and this reaction is controlled to produce expansive, or “shrinkage-compensating” cement.

In the absence of lime, ettringite and alumina gel (AH_3) are formed by:

$$C_4A_3\text{þ} + 2C\text{þ} + 38H \rightarrow C_3A{\cdot}3C\text{þ}{\cdot}H_{32} + 2AH_3$$

Ettringite formation will produce an earlier set and give early strength, but workability may be sacrificed. Both the amount of ettringite produced and the stability of the ettringite are highly dependent on the relative amounts of sulfates and aluminates present in the pore solution. If the aluminate concentration increases (perhaps due to renewed hydration of aluminate phases of the cement), the ettringite may be converted to monosulfate hydrate ($C_3A{\cdot}C\text{þ}{\cdot}H_{18}$). Additionally, should sulfate be present initially in insufficient concentrations, some proportion of monosulfate hydrate, instead of ettringite, will be produced as a hydration product. Thus, the proportions of $C\text{þ}$ and $C_4A_3\text{þ}$ in the cement must be carefully controlled to optimize the early setting and strength properties without compromising durability.

4.3.2 Resistance to Sulfate Attack: Calcium Sulfoaluminate Cements

As discussed in Sec 3.1, resistance to sulfate attack is dependent upon the permeability of the concrete and the hydration products present in the hydrated cement paste. Monosulfate hydrate and reactive alumina may be present in the hydrated calcium sulfoaluminate cement paste.

These products will react with sulfates to form ettringite. The reaction is potentially expansive, and may cause cracking in the concrete. Cracking increases permeability and also affects the strength and stiffness of the concrete. Additionally, calcium hydroxide, produced by the hydration of C_2S, may react with sulfates to form gypsum, which can produce microcracking, leading to a loss of stiffness and increased permeability. Loss of calcium hydroxide, by reaction to form gypsum or by leaching, also decreases pore solution alkalinity and can lead to the instability of C-S-H. Type K cements which are produced by blending ASTM Type II or Type V portland cement with C_4A_3þ show excellent durability to sulfate attack because they contain little reactive alumina or monosulfate after hydration.

The long-term resistance to sulfate attack is closely linked to the hydration products present in the concrete which is, in turn, determined by the exact proportions of calcium silicate, calcium sulfate, calcium sulfoaluminate, and other aluminates in the cement. Therefore, to assess long-term resistance to sulfate attack, accelerated tests must be performed with the particular calcium sulfoaluminate cements considered for construction in environments where sulfate attack may be a concern.

4.3.3 Resistance to Alkali-Silica Reaction: Calcium Sulfoaluminate Cements

Calcium sulfoaluminate cements are primarily composed of Portland cement, which may introduce a significant concentration of alkali into the pore solution. It is suggested that accelerated testing be performed to assess the potential for the alkali-silica reaction in concretes produced from calcium sulfoaluminate cements.

4.3.4 Resistance to Corrosion: Calcium Sulfoaluminate Cements

Because calcium sulfoaluminate cements are largely composed of Portland cement compounds, the corrosion resistance characteristics are expected to be similar. The permeability of the concrete will be the critical parameter to avoid corrosion of embedded steel. The pore solution alkalinity is expected to be adequate to passivate the steel.

4.3.5 Resistance to Freeze-Thaw: Calcium Sulfoaluminate Cements

Polivka *et al.* (33) examined the freeze-thaw characteristics of Type K shrinkage-compensating cement containing C_4A_3þ. Air-entrained shrinkage-compensating cement concretes displayed resistance to freeze-thaw action comparable to air-entrained Portland cement concrete. However, because some air entraining admixtures may be incompatible with certain sulfoaluminate cements, trial mixes should be produced and the air content of these mixes should be measured (34). Freeze-thaw resistance data of early-setting (i.e., *not* shrinkage-compensating) calcium sulfoaluminate cements has not been widely published.

4.3.6 Thaumasite Formation: Calcium Sulfoaluminate Cements

For general information on thaumasite formation, refer to Section 4.1.7.

The presence of ettringite is essential for the reaction to occur. Because ettringite is present in the hydrated calcium sulfoaluminate paste, the reaction should be considered when examining durability of such cements. Damage to concrete structures by thaumasite formation has been rarely reported. Concrete with low permeability should resist thaumasite formation, which may be considered to be a combination of sulfate attack and carbonation.

