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Alkali-Silica Reactivity: An Overview of Research

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Abstract

Part I of this report is a synthesis of our knowledge of mechanisms of damage to concrete by alkali-silica reactivity. Alkali-silica reaction gels are composed of two-component mixtures of alkali-calcium-silicate hydrate and alkali-silica sols of nearly fixed compositions. Cracking may be initiated by swelling of aggregate particles before copious production of gel and large expansions of cracks caused by swelling of gel occurs. External restraint reduces expansions and cracking, increases stress and the rate of dissolution of silica at reaction sites, reduces osmotic swelling of gel and causes gel to flow or creep from reaction sites, and causes creep of the matrix in compression. In practice the process is complicated by the effects of drying and growth of shrinkage cracks in exposed surfaces. The presence of chloride salts accelerates alkali-silica reactions. Formation of Friedel's salt and other complex chloride containing salts complicates test results.

Part II identifies 10 specific gaps in our knowledge of alkali-silica reactions in concrete that limit our ability to control these reactions or to predict performance of concrete with reactive aggregates. These involve rapid and reliable test methods; moisture conditions in highway structures; effects of salts, role of sulfate reactions accompanying expansions caused by reactivity; measurement of aggregate reactivities; effect of restraint on kinetics; mechanisms by which pozzolans prevent expansion; test methods and specifications for pozzolans; and inhibition of reactivity by chemical agents.

Executive Summary

This report summarizes the findings of a review of published literature concerning alkali-silica reactivity. The objective of the review was to identify gaps in our knowledge and sharpen the focus of laboratory and field investigations.

Part I of this report is a synthesis of our knowledge of mechanisms of damage to concrete by alkali-silica reactivity (ASR). It is the context in which gaps in our knowledge have been identified; these are presented in Part II.

Part I is a critical review of recent and older research on reaction chemistry, the physical nature of swelling gels, mechanical effects of ASR, and environmental effects on ASR in concrete. It includes some test results from this contract, and some reanalyses of published work. Major findings are as follows.

- The reaction chemistry of the swelling and dissolution of disordered silica in alkali hydroxide solutions in the absence of calcium hydroxide is reasonably well understood. When calcium hydroxide is present, dissolved silica reacts to form calcium silicate hydrate in the ASR gel.

- Portland cement hydration releases sodium and potassium ions into pore solutions so that concentrations stabilize after several weeks as essentially alkali hydroxide of 0.7 mol/L per percent equivalent $Na_2O\%$ in the cement, at 0.5 water/cement ratio. A simple equation was developed for hydroxyl ion concentrations that also includes w/c, and variations of the amounts of alkali retention by the cement gel. It then became possible to develop equations to estimate reductions of hydroxyl ion concentrations resulting from dilution and pozzolanic reactions when cements are replaced by pozzolanic fly ashes in order to control ASR. If low-alkali pozzolanic fly ashes are sufficiently reactive, they can reduce hydroxyl ion concentrations substantially when used with high-alkali cements.

- It is possible to explain the variable compositions of simple calcium-alkali-silicate-hydrate gels, and those of complex ASR gels in concrete, as relatively simple two-phase composites including precipitated calcium-alkali-silicate-hydrate of compositions near $0.16\,Na_2O \cdot 1.4CaO \cdot SiO_2 \cdot XH_2O$ in a swellable sol/gel matrix with a molar Na_2O/SiO_2 ratio of about 0.19.

- Consideration of the negative volume changes during dissolution of reactive silicas shows that increasing pressure does not stop the reaction, but tends to force it to completion. Hence the swelling pressure of the gel formed tends to accelerate the reaction

- Cracking of mortars or concretes may be initiated by swelling of solid aggregate particles before copious production of gel; large expansions of cracks caused by swelling of gel occurs progressively.

- Swelling pressures at reaction sites or in gel in cracks are balanced by tensile stresses in the nearby concrete, and by any external restraint, and are relieved when cracking occurs, or by gel flow and creep.

- Expansions are reduced by external restraint, which increases stress at reaction sites. Increased stress at reaction sites can 1) increase creep or the paste in the matrix, 2) increase the rate of dissolution of silica, 3) reduce osmotic swelling of gel, and 4) cause gel to creep or flow from the reaction sites through pores and/or microcracks.

- In practice these processes are complicated by the effects of drying and growth of shrinkage cracks in exposed surfaces, and differences in reaction rates caused by differences in moisture content.

- Powers and Steinour's model for ASR and criteria for safe and unsafe reactions, based on cement alkali contents and mortar proportions, are generally supported by recent research but have been challenged with respect to the effects of pozzolans and chloride salts. Some pozzolans (calcined kaolin, condensed silica fume) control ASR by rapid reduction of the pH pore solutions, as suggested by Powers and Steinour. Other materials (fly ashes and slags) may control ASR expansions without much reduction of, or even while increasing, the pH of pore solutions. These materials appear to facilitate the reaction of the aggregate so that it softens and dissolves without excessive swelling pressures.

- Chloride salts may aggravate ASR expansion whether added to mixing water or by penetrating mortars after hardening. Both sodium chloride and calcium chloride accelerate reactions with reactive silica at elevated temperatures. Friedel's salt ($C_3A \cdot CaCl_2 \cdot 10H_2O$,) and other complex salts are formed by reaction with tricalcium aluminate in cements. The reaction with NaCl causes an increase of hydroxyl ion concentration. Pozzolans reduce these expansions but may not prevent damage to specimens exposed to large amounts of salts. Under such accelerated test conditions the formation of calcium silicate hydrate when calcium hydroxide is present may prevent the escape of dissolved silica from the reaction zone. When calcium hydroxide is leached in hot calcium chloride solutions these expansions are prevented. However, the relationship between such accelerated tests and ordinary exposures is not well understood.

Part II includes descriptions of ten gaps in our knowledge of alkali-silica reactions in concrete:

- The Introduction is a summary of deficiencies described in Part I that limit our ability to predict accurately or to control the effects of different reactive aggregates, and of environmental effects on ASR.

- Rapid and reliable test methods to identify potentially reactive aggregates in concrete are required. ASTM and other test methods and specifications and their limitations are described, especially with respect to aggregates that react slowly, or release alkalies as they react. Even service records are not definitive because the information is usually incomplete.

- Moisture conditions of Concrete in Highway Structures determine the rates of reaction, the mechanical properties and drying shrinkage of the concrete, and hence its response to ASR.

- Effects of salts and direct participation of chloride ions in ASR are not yet well understood and of increasing importance because of the increasing use of deicing salts, "fast track" pavement construction practices, exposure of concrete to seawater, and the need for accelerated test procedures.

- The role of sulfate reactions accompanying expansions caused by ASR is illustrated by reports showing 1) delayed expansion and cracking of steam-cured concretes, 2) increased expansion caused by additions of sodium sulfate to mortars containing reactive aggregate, 3) ASR gel formed around reactive particles in cherty dolomites with gypsum inclusions in deteriorated concretes, and 4) ASR being initiated in concretes undergoing attack from sulfates penetrating from exterior sources, or concentrated locally by drying.

- Measurement of aggregate reactivities unimpeded by external diffusion processes has yet to be done on representative reactive aggregates, although the intrinsic reaction rate is probably the most important characteristic of reactive aggregates. Such measurements are difficult and complicated by the need for mixed solutions of alkali and calcium hydroxides, and suitable Na_2O/SiO_2 ratios or alkali concentration control.

- Effects of restraint of expansion on ASR kinetics are virtually unknown, although the effects on expansion have been studied. Increasing pressure reduces swelling, but should acceleratedissolution of reactive silica and gel production rates.

- There are apparently two or more mechanisms by which pozzolans inhibit ASR expansion. Some pozzolans (condensed silica fume, calcined kaolin) prevent expansions by rapid reduction of pore solution pH. Other materials (fly ash, slags) hardly reduce, or may even increase the pH of pore solutions at early ages. Other factors are important, especially in the presence of salts which increase ionic strength of the solutions, and increase the reaction rates rather than slow them.

- Pozzolan and mineral admixture test methods and specifications are inadequate to insure concrete performance. The use of Pyrex glass aggregate in ASTM C 441 may prevent a proper assessment of admixtures for ASR control. Some admixtures contribute alkali hydroxides to pore solutions, and proportions in such standard tests differ from most concretes.

- Inhibiting expansion due to ASR by chemical agents has been investigated to only a very limited extent. Crown ethers, cryptands, amines, alkyl-alkoxy-silane, phosphates, lithium compounds, sodium silicofluoride, and polymer cements are under study.

Part I: Mechanisms of Damage to Concrete By Alkali-Silica Reactivity

1 Introduction

The fundamental processes in alkali silica reactions are swelling and/or dissolution of soluble silica and formation of alkali silicate gels by their reactions with calcium ions supplied by cement hydration reactions (1,2,3,4). The chemistry of dissolution of silica to form alkali silicate solutions is complex even in the relatively simple industrial processes in common use (5,6). Not only are various crystalline solid hydrate species possible, but the solutions at high pH contain a variety of ionic species which tend to polymerize and form colloidal sols and gels without crystalline hydrates. Such systems tend to reach metastable equilibria, or approach equilibrium very slowly. When calcium hydroxide is present, as in most concretes, ASR* gels become even more complex entities. Analysis indicates that ASR gels of different compositions may be regarded as mixtures of different proportions of an alkali silicate hydrate sol or gel, and poorly crystalline calcium silicate hydrates containing some alkali as well as variable water content. Some of the transformed reactive aggregate particle remains in situ, and has effects different from the dissolved silica which diffuses and/or flows away from the reaction site and continues to react with calcium ions. Drying concentrates alkali hydroxide in pore solutions, and increases their pH and the solubility of silica. Rewetting dilutes the solutions, but permits swelling of gels formed by the concentrated solutions. Some of the alkali ions become immobilized during drying so that the net effect after rewetting is a reduction of alkali concentrations and pH of the pore solution.

An important mechanism is that of osmotic swelling of permeated rocks and gels. Although hardened cement pastes can function somewhat like semi-permeable membranes because of differences of mobility of water and ions in its pore structure, a membrane is not necessary (7). Reactive silica has a great affinity for hydroxyl and alkali ions, and water. It becomes its own membrane by concentrating ions as it swells.

A serious attempt was made by Powers and Steinour in 1955 (1,2) to describe the mechanism of expansion and safe and unsafe reactions in concrete. In their view, reactions with highly reactive opal rock particles could be safe or unsafe depending on the relative amounts of calcium and alkalies in the reaction product. High calcium content $CaO-Na_2O-SiO_2-H_2O$ gels do not swell and form safely at the particle surface as long as calcium ions can penetrate to the reaction zone.

However, if calcium ion concentrations are too low to form non-swelling gels, low calcium content swelling gels are formed. Also, for a safe reaction, some of the silica must diffuse out through the reacted layer as H_2O, calcium, and alkalies diffuse inward to the reaction zone.

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* Alkali-silica reaction or alkali-silica reactivity.

Recent research confirms major aspects of these concepts. Electron probe microanalysis (EPMA) and scanning electron microscope-energy dispersive X-ray (SEM-EDX) analyses have shown the penetration of alkalies and calcium into the reacted aggregate, and the increase in silica contents outside of the rock. EPMA has also permitted analysis of ASR gels exuded through cracks away from such reaction sites.

In addition, the reaction chemistry has been studied in more detail so that the effect of calcium on the compositions and properties of the reaction products are better understood. Despite these advances there is very little data available on swelling and swelling pressures that are developed by reactive aggregates and their gels. From the limited data available it is possible to calculate maximum osmotic pressures that can be used to assess potential for damage and the effects of restraint of expansion in concrete. Research on the effects of pozzolans on ASR has shown that different materials have very different effects. Some materials control ASR (as suggested by Powers and Steinour) by rapid reduction of pH of pore solutions. Others, including some fly ashes and slags, control ASR expansions while facilitating reaction of the reactive aggregate particles. Very different mechanisms are involved.

In most concrete pavements and structures, restraint of expansion of the reactive aggregates is developed both internally and externally to the concrete. The weight of concrete in a large structure can produce compression that increases with distance from the top. Steel reinforcement would restrain expansion parallel to the direction of the reinforcement, but drying shrinkage must be exceeded before compression can be developed in this way. Highway pavements afford an interesting example of one-dimensional restraint (parallel to their length) which minimizes transverse cracking so that longitudinal cracking is predominant. It is clear that average stress in the concrete, and localized stress at reaction sites, are important variables.

Environmental factors affect both reaction chemistry and the response of concrete to expansive processes. Partial drying shrinks expansive gels and delays expansion, but concentrates alkalies in pore solutions and may increase reaction rates. Moisture gradients create internal stresses. Stress relief by creep can occur more rapidly in moist than in dry environments.

Long-term effects while the concrete is moist, wet/dry cycles, and temperatures cycles each affect local stresses. Such cycles accelerate the destructive processes. In heterogeneous materials, like concrete, thermal and shrinkage (or swelling) stresses superimposed on stresses produced by service loads or expansion of reactive aggregates shorten service life by exceeding the strength of the material earlier and more often. Our objective is to eliminate or minimize these effects of ASR in concrete.

Another environmental factor now recognized to be of increasing importance in ASR is the use of soluble salts as deicers. It has been shown that certain soluble salts accelerate ASR expansions and deterioration processes. Study of those processes has led to reconsideration of Powers and Steinour's analysis of the reactions with calcium ions. Chatterji (8) has suggested that the presence of calcium hydroxide in the concrete system is a prerequisite for ASR expansion and cracking in some situations. He emphasized the influence of ionic strength of salt solutions on reactivity and how formation of gels containing considerable calcium did not assure safe reactions because the products impeded the escape of dissolved silica. With too little calcium in solution to form gels, the product sols may more readily diffuse or flow away from reaction sites. Although the escape of silica had been clearly recognized as essential by Powers and Steinour, Chatterji concluded that in ASR reactions accelerated by salt solutions, it was necessary to prevent or limit calcium hydroxide, derived from cement hydration, from providing calcium ions to react with silica and thereby impede migration of dissolved silica out

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from reactive grains. Powers and Steinour did not address the effects of salt solutions on ionic strength and solubility of silica. Research to date is incomplete and these effects do not yet appear to be well understood. To exploit the benefits of pozzolans and understand their limitations, further work must be undertaken on ASR accelerated by the effects of deicing salts.

In the following sections, research on various aspects of mechanisms of damage to concrete by ASR is critically reviewed and summarized. These aspects range from details of reaction chemistry and expansion processes, to effects of environmental conditions in mortars and concretes both in accelerated laboratory tests and in the field. The review provides the context in which gaps in our knowledge have been identified, and provides a basis for decision making in our current research for SHRP.

2 Reaction Chemistry

2.1 Reaction with Alkali Hydroxides

Reactive silicas have disordered internal structures. Even crystalline quartz is disordered at its surfaces, which have unsatisfied O^- surface charges and form acidic $\equiv$Si-OH (silanol) groups with water. Such dense and impermeable aggregates react very slowly. Rocks containing amorphous or poorly crystalline silica are somewhat porous and permeable, and a fraction of the internal silicon atoms also have silanol groups. In the absence of excess hydroxyl ions (i.e., in water without alkali or calcium hydroxide, not concrete pore solutions) reactive silicas can imbibe some water but do not swell appreciably because of extensive Si-O-Si (siloxane) cross linking of the silica structure. Excess hydroxyl ions present in alkali solutions cause reactive silicas to swell and dissolve at rates that depend on their external and internal surface areas and the completeness of the cross-linking of the silica structure.

Silicon atoms in silicas may be cross-linked with four bridging oxygen atoms, or less completely with only 3, 2, or 1 oxygen atoms. In a-quartz, cristabolite, and tridymite MAS-NMR Magic Angle Spinning-Nuclear Magnetic Resonance (MAS-NMR) spectra for ^{29}Si show only Q_4 peaks indicating complete three-dimensional polymerization, whereas opal shows in addition a peak Q_3 indicating a substantial fraction with only three bridging oxygens. This indicates less complete polymerization (9). Reacted specimens show decreased Q_4 peaks and increases in Q_3 and Q_2, which indicate loosening of the silica structure.

Since ASR phenomena in concrete are complex, simpler systems have been studied to isolate their different aspects. Silica in alkali solutions without calcium hydroxide cannot represent all of the chemical reactions in concretes because pore solutions in concrete tend to be saturated with calcium ions from calcium hydroxide. Although calcium concentrations are greatly reduced by alkali hydroxides by the common ion effect on the solubility of calcium hydroxide, there is an abundant supply of solid calcium hydroxide available for reaction through continuing dissolution. However, simple systems without calcium may represent swelling and dissolution of silica in concrete in zones remote from sources of calcium ions, as at the reaction front within coarse aggregate at later stages of reaction.

In order to examine the reaction of amorphous silica with alkali hydroxide solutions unimpeded by slow diffusion processes, a highly reactive, 770 m^2/g hydrated silica gel with loss on ignition (L.O.I.) of 7.8% was used as a model system (3,10). The surface area of this material indicates that the average thickness of the solid is only about 1.2 nm (0.05 microinch), or about twice the c-spacing in α-quartz. Thus, most of the silica is in exposed surfaces. This material was more than 95% dissolved in less than two hours when stirred in 0.1 M NaOH solution. Rate of dissolution of the silica gel was approximately proportional to the amount of undissolved silica (10).

In solutions containing appreciable alkali (potassium and sodium) hydroxide, this highly reactive silica gel tends toward dissolution in two stages. The first stage is neutralization of

the acidic silanol groups by OH^- ions. Charged O^- sites are created that attract positive ions. The reaction can be represented as:

$$H_{2x}SiO_{2+x} + 2xNaOH \rightarrow Na_{2x}SiO_{2+x} + 2xH_2O \qquad (2.1.1)$$
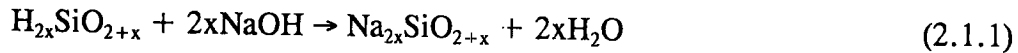
in which $2x$ is the fraction of silicon atoms with silanol groups. This fraction was about 0.38 for this particular silica gel. The reaction can be regarded as exchange of H^+ for Na^+ ions, which are ionically bonded and which attract hydration spheres of water molecules that slightly swell the rigid silica structure.

A second stage of reaction occurs when excess hydroxyl ions in alkaline solutions attack the siloxane bridges so that additional negatively charged O^- reaction sites are created that also bind Na^+ ions. The silica structure loosens progressively as the siloxane bridges are broken; additional oxygen-alkali sites become active and additional water is imbibed during an osmotic-like swelling of the loosened structure. This structure may become an alkali-silicate solution or alkali-silicate-hydrate gel (N+K-S-H), depending on moisture content. The OH^- concentration and pH both decrease as silica dissolves. This reaction may be written in simplified form as:

$$Na_{2x}SiO_{2+x} + (2-2x)NaOH + xH_2O \rightarrow 2Na^+ + H_2SiO_4^{2-} \qquad (2.1.2)$$
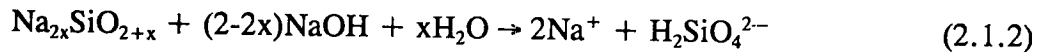
The actual reaction depends on pH and concentrations and the silicate species in solution may be polymeric.

Analysis by solid-state ^{29}Si MAS-NMR of reactive opal before and after reaction with alkali solutions (with or without calcium hydroxide) has provided direct evidence of structural breakdown of the silica structure as just described. These results, of current work by Kirkpatrick (9) at the University of Illinois, apparently refute results of an earlier NMR study using opal and flint aggregates. That study concluded (11) that these materials react by simple dissolution, without weakening the remaining lattice.

In contrast to results for silica gel, initial rates of dissolution of Beltane opal (6.5% loss on ignition and 0.13 m^2/g) and ground quartz (0.084 m^2/g) indicated that 31 and 54 days would be required for 100% dissolution if the rates had not been slowed as the reaction proceeded. These results indicate that the silica gel is more reactive than opal and quartz, mainly because of differences in measured surface areas. The reported values for the specific surface areas for the opal and quartz are probably much less than their true values because not all of the reactive surface area was measured by the method employed (Blaine Apparatus). Surface area of the silica gel was determined by titration, and was probably appropriate for this purpose. The internal surface area of the Beltane opal must be much greater than measured. For the quartz, crushing and grinding must have provided reactive internal surfaces by microcracking, which must have been extensive to account for the observed dissolution rate. Other work has shown that in mortar tests using coarser (sand-sized) reactive particles there are great differences between the effects of Beltane opal and those of less reactive materials, including quartz. These differences correlate well with chemical shrinkage rates (see Section 3.1) (12).

Beltane opal consists mainly of three reactive phases as well as 15% nonreactive quartz (13). Dissolution rates in 3 M NaOH measured at 77°F (25°C) showed that 71% of the 46% Opal-A, 8% of the 25% crystobalite, and 7% of the 11% tridymite dissolved in 3 days, whereas at 176°F (80°C) these amounts were 100%, 66%, and 31%, respectively. Because ASR did not usually occur when low alkali cements were used, Powers and Steinour concluded that there was some threshold alkali concentration for each reactive phase below which the reaction did

not occur. Results of Beltane opal dissolution measurements (10) in 0.1 m NaOH at 77°F (25°C) showed that, after 50 days, 46% of the sample had dissolved. Although it is not certain that the system had reached equilibrium, this result suggests that, at this NaOH concentration, all of the opal-A, but that none of the crystobalite or tridymite, had dissolved. If so, it indicates that 0.1 M NaOH as below the threshold for reaction of these two phases.

In closed systems with limited amounts of alkali hydroxide and silica, the concentration of silica in solution tends to increase until the equilibrium solubility curve ([SiO_2] vs. pH) is reached (14,10). The solubility of silica increases more than two orders of magnitude from pH 10 to 11.5. If there is less silica than alkali in the system, the silica concentration increases only until all of the silica dissolves and before the solubility curve is reached. If there is excess silica, its concentration increases until the solubility curve is reached, but then decreases as the pH continues to decrease because the remaining undissolved silica removes more OH^- ions from solution. The optimum proportions for a maximum concentration of silica is that for which all of the silica has dissolved when the solubility curve is reached. In 0.7M NaOH, the silica concentration reaches a sharp maximum at a Na_2O/SiO_2 mole ratio of about 0.2. When associated volume changes are considered (see Sections 3.2 and 4.3) this chemical balance has been suggested as the basis for the pessimum proportions found for maximum expansions in mortar bar expansion tests with opal and with at least some other aggregates (10). The actual process in mortars is complicated by the reaction with calcium ions, which greatly reduces silica concentrations (15). Furthermore, equilibrium conditions do not prevail and are approached very slowly in reacting mortars.

2.2 Reaction with Calcium and Alkali Hydroxides

The rates and course of the reactions of reactive silicas in concrete, and the compositions of the reaction products formed, depend upon the relative availability of moisture, and of alkalies and calcium in solution. Calcium hydroxide is much less soluble in pure water (20 m mol/L at 77°F [25°C]) than are the alkalies, and produces solutions of about pH 12.4.

Alkali contents and pH of pore solutions in concretes increase as alkalies are released and water contents reduced by cement hydration. When portland cement pastes and mortars are cured for several weeks as sealed systems, water in the pores becomes essentially a solution of alkali hydroxide that reaches nearly constant concentrations. The concentrations increase linearly with alkali content of the cements. Diamond showed that at 0.5 water/cement ratio the hydroxyl ion concentration is almost exactly 0.7 mol/L of OH^- per percent Na_2O equivalent alkali in the cement (4). This value indicates only about about 60% of the total alkalies are in solution. Powers and Steinour (1) showed that this is because the cement gel in hardened cement pastes removes alkalies from solution. Their analyses of contact solutions of specimens cured with water, so as to remain water-saturated, showed increasing retention of alkalies by cement hydrates as concentrations increased, although the amount of alkali held by the cement gel was much less than that held by reaction products at equilibrium with solutions, as studied by Kalousek (16). At low cement alkali contents virtually all of the alkali was in solution, and concentrations increased nearly linearly with alkali contents. At higher alkali contents concentrations increased less, and indicated that at 1% Na_2O_{eq} almost 30% of the alkali was retained by the cement hydrates. They also found that total alkali contents in solution in these water-saturated pastes were lower than Diamond has shown for solutions expressed from sealed specimens. This was because of lower evaporable water contents of the latter. Their graph of data (corrected for leaching of alkalies) indicates that, for cements with 1% Na_2O_{eq} at 0.5 w/c, Na^+ and K^+ concentrations totaled only 0.42 mol/L, instead of 0.7 mol/L, as in Diamond's graph for specimens cured without excess water.