4.4 Fly Ash-Based Cements

Fly ash is a byproduct of the burning of pulverized coal by power stations. Fly ash composition varies widely and is dependent upon the coal burned and the burning conditions. Most fly ashes contain 60-85 percent glass, 10-30 percent crystalline material, and up to 10 percent unburnt carbon. In the United States, fly ashes are given designations depending upon the SiO_2+Al_2O_3+Fe_2O_3 content. If the content is greater than 70 percent of the fly ash, it is designated Class F; if it is less than 70 percent, it is designated Class C.

One manufacturer has submitted a fly ash-based cement for consideration by Caltrans. The composition is described as:

90 percent Class C fly ash

4 percent Portland cement

6 percent other

From discussions with the manufacturer, it may be assumed that ‘other’ is a designation for a patented alkali accelerator. Thus, the focus of this discussion will be on the durability of alkali-accelerated cementitious materials, with an emphasis on Class C fly ashes.

4.4.1 Hydration and Strength Evolution of Fly Ash-Based Cements

Class C fly ash may contain 15-35 percent lime and may be termed ‘high-calcium’ fly ash. In general, high-calcium fly ash is more reactive than low-calcium (Type F) fly ash because the fly ash contains calcium in the form of crystalline reactive compounds (C_3A, Cþ, and C_4A_3þ). In addition, enough calcium is present in the non-crystalline phase to enhance the reactivity of aluminosilicate glass (4).

Reaction of fly ash is initiated by the dissolution of the particles, but the dissolution will only take place when environmental pH is at least 13.2. The addition of alkali to the fly ash, as is suggested by the literature provided by the manufacturer, would accelerate the dissolution of the fly ash and the hydration process. In fact, the manufacturer has provided several mix designs with varying amounts of alkali accelerator to produce material of varying setting time and rates of strength development.

Because fly ash composition varies widely and because the exact composition of the fly ash under consideration was not provided, the hydration products of this particular fly ash-based cement can not be predicted. Generally, the hydration of fly ashes will primarily produce some form of C-S-H.

4.4.2 Sulfate Resistance of Fly Ash-Based Cements

Sulfate resistance is largely determined by the permeability of the concrete and by the reactivity of the hydration products present. The hydration products of the cement submitted in this class are unknown. However, Class C fly ashes are generally known to contain relatively large proportions of sulfate, as well as alkalis. Thus, depending upon the relative amount of alumina present, the potential for monosulfate to form as a hydration product may exist. In addition, unreacted fly ash may contain alumina or lime, particularly in the non-crystalline phase, which may increase the potential for damage from sulfate attack. Accelerated sulfate testing of this cement type should reveal more information concerning its potential long-term durability in aggressive sulfate environments.

4.4.3 Resistance to Alkali-Aggregate Reactions: Fly Ash-Based Cements

Class C fly ash contains relatively large proportions of alkali, as compared to Class F fly ash. Additional alkalis are supplied in the form of an alkali accelerator. Should the fly ash-based cement be selected for pavement construction, a thorough investigation of the potential reactivity of both the fine and coarse aggregates to be used is recommended.

4.4.4 Resistance to Corrosion: Fly Ash-Based Cements

Because of the lack of information supplied by the manufacturer and because of the lack literature on the subject, the expected corrosion resistance of fly ash-based cements is difficult to predict. The use of a high- alkali accelerator would suggest that the pore solution alkalinity be adequate for steel passivation. However, the chloride binding capacity of the hydrated cement paste should be investigated.

4.4.5 Resistance to Freeze-Thaw: Fly Ash-Based Cements

Hydration of Class C fly ash is expected to produce a dense hydrated cement paste with a chemical composition similar to that of Portland cement. However, some studies have shown that high contents (>20 percent) of Class C fly ash produce concrete less resistant to freeze-thaw action (35). As a result, the fly ash content of concrete exposed to freeze-thaw cycles has been limited to 25 percent by mass of cement in ACI 318-89. Decreased resistance may result from an increased porosity in the hydrated cement paste caused by the movement of ettringite into air voids (24). The implications of these findings to a cement paste composed primarily of hydrated

Class C fly ash are unclear, but should be investigated before constructing fly ash-based pavements in areas likely to experience freeze-thaw cycles.

Like Portland cement concrete, air entrainment admixtures should be used in fly ash-based concrete for construction in regions where freeze-thaw resistance is necessary. The carbon content of the fly ash will affect the entrainment of air. Carbon has been shown to destabilize entrained air bubbles, perhaps by adsorption of the bubbles at the highly active carbon surface (36). The manufacturer should be consulted when selecting an air-entraining admixture to ensure compatibility of the admixture with the alkali accelerator.