Hydroxyl ion concentrations in the pore solutions depend on water/cement ratios as well as cement alkali contents. Data used by Diamond (4), and Nixon and Page (17) from eight different studies, and data from three others (18,19,20) were used during this review to determine the effects of both total alkali content and water/cement ratio, (w/c), on hydroxyl ion concentrations in pastes and mortars cured in sealed containers. The resulting multiple linear regression (MLR) equation (R = 0.94) for pore solutions expressed from 31 specimens is:

$$[OH^-] = 0.339Na_2O\%/(w/c) + 0.022 \pm 0.06 \, mol/L \qquad (2.2.1)$$

This equation agrees well with that determined by Diamond (4) at 0.5 w/c, and specifically includes the w/c as a variable. Other functions of these variables, including linear separation of variables and reduction of w/c by estimated nonevaporable water contents, were tried without significant improvement of fit. Unfortunately, scatter of these data is too large to distinguish between similar functions. If the equation is written with (c/w) instead of (w/c), the hydroxyl ion concentration is seen to be nearly proportional to the product of the concentration of alkali in the cement and the concentration of cement in water.

It is essential to an understanding of the effects of the use of pozzolans as replacements for portland cements to know the actual effect of w/c on hydroxyl ion concentrations, as will be shown below. It is also of interest because measured concentrations are often "corrected" and reported as for 0.5 w/c. Such corrections are usually made by using ratios of evaporable water contents, without allowance for differences in retention of alkalies by cement hydrates that are caused by concentration differences. That procedure is not justified by these data. On the basis of ratios of evaporable water contents, a 1.0% Na_2O_{eq} content cement used at 0.5 w/c and yielding an OH^- concentration of 0.7 mol/L would have an OH^- concentration of about 1.03 mol/L in the pore solution at 0.4 w/c, or slightly less if allowances are made for differences in bleeding and nonevaporable water contents. By contrast, Equation 2.2.1 shows that the actual concentration at 0.4 w/c would be only 0.81 mol/L, only one-third of the increase estimated from ratios of evaporable water contents. Concentrations of hydroxyl and alkali ions vary with water contents much less than would be the case without substantial retention and release of alkalies by the cement gel.

Measured pH values of pore solutions expressed from hardened mortars made with low and high alkali cements have been compared by Struble (15) with pH values calculated from their measured hydroxide ion concentrations using an assumed activity coefficient of unity. The calculated values scatter 0.2 above and 0.1 below measured values ranging from 13.4 to 14.0. Scatter was attributed to differences in the activity coefficients in different solutions as well as to experimental errors. Measured pH values were preferred.

The calcium ion concentration in pore solutions is much lower than for solid calcium hydroxide in water because the OH^- concentration in the solubility product is determined mainly by alkali concentration:

$$[Ca^{2+}] \cdot [OH^-]^2 = K_{sp} \cong [Ca^{2+}] \cdot [Na^+]^2 \qquad (2.2.2)$$

For accurate work, activity coefficients and products must be used (21,22).

Although the solution is saturated with respect to calcium hydroxide, the calcium ion concentration is greatly reduced as alkali increases. Kalousek showed that this is also true for the $Na_2O-CaO-SiO_2-H_2O$ system (16). Measured calcium concentrations in pore solutions expressed from mortars made with low and high alkali cements, but without ASR, ranged

from 0.6 m mol/L to 2.5 m mol/L (15). Silica concentrations ranged from 0.002 to 0.04 m mol/L. These values for silica concentrations are very much below those in alkali-silica sols without calcium at high pH, but are consistent with the equilibrium phase diagram for the Na_2O-CaO-SiO_2-H_2O system recently constructed by Brown (23).

Highly reactive silica gel in laboratory solutions saturated with respect to calcium hydroxide (as are the pore solutions in concretes), but without alkalies, produce two products, silica gel with c/s ratio of about 0.15 to 0.20, and poorly crystalline calcium silicate hydrate (C-S-H) with c/s ranging from about 1.2 to 1.4 (24). In dilute solutions containing both calcium and alkali hydroxide, highly reactive silica dissolves but is promptly precipitated as a calcium silicate hydrate containing some alkali (C-N+K-S-H). If the calcium concentration is reduced by this reaction to a very low value, the reactive silica continues to dissolve until an equilibrium concentration is reached at reduced pH. This reaction may represent the situation in the interior of a reactive aggregate particle in concrete. When calcium diffuses into this reaction zone it may replace the alkali, which may then be regenerated to continue the reaction (1,2,25,26).

In concrete, hydration of cement provides an abundant supply of solid calcium hydroxide that can continuously replace calcium in solution as C-N+K-S-H is formed. In this way reactions may gradually consume all of the alkali or reactive silica, or both. Earlier studies (16,25) have shown that the C-N+K-S-H can have Na_2O/SiO_2 molar ratios up to about 0.2 in NaOH solutions at concentrations above 10g Na_2O/L (0.32 M NaOH). This OH^- concentration is well below that produced by portland cements containing only 0.6% equivalent Na_2O at 0.5 w/c in sealed systems. Reactive silicas in such an environment will react readily, but may exhaust all of the alkali by forming C-N+K-S-H, which is relatively insoluble. As the alkali is consumed, the pH decreases, the concentration of Ca^{++} increases, and the concentration of silica in solution decreases. The reaction product then tends to become more nearly C-S-H.

If alkali concentrations remain high, calcium concentrations are very low, and the loosened silica structure imbibes more liquid and hydroxyl ion that continue the process of swelling and dissolution of the silica. Precipitation of C-N+K-S-H may occur only after diffusion or flow through large pores or cracks to calcium-rich areas.

The reaction chemistry of ASR is strongly affected by pozzolans and by salts used as deicers or admixtures in concrete, such as sodium or calcium chlorides. The effects of pozzolans and added salts on ASR are discussed in Section 4.1. The effects of external salt solutions on concrete made with and without pozzolans are reviewed in Section 5.3.

Pozzolans consist of highly reactive, mainly siliceous, fine particles. They are commonly used as mineral admixtures in concrete to control ASR. Hydroxyl ion concentrations in pore solutions in hydrating cement pastes and concretes depend on pozzolan contents and characteristics, as well as cement alkali contents, water/cement ratios, and curing time and conditions. The trends in these relationships have been summarized by Nixon and Page (17), and Canham et al. (18). They have shown that in mixes made with high-alkali cements, hydroxyl ion concentrations are reduced by pozzolanic fly ashes and depend on: alkali content of the ash, reactivity of the ash, and alkali content of the portland cement, the last item being the most important. They found that fly ashes need a minimum of about 28 days at room temperature to have a significant effect, and that high alkali content fly ashes are ineffective with low alkali cements for reduction of hydroxyl ion concentrations. They recognized that release of alkalies is favored in low concentration solutions, and that hydrates can incorporate alkalies to reduce their concentrations. However, they did not seem to appreciate the magnitude of alkali retention by the cement hydrates, or the activation of fly ash by cement

alkalies, or acceleration of cement hydration by the fine particle effect (27). They concluded that more work was required to understand the complexities.

Pozzolans have three major effects when used as replacements for portland cement at equal water/solids ratios.

1) because the cement is diluted by pozzolan, less cement alkali is dissolved during hydration of the cement, and concentrations are reduced;

2) alkalies released by pozzolans increase concentrations of dissolved alkali and hydroxyl ions;

3) reaction of pozzolans to form alkali-calcium-silicate-hydrates decrease concentrations of alkalies and hydroxyl ions in pore solutions.

Appendix A shows how Equation 2.2.1 can be generalized to include the effects of fly ash substitutions for portland cement on pore solution hydroxyl ion concentrations. Portland cement paste and mortar data for Equation 2.2.1 ranged from 28 to 180 days at ordinary temperatures. If a pozzolanic fly ash is used under such conditions the percentage reacted may be expected to increase with time and alkali contents to as much as 40% (27c). Although degree of reaction of fly ashes is not usually determined or reported for such tests, trial calculations have been made, using equations derived in Appendix A and assumed values for percentage reacted, with several sets of data for which hydroxyl ion concentrations were measured. Results are given in Figures 2.2.1 and 2.2.2. Figure 2.2.1 is derived from data (28) after 90 days of curing of pastes made with portland cements of either 0.95 or 0.50% Na_2O_{eq} with 15% fly ash, the ashes having 3.6 or 1.2% Na_2O_{eq}. Figure 2.2.2 is derived from data reported by Canham, et al. (18) using one cement of 0.67% Na_2O_{eq} with four fly ashes of different alkali contents after 84 days of curing. Representative results for ashes with 3.37% and 0.97% Na_2O_{eq} are shown. The figures show that:

1) [OH$^-$] increases with both cement and fly ash alkali contents,

2) [OH$^-$] decreases as the percentage fly ash reacted increases and reaches the measured values, indicated on each figure, within the expected range,

3) the percent fly ash reacted increases strongly with the hydroxyl ion concentrations at constant fly ash content but is nearly independent of fly ash content for the same materials.

This general agreement between experimental and calculated results for portland cements and fly ashes of different alkali contents, and different proportions, lends support to the assumptions used in the model and provides a quantitative understanding of the effects of pozzolans on the compositions of pore solutions.

2.3 Compositions of Products of Alkali-Silica Reactivity

Results of research on the products of ASR in mortars and concretes was recently reviewed by Moranville-Regourd (29). Table 2.3.1 summarizes the compositions reported in recent investigations using different combinations of materials and instrumental methods. Most of these studies were done with semi-quantitative SEM-EDX, and X-ray diffraction (XRD) analyses. In this investigation, ASR gels are described as either massive (dense) or spongy (textured or grainy). The massive gel appears very smooth by SEM while spongy gel has a distinctive open structure on a scale of about 10 mm. The massive gel is usually sponge-like at higher magnification, and is found in every structure with ASR expansions and cracking

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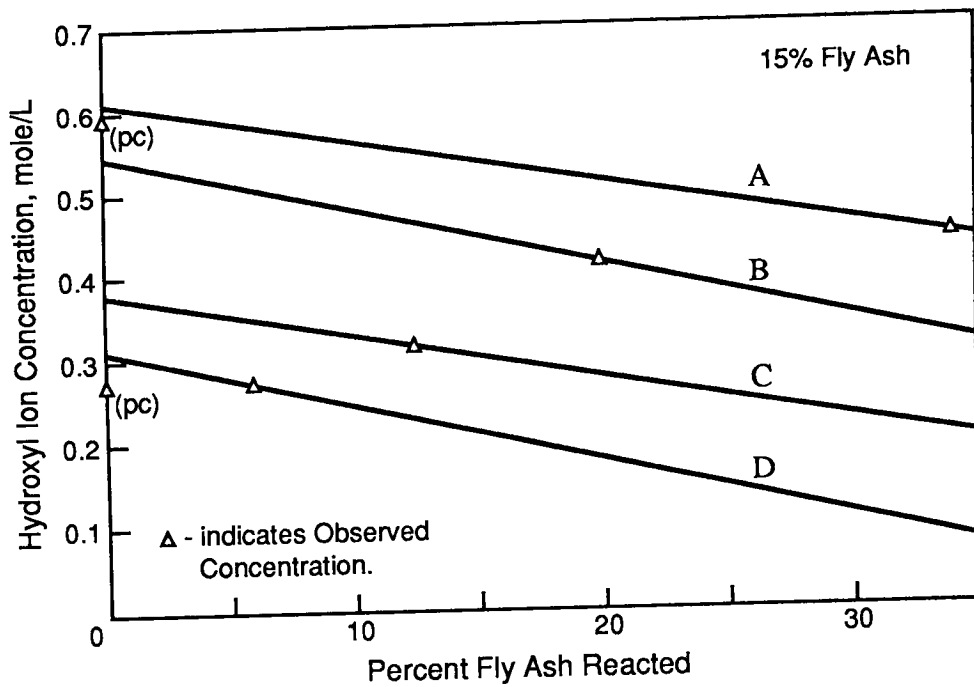
Figure 2.2.1 Calculated Reduction of Hydroxyl Ion Concentration Caused by Reaction of 15% Fly Ash Blends With Different Na_2O_{eq} (cement + fly ash) Contents. A: (0.95% + 3.6%), B: (0.95%+1.2%), C: (0.50%+3.6%), D: (0.5%+1.2%), (Data from ref. 28).
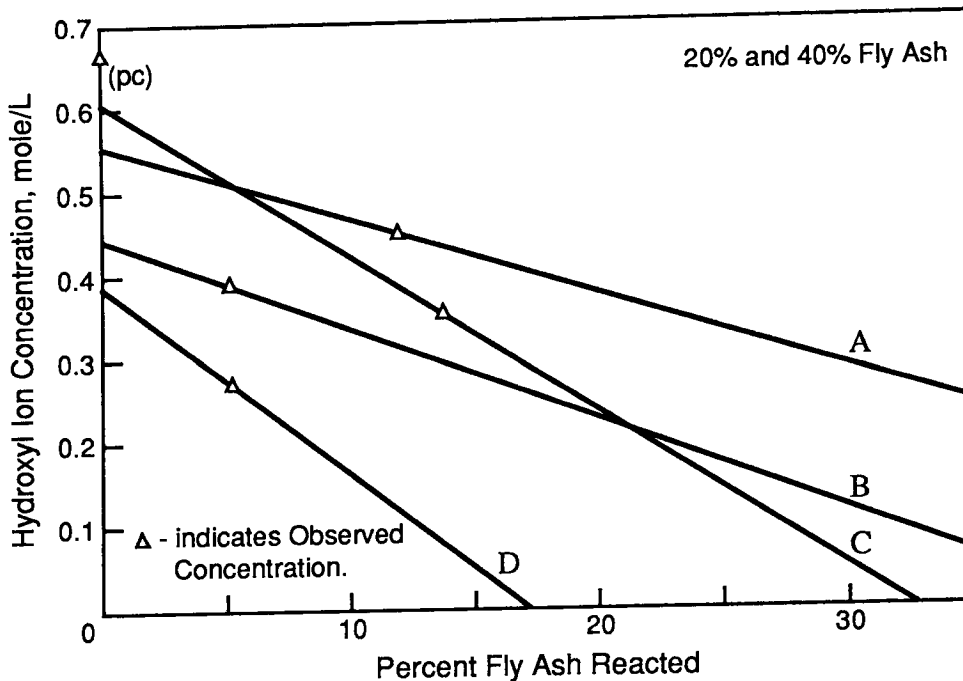
Figure 2.2.2 Calculated Reduction of Hydroxyl Ion Concentration Caused by Reaction of Fly Ash Blends With 0.67% Na_2O_{eq} Portland Cement With Fly Ashes of Different Na_2O_{eq} Contents. A: 20% Fly Ash (3.37%), B: 20% Fly Ash (0.97%), C: 40% Fly Ash (3.37%), D: 40% Fly Ash (0.97%), (Data from ref. 18).

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(30). The difference between the appearances of massive and spongy ASR gels may result from differences in the modes or amounts of shrinkage during drying, in the SEM, of gels of different compositions.

The results in Table 2.3.1 show that products of similar composition are formed by reactions in concretes made with different aggregate types. Results for accelerated tests at 176°F (80°C) in alkali hydroxide solutions are included because that work has been an important part of studies to establish the validity of the NBRI (National Building Research Institute, S.A.) accelerated test method. It has been concluded that products of the reaction in 1N NaOH solution at 176°F (80°C) are of similar morphology and chemistry to those formed in concrete structures in practice (31,32).

Before washing, the spongy gel had a much higher alkali content than the massive gel. Washing in distilled water showed that the alkalies could be removed in a matter of days for NaOH-reacted, or weeks for KOH-reacted gels. Apparently the alkalies are adsorbed rather than chemically bound, and are readily exchanged for calcium. Nearly all of the gels reported had substantial calcium contents even before washing.

Crystalline products of three distinct morphological types are also formed. These are described as lamellar or rosette-like, needle or rod-like, and blade-like crystals. However, such terms are not always used consistently. Most of these crystalline reaction products from concrete structures have compositions not much different from the ASR gels analyzed. Also, the crystalline products formed in cracks and air voids in mortars and concretes in accelerated tests at 176°(80°C) had compositions not greatly different from gels in the same samples. However, the atomic C/S ratios of the washed gel samples were much higher, and the crystalline products lost alkalies to a much smaller extent than did the gel samples.

X-ray diffraction patterns of crystalline reaction products exhibit numerous peaks indicating a mixture of coexisting phases. Okenite, $10CaO \cdot 18SiO_2 \cdot 18H_2O$, tobermorite, zeolites, and other phases have been suggested (29,30), but it may be that there are new minerals yet to be indexed in these reaction products. Brown has suggested that a quaternary compound, $0.25Na_2O \cdot CaO \cdot SiO_2 \cdot 3H_2O$, should be a stable phase in equilibrium with C-N-S-H or calcium hydroxide, or both, at the invariant solution composition of 0.39 M Na_2O, 0.16 m mol/L $Ca(OH)_2$, and 0.72 m mol/L SiO_2 (23). The existence of this compound or a K_2O analog in concrete does not seem to have been reported.

The compositions of ASR gels found in concretes are highly variable, but analysis of published data indicates that it may be possible to regard them as belonging to one of several relatively simple compositional categories: 1) partially reacted and swollen silica, 2) relatively pure alkali silicate solutions or gels of various alkali and water contents, and 3) simple mixtures of two components of nearly constant composition (except for their water contents). This latter possibility is supported by current MAS-NMR studies by Kirkpatrick who has tentatively concluded ASR gels to be mixtures of alkali silicate hydrate and calcium silicate hydrate phases (9). It is also supported by work done by Gutteridge and Hobbs (13) who used X-ray photoelectron spectrometry (XPS), a surface analysis technique, that showed a change in the binding energy of Na1s, O1s, Ca2p and Si2p electrons after the alkali-silica reaction. XPS data suggested that the reaction rim around Beltane opal grains was composed of two hydrated silicates: a sodium silicate and a sodium-calcium silicate.

Electron probe microanalysis (EPMA) of ASR gels found in concrete has shown (36) that gels in cracks close to the reactive aggregate particle contain little calcium, but at greater distances their calcium contents progressively increased, presumably because of the longer time of

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Table 2.3.1 Semi-Quantitative Analyses (in mass percent) of ASR Products (29)

Reaction Product	Aggregate	SiO_2	CaO	Na_2O	K_2O	Other	Reference
ASR Gels from Concrete Structures						H_2O	
Various Origins	Various	56-86	1-28	0.4-20	2-8	10-30	(33)
Gels from Seven Concrete Structures	Quartzite	73	15	1.8	9.6	--	(34)
	Greywacke/ Hornfels	72	16	1.8	9	--	(34)
Gels in Veins in Aggregate (5 Structures)	Siliceous Limestone	51	12	6	8	--	(35)

Gels from tests at 176°F (80°C) in 1N NaOH or KOH

Reaction Product	Aggregate	SiO_2	CaO	Na_2O	K_2O	Atomic C/S	Reference
Exuded Surface Gels Massive Gel (concrete pat)	Quartz-Bearing metasediment	49.4	28.2	22.5	--	0.61	(31)
As above, Washed	"	61.9	31.9	--	--	0.55	(31)
Spongy Gel (mortar prism)	"	18.5	20.8	56.6	4.1	1.2	(31)
As above, Washed	"	56.6	43.4	--	--	0.82	(31)

Gels in Cracks and Air Voids

Reaction Product	Aggregate	SiO_2	CaO	Na_2O	K_2O	Atomic C/S	Reference
Massive Gels (mortar prism)	"	61.7	16.3	17.7	1.2	0.28	(31)
As above, Washed	"	60.8	37.6	--	--	0.66	(31)
Massive Gel (concrete pat)	"	63.3	12.9	--	23.8	0.22	(31)
As above, Washed	"	52.4	47.6	--	--	0.97	(31)

ASR Crystals from Concrete Structures

Reaction Product	Aggregate	SiO_2	CaO	Na_2O	K_2O	Other	Reference
Rosette-Like (a)	Not identified	68.6	18.2	--	13.2	--	(30)
Rosette-Like (a)	"	71.1	17.1	--	11.8	--	(30)
						% Al_2O_3	
Rosette-Like (a)	"	76.9	9.4		9.1	4.6	(30)
Needle rod-Like	"	63.7	8.9	13.1	14.3	--	(30)
Needle rod-Like	"	60.3	1.1	8.4	18.2	--	(30)
Blade-Like	"	71.2	11.6	--	17.2	--	(30)

ASR Crystals from Cracks and Air Voids from Tests at 176°F (80°C) in 1N NaOH or KOH		SiO_2	CaO	Na_2O	K_2O	Atomic C/S	Reference
Rosette-Like (a) (mortar prism)	Quartz-Bearing Metasediment	71.7	12.4	14.8	0.4	0.18	(31)
As above, Washed	"	71.0	26.5	1.7	0.8	0.40	(31)
Rosette-Like (a) (concrete pats)	"	63.5	20.7	--	15.8	0.35	(31)
As above, Washed	"	67.0	21.7	--	11.3	0.35	(31)

(a) Possibly lamellar

exposure to the calcium-rich environment during transit. Low-calcium content ASR gels commonly found on concrete surfaces are thought to not have been so exposed, presumably because of too rapid transit.

When the compositions of these ASR gels in cracks in concrete were examined they were found to agree remarkably well with those of CaO-Na_2O-SiO_2-H_2O gels prepared by Kalousek (16). Straight lines in Figure 2.3.1 represent both sets of results on an anhydrous weight percent basis. In Appendix B it is shown that these linear relationships can be simply explained if it assumed that the ASR gels are composed of various proportions of N+K-S-H gel which is 83% SiO_2 and 17% (Na_2 + K_2O), and an amount of C-N+K-S-H required to account for the calcium content. The composition of the alkali-calcium-silicate-hydrate on a molar basis is found to be $N_{0.16}C_{1.4}SH_x$ if the only alkali is Na_2O, as in Kalousek's data. Figure 2.3.2 shows the percentages of both the C-N+K-S-H and N+K-S-H over the range of SiO_2 contents from 40% to 83%. The analysis in Appendix B shows that ASR gels containing calcium appear to be simple two-component mixtures in which the swelling component is of nearly constant alkali-silica ratio, and should have constant swelling characteristics. To be free of the swelling component, the CaO content of ASR gels must be more than 53% and the SiO_2 content less than 40%, on an anhydrous weight basis.
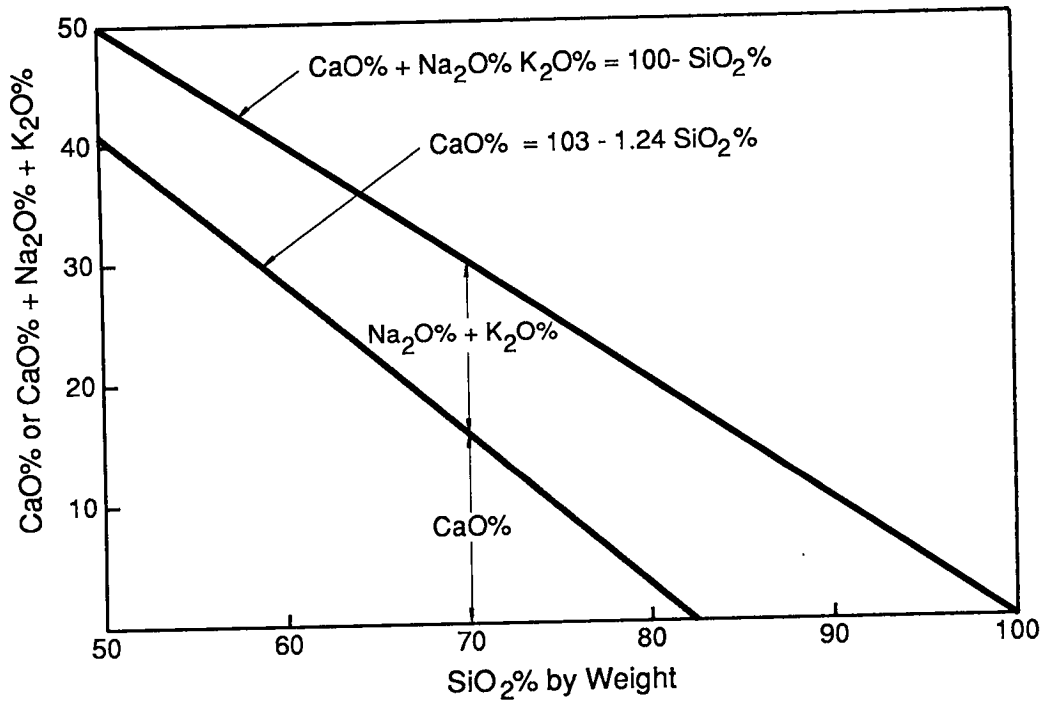
Figure 2.3.1 CaO and Alkali Contents of ASR Gels (36). By permission from Pergamon Press.
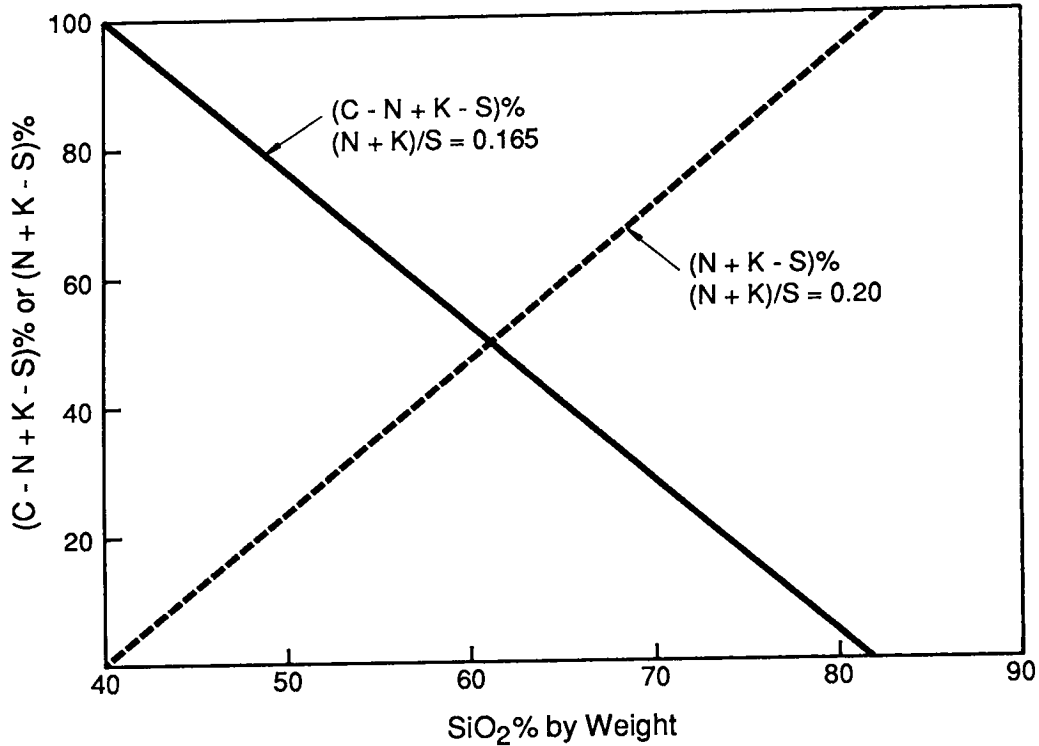
Figure 2.3.2 Composition of ASR Gels Considered as a Two-Component Mixture.