5.0 TEST PROGRAM

From the discussions in the previous sections, it is clear that further investigations will be required to better assess the potential long-term durability of the cements under consideration for rigid pavement construction in California. Accelerated testing is underway to measure sulfate resistance of the cements under consideration. Tests for aggregate reactions and conversion of calcium aluminate cements are planned, and test descriptions will be provided in subsequent reports.

Accelerated tests for sulfate resistance should predict field performance. Sulfate attack characterized by loss of strength, spalling, and cracking is typical of the gypsum-formation type of attack and is more common in structures than the ettringite-formation type of attack. However, currently accepted ASTM tests fail to evaluate resistance to the more common gypsum-formation type of attack, and only measure the far less common ettringite-formation type of attack. For these reasons, a revised test method is being used to measure the sulfate resistance of the cements under consideration.

5.1 Review of Accepted ASTM Accelerated Test Methods

Two accelerated test methods have been adopted by ASTM to evaluate performance of hydraulic cements in sulfate-rich environments:

- ASTM C452 Standard Test Method for Potential Expansion of Portland-Cement Mortars Exposed to Sulfate
- ASTM C1012 Test Method for Length Changes of Hydraulic-Cement Mortars Exposed to a Sulfate Solution

ASTM C452, adopted in 1960, specifies that mortar bars made from a mixture of Portland cement and gypsum (to increase the sulfate content to 7 percent by mass). The samples are cured 22-23 hours in water, measured, and measured again after soaking 14 days in water to determine the amount of expansion. Because of the short curing time, ASTM C452 is suitable only for Portland cements. ASTM C1012 was introduced as a supplement to ASTM C452 for the testing of blended cements and blends of Portland cement and slag or pozzolanic material. Mortar bars and cubes are produced and cured until the mean compressive strength of two cubes measures 20 MPa (2850 psi) or more. At this point, an initial length measurement is made, and the bars are immersed in a sulfate solution. Subsequent length measurements are required at 1, 2, 3,4, 8, 13, and 15 weeks and additional measurements may be required at 4, 6, 9, and 12 months if the length change is slight, gradual, and uniform.

Both standard test methods have been the subject of much criticism. Many researchers (37) have expressed concern that the results may not be indicative of in-situ performance of the cements tested. Table 6 lists specific criticisms of these test methods with the corresponding reference.

An example of the inadequacy of the accepted test methods is described by Mehta *et al.* (43). Alite cements tested by ASTM C452 exhibited minimal expansion because the cements contained no C_3A and could not produce ettringite. However, after six years of curing, spalling occurred and it was discovered that the C-S-H had converted to aragonite and gypsum. The spalling observed was attributed to the crystallization of gypsum, which could not have been predicted by either of the currently accepted test methods.

Table 6 Criticism of Accepted Sulfate Durability Tests.

Criticism	Reference
Cause of expansion not determined by the tests; tests do not address formation of ettringite during storage and expansion.	Idorn, Johansen, and Thaulow, 1992 (38).
Addition of sulfate in ASTM C452 is not representative of field conditions; both tests are too sensitive to specimen size and geometry.	Tumidajski and Turc, 1995 (39).
ASTM C452 does not represent field conditions because inadequate curing of cement results in anhydrous cement compounds being exposed to attack; softening-spalling attack is ignored by ASTM C452 and ASTM C1012.	Mehta and Gjorv, 1974 (40).
Standard specifications for sulfate-resisting cements (ASTM C452 and C1012) generally ignore the acid-type sulfate attack, which is the more typical type of attack in the field.	Mehta, 1975 (41).
Cement composition affects the rate of consumption of sulfate ion and introduces variability in ASTM C1012; pH during testing is 3- to 5 orders of magnitude different from field conditions; C1012 tests are protracted because of decrease in the sulfate concentration in solution.	Brown, 1981 (42).

5.2 Accelerated Test Method

The accelerated test method used for evaluation of sulfate resistance is based upon a method proposed by Mehta and Gjorv (39, 40). The conditions provided in this accelerated test method are more representative of field conditions, and, therefore, results will be more indicative of field performance than the currently accepted ASTM methods.