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3 The Physical Nature of Alkali-Silica Reaction Swelling Gels

The aforementioned results are important because they show that although the compositions of ASR gels vary widely the composition of the swelling N+K-S-H component, which has not yet reacted with calcium hydroxide, may vary only slightly. They suggest that such ASR gels are two-phase composites, with the C-N+K-S-H being dispersed in the swelling component. This component does not necessarily provide elastic solid structure to the gel unless the concentration of the calcium component becomes very high, as in hardened cements. Even at low concentrations of C-N+K-S-H, viscosity should increase with concentration but, without definite structure, stresses can be relieved by deformation and flow. However, the viscosity of the composite will be very high not only because of the calcium component, but also because viscosities of low Na_2O/SiO_2 ratio gels are much higher than gels of higher Na_2O/SiO_2 ratios. The latter may be fluid and can relieve stress more rapidly by flow.

Nevertheless, it is much easier to calculate ultimate swelling pressures for such high viscosity gels than for solid elastic gels, such as hardened cements or wood. In the latter cases the swelling pressure is balanced elastically within the gel and the sorption characteristics and internal elastic restraint of the gel must be known to calculate the net swelling pressure (37). For fluid gels osmotic pressure calculations can be used to calculate maximum swelling pressures (3,4). The above results suggest that maximum pressures may be independent of ASR gel compositions over a wide range, that is, until they become solid and their volume changes are too small to be important.

Volume change of reactive silica can involve both chemical shrinkage and swelling. Silica swells as it is attacked by hydroxyl ion and is in the process of dissolution. The dissolved silica diffuses out of the reaction site into cracks or large pores in the matrix, where it forms swelling ASR gels.

3.1 Chemical Shrinkage

There are at least two kinds of volume changes when reactive silicas are exposed to alkali solutions in closed systems: decreases caused by dissolution of silica, and increases caused by expansion of any undissolved silica (10). The apparent specific volume of silica in alkali hydroxide solutions can be calculated from known values of solutions before and after dissolution of the silica. A solution containing 6.75% Na_2O, 25.3%, SiO_2, and 67.95% H_2O has a density of 1.318 g/mL (6a). This solution can be considered to be a product of dissolution of 25.3 g of SiO_2 in 74.7 g of 3.30M NaOH of density 1.1278 g/mL (38). The apparent specific volume of silica in that solution is calculated to be 0.384 mL/g SiO_2. This value is nearly the same as the specific volume of a-quartz, 0.377 (density 2.65) or chalcedony, so that their volume changes during dissolution are very small. Before dissolutionoccurs, amorphous hydrated silicas have specific volumes ranging from 0.45 to 0.50. Their volume changes of dissolution should then be about -0.07 to -0.12 mL/g SiO_2. Measured changes are even larger.

Such negative volume changes during partial dissolution of various alkali reactive aggregates have been reported and proposed as a basis for characterization of their reactivity (39). Direct measurements with opaline and chalcedonic flint sands yielded volume changes of -0.143 ml/g SiO_2 during dissolution in 10M NaOH solutions. From this value and the density of chalcedony (2.6 g/cm^3), the apparent specific volume of silica in this more concentrated solution is calculated to be 0.242 mL/g.

3.2 Swelling of Undissolved Silica

Volume changes measured during dissolution of highly reactive silica gel in an excess of 0.7 NaOH solution showed rapid volume decreases (10). When completely dissolved, the data indicated that silica in solution had an apparent specific volume of only about 15 mL/mol (0.25 mL/g). This is in good agreement with the results for flint sands in 10M NaOH. When an excess of this silica gel was exposed to a limited amount of NaOH solution, only a small amount of silica was dissolved before the solubility curve was reached. However, the remaining undissolved silica continued to be neutralized by OH^- ions, attract Na^+ ions, and swell. The swelling was calculated by correcting for the volume change of partial dissolution. When proportions of silica and solution were optimized with 0.05M or 0.7M NaOH solution, the silica concentration reached sharp maxima at Na_2O/SiO_2 ratios of about 0.32 or 0.23, respectively. These ratios for maximum swelling of the undissolved silica were near to those for which maximum pH was observed. For the 0.7 M NaOH solution at that ratio, the undissolved silica swelled from 2.0 mL/g to about 4.4 mL/g, or about 120%. At Na_2O/SiO_2 ratios of 0.091 and 0.455, the undissolved silica swelled to only 2.17 mL/g and contracted to 1.5 mL/g. These are changes of about 8% and -25%, respectively. These phenomena were suggested to be the chemical basis (10) for maximum expansions at pessimum proportions found in mortar bar tests with opaline aggregates, an idea which has gained some acceptance (40) despite various complexities, such as neglect of the effects of reactions with calcium ions.

The apparent contraction of the silica gel at high Na_2O/SiO_2 ratios in these tests evidently results from loosening and imbibing fluid into the structure to the point where much of the silica is in a state beginning to approach dissolution. At this point the apparent specific volume is only 0.25 mL/g. Hence measurements of the sum of volumes of fluid and solids in the mixture do not determine the volume of swollen particles. It may be even larger than at the observed maximum because of high water contents.

There do not appear to be any comparable data for natural reactive aggregates. In the chemical shrinkage measurements with opaline and chalcedonic flint sands (10,39), no swelling of undissolved silica was reported. However, no corrections were made for silica dissolution, nor were Na_2O/SiO_2 ratios varied. The Na_2O/SiO_2 ratios were probably between 0.2 and 0.4. The surface areas of the sands were much less than the 770 m^3/g for the silica gel, with which silica saturation was achieved rapidly and for which there was no delay of diffusion of fluid into the silica to cause swelling. In the tests with opaline flint sands rapid dissolution at high pH occurred until the solubility curve was apparently reached, because chemical shrinkage of the finer fraction samples stopped in less than 7 hours at 122°F (50°C),after which no swelling was observed (10). Chemical shrinkage and the time to reach equilibrium increased with *decreasing* fineness. Apparently the finest fraction had the least amount of dissolution and the greatest swelling of undissolved silica. In mortars and concretes the situation is more complex because of precipitation of dissolved silica by calcium ions and penetration of calcium into undissolved silica. It appears that such measurements need to be made with solid calcium hydroxide in the mixtures.

3.3 Shrinkage and Swelling of Gels

Vivian (41) concluded in 1950 that clear gel produced by the action of alkali solutions on reactive forms of silica was the cause of ASR expansions of mortar and concrete. To understand the swelling behavior of clear ASR gel, Vivian prepared and tested synthetic sodium silicate gels with Na_2O/SiO_2 ratios of about 0.2 and different water contents. Samples of gel made with water contents of 73.9%, 48.7%, and 22.0% water were equilibrated in containers in which the relative humidities were controlled by NaOH solutions at about 97%, 93% and 85% RH. Although the silicate gels did not reach equilibrium with the NaOH solutions in all cases, data after 28 days permit a close approximation to equilibrium values for desorption-adsorption isotherms at 20°C for these gels, as given in Table 3.3.1. Also given are similar data published in 1975 by Krogh (42) for gels prepared at Na_2O/SiO_2 and K_2O/SiO_2 molar ratios of 0.31 and 0.32, respectively. Values in the table are weight ratios.

Table 3.3.1 Water Sorption by Alkali Silicate Clear Gels (41,42)

M	M_2O/SiO_2 and Temperature	Relative Humidity %	Water Content g water/ 100g dry gel	%	Solids Content %	Na_2O or K_2O Content weight %
Na	0.2	?*	--	74	26	4.3
	68°F (20°C)	97	--	57	44	7.3
	(41)	93	--	49	51	8.5
		85	--	40	60	10.0
Na	0.33	97	230	70	30	7.5
	77°F (25°C)	?*	160	62	38	9.4
	(42)	90	69	41	59	15.7
		86	48	32	68	16.9
		60	33	25	75	18.7
K	0.48	97	276	73	27	8.6
	77°F (25°C)	?*	190	66	34	10.9
	(42)	90	75	43	57	18.2
		86	54	35	65	20.8
		60	36	26	74	23.7

* as prepared

Vivian also dried small blocks of gel, about 0.1 in. (2.5 mm) thick, over calcium chloride (29% RH if a saturated solution). Deformations of partly dried samples under compressive loads on known areas were then measured. At 72% water, only 0.42 psi (30 g/cm²) produced deformations ~0.08 in. (~ 2 mm). At lower water contents, the gel were more viscous and deformations decreased to very low values. Even at 85.3 psi (6000 g/cm²), they were only about 0.02 in. (0.5 mm) at 30% water content. However, the thickness of the blocks decreased markedly as water was removed; at less than 30% water it was decreased to about 0.2 in. (0.5 mm).

These gels remained comparatively clear until dried to water contents between 13.7% and 8.2%, when they became white and opaque. Vivian considered the solid phase to become continuous at that point and that gel volume should remain relatively constant as the remaining water was removed.

Additional samples of gel with 72.3% water were used to measure volume changes of the gel during drying. Some were allowed to reabsorb water after desorption to 26.05% water. The gel volume V_g (cm^3/g solids) data was shown to lie nearly on a straight line when plotted against water content, w_g (g water/g solids) of the gel (41). The equation of that line is:

$$V_g = 0.46 + 0.98\,w_g \qquad\qquad (3.3.1)$$

These are the only data yet located that permit calculation of apparent and partial specific volumes for partly dried alkali silicate gels. Such data are necessary for calculation of swelling pressures. Partial specific volumes were determined by the method of intercepts (43) by calculating and plotting the specific volume of the gel versus the percentage of water in the gel. Figure 3.3.1 shows that the data actually fall into two straight lines. A first desorption line shows a transition at about 25% water to a lower straight line for adsorption by strongly dried gel, and two other points, perhaps for samples that may also have been pre-dried. The values of the intercepts are as follows:

Table 3.3.2 Na$_2$O-SiO$_2$ Volume Data (Data from Ref. 41)

	Desorption	Adsorption*	Average
Partial specific volume of water (cm^3/g)	0.995	0.95	0.97
Partial specific volume of solids (cm^3/g)	0.555	0.420	0.49
Apparent density of solids (g/cm^3)	1.80	2.38	2.09

*includes two other points (perhaps pre-dried)   1 g/cm^3 = 62.4 lb/ft^3

The average values for partial specific volumes are seen to agree with the constants in Equation 3.3.1; the average apparent density of the solids in these gels also agrees well with values for opal.

3.4 Osmotic Swelling Pressures

If ASR swelling gels that cause expansions and cracking in concrete are not too viscous, the gel can deform and relieve internal elastic stress. The swelling pressure can then be regarded as an isotropic osmotic pressure calculated from:

$$P_i = -(RT/u) \ln (p_i/p_o) \qquad\qquad (3.4.1)$$

In an arbitrary initial (partly dried) state, p_i is the equilibrium vapor pressure of the gel, P_i is the pressure that must be applied to the solution or gel to prevent imbibition of water at vapor pressure p_0 and p_i/p_0 is the equilibrium relative humidity (RH), or the activity of the water, in the dried gel. R is the gas constant (8.314 J/mol°K) T the temperature in °K, and u is the partial molar volume of solvent in the solution or gel. This is an approximate integrated form based on the assumptions that water vapor is an almost ideal gas at these vapor pressures, and that u is essentially constant over the range of the integration. Both are quite good approximations for NaOH and KOH solutions. Values of u calculated from density data (38a) range from 1.0 to 0.967, or 0.988 L/kg, for solutions containing 0 to 18.6% Na$_2$O, or K$_2$O, respectively. Osmotic pressures calculated from Equation 3.4.1 at 77°F (298°K) are given in Table 3.4.1 for NaOH solutions of various concentrations, and relative humidities, p_i/p_0.
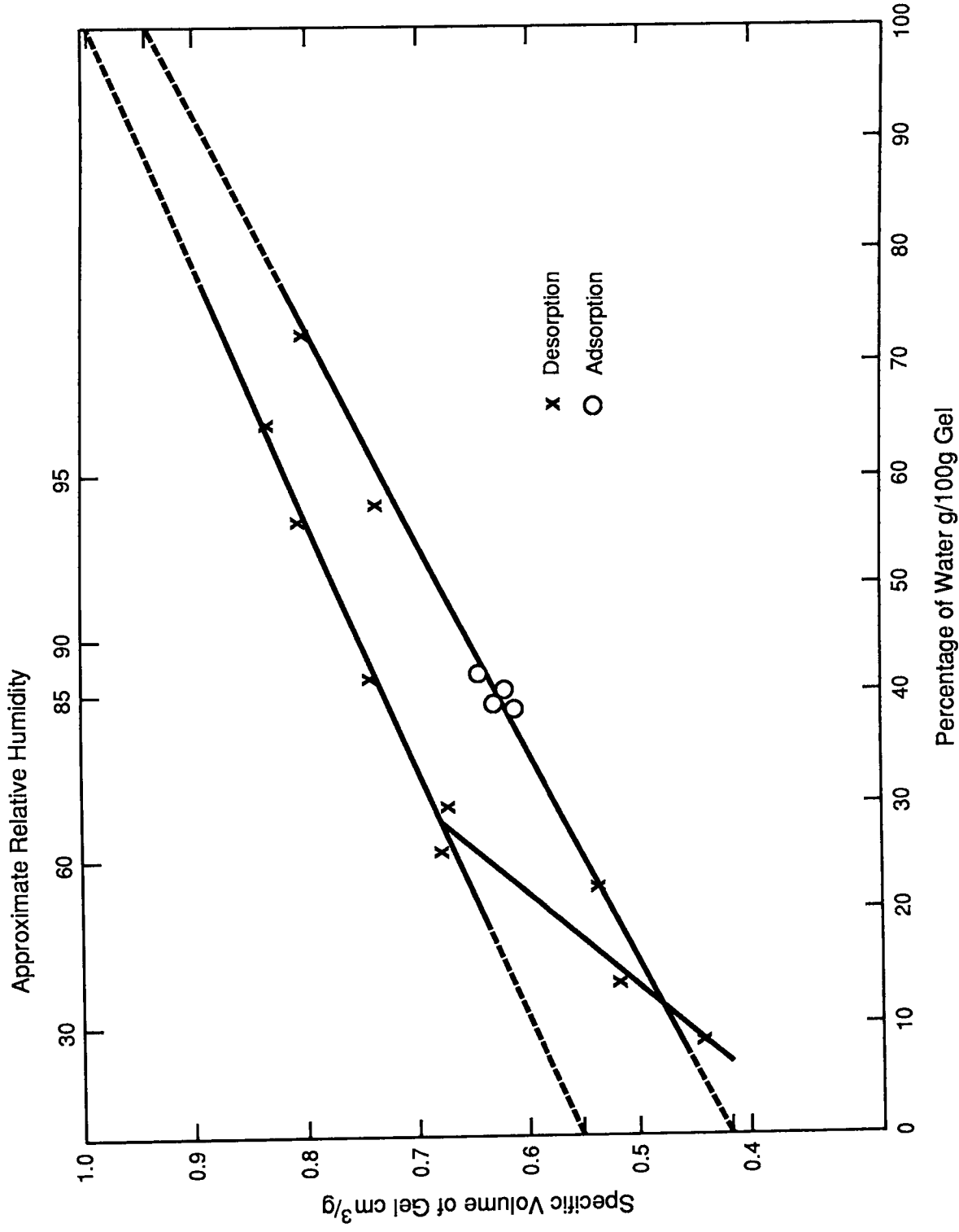
Figure 3.3.1 Partial and Apparent Specific Volumes of Sodium Silicate Gels Calculated From Data by Vivian (41).

Table 3.4.1   Calculated Osmotic Pressures for NaOH solutions at 77°F (25°C)

% Na$_2$O by wt.	% NaOH by wt.	NaOH mol/L	RH(44) %	P (MPa)	P (psi)
0.0	0.0	0.0	100.0	0.0	0
2.11	2.73	0.70	97.7	3.1	450
4.29	5.54	1.50	95	6.9	1000
7.62	9.83	2.71	90	14.2	2067
10.32	13.32	3.8	85	22.0	3188
12.47	16.10	4.7	80	30.2	4378
14.41	18.60	5.5	75	38.9	5644

1 psi = 6.895 kPa

The NaOH concentration at 0.7 mol/L corresponds to the pore solution concentration for mature hardened cements and mortars made with cements with 1% total alkalies as equivalent Na$_2$O at 0.5 w/c. The calculation shows that such solutions at equilibrium at 97.7% RH would develop osmotic pressures of 450 psi (3.1 MPa) if confined and when exposed to 100% RH. More concentrated solutions in equilibrium with drier atmospheres can develop much greater pressures when so exposed. However, this kind of calculation actually overestimates the expected pressures to be developed in a real situation because the solution imbibes additional water to develop pressure, because of dilution, and because the container may dilate, permitting additional dilution.

Data for partial molar volumes and vapor pressures of alkali silica gels at equilibrium moisture contents are very limited. Vivian's data, used to obtain the values given in the last section, show that partial specific volumes for water in clear Na$_2$O-SiO$_2$ gels are about 0.95 to 1.0, mL/g at atmospheric pressure. Thus, the usually assumed value of 18x10^{-6} m^3 for u is a good approximation and is probably valid in the pressure range of osmotic swelling in concrete.

These data show that partial specific volumes of water in clear alkali silicate gels are nearly the same as those of NaOH and KOH solutions. However, the compositions at equal relative humidities are very different, as may be seen by comparing the Na$_2$O% at equal RH in Table 3.4.1 with those given in Table 3.3.1 for Vivian's Na$_2$O-SiO$_2$ gel sorption data. At 85% RH both the Na$_2$O-SiO$_2$ gel and the NaOH solution contain about 10% Na$_2$O, but the solution contains 89.7% H$_2$O, whereas the gel contains only 40% H$_2$O and 50% other solids, mostly SiO$_2$. It appears that the SiO$_2$ effectively removes so much Na$_2$O from solution that the activity of the water in this gel is as high as in the solution. This capacity for alkali is even more evident near 100% RH, at which level the gel can retain 4.3% Na$_2$O while having little effect on the activity of the 74% water. However, the activity of Na$_2$O is very low, as has been shown by the reduction of pH values during dissolution or swelling of silica in NaOH solutions. Hence the reactive silica and the resulting gel absorb alkalies even from very dilute alkali hydroxide pore solutions, and concentrate and immobilize the alkalies while swelling the silica in the process. But this does not generate very large swelling pressures in wet systems.

Attempts to measure swelling pressures of synthetic alkali silicate gels have not yielded very systematic results. Values obtained for gels prepared from dried sols of various Na$_2$O/SiO$_2$ molar ratios, ranging from 0.27 to 0.53, varied from 8.7 to 1580 psi (0.06 to 10.9 MPa) when exposed to water after drying to 18% to 30% water contents in vacuum (45). The gels may

have formed densified surfaces during drying that could not be reswollen, as had been reported by Vivian. Thus they probably could not have been equilibrated at a known RH, so that the results cannot be compared with those expected from Equation 3.4.1.

In another study (3) a different approach was used to avoid the experimental difficulties associated with direct measurements. Solid alkali silicate gel was formed from silica gel in sodium hydroxide and eventually reached a quasi-equilibrium with the solution. The solids had Na_2O/SiO_2 mole ratios ranging from 0.024 to 0.295. Since the activity, or chemical potential, of the water must be equal in each phase at equilibrium, it was assumed that the imbibition pressure of the gel was equal to the osmotic pressure of the contact solution. The pressure was then calculated from the measured concentrations of the species in solution. Osmotic (and swelling) pressures calculated for exposure of the 15 solutions (and solid gels) to 100% RH ranged from 4.6 to 790 psi (0.03 to 5.5 MPa).

Results in both studies showed very large changes of swelling pressures with composition of these gels. Such large changes of properties with compositions are characteristic of sodium and potassium silicate sols and gels. Viscosities of sodium silicate solutions of Na_2O/SiO_2 ratios higher than 0.25 increase greatly with increase in concentration and decrease with increasing Na_2O/SiO_2 ratios (46). Data for solutions in the Na_2O/SiO_2 range of interest, 0.15 to 0.2, have not yet been found, but the trend at higher ratios clearly indicates that they should have even higher viscosities, ranging from 10 to above 100,000 centipoise (mPa·sec) over a rather narrow concentration range. The viscosities become extremely sensitive to concentration at these lower Na_2O/SiO_2 ratios. Slight changes in temperature are also known to cause liquification of seemingly solid gels (5a, 45).

Such very large changes of viscosity with water content should permit osmotic swelling pressures to be relieved by flow of gel through pores, microcracks, or cracks in the matrix if sufficient moisture is available. Krogh (42) concluded from Vivian's data that maximum expansion of mortars should occur when the water contents of the gel are between 0.70 and 1.6 g water/g dry gel (41% and 62% water), based on the assumption that maximum expansions occur when 1) the gel fills cracks completely but 2) is not so fluid as to impregnate the mortar (and presumably escape through pores).

3.5 Osmotic Cell Tests

A simple test method that combines both physical and chemical effects of ASR is the osmotic cell test developed by Verbeck and Gramlich (47). Its use eliminates the mechanics of materials effects that complicate mortar and concrete test data. It has been used for a separate study of certain variables and the direct observation and control of some of the chemical and physical aspects of the reaction mechanism. Recent progress has been made by Stark and Schmitt in development of the test to determine potential for reactivity of aggregates (48.49).

Verbeck and Gramlich used the test to examine the effects of increasing amounts of solid calcium hydroxide and other factors in reaction mixtures with opal in sodium hydroxide solutions. In these tests the reaction mixture in the reaction chamber (20 mL) was separated by a hardened cement paste membrane from a reservoir chamber containing equal amounts of solution and solid calcium hydroxide, but no reactive aggregate. Capillary tubes attached to each chamber permitted measurements of changes of volume of the contents in each chamber, by dissolution, reaction, or by the transport of solution required to eliminate concentration and osmotic pressure differences. Reaction products formed, imbibed water, and swelled, causing liquid movement from the reservoir chamber to the reaction chamber.

Results of such tests for 4-gram No. 50 to No. 100 sieve samples of opal (300 to 150 mm) are shown in Figure 3.5.1. The major effect of reaction in the 3% NaOH solution without calcium hydroxide is the imbibition of solution by the reaction products. The volume in the reaction chamber tended to decrease initially because of some dissolution and reaction of the opal surfaces, and because of reverse flow caused by the reduction of solute concentration in the reaction chamber. After several days, the rates of swelling of reaction products predominated and flow into the reaction chamber reached a steady state that continued for some weeks. The effects of mixing various amounts of calcium hydroxide (less than 45 mm) with opal was to reduce flow rates progressively until, with 3 grams added, flow into the reaction chamber was apparently stopped. Subsequent work has shown that the flow may begin after some further delay.

It was not clear to Verbeck and Gramlich why variations in the amounts of calcium hydroxide would have such large effects. They believed that 2 and 3 grams of calcium hydroxide were large excesses relative to both its solubility and reactivity requirements, and attributed the effect to supposed low mobility of calcium ions. Their attempts to interpret these and other results were hampered by several other misconceptions of the processes in the osmotic cell test. Although they referred to flow into "the reaction chamber as required by the tendency of the reaction products to imbibe water" (p.1112), their discussion (p.1114-1115) indicated that the results were misunderstood, as follows.