The method involves the immersion of 0.500 in. (1.270 cm) hydrated cement paste cubes in a 4 percent Na_2SO_4 solution (pH=7.2). Sample dimensions have been selected to maximize the surface to volume ratio, thus increasing the potential for reaction with the sulfate solution. This reduces the testing period required and eliminates effects of size and geometry. The sulfate solution pH is suitable for testing sulfate attack under slightly acidic conditions typically present in the field. The pH is maintained through constant monitoring and adjustment by additions of aliquots of 0.1N H_2SO_4. It should be noted that the sulfuric acid is added to a large reservoir and not to the sample reservoir. Figure 2 is a schematic of the test apparatus.

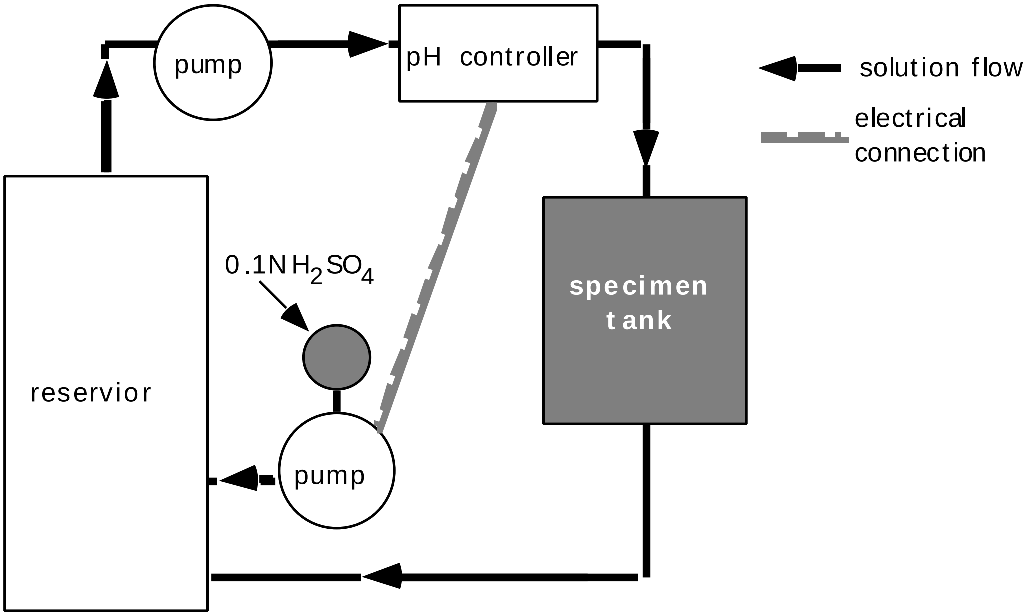

Figure 2: Depiction of pH-controlled accelerated test method.

Because the pH is controlled, the effect of leaching of CH from the paste into the sulfate solution is eliminated. In addition, Brown (42) demonstrated that controlling the pH through additions of sulfuric acid ensured that the sulfate ion concentration of the solution remained constant over time. By maintaining a constant sulfate concentration through pH control, field conditions are better replicated.

Cement paste cubes are cured for 7 days prior to testing. Research has indicated that normally slow-hydrating cements, such as blended or pozzolan-containing or slag-containing cement, are well hydrated after 7 days moist curing at 50C. The cubes are prepared in watertight molds at a w/c=0.50. The cubes cure in the molds for 24 hours before de-molding. The samples are cured at constant temperature: 20C for CAC and 50C for other cement classes. However, conversion is induced in some CAC cubes before testing by subjecting the samples to increased temperature and water over time. Table 7 provides details about the curing regimen for the cements tested. Loss of strength for Type I/II, III, and V Portland cement cubes serves to distinguish between cements that perform well (Type V) and those that perform poorly (Type III).

Table 7 Description of Curing Regimen for Cements Evaluated.

Curing Regimen	Cements
20C; moist cure; 7 days	CA1, CA2, CA3
50C; moist cure; 7 days	PC1, CSA1, Type I/II, Type III, Type V
50C; 7 days	FA1
50C; moist cure; 90-180 days (until strength loss due to conversion)	CA1, CA2, CA3

After curing, a set of control samples is tested to measure compressive strength prior to sulfate immersion. After 28 days of immersion, compressive strength is measured and compared to 7-day strength. Mehta (41) evaluated the sulfate resistance of a variety of cement pastes, including those made from Type I cement, Type V cement, and pozzolan- and slag-containing cements, by this accelerated test method. Twenty-eight days proved to be an adequate time period to distinguish between the sulfate resistance of the cements tested, indicating the method is quick and reproducible. However, compression tests will be repeated after 60 days of immersion for further verification. Table 8 describes the test plan and the number of samples to be tested at each interval. The number of samples tested at each interval depends upon the agreement of the compression test data, but will range from 5-10 samples per test period.