1. The rate of flow at any time was a function of the solute concentration difference between the two chambers. Actually, their calculated potential osmotic pressure differences would cause steady flow in the reverse direction to that observed.
2. A concentration difference between the reaction chamber and reservoir solution was established by the reaction going to completion quite early in the test.
3. This concentration difference was the cause of the constant rate of flow which then continued generally for more than 30 days.

As a result of this review the actual processes now appear to be about as follows.

1. There is an initial surface reaction with some dissolution of opal followed by continuing penetration and reaction with OH^-, Na^+, and Ca^{++} ions to form C-N-S-H or N-S-H.
2. The volume measurements in each chamber include volume changes of dissolution, reaction, and liquid flow.
3. Water, NaOH solution, and ions move freely through the cement paste membrane; silicate ions are contained by cement paste of w/c less than about 0.5.
4. In the tests of Figure 3.5.1 without solid calcium hydroxide there is no "safe" reaction; solution penetrates, partially dissolves, and swells the opal to increasing depths with time. Initially, water molecules diffuse out and Na^+ and OH^- ions into the reaction chamber to restore equal activities in each solution; a steady flow into the reaction chamber is established by the diffusion of solution into the swelling opal particles to form swelling N-S-H gel. pH and Na^+ concentrations decrease in both chambers.
5. With solid calcium hydroxide there is initially a period of safe reaction; some silica dissolves and precipitates C-N-S-H on opal particle surfaces; OH^-, Na^+, and Ca^{++} penetrate and react with silica to form C-N-S-H in the interior. There is some negative volume change of dissolution and reaction, and some initial diffusion of water out and ions into the reaction chamber.

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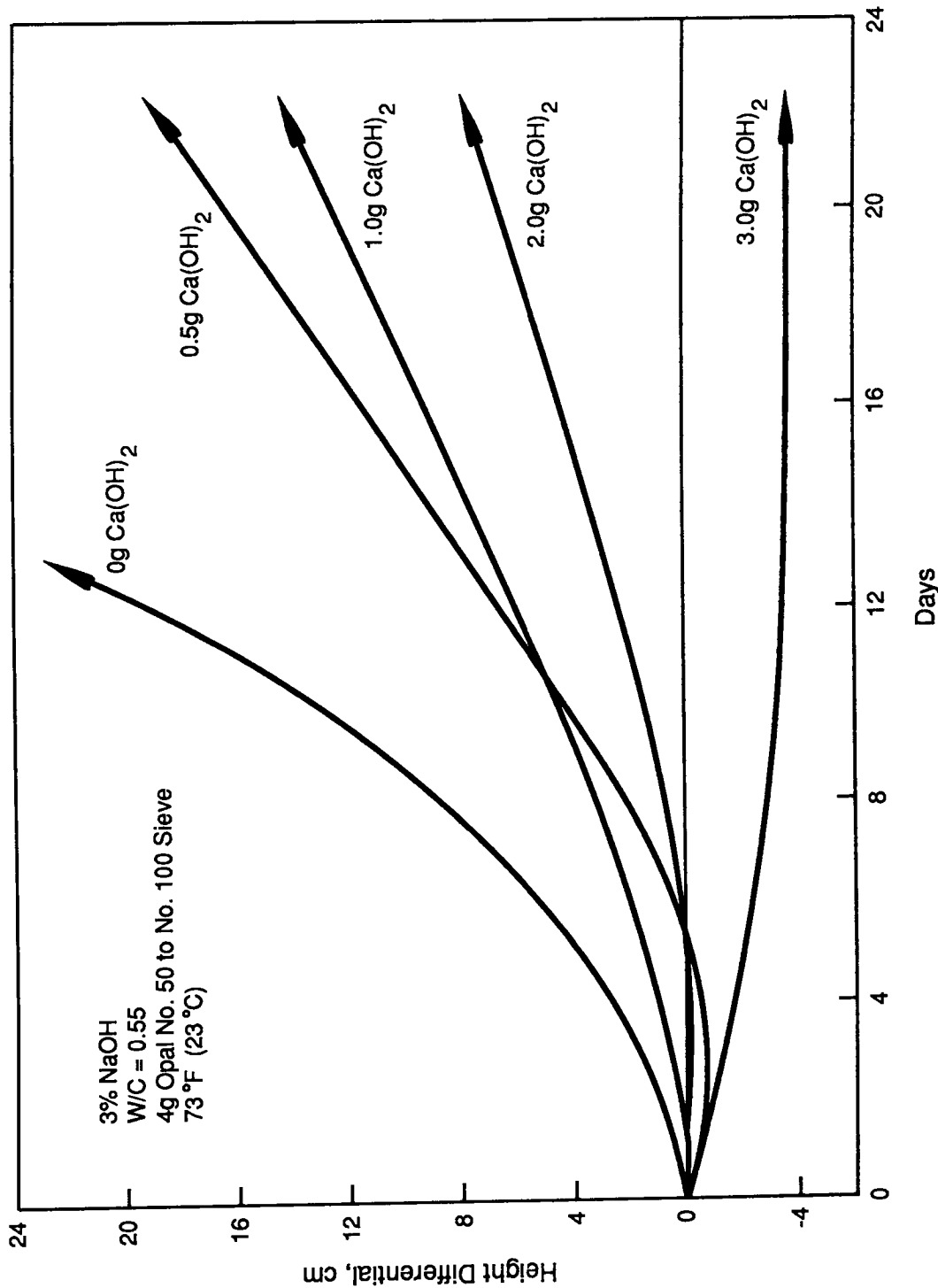
Figure 3.5.1 Effect of Calcium Hydroxide on Observed Height Differentials in Osmotic Cell Tests (50).

6. When the supply of calcium hydroxide is exhausted in the reaction chamber, the reaction product at the reaction fronts in the opal particles begin to become more nearly N-S-H swelling gel. Already formed C-N-S-H begins to become swelling gel as it supplies calcium to the new product. A steady flow into the reaction chamber is established by the diffusion of solution into the swelling opal particles as in point 4.

7. Increasing amounts of calcium hydroxide produce thicker layers of C-N-S-H in the reacted opal surface layers, and delay the onset of swelling and flow into the reaction chamber.

8. The steady rate of flow then depends on:
   a. The thickness of the reacted surface layer that must be penetrated by the OH^- and Na^+ ions and water, and
   b. The amounts of unreacted opal.

   These two factors are believed to be the major causes for the differences of slope of the nearly linear portions of the curves in Figure 3.5.1.

The results in Figure 3.5.1, and others in the same paper, now appear to be completely consistent with Powers and Steinour's model for ASR (See Figure 4.1.1). Verbeck and Gramlich therefore provided indirect evidence of formation of non-swelling reaction product within the opal when there was sufficient calcium hydroxide to prevent flow into the reaction chamber, and swelling reaction product when there was not. The delay of flow into the reaction chamber in tests with sufficient calcium hydroxide should correspond to the time required for reaction to a depth to which calcium ions cannot penetrate as rapidly as hydroxide and sodium ions.

The relationship of the delay time in the osmotic cell test to the delay time in mortar bar tests with pore solutions of the same concentrations may depend also on the diffusion rates outside of the reactive aggregate particles, if that becomes the rate limiting step in the reaction.

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4 Mechanical Effects of Alkali-Silica Reactivity

4.1 Mortar and Concrete Expansion and Cracking

Mortars and concretes made with reactive aggregates that are commercially available show maximum expansions in certain ranges of compositions as Na_2O/SiO_2 ratios or finenesses of reactive silica are varied. However, these phenomena depend on several factors in addition to maximum swelling of the undissolved silica. Most important is the fact that maximum expansions of mortars are the result of large expansions of cracks, which apparently result from copious production and swelling of gel. In addition, reaction of swollen N+K-S-H with calcium ions may regenerate alkalies to swell and dissolve more silica. This process enlarges the reacted zone in the aggregate, but it may not cause greater swelling because the alkali silicate gel becomes diluted, and eventually stabilized, by increasing amounts of C-N+K-S-H. Nevertheless, reaction with calcium, and relatively high ratios of alkali contents to surface areas of reactive silica particles in mortars and concretes, must establish the conditions for initial cracking. These conditions may depend strongly on the swelling of undissolved silica.

Reaction of silica with alkalies in mortar bars may begin to reduce alkali concentrations in pore solutions almost immediately (50,51) or in the case of some pozzolans, may require some time (16,17). When reactions are occurring prior to cracking, elastic expansions are extremely small. The threshold for cracking is less than about 0.03% expansion, and Hobbs found that no cracking occurred in mortars made with either portland cements or cements with fly ashes if the total alkali contents (as Na_2O) were less than about 5.7 lb/yd^3 (3.4 kg/m^3) (52). Cracking and large expansions (0.05 to 2%) begin after some delay, after which the rate of reduction of alkali or hydroxyl ion concentrations correlate well with expansion rates (50,51).

When it is assumed that the amount of expansion at each stage of the process is proportional to the interaction between the amount of reaction product and the balance of unreacted alkalies, Ozol showed by a simple mathematical model that there will be pessimum proportions for maximum expansions (53). Reactive aggregates with high capacity for alkalies then show sharper maxima with varied reactive aggregate content than aggregates with lower capacities.

Hobbs (54,55) developed a more complete model for expansion of mortars and concretes containing opaline silica based on the assumption that the reaction occurs in two stages and proceeds according to additional assumptions. The model was based on an extensive body of mortar test data developed to explore the effects of reactive and total aggregate contents, cement alkali contents, and water/cement ratios (56). Mortars made with cement of 1% total alkali content at fixed proportions, but with variable amounts of reactive aggregate, had expansions that increased with Beltane opal content up to 6% of the aggregate content, and then decreased (54). Similar variations occur at different alkali contents.

Hobbs found that the *maximum* expansions of mortars made with Beltane opal, and cements of different water-soluble alkali contents $(Na_2O)_{cw}$, and reactive aggregate contents $(SiO_2)_r$, occurred at proportions for which $(Na_2O)_{cw}/(SiO_2)_r$ remained constant at 0.067 (54), or 0.09

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using the total alkali content (56). Better correlations were found with water-soluble alkali contents than total alkali contents of the cements with this highly reactive aggregate. If total alkali contents and only the most reactive component of Beltane opal, the 46% that is Opal A, is used, the ratio is 0.19. This ratio is not much different from the proportions of about 0.2 for proportions for maximum swelling of undissolved silica gel, and not much different from the compositions of the alkali silica gel and ASR gels found in Appendix B (and discussed in Section 2.3) of about 0.195. Hence, proportions for maximum swelling in chemical tests without calcium and maximum expansions in mortar tests, are in reasonably good agreement despite several complications.

When water/cement ratios are varied aggregate/cement ratios, (a/c), must also be varied to produce plastic mortars. Hobbs used a/c from 0.5 to 5, with replacements by Beltane opal of up to 23% (10.5% Opal A), in order to vary w/c from 0.29 to 0.65. Total alkali content of the cement was 1.04%, with 0.80% $(Na_2O)_{cw}$. He showed that as w/c and a/c are varied, at fixed reactive aggregate percentages ranging from 2% to 23% of the total aggregate, a family of curves with maximum expansions is obtained. Maximum expansions increased from low values above 0.60 w/c, for mortars of less than 4% replacement by opal at $(Na_2O)_{cw}$/Beltane opal ratios near 0.12, to about 2% with 4% opal at a $(Na_2O)_{cw}$/Beltane opal ratio of 0.07 at 0.47 w/c. The latter mortar had a total alkali/Opal A ratio of 0.19. At lower w/c and a/c at higher opal contents maxima occurred at the same alkali/silica ratio, but expansions did not increase.

Hobbs' model simplifies the expansive reaction processes so that 1) all of the reactive silica is assumed to react to form an initial product, before any 2) ASR gel forms by reaction with excess hydroxyl ions, and begins to swell. These two stages differ from the stages of swelling and dissolution of reactive silica described in Section 2.1, and the initial and subsequent reactions in Powers and Steinour's model. Specific assumptions were as follows.

In the first stage, accessible reactive silica reacts rapidly with alkalies until one of the reactants is depleted. If there is an excess of silica, no expansion is predicted. If there is an excess of alkalies, the first stage reaction product imbibes water and hydroxyl ions in the second stage to form an ASR gel. The rate at which ASR gel imbibes water and swells is assumed to be proportional to the quantity of ASR gel and to the alkali concentration in the pore solution at the time the first stage reaction is completed. Any ASR gel formed during setting and hardening of mortars and concretes up to 1.5 days (in laboratory tests at 20°C [68°F]) is assumed to be accommodated without development of significant stress. Cracking is induced only when the volume fraction of gel formed in the mortar after early hardening exceeds 0.004. Expansion is taken to be proportional to the volume of gel formed after cracking begins. If sufficient alkali is present, the second reaction goes to completion stoichiometrically for mixtures of a particular value of alkali/opal ratio (about 0.07), at which maximum expansions are produced.

Analytical expressions (including five adjustable parameters) for reaction rates, alkali concentrations, time to cracking, and expansion after cracking, permitted Hobbs to fit experimental expansion data reasonably well for mortars made using a wide range of mix proportions. This study is probably the most complete attempt to date to model quantitatively cracking and expansions caused by ASR. Hobbs noted that the assumption that expansion is proportional to the volume of gel formed (after cracking occurs) implies that expansion is not influenced by porosity of the mortar or concrete or rate of gel formation, and that the physical properties of the gel are independent of reactive aggregate content, mix proportions, and cement alkali content.

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These observations are somewhat surprising since the results clearly showed that expansions depended on water/cement and aggregate/cement ratios. They must be considered in the context of the data base which was focused around the pessimum proportions for maximum expansions; that is, with alkali/Beltane opal ratios near 0.07. It was argued that combinations that were safe at that ratio would be safe at any other ratio. Other conclusions might have been reached if the focus were instead on the region of safe reactions, with expansions smaller than those causing cracking, that is, on the time to cracking. Alkali/(reactive silica) ratios are much lower in practice than at pessimum proportions. Added alkalies decrease expansions only with unusual formulations or exposure conditions. Excess alkali dissolves silica and can accelerate ASR while reducing expansions, as discussed in Sections 4.1.3 and 5.3.

4.1.1 Powers' and Steinour's Hypothesis

Powers and Steinour (1,2) examined the proportions required for safe and unsafe (expansive) reactions between cement alkalies, calcium, and opal in mortars and concretes in terms of the effect that reacting silica has on the alkali content of pore solutions. They used opal as an example of reactive silica because considerable data was available for expansions of mortars made with opal. Safe reactions were explained as those with solutions with alkali and calcium contents that produce non-swelling, high calcium content gels. The initial surface reaction product (see Figure 4.1.1) was assumed to be produced in close proximity to calcium hydroxide and to have compositions given by Kalousek's equilibrium data (16). Water, alkali and hydroxyl ions penetrate the opal to form a swelling solid alkali-silica complex and to dissolve silica, followed by reaction with calcium ions that regenerate some alkali into solution. The reacted layer thickens as the reaction proceeds.

Because opal is porous and relatively permeable, the boundaries between reaction zones may not be as sharply defined as indicated in Figure 4.1.1. Pore solutions within the opal would have compositions that differ from those in the cement paste, depending on the distance from the cement paste/opal interface, until the reaction is completed.

Powers and Steinour reasoned that the consumption of alkali progressively reduces alkali concentrations in pore solutions and that the resulting increase in calcium concentration provides the increasing gradient required to continue to supply calcium at the reacting interface to form non-swelling product. These safe reactions usually begin and continue without expansion if the initial alkali concentration is no more than produced by cements of about 0.6% Na_2O equivalent (about 0.4 mol/L NaOH at 0.5 w/c). For higher alkali contents, particles with insufficient surface area consume little alkali from solution so that the calcium concentration remains low and the reacted layer eventually becomes too thick for sufficient calcium to be supplied at the reaction front. Swelling gel is formed there and expansion results. However, if the amount of reactive silica, or its fineness, is sufficiently increased, the alkali content of the solution is rapidly reduced to a safe level so that non-swelling, high calcium content, gel forms until the alkali, or reactive silica, is completely reacted.

From portland cement mortar test data they also showed that as alkali contents of cements increased from 0.5 to 1.0% Na_2O equivalent, Na_2O/SiO_2 ratios for unsafe (expansive) reactions *decreased* from 0.09 to 0.04 and Na_2O/SiO_2 ratios for "just safe" reactions decreased from 0.05 to 0.014. The reactive SiO_2 content must increase much more than the Na_2O content to assure safe reactions in closed systems.

In this way, Powers and Steinour used both chemical data and mortar expansion data to explain pessimum proportions for maximum expansion, and why low alkali cements and
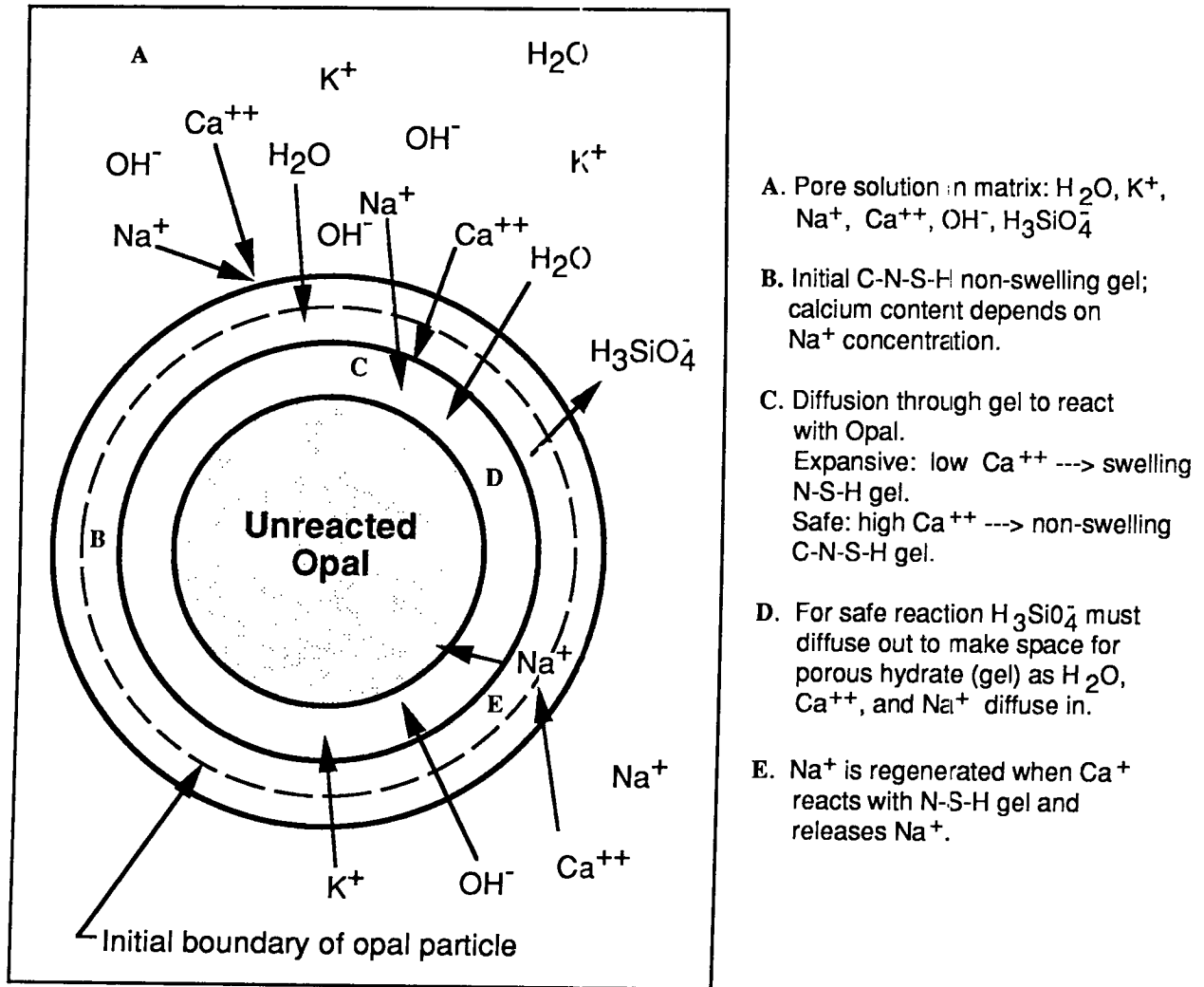
Figure 4.1.1 Powers and Steinour's Model for Reaction With Opal Particles (1.2).

pozzolans are effective in preventing expansion. However, in Sections 4.1.3 and 5.3 it will be shown that the effects of pozzolans and of salts can be much more complicated than described by Powers and Steinour.

Chatterji (8) has presented a description of the role of calcium hydroxide in ASR expansion processes very different from that of Powers and Steinour. He suggested that its reaction products cause or aggravate expansions, rather than prevent them, by impeding the escape of dissolved silica from reacting silica particles. Wang and Gillott (57) recently compared these mechanisms when reporting results of ASTM C 227 tests of mortars made with nonreactive aggregate, except for 2% replacement by opal, and added NaOH to increase cement alkalies to 1%. They reported test results that showed increased expansions, caused by additions of calcium hydroxide (9% by wt. of cement), to mortars made together with, or without, 20% by wt. replacement by condensed silica fume. The control mortar expanded about 0.6% in 1 year at 100°F (38°C), while mortar with added calcium hydroxide expanded about 0.8%. Mortar with silica fume showed no expansion to 560 days, but with added calcium hydroxide began to expand before 180 days and reached 0.4% at 560 days.

Wang and Gillott concluded that these results show that additional calcium hydroxide aggravates ASR expansions, but did not agree with Chatterji's suggested interpretation, while retaining   Powers and Steinour's model in their discussion. Instead they concluded that expansions increased because:

1) calcium hydroxide provides an abundant source of hydroxyl ions, and
2) calcium ions replace alkalies in partially reacted silica to regenerate alkalies that maintain high pH and continue the reaction within aggregate particles.

Since these conclusions agree with those of Powers and Steinour, some additional reason, such as suggested by Chatterji, must be given as a basis for increased expansions. Powers and Steinour based their analysis (2) of conditions for safe and unsafe reactions on the assumption that silica was able to diffuse out through the reaction layer during a safe reaction. The expansion controlling processes were the alkali and calcium diffusion rates required to produce nonexpansive products. They did recognize uncertainties in making the same assumption for silica diffusion for unsafe as for safe reactions.

The alkali/opal ratio in Wang and Gillott's mortars without silica fume were 0.22, much higher than the 0.07 for maximum expansions found by Hobbs for Beltane opal, and the 0.014 for safe reactions under the conditions considered by Powers and Steinour. In this above-pessimum case, increasing the alkali should decrease expansions if more silica is dissolved and can escape. When calcium hydroxide is added, the rate of escape of silica should be impeded because of increasing reaction to form solid C-N+K-S-H, which increases the viscosity of the gel mixture. In such situations Chatterji's suggestion that calcium hydroxide is necessary to cause, or may aggravate, expansions appears to be correct.

In the case of the mortars containing silica fume, the alkali/(opal + silica fume) ratio was only 0.033, very close to the value at 1% Na_2O_{eq} estimated by Powers and Steinour for unsafe reactions (0.04). They also estimated that 20 grams of pozzolanic silica per gram of alkali in excess of 0.5% was needed to maintain safe reaction conditions with higher alkali content cements. That was apparently achieved with the silica fume without added calcium hydroxide, but not when 9% by wt. of cement of calcium hydroxide was added. Since expansion was not detected by C 227 until 180 days, these results confirm Powers and Steinour's estimate for this marginal case. Hence, in this low-alkali/silica ratio, below-pessimum case, it appears that the reaction was well controlled for some time, but that expansion eventually occurred either because effectiveness of the silica fume for long-term pH control was reduced by its reaction with added calcium hydroxide, or by impeding escape of dissolved silica, or both.

These results, in both the high and low alkali/silica ratio cases, are consistent with Powers and Steinour's criteria for safe and unsafe reactions. Chatterji's suggestion appears to apply in the case of unsafe reactions at very high alkali/silica ratios.

One other aspect of Powers and Steinour's hypothesis has been difficult to verify. They reasoned from phase equilibrium data that consumption of alkali and hydroxyl ion by silica should increase calcium ion concentrations in pore solutions. Although alkali and hydroxyl ion concentrations in pore solutions expressed from mortars are often measured, calcium concentrations are seldom reported, perhaps because they are relatively small. In the study by Struble (15) values ranged from 0.6 to 2.5 m mol/L for mortars made without reactive aggregates, and showed little correlation with cement alkali content. However, these calcium concentrations are in the range to be expected from the equilibrium phase diagram for solutions in contact with C-N-S-H and calcium hydroxide (23). It appears that the pore solution samples are expressed from the largest and interconnected capillary pores in the

cement paste and are essentially in equilibrium with those phases as assumed by Powers and Steinour, which tends to confirm their reasoning. Direct verification requires data for reacting mortars that show decreases in calcium concentrations as cement alkalies are released, followed by increases as alkalies are consumed by reactive aggregates. Struble's data were inappropriate because they did not contain reactive aggregate. Such measurements for mortars containing pozzolans or highly reactive aggregates may not show increased calcium concentrations because of 1) reaction of calcium with the pozzolan or 2) encapsulation of calcium hydroxide by a protective coating of reaction products which isolate it from the pore solution (27d).

Local equilibrium may exist between the solids and solution in the large pores in hardened mortars, but this does not mean that the entire system is in equilibrium. Alkali, calcium, and hydroxyl ions are consumed in the reaction zones of silica particles. Those solution concentrations are different from those in large pores, but not measurable. For this reason, it is advantageous to examine the compositions of the reaction products.

4.1.2 *Reaction Zone Compositions*

Twenty years after Powers and Steinour's review, Thaulow and Knudsen (58) used SEM-EDX and light microscopy to examine the interface between a 0.35-in. (9-mm) rock core embedded in an 0.43-in. (11-mm) thick hull of 0.4 w/c paste after 8 months of moist curing. The cement was an Icelandic cement with 1.65% Na_2O and 0.37% K_2O (1.89% Na_2O equivalent). Nearly all of the potassium and one-third of the sodium was water-soluble. Light microscopy showed the center of the opal core to be unaltered, but from 0.2 to 1.5 mm from the interface the opal was less transparent. From 0.004 to 0.002 in. (0.1 to 0.5 mm) a white opaque rim had formed. The cement paste showed alteration with a dark glassy rim about 0.004 in. (0.1 mm) thick. Nine empty cracks radiated through the paste from the core. It was uncertain whether the cracks formed during curing or during drying prior to examination.

SEM examination revealed an irregular circumferential crack in the opal 0.002 to 0.006 in. (50 to 150 μm)from the original interface. Radial cracks began at this crack in the opal. The largest cracks penetrated the reaction zones and the cement paste hull. The cracks were not gel-filled.

Figure 4.1.2 shows results of SEM-EDX line scans and spot analyses. Variations of intensities for silica, calcium, and potassium concentrations are shown from the unreacted opal core, through the crack and several reaction zones in the opal, and into the cement paste, all with good sensitivity and resolution. Sodium was not detected by this method with adequate sensitivity.

The reaction zones identified were as follows:

1. Reacted opal with decreased silicon and increased calcium contents. Cracks normal to interface.
2. Reacted opal with less calcium, more silicon and some potassium.
3. Zone in cement paste impregnated with calcium-rich potassium-silica gel.
4. Cement paste not penetrated by gel.

The molar C/S ratio of the reacted opal in Zones 1 and 2 are about 0.8 and 0.13, respectively. Thaulow and Knudsen recognized that this reaction was apparently not a safe reaction despite the significant calcium content of the reacted opal, and that a reexamination of the role of calcium in ASR was required. These results led them to ask why the calcium concentration in
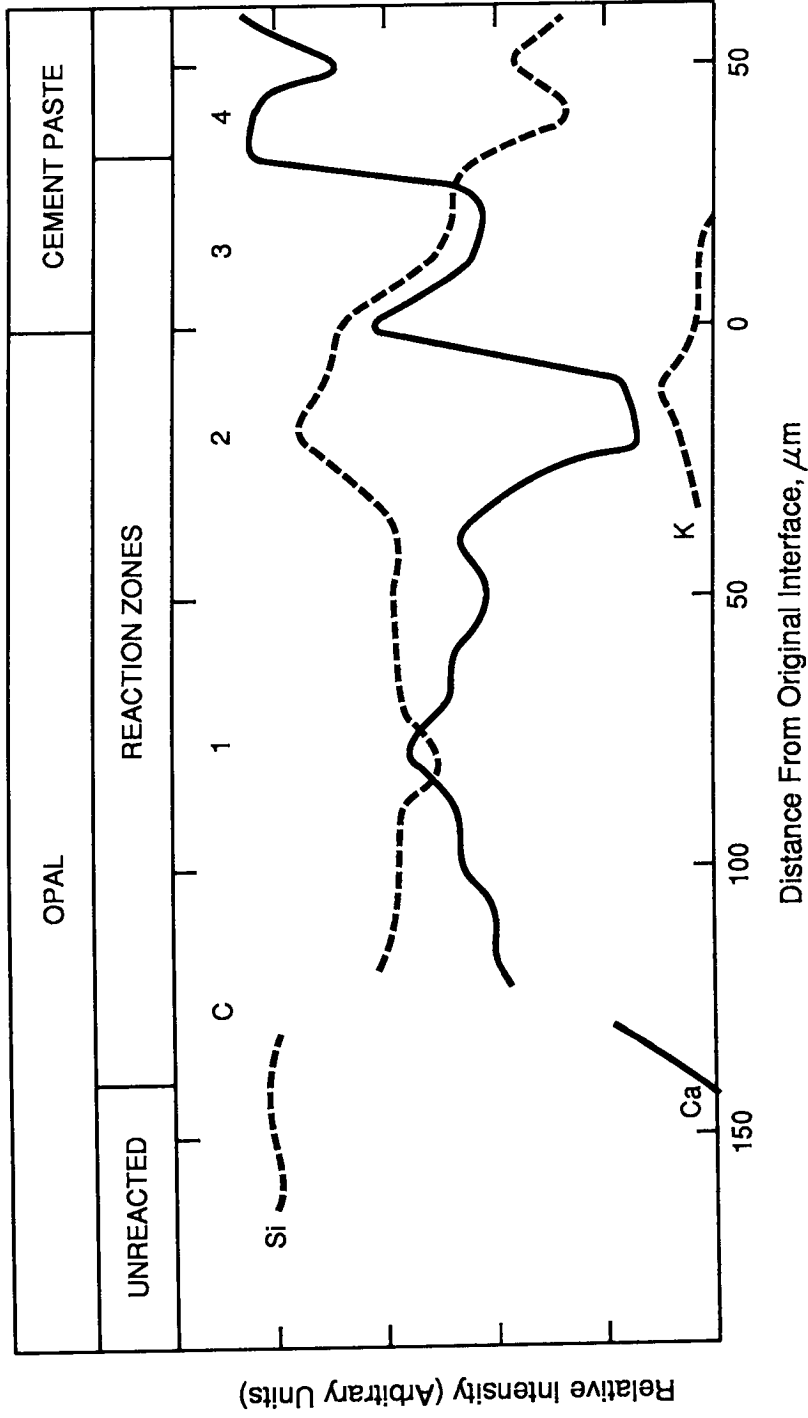
Figure 4.1.2 SEM-EDX Microanalysis of Opal-Cement Paste Reaction Zones After 8 Months Moist Curing
C: Open Crack Parallel to Interface (58). By permission from the Icelandic Building Research Institute.

the opal reaction zones should be so high with high alkali and low calcium ion concentrations in the pore fluid. The presence of calcium must mean that the calcium reaction product is very insoluble, as would be expected in the high alkali, high pH environment.

The results of the SEM-EDX analyses are given in Table 4.1.1.

Table 4.1.1 SEM-EDX Analyses (in mass percent) of Interfacial Reaction Zones and Opal (58).

Zone	SiO_2	CaO	Na_2O	K_2O	H_2O	C/S molar
Opal	97.6	-	.	-	2.4	-
1	40	28		0.2	32	0.75
2	73	9	0.5	2.1	15	0.13
3	41	20		0.5	38	0.52

By permission from the Icelandic Building Research Institute.

Examination of the original X-ray line scan trace shows penetration of potassium through all of Zone 1 and even to the unreacted opal interface, although the trace may be only slightly above background noise. Sodium was more abundant than potassium in this cement but hardly detectable by this method. In later work with quartzite aggregate (34), analyses showed K_2O/SiO_2 and CaO/SiO_2 ratios of about 0.2 all the way into the aggregate particle and to the unreacted silica interface. It appears that alkali hydroxides must precede calcium into the reaction zone, although calcium contents may eventually become higher. Such data tend to confirm Powers and Steinour's model for the process.

Although the reacted opal of Figure 4.1.2 contains considerable calcium, its distribution is not as expected from Powers and Steinour's model. The calcium content in most of Zone 2 is lower than in Zone 1. In Appendix B and Section 2.3 we showed that, for ASR gels to be free of swelling component, the CaO content must be above about 53% and the SiO_2 content less than about 40% on an anhydrous basis. CaO contents in Zone 1 and Zone 2 are only 41% and 10.6%, and the SiO_2 contents 59% and 86%, respectively, on that basis. The data thus suggest that some silica remains undissolved and unreacted, and that the products contain swellable gel.

In addition, the opal/paste cylinders also cracked in ways that indicate expansion as well as drying shrinkage, and that the calcium-rich layer of reacted opal may have expanded away from the core. Similar observations in concrete had been reported by Brown (59), who attributed cracks in reactive aggregates to tensile stresses produced by expansion of the reacted rim.

4.1.3 Effects of Reactive Particle Size and Pozzolans

Eight years after Thaulow and Knudsen's pioneering work Kawamura, et al. (60) examined the reaction of opaline rock (Akase opal) aggregates in mortars by using improved SEM-EDX analyses and microhardness measurements at 3, 7, 14, and 28 days. Companion mortar bars were used for expansion measurements at up to 50 days' storage in a fog box at 100°F (38°C). Some leaching of alkalies must have occurred. Seven different size fractions of reactive aggregate were included at 7.5% by weight of cement as 10% of the total aggregate.

Mortars with all of the size fractions except the finest (less than No. 200 sieve or 0.074 mm) began to expand after 3 days' curing. The mortar made with the finest fraction, and one mortar made with fly ash and No. 16 to No. 30 sieve (1.2 to 0.6-mm) reactive aggregate, did not expand significantly. Expansions were about 0.3% at 30 days for mortars made with the intermediate size fractions. Mortars made with the two coarse fractions, No. 4 to No. 8 and No. 8 to 16 sieve (5 to 2.5 mm and 2.5 to 1.2 mm), had reduced expansions partly because the particles were not fully penetrated by the reaction as were the finer fractions.

EDX analyses showed substantial increases in alkali contents in the reaction rim to a depth of about 0.01 in. (250 mm) in only 7 days. $(Na_2O + K_2O)/SiO_2$ ratios increased in 28 days to about 0.2 near the surface. Calcium contents remained low for 7 days but, at 14 days, showed penetration to depths of 0.008 or 0.004 in. (200 or 100 μm) for mortars made with or without 1% NaOH, respectively, added to the cement. The increase in alkali content in the aggregate caused drastic reductions in microhardness of the rock. Solidification of the softened region within about 0.002 in. (50 μm) from the interface corresponded to its increase in calcium content. However, $(Na_2O + K_2O)/SiO_2$ and CaO/SiO_2 molar ratios in the reaction zones were never more than about 0.2; such CaO contents seem too low to form non-swelling gels. Indeed, most of the mortars expanded 0.1 to 0.4% in 30 days.

Most of these data appear to be consistent with Powers and Steinour's model for unsafe reactions. Kawamura, et al. showed that alkalies preceded calcium into reacting particles. They concluded that expansion, at least up to about 30 days at 100°F (38°C), depended upon the amounts of gels, rather than on their chemical compositions. However, their results for mortar made with the addition of fly ash were not consistent with Powers and Steinour's hypothesis for the effects of pozzolans because alkalies penetrated the opal in *greater* amounts up to age 14 days than in mortar without fly ash. Just as important was the fact that calcium contents in the opal, to a depth of 0.012 in. (300 μm) in the mortar made with fly ash, increased as rapidly as alkali contents at 3 days, and even more so by 28 days. Fly ash did not inhibit alkali-silica reactions, but facilitated more reaction to produce higher calcium content products without expansion, although CaO/SiO_2 ratios were less than about 0.3. They concluded that expansion was eliminated by 1) formation of gels with "high" calcium concentration and/or 2) reduction of mobility of water through the paste matrix. They also recognized that reduction of pH of the pore solutions by pozzolans, such as calcined kaolin, can inhibit ASR and expansion.

In a later paper Kawamura and Takemoto (61) showed that alkali levels in pore solutions expressed from control mortars made with standard sand *without* reactive Akase opal were reduced from about 0.7 mol/L at 7 to 28 days to less than 0.3 mol/L by addition of 30% by weight of cement of calcined kaolin. Ordinary portland cement with an alkali content of 0.79% Na_2O equivalent was used. Alkali concentrations were only slightly reduced by addition of 5 or 30% fly ash, and slightly *increased* by additions of 5% or 30% blast furnace slag. The result for this slag may be unusual. In another study (18) slags were found to reduce alkalinity of pore solutions, although not as effectively as fly ashes. The available alkali content of this slag was 0.45% Na_2O. This was *less* than that of the fly ash (0.57% Na_2O eq), but much greater than that of the calcined kaolin (0.13% Na_2O eq.). Addition of 5% of two different condensed silica fumes reduced the alkali concentrations about the same as that of 30% fly ash; addition of 10% silica fume reduced alkali levels to about 0.4 mol/L after 7 days.

Expansions of mortar bars made with the same materials, but with 10% of the standard sand replaced by Akase opal, also were reduced by the mineral admixture additions. Expansions of these mortars, and controls made without such additions, are shown in Table 4.1.2. Additions

of 30% fly ash or calcined kaolin, or 10% silica fume B, were highly effective in reducing mortar expansions. Pozzolanic reactivity of silica fume B was shown to be much greater than that of silica fume A. Results for 5% and 10% silica fume A seem to have been interchanged. Mortar bars made without reactive aggregate and with 30% calcined kaolin showed that any expansion caused by the alkali-silica pozzolanic reaction was at most very small. This was also found with finely ground Akase opal in the earlier study (60).

Table 4.1.2   Expansions of Mortar Bars Made with Akase Opal and Mineral Admixtures (61)

Mineral Admixture	Amount Added % by wt. of Cement	Mortar Bar Expansions	
		3 months %	6 months %
None	0	0.46	0.46
Fly ash	5	0.23	0.23
Fly ash	30	0.00	0.04
Slag	5	0.14	0.14
Slag	30	0.13	0.16
Calcined Kaolin	30	0.07	0.07
Calcined Kaolin*	30	0.03	0.03
Silica Fume A	5†	0.02	0.24
Silica Fume A	10†	0.29	0.40
Silica Fume B	5	0.32	0.41
Silica Fume B	10	-0.02	-0.03

*Mortar without Akase opal replacement of standard sand.
†Results for 5% and 10% appear to this writer to have been interchanged.

Comparison of these expansion data with the pore solution data is complicated by the fact that the mortars used for pore solution analyses did not contain reactive aggregate, as did the expansive mortar bars. Since reaction of opal also reduces alkali concentrations, actual reductions of concentrations in the expansive mortars should be greater than those measured values. Kawamura and Takemoto nevertheless discussed relationships between expansions and alkali concentrations as if any such differences did not exist. Although neither the fly ash or slag significantly reduced alkali concentrations in the pore solutions, both reduced expansions substantially, even with only 5% additions. Additions of 5% silica fume had about the same effect on alkali pore solution concentration as that of 30% fly ash, but were not nearly as effective in reducing expansions as the fly ash. For the mortar with 30% calcined kaolin, both the alkali concentration and expansion were greatly reduced.

Microhardness and EDX measurements of the opal particles in mortars with 30% calcined kaolin showed no changes from 3 to 28 days; reaction of the opal was virtually stopped by reduction of alkali concentration by the calcined kaolin. For mortars made with 30% fly ash, the opal particles were considerably softened to depths of 0.012 in. (300 μm) as alkalies diffused into the opal between 3 and 28 days. For the case of mortars with only 5% added

slag it was suggested that expansions may be reduced by activated reaction of the opal particles, which soften to relieve the expansive pressure. It was concluded that factors other than removal of alkali hydroxides from solution by reaction with fly ash or slag reduced the mortar expansions.

It was also clear that different pozzolans inhibited mortar expansions by quite different mechanisms. In the case of calcined kaolin, the reaction with opal was virtually stopped by sufficient reduction of alkali concentration in solution. In the case of fly ash, the alkali concentration was hardly reduced, and the reaction of the opal with alkalies was more rapid. Also, the reaction with calcium within the opal particles was facilitated. Addition of only 5% slag reduced expansion greatly despite an increase of alkali concentrations. They concluded that when only one kind of mineral admixture (fly ash, slag) is used, correlations are found between pore solution concentrations and expansions, but when different kinds are compared, other factors become important.

Other characteristics of mineral admixtures that must affect the mechanism of control of mortar expansions are those which influence transport of moisture and dissolved species to and from reaction sites. Solutions in large pores are separated from reactant surfaces by porous reaction products. There will be concentration gradients through these porous layers as long as ASR, diffusion, and expansion continue. Since different pozzolans can have different effects on the distribution of reaction products and their permeabilities, they can affect expansions by their effects on diffusion rates as well as pore solution concentrations.

These two studies (60,61) have shown that pozzolans, such as calcined kaolin, appear to function as described by Powers and Steinour, but that fly ashes function instead by facilitating alkali-silica reactions without excessive expansions. In Section 2.2 it was shown that hydroxyl ion concentrations in pore solutions can be substantially reduced when low alkali content fly ashes are used, but that did not seem to occur in these accelerated tests at 100°F (38°C). The results with fly ash indicate that silica diffused freely out while alkalies and calcium diffuse into opal. Other studies (27,62) show that fly ash particles nucleate early formation of C-S-H (or C-N+K-S-H) and promote more uniform distribution of hydrates in the paste. These phases should also nucleate on opal particles and keep calcium and silica concentrations low at the opal-paste interface. If the hydrates form in the pore space outside the opal, they might not form in the opal and interfere with further diffusion and reaction, as Chatterji has suggested (8), and may occur at high alkali/silica ratios as explained in Section 4.1.1.

4.1.4 Effects of Chloride Salt Additions

Research has recently begun to focus on the effects of soluble salts on ASR, something that was not considered by Powers and Steinour in 1955. Calcium chloride has been a common accelerating admixture for concrete. Its use is being restricted in steel reinforced concrete but will continue in plain concrete where steel corrosion is not a concern. Seawater and sea dredged sands may be used to make concrete where use of fresh water is not economical. In addition to the effects of salts added to the fresh concrete, there are the effects of exposure of hardened concretes to salt solutions. Seawater and NaCl deicing salts can provide unlimited amounts of alkali. Accelerated tests for ASR are being done in salt solutions. The physical and reaction chemistry in these situations is complex, and results may be misinterpreted unless the complexities are understood.

The effects on ASR in hardened mortars and concretes exposed to external salt solutions will be reviewed in Section 5.3. In such exposure the pore solution concentrations can become very high, up to saturation with salt. In this section the effects of chloride salt additions to

fresh mixtures on the reaction chemistry and expansions will be described. There are substantial differences between these effects. When salts are present in mortars before hardening, cement hydration reactions may be accelerated or retarded and chloride ions may be incorporated into chloroaluminate hydrate phases during early hydration of the aluminate phases in cements. In addition, reactive aggregate particles are not yet sealed in dense, relatively impermeable, hardened cement paste, and penetration of various ions may occur more readily. Without additions or external sources of salts, pore solutions in concretes are complex mixtures of various ionic species in solution. After several days, however, they become essentially alkali hydroxide solutions, calcium and other species being reduced to very low concentrations (see Equation 2.2.1).

During this period much of the C_3A and some of the ferrite phase in the portland cement hydrates to AFt (trisulfate) and AFm (monosulfate) phases, with much of the AFt phase decomposing to AFm phases when the calcium sulfates have been exhausted. The compositions and properties of these and related phases have recently been reviewed by Taylor (63).

In ordinary portland cements, the composition of the common monosulfate hydrate phase may be represented by: $C_3A \cdot C\bar{S} \cdot H_{12}$. There are analogs in which the SO_4^{-2} is replaced by other ions, such as CO_3^{-2} or $2Cl^-$. When either $CaCl_2$ or $NaCl$ is used as an addition, an AFm phase known as Friedel's salt is formed: $C_3A \cdot CaCl_2 \cdot H_{10}$. This compound does not form solid solutions with sulfate AFm phases. Instead, an ordered compound exists: $2C_3A \cdot CaSO_4 \cdot CaCl_2 \cdot H_{24}$. Friedel's salt transforms reversibly at 82°F (28°C) from α (monoclinic) to β (triclinic) at higher temperatures. These phases can also form in concrete exposed to chloride solutions. The chloride containing AFt phase is stable only below 32°F (0°C) where it has been reported to cause destructive expansions in concrete containing large amounts of $CaCl_2$ (63a).

Studies of the effects of chloride salts and pozzolans on compositions of pore solutions have been done in connection with their effects on corrosion of steel in concrete and on ASR. High C_3A content portland cements have higher chloride binding capacity by formation of Friedel's salt and thus tend to reduce steel corrosion. The overall reaction with NaCl to form Friedel's salt will tend to increase alkalinity:

$$C_3A + 2NaCl + Ca(OH)_2 + 10\,H_2O \rightarrow C_3A \cdot CaCl_2 \cdot 10H_2O + 2Na^+ + 2(OH)^- \qquad (4.1.1)$$
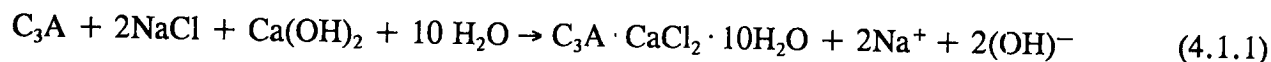
whereas that with $CaCl_2$ does not:

$$C_3A + CaCl_2 + 10H_2O \rightarrow C_3A \cdot CaCl_2 \cdot 10H_2O \qquad (4.1.2)$$
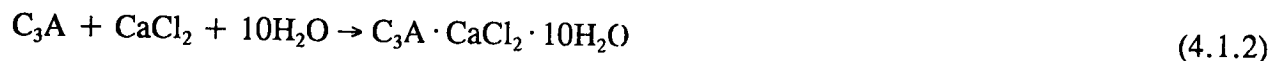
These equations suggest that NaCl additions may aggravate ASR more than $CaCl_2$ additions, especially with high C_3A content cements. However, the reaction with NaCl solutions converts some calcium hydroxide to the less soluble Friedel's salt. $CaCl_2$ also dissolves some of the calcium hydroxide, at least in concentrated solutions, to produce calcium oxychloride: $CaCl_2 \cdot Ca(OH)_2 \cdot H_2O$. This is a destructive expansive reaction (63b, 64). These reactions, together with leaching and expansive effects, must be kept in mind when attempting to interpret changes of expansions or changes of chloride and hydroxyl ion concentrations in pore solutions in terms of reactions with pozzolans or reactive aggregates.

Kawamura et al. (51,19), and others (65) have recognized that different combinations of cements and mineral admixtures have different chloride binding capacities and different effects on pore solution compositions. Pozzolanic reactions consume calcium hydroxide, form additional C-N-S-H of lower C/S ratio and higher alkali capacity, and thereby reduce pore

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solution alkalinity. In some circumstances these effects may aggravate corrosion of steel by chlorides while controlling ASR, unless chloride concentrations are also adequately reduced. Kawamura et al. (19), examined variations of pore solution compositions in the absence of reactive aggregates in mortars made with and without 30% fly ash replacement for low alkali portland cement, (0.38% Na_2O) and additions of $CaCl_2$ or NaCl. Chloride ion additions of 0.5%, 1.0%, and 2.0% by weight of cementitious materials were introduced as salts dissolved in the mix water of mortars. The initial chloride ion concentration of pore solutions with the 1.0% addition was 0.59 mol/L. The mortars were cured in sealed plastic bags at 73°F (23°C). Pore solutions were expressed from the mortars after 1, 3, 5, and 12 weeks of curing and analyzed for Cl^- and OH^-.

Some of their results of pore solution concentration measurements are given in Table 4.1.3. Results for the mortars made without salt additions showed that 30% fly ash reduced hydroxyl ion concentrations to 64% to 72% of the values of those made without fly ash. Results for mortars with 2% NaCl additions show that the chloride concentrations increased above their initial values. This increase results from the reduction of pore water during hydration of the cement. When concentrations are adjusted to constant (initial) water contents, they show that chloride ions were consumed by reactions. Actual concentration reductions at 1.0% NaCl indicate that the reactions with C_3A were sufficient to overcome the effect of pore water reduction. XRD and DTA confirmed the formation of Friedel's salt, and that greater amounts formed with $CaCl_2$ than with NaCl. Results in Table 4.1.3 for mortars made with $CaCl_2$ show much greater reductions of chloride ion concentrations than found with NaCl.