Table 8 **Number of Samples for Each Cement to be Tested in Compression Prior to Exposure (7 day), After 28 Days of Sulfate Exposure, and After 60 Days of Sulfate Exposure.**

	Number of Samples		
Cement Designation	**7 days**	**28 days**	**60 days**
PC1	5-10	5-10	5-10
CSA1	5-10	5-10	5-10
FA1	5-10	5-10	5-10
CA1	5-10	5-10	5-10
Converted CA1	5-10	5-10	5-10
CA2	5-10	5-10	5-10
Converted CA2	5-10	5-10	5-10
CA3	5-10	5-10	5-10
Converted CA3	5-10	5-10	5-10
Type I/II PC (control)	5-10	5-10	5-10
Type III PC (control)	5-10	5-10	5-10
Type V PC (control)	5-10	5-10	5-10

Note that the calcium aluminate cements will be tested both as unconverted cement paste and as converted cement paste.

6.0 SUMMARY

The cementitious materials under consideration by Caltrans for rigid pavement construction may be classified into four categories: Portland cements and blends, calcium aluminate cements and blends, calcium sulfoaluminate cements, and fly ash-based cements. For rigid pavements to achieve the 30+ year service life defined by Caltrans, the characterization of the long-term resistance of the concrete to sulfate attack, aggregate reactions, corrosion, and freeze-thaw action is essential.

However, assessment of the long-term durability of these cement classes by literature review alone is questionable. First, most of the cementitious materials under consideration have not been extensively used for pavement construction in the United States, and little information about their long-term durability is available. Second, many of the manufacturers are protective of their products and are not comfortable revealing the chemical composition of their cements. While durability test results have been provided by some manufacturers, these results have been largely neglected in this review because the testing was not performed by or published by an impartial source. Of course, a vast amount of information concerning the durability the Portland cements and Portland cement blends is available, and a detailed review of the expected performance has been provided. Accelerated testing to measure the sulfate resistance of the cements submitted to Caltrans has been described. Further testing for aggregate reactions, corrosion resistance, and air entraining admixture content and compatibility may be required in the future.

A summary of the potential durability issues for each cement class is provided in Table 9. Because of potential differences in durability characteristics, Portland cements are treated separately from Portland-pozzolan blends, as are calcium aluminate cements and calcium aluminate blends. The summary in Table 9 is intended as a guide only. The designations are meant to describe *potential* for the reaction to occur with a particular class of cements. The descriptions in Table 9 are not based upon experimental evidence, but are based upon a literature review of durability of the various cement types with specific regard to long-term durability. The reader should refer to the discussion of each performance issue for detailed information.

Table 9 Summary of Potential Durability Issues for Cement Classes Investigated for Rigid Pavement Construction in California.

Cement Class	Sulfate Attack	Aggregate Reactions: Alkali Oxidation		Corrosion	Freeze-Thaw Action
		Alkali	**Oxidation**		
Portland Cements	Specified by the building code (see Table 1)	Specify low-alkali cement		Maximum water soluble chloride ion in concrete is 0.15 percent by weight of cement	Resistance is a function of amount of air-entrainment
Portland-Pozzolan Blends	Potentially improved performance	Potentially improved performance (see 4.1.3).	Potentially improved performance	Potentially improved performance (see 4.1.4)	Resistance is a function of amount of air-entrainment (see 4.4.5)
Calcium Aluminate Cements	Potentially improved performance (see 4.2.3)	Potentially improved performance (see 4.2.4)		Limited information (see 4.2.5)	Resistance is a function of amount of air-entrainment (see 4.2.6)
Calcium Aluminate Blends	Potentially improved performance (see 4.2.3)	Potentially improved performance		Limited information (see 4.2.5)	Resistance is a function of amount of air-entrainment (see 4.2.6)
Calcium Sulfoaluminate Cements	Potentially improved/worse performance (see 4.3.2)	Similar to Portland cement (see 4.3.3)		Similar to Portland cement (see 4.3.4)	Resistance is a function of amount of air-entrainment (see 4.4.5)
Fly Ash-Based Cements	Potentially improved performance (see 4.4.2)	Potentially improved / worse performance (see 4.4.3)	Potentially improved performance	Complex interaction (see 4.4.4)	Resistance is a function of amount of air-entrainment (see 4.4.5)

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