Hydroxyl ion concentrations with NaCl additions were higher than without salt, consistent with Equation 4.1.1, and were similarly reduced by 30% fly ash in the mortars. The degree of reaction with $CaCl_2$ was much greater than with NaCl, as indicated by the greater reduction of chloride and hydroxyl ion concentrations. The reduction also was shown by the greater DTA peaks for Friedel's salt, both with and without fly ash. DTA also showed that the amounts of Friedel's salt formed did not appear to be reduced by replacement of cement by fly ash; that is, the chloride binding capacity of the cement was reduced very little, if any, by fly ash. These facts suggest that release of Al_2O_3 by fly ash during reaction contributed to formation of Friedel's salt. The results up to this point all seem simply explainable by the reactions with aluminates to form Friedel's salt, as in Equations 4.1.1 and 4.1.2, and by the pozzolanic reactions with fly ash.

Kawamura et al. also found (Table 4.1.3) that the ratio of Cl^- to OH^- increased rapidly with salt addition from 1% to 2% and concluded that the effects of chloride salts on corrosion of steel reinforcement are more serious in concretes containing fly ash, and in concretes containing $CaCl_2$, than those containing NaCl. The results in Table 4.1.3 show that these same concretes should have less severe ASR because of reduced OH^- concentrations. While Equation 4.1.1 indicates the reason for the increase of hydroxyl ion concentration with NaCl, Equation 4.1.2 does not explain the reduction of OH^- concentration with $CaCl_2$ relative to mortars without either salt. However such an effect would be expected from the formation of complex salts that incorporate the limited amount of alkalies released by the cement. $[Ca_2Al(OH)_6] \cdot K(ClO_4) \cdot XH_2O$ and $C_4A_{0.9}N_{0.5}S_{1.1}H_{16}$ are such AFm phases (63c) that may have formed in amounts too small to be detected by XRD.

An important result of this work is that considerable reduction of chloride ion concentrations and changes of pH can result from reactions with portland cements and pozzolans in the absence of ASR, and that such changes need not be attributed to chloride participation in alkali silica reactions without more specific evidence. Kawamura and Ichise (51) have recently

Table 4.1.3 Pore Solution Data for Mortar Cylinders Made With and Without 30% Fly Ash and Additions of NaCl and CaCl₂ After Curing at 73°F (23°C) (19)

Mortar Compositions [a,b]		[Cl⁻] mol/L [c]				[OH⁻] mol/L			[Cl⁻]/[OH⁻]
Salt %Cl⁻	Fly Ash %	0d	7d	35d	84d	7d	35d	84d	35d
None									
0	0	n.r.	n.r.	n.r.	n.r.	0.25	0.28	0.25	n.r.
0	30	n.r.	n.r.	n.r.	n.r.	0.16	0.20	0.18	n.r.
NaCl									
1.0	0	0.59	0.56 (0.38)	0.51 (0.35)	-- (0.28)	0.33	0.38	--	1.3
1.0	30	0.59	0.48 (0.34)	0.47 (0.34)	0.40 (0.28)	0.28	0.23	0.23	2.0
2.0	0	1.18	1.48 (1.00)	1.44 (0.97)	1.34 (0.85)	0.27	0.36	0.34	4.0
2.0	30	1.18	1.25 (0.91)	1.25 (0.91)	1.22 (0.85)	0.25	0.23	0.20	5.4
CaCl₂									
1.0	0	0.59	0.21 (0.15)	0.20 (0.13)	0.19 (0.10)	0.14	0.16	0.15	1.2
1.0	30	0.59	0.19 (0.14)	0.17 (0.13)	0.21 (0.15)	0.09	0.10	0.11	1.7
2.0	0	1.18	0.46 (0.30)	0.41 (0.25)	0.45 (0.24)	0.07	0.09	0.09	4.8
2.0	30	1.18	0.46 (0.32)	0.42 (0.30)	0.42 (0.28)	0.05	0.06	0.06	6.6

a. %Cl⁻ or Fly Ash by weight of cement

b. Stored sealed in vinyl plastic bags in a fog box at 73°F (23°C).

c. Values in parentheses are adjusted to constant water content; pore water contents are reduced by hydration.

n.r. Not reported, presumed to be zero.

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investigated the effects of added sodium and calcium chlorides on ASR expansions and pore solutions of mortar on their expansions when stored in a fog box for 180 days at 38°C. Mortars were made with and without 10% of the total aggregate replaced by Beltane opal. Additions of NaCl and CaCl₂ were used to produce chloride ion contents of 0.65, 1.23, 1.80. 2.37, and 3.52% by weight of cement. The alkali content of the portland cement was 0.93% Na₂O eq. Concentrations of hydroxyl and chloride ions in their pore solutions were measured for up to 28 days. Unfortunately, the procedures used resulted in leaching of ions from specimens made with Beltane opal, whereas the control specimens were sealed in plastic bags to prevent leaching. Nevertheless the results have some utility, but may require reinterpretation.

Results of expansion and pore solution concentration measurements are summarized in Table 4.1.4. In this table the concentrations are adjusted to constant water content, as were the data in parentheses in Table 4.1.3; the measured values for Table 4.1.4 were not reported.

Expansions were accelerated by both salts at all addition levels, except for the highest level with CaCl₂, for which expansion was initially delayed. Expansions close to their ultimate

values were reached in about 30 days with added salts. Ultimate values at more than 1.23% Cl^- were approximately 3 times, and 1.5 to 2 times, as large as without NaCl and $CaCl_2$, respectively.

Table 4.1.4 Expansion and Pore Solution Data for Mortars Made With and Without 10% Reactive Aggregate (Beltane opal) and Additions of NaCl and $CaCl_2$ (51)

Mortar Compositions[a]		Storage[b]	Expansion %		[Cl-] mol/L[c]				[OH—] mol/L[c]		
Salt %Cl⁻	Opal %		7d	28d	0d	1d	7d	28d	1d	7d	28d
None 0	0	sealed	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	(0.4)	(0.53)	(0.5)
0	7.5	leaching	0.15	0.22	n.r.	n.r.	n.r.	n.r.	(0.4)	(0.20)	(0.1)
NaCl 1.0	0	sealed	n.r.	0.03	0.9	(0.9)	(0.6)	(0.5)	(0.42)	(0.6)	(0.55)
1.0	0.75	leaching	0.58	0.61	0.9	(0.5)	(0.25)	(0.2)	(0.48)	(0.62)	(0.40)
CaCl₂ 1.0	0	sealed	n.r.	n.r.	0.9	(0.4)	(0.3)	(0.3)	(0.24)	(0.3)	(0.35)
1.0	0.75	leaching	0.37	0.45	0.9	(0.4)	(0.2)	(0.1)	(0.2)	(0.1)	(0.05)

a. %Cl⁻ or opal by weight of cement
b. Stored in a fog box at 100°F (38°C) either sealed in vinyl plastic bags, or without such protection from leaching.
c. Values in parentheses were adjusted to constant water content. Measured values were higher but not reported. Values at 0 days were calculated from mix proportions.
n.r. Not reported.

In mortars without opal or salts, hydroxyl ion concentrations increased during the first seven days to about 0.5 mol/L; with opal the hydroxyl ion concentration decreased to about 0.2 and 0.1 mol/L in 7 and 28 days, respectively. With 1.23% Cl⁻ in mortars made with added NaCl, the hydroxyl ion concentration increased nearly equally to about 0.6 mol/L at 7 days for both mortars, whether made with or without the reactive aggregate, but after 7 days decreased in the mortar containing opal. Cl⁻ concentrations decreased from about 0.9 mol/L at 1 day to 0.5 at 28 days for the mortar without opal. For the mortar containing 1.23% Cl⁻ and opal, large expansions occurred but the OH⁻ concentration decreased only slightly. Instead, the Cl⁻ concentration decreased more rapidly than in the mortar without opal. The increase of expansion in mortars containing NaCl additions was interpreted to result from acceleration of ASR in the early stages without consuming OH⁻ ions and with consumption of a large percentage of the chloride ions from solution in the first 24 hours, after which expansion began. This suggestion that chloride ions are consumed in the alkali-silica reaction is in direct conflict with EPMA results reported by Chatterji et al. (66), and discussed in Section 5.3. They found chlorine contents were much lower than Na_2O contents in reactive grains inmortars tested at 50°C in solutions saturated with NaCl. Chlorine contents were only about 1% while Na_2O contents were above 10%. In the case of these mortars made with Beltane opal (7.5% by weight of cement), if the decrease of Cl⁻ concentration by, for example, 0.4

mol/L had been caused by reaction with opal, the Cl⁻ content of the opal would be more than 9%, and proportionately higher in the reacted part of the opal.

It does not appear that Kawamura and Ichise took into account the combined effects of leaching and formation of Friedel's salt in accounting for the Cl⁻ concentration changes. Comparison of data in Table 4.1.4 with those in Table 4.1.3 shows definite evidence of leaching of Cl⁻ from the specimens containing opal reported in Table 4.1.4. Sealed specimens without opal made with 1.23% Cl had Cl⁻ adjusted concentrations at 0, 7, and 28 days between, and consistent with, specimens in Table 4.1.3 made with 1.00 and 2.00% Cl at 0, 7, and 35 days. Comparison of results for the specimens containing opal (which were not sealed) in Table 4.1.4 with those containing fly ash in Table 4.1.3 show that the latter have much larger values, and indicate leaching of the unsealed specimens. Each set of data indicates significant reaction by fly ash or opal at 7 days.

Similar comparisons made for the mortars with 1.23% Cl⁻ as calcium chloride in Table 4.1.4 with comparable mortars in Table 4.1.3 also indicate no leaching of Cl⁻ at 7 and 28 days for the sealed specimens. However, they show lower values for the mortars exposed to leaching. Hydroxyl ion concentrations for mortars in Table 4.1.4 are higher for the sealed mortar because of the higher alkali content of the cement, but they were reduced to 0.05 mol/L at 28 days by reaction and leaching of alkalies.

In view of the above evidence it appears that the results in Table 4.1.4 should be explained instead as follows. Formation of Friedel's salt occurred with NaCl additions according to Equation 4.1.1 in mortars both with and without opal. In mortars without opal (and without leaching) the Cl⁻ concentration was reduced and Na⁺ and OH⁻ concentrations were increased by that reaction and by alkalies released by cement hydration. In mortar with opal (and leaching in the fog box) Cl⁻ concentration was further reduced but Na⁺ and OH⁻ concentrations remained high beyond 7 days by these reactions despite some leaching and uptake of alkalies by the alkali silica reaction.

It is apparent that uncertainties remain concerning the mechanisms by which chloride salts influence ASR. Large effects are evident, as will also be seen in Section 5.3 for mortars exposed, after hardening, to salt solutions.

4.1.5 Aggregate Fracture by Alkali-Silica Reactivity in Concrete

Cracking and the mode of reaction of reactive quartzite aggregate particles in concrete has been documented and described by Davies and Oberholster (30). When samples of concrete were fractured along cracks caused by ASR, fractures through the aggregate showed there was always an elevated rim of tough, colorless, gel between the cement paste matrix and aggregate along the periphery of the particle. Inside the gel rim, white reaction products became less abundant on the fractured aggregate surface toward the center of the particle. These crystalline products appear to be rosette-like when examined by SEM and often appeared to have nucleated on quartz or silicate grains. They suggested that reactive aggregates contain ideal sites for reaction and gel production at the intersection of the crack surface and the paste-aggregate interface. Alternatively, the aggregate may contain flaws which fracture readily when pore solutions produce swelling of the rim or swelling gel on the rim. Further reaction produces gel which partly fills the crack and swells to enlarge the crack.

Examination by SEM-EDX of a polished section through such a crack in a meta-argillite aggregate particle in concrete clearly showed the crack had been widened at the paste/aggregate interface by a plug of massive gel. The crack was only partly filled farther

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from the interface into both the aggregate and paste matrix. Reaction products in the crack varied in composition with distance from the interface, and became more crystalline farther from the interface, as shown in Table 4.1.5.

Table 4.1.5 SEM-EDX Analyses (in mass percent) of ASR Products in a Crack in a Meta-Argillite Particle in Concrete (30)

Distance along Crack into Particle in. (μm)		Material in Crack	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	C/S molar
0	0	Mixed Products	46.1	6.4	3.5	39.8	4.2	0.92
0.004	100	Massive Gel	66.4	-	-	25.4	8.2	0.41
0.007	180	Crystalline*	68.5	-	-	20.2	11.3	0.31

*Based on similarity to rosette-like crystals.   1 μm = 0.0000393 in.

These results agree with those of Knudsen and Thaulow (36) (see Section 2.3) in the sense that they show increasing CaO contents and lower SiO_2 contents in the crack toward the paste matrix. However, in that case CaO contents were only about 15% to 25% near the paste/aggregate interface. Results of Davies and Oberholster also show much lower C/S ratios for the products in the crack than those in Figure 4.1.2 and Table 4.1.1 at comparable depths into opal Zone 1.

4.2 The Effect of Pressure on Alkali-Silica Reactivity

Since concrete in service is under stress, the effect of stress on ASR must be considered. It is also important to recognize that since the volume change for dissolution of reactive silica is negative (Section 3.1), its solubility increases with pressure (6b). These phenomena, related through Le Chatelier's Principle, show that the reaction cannot be stopped by increasing pressure, whether generated by osmotic swelling (Section 3.4) at the reaction sites in concrete, or applied externally. By contrast, osmotic swelling will occur only until an equilibrium pressure, and vapor pressure, are reached. Since dissolution reduces the volume, it relieves swelling pressure, and more OH^- and alkali and water will be imbibed. If the concrete is able to sustain the pressure at the reaction site, the process can become auto-accelerating and will tend to consume all of the reactive silica if sufficient alkali and moisture are available. For quartz, increased pressure should reduce solubility because the volume change is slightly positive.

4.3 Stresses on Expanding Particles

The problem of estimating stresses on expanding aggregate particles, and the restraint of expansion, is similar to the problem solved by Pickett for the restraint of drying shrinkage by elastic aggregate particles (67). Figure 4.3.1 is a graph, calculated from Pickett's equations, of radial compressive stresses and maximum tangential tensile stresses induced by drying shrinkage in the cement paste film around a spherical aggregate particle, as a function of the paste film thickness. The stresses in Figure 4.3.1 were calculated for paste shrinkage of 0.05% and paste elastic modulus of 2×10^6 psi (13.8 GPa). The same calculation yields the
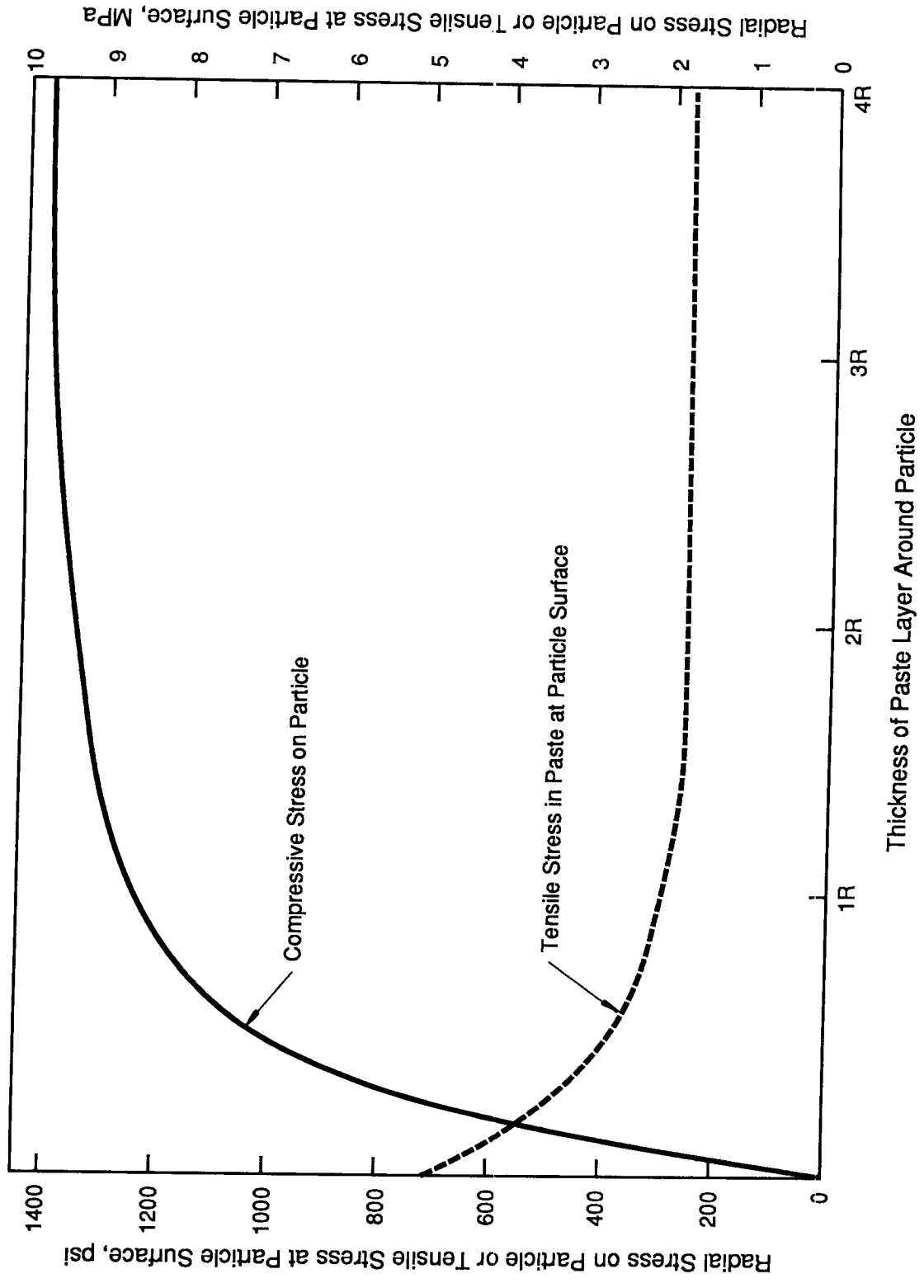
49

Figure 4.3.1 Stresses on Particle of Radius R and in Paste at Particle Surface Caused by Paste Shrinkage, or Particle Expansion, Calculated for 0.05% Expansion and Selected Properties.

stresses caused by aggregate particle expansion, rather than paste shrinkage, or combined shrinkage and expansion.

Average paste film thickness in standard mortars and concretes vary considerably, but are generally less than the average radius of even the finest fraction No. 50 to No. 100 sieve (300 to 150 μm) sand used in ASTM C 227 for alkali reactivity tests. Hence the surrounding "paste" around each particle is actually mortar. For these and coarser aggregate particles the stresses in the surrounding mortar film could be calculated in the same way using appropriate values for the shrinkage and elastic properties of the materials. Although creep and stress relaxation effects in mortars and concretes are substantial, Pickett's simple model indicates that for thick films, or for continuous composites, the stresses at the interfaces approach constant values.

Even with the small expansion assumed for this calculation, the stresses on the particle are large enough to cause flow and to balance calculated swelling pressures of moist gels, if cracks do not develop.

Stresses produced by expanding aggregate particles may exceed the strength of the restraining matrix, resulting in crack initiation and propagation. Hobbs (54) developed a model that includes both the time-to-cracking and the expansion after cracking for mortar bar tests using Beltane opal, a fast reacting aggregate. Hobbs' paper makes it clear that until the mortar cracks the expansion is negligible (when averaged over the length of the sample), but after the first crack forms it goes at a fast rate. This suggests that the rate greatly increases by growth of the crack (or cracks) because of the lack of restraint. Gel exudes into the crack, causing it to widen rapidly, while relieving internal pressures and stress concentrations in the porous structure.

4.4   Restraint of Expansion of Moist Mortars

The effect of mechanical restraint on ASR expansions has been recognized at least since 1955 when McGowan and Vivian reported mortar bar tests done with uniaxial loads. They showed reduced expansions in the direction of loading (68,55). A compressive stress as low as 50 psi (0.34 MPa) applied after demolding was sufficient to delay expansion and cracking about 120 days, and then reduce cracking expansions from 1.05% to 0.19% at one year, relative to unloaded specimens. An equal stress applied instead at 112 days, after about 0.8% expansion, was sufficient to stop expansion. The mortars were made with aggregate containing 95% quartz sand and 5% opaline rock (No. 50 to No. 20 sieve size or 0.3 to 0.85 mm), and portland cement with 0.98% alkali as Na_2O, so that the Na_2O/SiO_2 ratio was about 0.1. Tests were also done with mortars made with low alkali cement and additions of NaOH, for total alkalies of 0.3 up to 1.0% as Na_2O. Expansion at one year was 0.12% at 0.5% alkali without load, but even 1 psi (0.007 MPa) was sufficient to prevent expansion at that Na_2O level for that time. At 0.75% and 1.0% alkali, expansions exceed 1% at low loads, decreasing with load to only about 0.5% at 50 psi at 1 year. It should be noted that under the stress of 50 psi the control specimens, without reactive aggregate, contracted 0.07% after one year, so that if the expansion measurements had been corrected for this creep under stress they would have been somewhat higher, but not nearly enough to account for the reduction of expansion caused by even these very small loads.

Examination of the crack patterns on the mortar bars showed that the width and numbers of cracks diminished for specimens tested at higher loads. At low loads the orientation of cracks tended to be random. At higher loads the larger cracks tended to become oriented in the

direction of the applied load. They concluded that crack patterns in concrete structures must be governed by the restraints imposed by the design and size of the structure.

4.5 Restraint of Expansion of Moist Concretes

Hobbs (55a) reported that concretes made at pessimum proportions with Na_2O contents of 8.4 lb./yd.[3] (5 kg/m^3) and opaline silica expanded against restraint after loading in compression to 360 psi (2.5 MPa). The stresses induced by the restraint increased to 580 or 508 psi (4.0 or 3.5 MPa) with different silica fineness No. 100 to No. 50 or No. 50 to No. 16 sieve fractions (0.15 to 0.30 mm or 0.30 to 1.2 mm), respectively in 50 to 100 days. These stresses are about ten times the greatest stress in the mortar tests. The major causes of this large difference appears to be a result of the expansive reaction products being much more completely confined within the concrete by the concrete under higher stress than in the small mortar specimens, rather than differences in proportions or leaching of alkalies from the mortars during testing.

Tests by Fujii, et al. of reinforced concrete beams (69) also show compressive stress induced in the concrete by ASR of about 580 psi (4 MPa). These concretes were mixed with added NaOH or NaCl to produce total alkali contents of 10.1 lbs/yd^3 (6.0 kg/m^3) (as Na_2O) to accelerate ASR. Strain of the compression steel and stirrups reached about 0.2% in about 70 days after 14 days curing at 68°F (20°C) and testing at 100% RH and 104°F (40°C). Crack patterns were determined by restraint of the reinforcement, as has also been discussed by Hobbs (55b).

4.6 Triaxial Restraint of Expansion of Moist Concrete

In SHRP's research on ASR, (C 202) a unique restraint of expansion experiment was done using external triaxial loading imposed on sealed concrete specimens under hydrostatic pressure. In these tests the effects of directional stress, drying gradients, and cracking were minimized, and the swelling pressures were more completely confined within the concrete than when directional restraint occurs. It was not known what pressure was required to stop ASR expansions or reactions in concrete under these conditions, or if there was any pressure at which the reaction could be stopped, although field and other evidence strongly indicated at least temporary benefits of restraint. These tests clearly demonstrated that expansions could be stopped, or slowed, or reversed by adjusting the pressure applied, and that the reversal resulted from simultaneous creep and expansive reactions because control (non-expanding) specimens also showed creep contraction under compressive stress.

The results also show elastic rebound and creep recovery effects when pressures are changed. The expansion rates were sensitive to pressure, becoming small at 250 to 300 psi (1.7 to 2.0 MPa). The creep rate of the control specimens at these low pressures is still significant (70), (Figures 4.6.1 and 4.6.2).

External pressure may stop or reverse the expansion, but that does not mean that the reaction is stopped. It must mean that the sum of the rates of expansion, and creep in compression, produce zero net strain rates. Increased stress at reaction sites can 1) increase creep of the paste in the matrix; 2) increase the rate of dissolution of silica; 3) reduce osmotic swelling of gel; and 4) cause gel to creep or flow from the reaction sites through pores and/or microcracks. Such effects depend on the degree of the reaction. Initially there is pore space available (containing some water), but free of gel, and no microcracks. Later the pores and microcracks may become filled with gels of differing properties. These results are extremely important not only because they indicate how the expansion rate depends on restraint, but
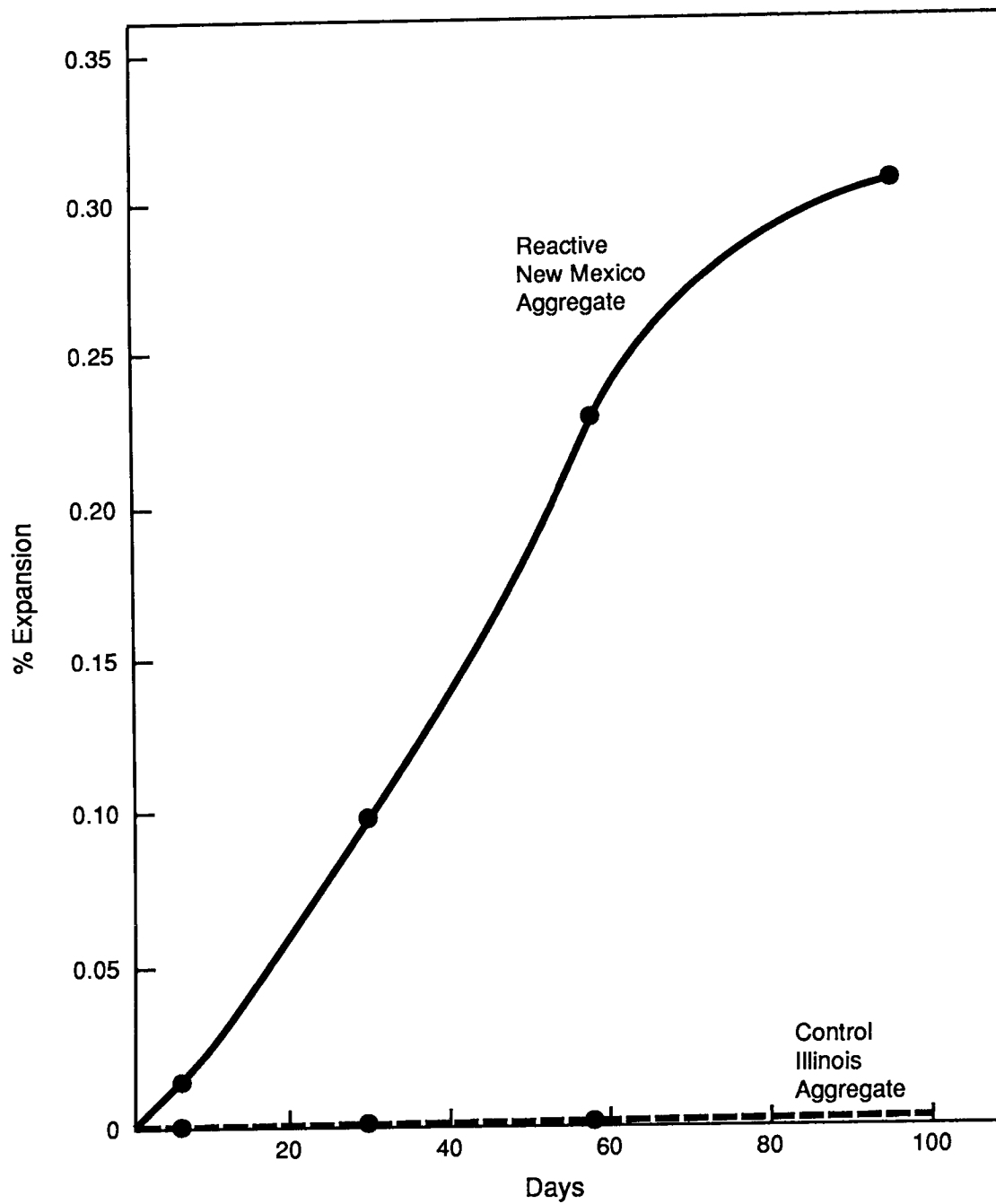
Figure 4.6.1 Expansion of Concrete Prisms Stored Over Water in Sealed
Containers at 100°F (38°C) (70).
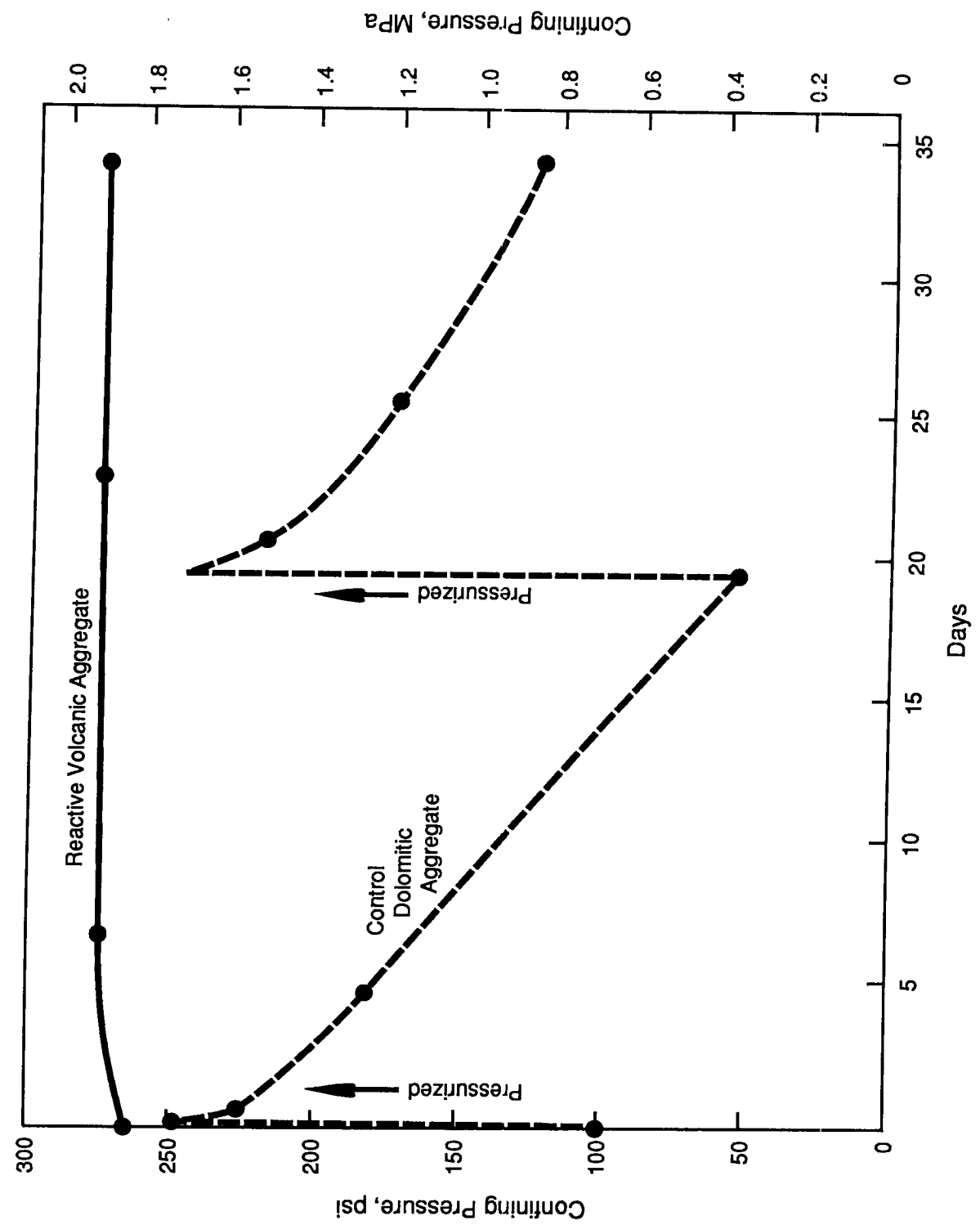
Figure 4.6.2 Pressure Developed Due to ASR in Triaxally Confined Concretes Stored at 100°F (38°C) (70).

because they show that creep of the matrix and ASR expansions of these fast reacting aggregates are of comparable magnitudes in moist concretes.

4.7 Stresses in Moist Mortars and Concretes

Relating the swelling pressures of ASR gels to the external stress at which expansion stops requires an examination of the relationship between the average stresses at the expansive sites and in the matrix and how it depends on the external pressure or restraint. The following simple balance of forces analysis does not depend on elastic behavior, and does not permit calculation of strains, but does relate expansive stresses to tensile stresses in the matrix and external restraint (71).

There are several cases to be considered when concrete is sealed and under a pressure P that produces axial stresses, σ_x, and radial stresses, σ_r, at the surfaces of a concrete cylinder. Consider $P > 0$ and <u>compressive</u> stresses to be positive so that $P = \sigma_x = \sigma_r$. To consider a balance of forces on planes normal to the cylinder axis of area, A_x, equal to the external area of the end of the cylinder:

$$A_x = A_a + A_m; \quad A_a = \text{Sum } A_i \tag{4.7.1}$$

in which A_a is the summation of areas A_i of reactive silica particles in a section, and A_m is the area of the matrix (everything but reactive silica in the section).

A balance of forces through any plane section requires:

$$\sigma_x A_x = \sigma_a A_a + \sigma_m A_m \tag{4.7.2}$$

where $\sigma_x A_x$ is the load on the end of the specimen, and σ_a and σ_m are the average stresses in the reactive silica and the matrix, respectively.

Case 1

For $\sigma_x = 0$, i.e., no external load (free expansion):

$$\sigma_a A_a = - \sigma_m A_m \tag{4.7.3}$$

For $\quad A_x \sim A_m$ or $A_a/A_x << 1$

$$\sigma_a = - \sigma_m A_m/A_a >> - \sigma_m \tag{4.7.4}$$

i.e., the compressive stress on the reactive aggregate σ_a is much greater than tension in the matrix.

If, however, $A_m \sim A_a, \quad \sigma_m \sim - \sigma_a$ \qquad (4.7.5)

Case 2

For $\sigma_m = 0$, i.e., tension in the matrix caused by expansive particles is exactly balanced (eliminated) by compression from external stress:

$$\sigma_x A_x = \sigma_a A_a \tag{4.7.6}$$

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Then
$$\sigma_a = A_x/A_a \sigma_x$$

and if

$$A_x/A_a >> 1$$

$$\sigma_a = A_x/A_a \sigma_x >> \sigma_x \qquad (4.7.7)$$

i.e., the compressive stress σ_a is much greater than the applied stress.

If, however, $A_a \sim A_m \sim A_x/2$

$$\sigma_a \sim 2\sigma_x \qquad (4.7.8)$$

This fact indicates a factor that may be very important: A_a may slowly increase as gel spreads through the pores as a result of continuing reaction under restraint that is sufficient to stop the expansion. In such cases σ_x may need to be increased to very high values to prevent cracking.

Case 3

External load $P \neq 0$ and $\sigma_m \neq 0$

Expressions for σ_a and σ_m in terms of the measured pressure $P = \sigma_x = \sigma_r$ are required. We have found experimentally that there are values of P that stop ASR expansion.

We want to be able to limit σ_m to prevent cracking. From Equation 4.7.2:

$$\sigma_m = \sigma_x A_x/A_m - \sigma_a A_a/A_m \qquad (4.7.9)$$

Equation 4.7.9 shows that σ_m can be made > 0 for any σ_a by sufficiently increasing σ_x, or can become very negative (i.e. tension) if σ_a is large enough. Also from Equation 4.7.2:

$$\sigma_a = \sigma_x A_x/A_a - \sigma_m A_m/A_a \qquad (4.7.10)$$

which shows that the stress on the reactive aggregate is the sum of two terms that depend on 1) external stress, and 2) tensile stress in (and strength of) the matrix.

5   Environmental Effects

The major environmental effects on ASR are those of moisture content and temperature variations, and exposure to soluble salts which penetrate into the concrete (8,55,72,73). Every climate area in North America has seasonal variations, during which concretes are exposed to slow cycles of temperature and moisture content changes that have major effects on ASR cracking. The widespread use of deicing salts on pavements and their drainage onto other structures has been responsible for much deterioration. The interaction between such environmental effects and ASR is as yet not well understood. The results of accelerated test methods of reactive aggregates using salt or alkali hydroxide solutions at elevated temperatures may also be misleading if our understanding of reaction processes under those conditions is not improved.

5.1   Moisture Conditions in Field Concretes

One of the major tasks of this research has been to obtain good documentation of the actual relative humidity conditions that exist in field concretes. Some of these results are reported here (70,70a).

Figures 5.1.1 and 5.1.2 show variations of relative humidity (RH, corrected to 75°F, 24°C) measured in pavements at various depths from the top surface at different times of the year and geographic locations with different climates. Such data show that RH values are high enough (RH > 80%) to sustain expansive alkali-silica reactions in most of the pavement below the top surface layer, even in the summer in a hot desert climate. Figure 5.1.3, for a bridge column in this area, also shows pronounced seasonal differences, but a similar moisture profile. Measurements were made about 4 ft (1.2 m) above grade, in holes bored to various depths from the column vertical surfaces.

The drying profile is a familiar one, superficially similar to the characteristic profile for concrete specimens drying in the laboratory. These data are, however, for seasonal variations that we assume are approximately repeated each year. The concrete is about 20 years old. For the column in August, 1988 to have reached the condition in February, 1989 (near the end of the cooler wetter season), it does not appear that moisture entered from the vertical surfaces of the column; the curve would be concave upwards if it had been absorbing moisture from these wet surfaces. Since the interior concrete responds only very slowly to surface fluctuations, it appears that the average RH even in February, only 2 in. (50 mm) below the surface, is less than 70%, although the surface RH may vary widely from a short-time average of about 40%. It is apparent that, even in the wetter season, moisture is flowing outward from the interior to the surface, and must be coming up through the core from the underground base of the column as water evaporates from the vertical surfaces.

Relative Humidity, % at 75°F (24°C)
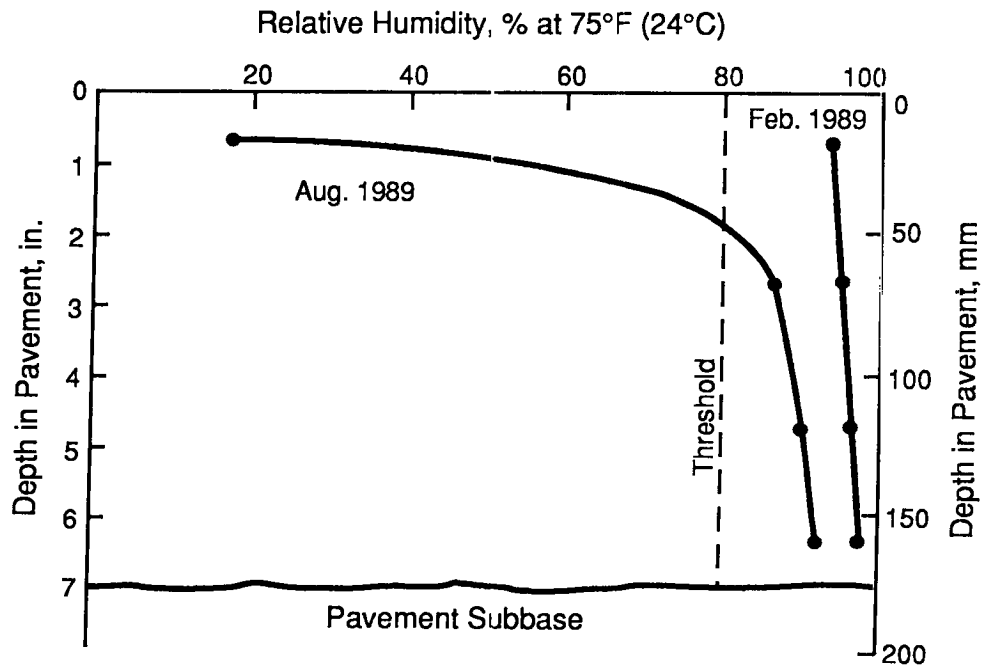
Figure 5.1.1 Relative Humidity in Concrete Pavement Located in Hot
Desert Area (70).

Relative Humidity, % at 75°F (24°C)

CA - California
DE - Delaware
GA - Georgia
NM - New Mexico
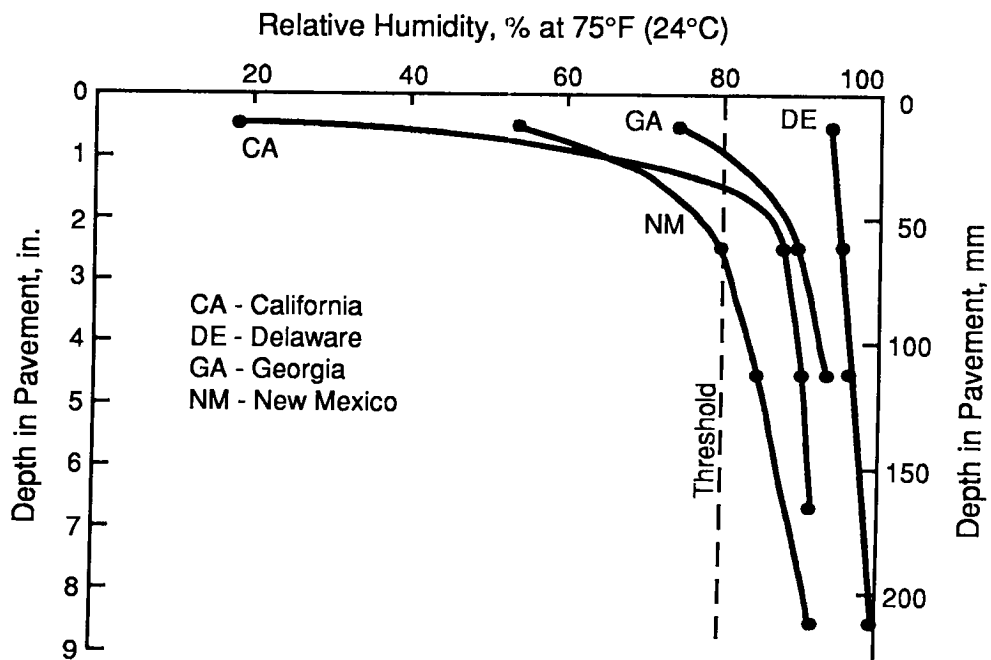
Figure 5.1.2 Relative Humidity in Concrete Pavements Located in
Different Climatic Regions (70).

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Depth Into Column, in.
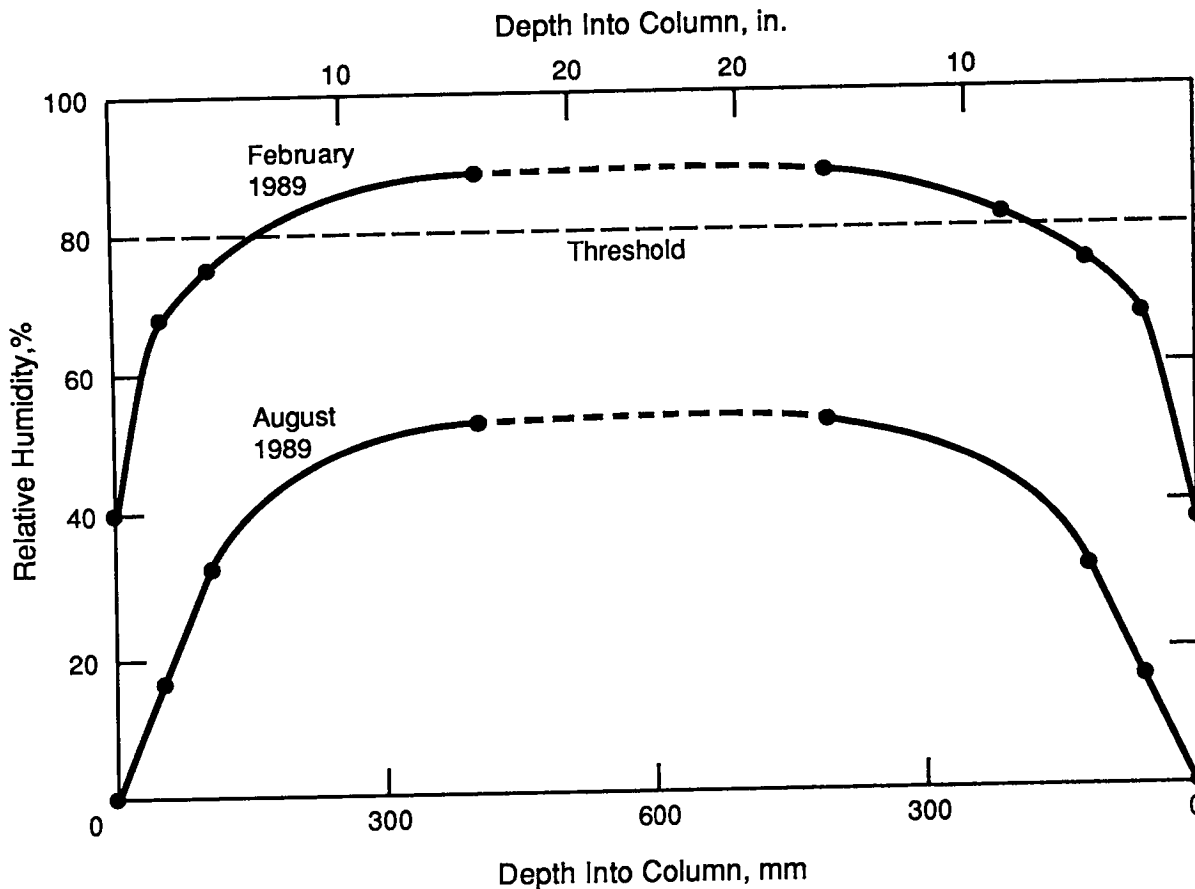
Figure 5.1.3 Relative Humidity in Column of Bridge Located in Hot Desert Area
in California (70).

These data are convincing evidence that humidity conditions moist enough to support
expansive ASR exist in much of the concrete in pavements and structures for a part of each
year in most of the continental United States. Only concrete isolated from sources of moisture
(including groundwater), such as a bridge deck, can dry sufficiently to remain below the
threshold and arrest expansion due to ASR. The data also show that drying at exposed
surfaces creates moisture and humidity gradients in field conditions similar to those measured
and analyzed by Pickett (74).

5.2 Effects of Drying and Creep

In Section 4.7, we examined the effects of mechanical restraint and internal stresses on ASR
and cracking. The situation in real concrete pavements and structures is complicated by the
effects of drying. During the early stages of drying, the interior of the concrete is in
compression but the exterior is in tension. ASR in the moist interior will increase the
compressive stress in the interior and the tensile stress in the surface. Stresses in concretes are
relaxed by creep of the cement paste. A complexity of concrete is the increase of creep rate
on simultaneous drying ("drying creep") as opposed to creep at constant RH ("basic creep").
Total creep during drying can be much greater than basic creep, although basic creep
decreases with RH.

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Examples of modern treatments of concrete shrinkage and creep data are given by Bazant, et al. (75,76). In both papers one of the best sets of data analyzed is that in a paper by Hansen and Mattock (77). The data in Table 5.2.1 are taken from the figures in the Appendix in this reference. These specimens were loaded to 1200 psi (8.3 MPa) after eight days curing and dried at 50% RH, except for specimens sealed to prevent drying. Strains at drying times of 0, 10, 100, and 1000 days are shown. Strains were measured on the surfaces of the concrete cylinder specimens, rather than axially. Drying shrinkage specimens were not loaded. Creep strain (e_c) was calculated as the total strain (e_t) less the instantaneous strain (e_i) when loaded, and the drying shrinkage strain (e_s).

Drying shrinkage increases as expected with time and decreases with specimen size, as does the total strain. Except for the 24-in. (61-cm) specimens at 10 days, creep during drying is always greater than the basic creep of sealed specimens. This is not because cement pastes creep more rapidly when in a dried state (they creep less rapidly). The creep is greater during drying partly because the compressive stress on the moist core of the specimen is increased by drying of the surface. During drying, the surface also creeps in tension until the interior has shrunk sufficiently. The eventual effect is greater total strain, except in the case of the 24-in. specimens at 10 days.

Creep strain during drying exceeds the initial (elastic) strain in less than 100 days. Creep strains are only partially reversible because of irreversible changes in the cement gel caused by drying and other factors.

For some purposes, as in ACI 209R (78), it is assumed that creep, drying shrinkage, and elastic strains are "mutually additive and independent." Table 5.2.1 shows representative values for concrete shrinkage and elastic and total strains, from which creep strains were calculated on the assumption of additivity. The increase of creep during drying (drying creep) values are also shown. They are simply the differences between the creep strains $(e_t-e_i-e_s)$ of drying creep specimens and those of the 6-in. (15.2-cm) sealed (basic creep) specimens. Also shown are the values calculated for the total strains assuming additivity of elastic, basic creep, and shrinkage strains. These values show that the drying creep was very small for these 24-in. (61-cm) diameter specimens but quite large (more than 40% of the creep at 10 and 100 days) for the 6-in. diameter specimens. Total strains calculated assuming additivity of elastic, basic creep, and drying shrinkage strains for the 24-in. cylinders are within 3% of the measured strains; for the 6-in. cylinders the measured strains are about 15% greater. Hence, the assumption of additivity of strains is not very accurate, but not grossly in error even for these data.

Reacting aggregate particles are restrained by both the strength of the non-expansive part of the concrete, and by forces transmitted from external restraints. Drying shrinkage of the concrete also increases compressive stress on reactive particles, and shrinkage of the drying surface produces compression in the interior even before the interior begins to dry. Surface cracking reduces stresses and accelerates drying. Drying slows and eventually stops ASR swelling. Drying also immobilizes alkalies by mechanisms not yet established so that they are not immediately released into solution after rewetting (70).

Restraint stresses required to prevent growth of surface cracks when the continuously moist base of a concrete pavement expands by ASR against longitudinal and transverse restraint while the top surface is drying must depend upon the drying condition, expansion of the base, and creep of the concrete. Such growth is depicted in the diagram for ASR cracking of concrete, (Figure 5.2.1) but the effects of external restraint and internal creep are not yet

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specifically indicated in this diagram. It represents a section of pavement with negligible transverse restraint.

Experiments to simulate this situation with longitudinal restraint typical of concrete pavements in practice are now in progress under SHRP's research on ASR (C-202).

Table 5.2.1 Concrete Creep and Shrinkage (Millionths) After 8-Day Cure (77)

	Specimens	Initial Strain e_i at 1200 psi	Drying at 50% RH, 70°F Time (Days)				Projected Final Strain
			0	10	100	1000	
Drying	6 in. (15.2 cm)	---	0	200	650	870	942
Shrinkage	12 in. (30.5 cm)	---	0	150	450	700	752
Strain, e_s	24 in. (61 cm)	---	0	20	160	420	500
(No Load)	6 in. Sealed	---	0	30	70	30	0
Creep	6 in.	340	0	252	564 (108)a	744 (264)	787 (252)
Strain, e_c	12 in.	310	0	180	408 (36)	588 (108)	656 (96)
$= e_t - e_i - e_s$	24 in.	330	0	132	360 (-12)	528 (60)	637 (36)
e_{cb} Basic	6 in. Sealed	410*	0	144	300	492	694
Total	6 in.	340	340	792	1554 (684)b	1954 (1290)	2029 (1202)
Strain, e_t	12 in.	310	310	640	1168 (604)	1598 (1060)	1718 (1502)
$= e_t + e_i + e_s$	24 in.	330	330	482	850 (492)	1278 (790)	1467 (1142)
	6 in. Sealed	410*	410	584	780	932	1104

a. Values in parentheses are Drying Creep, $(e_d) = e_c - e_{cb}$
b. Values in parentheses are (e_t)calc $= e_{cb} + e_i + e_s$
*Measurement at 970 psi (6.7 MPa); calculated at 1200 psi (8.3 MPa)

1 in. = 2.54 cm
1 psi = 6.895 kPa

5.3 Effects of Salt Solutions

Some of the same chemistry and effects of chloride salt additions discussed in Section 4.1.4 are involved when hardened mortars or concretes are exposed to salt solutions. NaCl deicing salt solutions and seawater can provide unlimited amounts of alkali. NaCl has been shown to accelerate ASR, especially in tests at elevated temperatures. Tests of mortars and concretes in NaCl saturated solutions at 176°F (80°C) correlate well (79) with tests of reactive aggregates by ASTM C 227-81; at 72°F (22°C) these solutions caused contractions of concretes with ASR aggregates (80).

Relative
Humidity, %

100   50   Drying surface
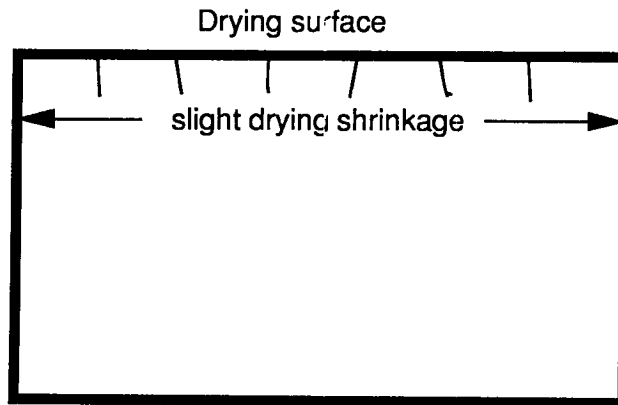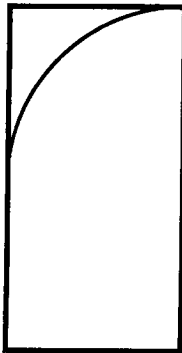
FIRST STAGE
Drying shrinkage and
fine cracking at
concrete surface.
No appreciable alkali-
silica reaction or
expansion.

slight drying shrinkage
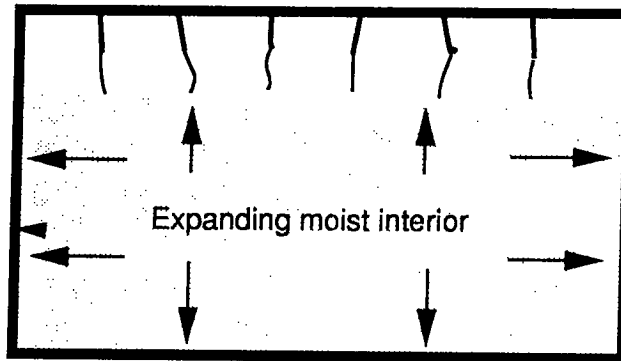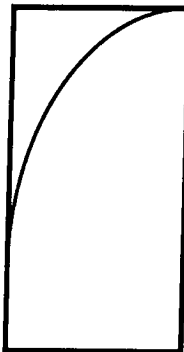
100   50

SECOND STAGE
Reaction ,expansion,
and microcracking in
interior at RH >80%.
Surface cracks grow
by expansion of concrete
in the moist interior. Soft
gel may exude into
surface cracks.

Expanding moist interior

100   50
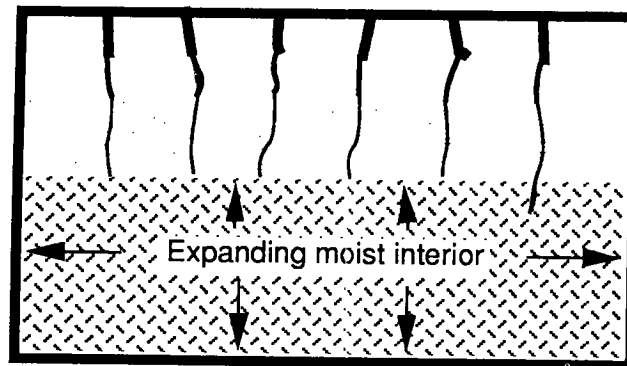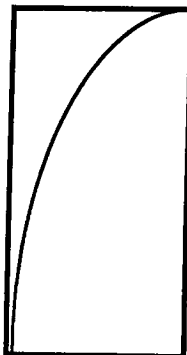
THIRD STAGE
Continued drying slows
reaction in zone
below surface. Continued
reaction and
microcracking in moist
interior causes
growth and widening of
surface cracks.

Expanding moist interior

The reaction will go to completion in the moist zone by depletion of either reactive silica
or alkalies. If the section is very deep, expansion continues and surface cracks continue
to grow. If the section is shallow, drying will stop the reaction and expansion. If a source
of moisture is available at the base, a more or less steady-state gradient to the surface
will develop so that reactions in the moist interior will go to completion.

Figure 5.2.1 Model for ASR Cracking in Concrete Pavements.

Equations 4.1.1 and 4.1.2 show how the reaction between NaCl and C_3A increases OH^- concentrations while that with $CaCl_2$ does not. Both may cause dissolution of calcium hydroxide to form Friedel's salt. Aside from the uptake of Cl^- to form chloroaluminates the major effects of these salts are the common ion effects and the effect of salts on ionic strength on the solubility of solid phases.

Chatterji has shown that NaCl can be even more aggressive than NaOH in causing ASR mortar bar expansions (81). Reactions of aluminates with chloride ions can convert NaCl solutions to NaOH solutions in the pores to increase pH to high values. In addition, there is the effect of salts on ionic strength and on solubilities of silica and calcium hydroxide. Instead of a common ion effect, the effect of different ions in solutions of strong electrolytes is to *increase* solubility of solid phases (82,22, 6c). For example, the rate of dissolution of quartz in water is increased by a factor of 67 in 0.1 N NaCl solutions (6d). Hence, silica reactivity is increased, and calcium hydroxide may dissolve more readily, which should increase transport and reaction rates. Both effects should increase the rate of formation of N+K-S-H gel in the reactive particle and also the rate of formation of C-N+K-S-H. Thus the rate of reaction in NaCl solutions should be accelerated, but that does not necessarily mean that the expansions should also increase. It has been shown that expansions increase at 100, 122, and 176°F (38, 50, and 80°C) (51,66,79), but decrease at 72°F (22°C) (80).

$CaCl_2$ in solution can also increase the ionic strength of pore solutions, but has very different effects from those expected from the common ion effect on the solubility of calcium hydroxide. $CaCl_2$ decreases OH^- ion concentrations (83) but apparently causes dissolution of $Ca(OH)_2$ and reactions to form complex salts (84). Mortars made with reactive opaline limestone developed cracks and expanded 0.1% in 5 weeks of accelerated testing at 122°F (50°C) in NaCl-saturated solutions after curing 28 days, followed by four weeks of leaching at 40°C in water (85). Companion mortars leached at 104°F (40°C) in 30% $CaCl_2$ solutions showed no expansions, or any sign of destructive ASR, up to 12 weeks. Differential thermal analysis (DTA) showed that prisms leached in $CaCl_2$ solutions were free of calcium hydroxide, whereas those leached in water contained large amounts. This lack of expansion without calcium hydroxide indicates that such processes are different from the safe reactions described by Powers and Steinour.

Electron probe microanalysis (EPMA) has been used by Chatterji et al. (66) to examine reacted particles of three different reactive aggregates in accelerated tests of mortar bars at 122°F (50°C) for 45 weeks after 27 days' curing at 73°F (23°C). Results with opaline flint aggregate showed that Na_2O, K_2O, and CaO had increased substantially in the silica particles and that the SiO_2 had increased in the paste outside of the particles. Mortars with 0% to 25% replacements of portland cement by a highly reactive pozzolan (diatomaceous earth) were tested under two reaction conditions at 122°F (50°C). Specimens were stored either in water, or in solutions saturated with respect to solid NaCl. XRD showed that mortars made with 25% pozzolan contained only about 10% as much calcium hydroxide as those made without pozzolan.

Specimens tested in water did not expand, probably because leaching of cement alkalies had stopped ASR at an early age. They contained tenths of percents of K_2O and Na_2O in the paste matrix despite possible leaching. Concentrations in the reacted particles were several percent. With 25% diatomaceous earth in the cement, alkalies were less concentrated in the reacted aggregate. Concentration gradients of CaO and SiO_2 showed that migration of SiO_2 from particles to paste, and CaO from paste into the particles, had occurred. K_2O and Na_2O contents in the reactive grains were less than 2.9% and 2.4% respectively, without pozzolan,

and 2% and 0.7% for specimens made with diatomaceous earth. Chlorine contents were only about 0.1% without pozzolan, and less with pozzolan.

Specimens made without pozzolan were heavily cracked after testing in NaCl solutions. With 25% diatomaceous earth, linear expansions were reduced but mortars still had a low degree of cracking. Na_2O was concentrated in the reactive grains, but less so in mortar containing pozzolan. The most remarkable effect with these specimens was the wider and much more uniform distribution of SiO_2, CaO, and Na_2O through the aggregate and into the paste, rather than the steep concentration gradients at the interfaces found in the other cases. The SiO_2 content (72-80%) inside the reactive grain was higher than without pozzolan (45-56%) and the CaO content inside the grain (13-22%) was lower than without pozzolan (27-52%). Reactions inside the reactive grains were apparently slowed by the pozzolan in the paste rather than accelerated by calcium hydroxide, as suggested by Chatterji. In the surrounding paste, however, the SiO_2 increased and CaO decreased more, and to greater depth, with the pozzolan than without. Paradoxically, the pozzolans seemed to increase the rate of reaction outside the grain while that inside decreased, which suggests that silica sources more remote from the observed zone participated in the reaction.

Na_2O contents inside the reactive grain reached 13.8% without and 11.7% with pozzolan, while chlorine contents were about 1% without pozzolan and 0.6% or less with pozzolan. Chatterji et al. concluded that the chloride in solution does not participate directly in the reaction, although the salt solution had large effects. They reasoned that during accelerated reactions at 122°F (50°C) dissolved silica must escape rapidly from the reaction zone, and that when calcium hydroxide is abundant, as in the absence of pozzolans or prior leaching, diffusion of silica out of the reactive grains is impeded while silica is precipitated as C-S-H close to the interface.

On the basis of such results, Chatterji concluded that the presence of solid calcium hydroxide, as well as reactive silica and alkali hydroxides, is necessary for destructive ASR (8,66,85,86),. In his 1989 paper (8) he summarized differences between Powers and Steinour's model and his proposed revision. In addition to concentration differences he notes that more alkali than calcium ions will follow hydroxyl ions diffusing into aggregate particles because of smaller sizes of the hydrated alkali ions. The two hypotheses have many features in common, but they are presented as diametrically opposed with respect to the role of calcium in the reaction. The essence of Powers and Steinour's conditions for safe reaction is not, as Chatterji presented it, that more lime than alkali initially penetrates the reactive silica, but that: 1) the rates of these processes permit escape of sufficient amounts of dissolved silica; and 2) high C/S ratio non-swelling products be formed both within the aggregate particles, and in the ASR gel in pores in the matrix. Chatterji's view was that the presence of calcium hydroxide is necessary to have *unsafe* reactions (in accelerated tests) because the diffusion of silica out of the reaction zone is controlled by formation, from the available Ca^{++}, of reaction products that impede diffusion. Diffusion of more water and ions into the zone than diffuses out causes expansion in both views of the process.

Although some of Chatterji's contributions may be highly significant with respect to the mechanisms of ASR and the role of soluble salts and pozzolans there are some complex and unresolved aspects. One of his criticisms of Powers and Steinour's analysis seems justified on the basis of this review:

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Chatterji concluded that in Powers and Steinour's model pozzolans cannot be very effective in control of ASR with unlimited external sources of NaCl. In these cases expansions appear to be controlled by factors that permit rapid escape of silica from reactive aggregate particles (8).

Powers and Steinour's analysis seems to apply well to situations in which alkali contents are not very excessive, whereas Chatterji has focused on results of tests at 122°F (50°C) with excess alkali as soluble salts. In this latter case, high alkali concentrations may dissolve silica so rapidly, and so limit Ca^{++} concentrations in the reaction zone, that non-swelling products cannot be produced. In that case the only way that pozzolans can be effective is to further limit the calcium in the reaction zone so that alkali can dissolve the reactive silica and allow it to diffuse or flow to sites where it is not confined. This requirement, that silica escape for a safe reaction, is not different from that in Powers and Steinour's model. But it is beyond the range of alkali contents they considered, and also extends the conditions for testing the effectiveness of pozzolans in preventing damage by ASR beyond those in ASTM C441.

If the lack of expansion is a result of accelerated dissolution of the aggregate and pozzolan, however, it appears that these mortars must have contained considerable alkali silicate solution and gel which has not been made non-swelling by reaction to C-N+K-S-H. If so, their mechanical properties during drying and rewetting need to be investigated to establish whether the reaction was actually safe. If the high ionic strengths of the salt solutions facilitate ASR transport processes to the point where ASR becomes actually non-destructive pozzolanic reactions without adverse effects, they can be very different kinds of "safe" reactions.

There is already some precedent for utilization of such high alkali concentration reactions in concretes made with alkali-activated binders (87) or geopolymers (88).

6 Concluding Discussion

This summary of mechanisms of damage to concrete by ASR has attempted to utilize and synthesize the results of both older and current research. The framework of selected information includes the most important elements of reaction chemistry and physical chemistry as well as very practical engineering concerns related to laboratory testing, and performance of concrete pavements and structures in field environments. Data on several crucial points have been found to be very limited, or non-existent. On other points it has been possible to use data to develop relationships beyond the intent of the original authors, to whom we are much indebted.

In the following conclusions, specific mechanisms of damage which need further research are identified. In Part II, descriptions of gaps in our knowledge of all aspects of ASR will be presented.

1. The basic reaction chemistry of the swelling and dissolution of disordered silica in alkali hydroxide solutions is reasonably well understood. However, little comparable work has been done with calcium ions present.

    Portland cement hydration releases sodium and potassium ions into pore solutions so that concentrations stabilize after several weeks as essentially alkali hydroxide of 0.7 mol/L per percent equivalent Na_2O in the cement, at 0.5 water/cement ratio. During this review, this relationship was extended to include variations of w/c, which involve variable amounts of alkali retention by the cement gel. It then became possible to develop equations to estimate reductions of hydroxyl ion concentrations resulting from dilution and pozzolanic reactions when cements are replaced by pozzolanic fly ashes in order to control ASR. The validity of these equations needs to be experimentally investigated.

    The presence of calcium ions from solid calcium hydroxide produced by cement hydration does not greatly affect the composition of the mainly alkali hydroxide solutions in mortars and concretes, but it has a large effect on ASR and pozzolanic reactions. Relatively little is known about these reactions and the compositions and properties of the reaction products formed within the reactive aggregate. Studies by SEM-EDX with only a few reactive aggregates have shown that pore solutions containing alkali and calcium ions diffuse into the reactive aggregate particles. It is concluded that OH^- and alkali ions and water cause swelling and that the swollen silica can react with calcium ions to form calcium alkali silicate hydrate gel in the solid state, regenerating alkalies in the process. Silica also dissolves to form alkali silicate solutions or gels which imbibe water and escape from the reaction zone. Calcium ions cause precipitation of calcium silicate hydrates containing alkalies in these gels. The effects of the reactions depend on the compositions of the reaction products, which in

turn depend upon the concentrations of ions in solution and their rates of transport to and from the reaction zone.

These processes have been shown to be greatly affected by the concentrations of soluble salts, and by the presence of pozzolans. We need to understand how different concentrations of alkali and calcium ions influence the rates and effects of the reactions within aggregate particles, and we need much better measures of reactivities of real aggregates under realistic conditions.

2. Many gels that have been analyzed have compositions that can be regarded as simple mixtures of two components: 1) an alkali-silicate-hydrate gel; and 2) calcium-alkali-silicate-hydrate gel. Data analysis shows that the compositions of each component appear to remain nearly constant as their proportions vary over the compositional range of ASR gels from 40% to 83% SiO_2 on an anhydrous basis. The ASR gel must contain at least 53% CaO to be free of swelling component. These findings need to be confirmed with additional reactive aggregates, and correlated with studies of properties of such gels.

3. Cracking of mortars occurs at very small expansions (less than about 0.03%), long before maximum expansions resulting from copious production and swelling of ASR gel are reached. Despite the apparent importance of early reaction control, there are few, if any, measurements of volume changes of real reactive aggregates at stages of swelling and reaction (prior to dissolution) that cause initial cracking of mortars. Such early indicators of reactivity could be very useful for aggregate characterizations as well as testing the effectiveness of control measures.

4. Although cracking may be initiated by expansion of aggregate particles, swelling pressure of gels is a major ASR damage mechanism for enlargement of cracks. Reliable data for swelling pressures produced by ASR or synthetic gels made with representative calcium contents, and brought to equilibrium RH before exposure to a higher RH, are almost nonexistent. As a result, little is known about the effects of compositions of ASR gels on swelling or swelling pressures, or the effect of stress on reactions.

Stresses of only 50 psi (0.34 MPa) have been shown to delay the beginning of expansions and cracking of mortars or to stop expansions already began. Expansions of concretes against 360 psi (2.5 MPa) increased the restraining stress to even higher values over 500 psi (3.5 MPa). In accelerated tests of reinforced concrete beams ASR expansions developed compressive stress of 580 psi (4 MPa) and excessive strains in the reinforcing steel. Swelling pressures at reaction sites are balanced by tensile stresses in the remaining concrete, and by external restraint, and are relieved when cracking occurs, or by gel flow and creep. Despite the great potential for damage to concrete by ASR gels, we have very little data on their response to stress under known conditions.

5. Work under SHRP C-202 showed that sealed concretes with ASR expanded and developed pressures against triaxial (hydrostatic) restraint. At about 300 psi (2 MPa) expansion rates are small, or slightly negative. The sum of the rates of expansion, and creep in compression, produce zero net strain rates. Increased stress at reaction sites can 1) increase creep of the paste in the matrix 2) increase the rate of dissolution of silica 3) reduce osmotic swelling of gel and 4) cause gel to creep or flow from the

reaction sites through pores and/or microcracks. Expansive pressures at reaction sitesare balanced by tensile stresses in the remaining concrete and any external restraint.

In practice, the situation is complicated by stresses caused by shrinkage of the drying surfaces. Shrinkage is restrained by, and causes compression of, the moist interior concrete. These long-term stresses cause tensile creep and growth of cracks in the drying surfaces, and compressive creep of the interior. Expansions and cracking of the concrete in such situations are then affected not only by external restraint, but by creep and the complex, time-dependent stresses produced by drying. These factors complicate analysis to determine the effects to be expected from the use of aggregates of different reactivities, or the future course of deterioration of existing structures, or the probable effects of remedial measures. This is at least partly because, until now, there has not been a single structure that has been fully instrumented to determine drying shrinkage, expansion, and creep, under controlled restraint, temperature, moisture gradient, and drying conditions. Such tests have been done in SHRP C-202.

6. Powers and Steinour's model for ASR and criteria for safe and unsafe reactions are generally supported by recent research but have been questioned because expansions and cracking (unsafe reactions) have occurred even when the calcium contents of the reacted particles are 27% to 52% CaO (anhydrous basis). In the present study it is concluded that CaO contents higher than 53% are required in ASR gels to eliminate the swelling component. Hence such data do not seem inconsistent with Powers and Steinour's criteria. However, they did not specifically consider the effects of alkali/silica ratios above those for pessimum proportions for maximum expansions, or external sources of alkalies, such as soluble salts, on the effectiveness of pozzolans in controlling ASR expansions, or the formation of Friedel's salt ($C_3A \cdot CaCl_2 \cdot 10H_2O$), or other complex salts, from chloride salts.

Direct verification of Powers and Steinour's model would also require data that show the effects of changes of alkali concentrations in pore solutions in reacting mortars on the calcium concentrations and compositions and properties of the ASR products. Alkali and hydroxyl ion concentrations are commonly measured, but appropriate data for calcium concentrations is almost nonexistent and may be impossible to obtain because of the difficulty of determining concentrations at the reaction interface. Solutions expressed from large pores in the matrix must have higher calcium and lower silica concentrations than in the reaction zone.

Powers and Steinour's model for the effect of pozzolans on ASR by reduction of alkali and hydroxyl concentrations appears valid for some mineral admixtures, such as calcined kaolin and some silica fumes, but other factors appear to be more important for fly ash and slags. These materials appear to facilitate the reactions of the aggregate so that it softens and dissolves without development of excessive swelling pressures. Requirements for safe reactions by this mechanism have not been defined, and appear to be strongly influenced by ionic strength in salt solutions as well as by characteristics of pozzolans.

7. Accelerated tests of mortars in water and in NaCl solutions have shown that reactions and expansions are greatly accelerated by that salt, and that pozzolans can still be effective in reduction of expansions and cracking. However, it has been suggested that pozzolans cannot be effective with unlimited alkali available (as salts) by forming high calcium content, non-swelling, reaction products because they impede escape of

dissolved silica. Instead, pozzolans must limit formation of such products to permit dissolved silica to escape. Very little is known about this kind of "safe" reaction to dissolve the reactive aggregate without forming non-swelling products or the properties of the resulting mortars or concretes.

In such tests the reactions between C_3A, $Ca(OH)_2$, and chloride ions that produce Friedel's salt also increase the pH so that the severity of the test of the aggregate depends on the C_3A content of the cement. Attempts by researchers to study these systems have been complicated by the effects of uncontrolled leaching of ions from test specimens, making it difficult to determine whether or not chloride ions have participated in the ASR, as well as in complex salt formation. In addition, the ionic strength of the solutions is increased so that solubilities of solid phases without common ions are increased. These effects require further research in order to understand the effects of different pozzolans on ASR under a variety of field and accelerated test conditions, and to relate test results to field performance.

Appendix A. Effect of Fly Ash on Hydroxyl Ion Concentrations

Use of Equation 2.2.1 and a few reasonable assumptions make it possible to calculate approximate values for concentrations of solutions derived from cement blends with pozzolanic fly ashes, after most of the portland cement has hydrated, as follows.

1) Since portland cement reacts much more rapidly than pozzolanic fly ashes, the reactions may be assumed to occur in sequence: a) reaction of the portland cement to a nearly constant concentration; followed by b) partial reaction of fly ash.

2) That nearly constant concentration is given by Equation 2.2.1 with two corrections. Assuming no pozzolanic reaction of the fly ash, and that the water/solids ratio is $w/(c+p)$, dilution of cement by fly ash increases w/c to:

$$w/c = [w/(c+p)](c+p)/c \qquad (2.2.3)$$

The second correction is based on the fact that about 70% of the alkali in fly ashes is contained in glassy phases (27a) and is released only by pozzolanic reaction, but that some is released earlier. We assume that 30% of the total alkali of the fly ash, $(Na_2O_{eq})_{fa}$, is released along with, and adds to, that coming into solution from portland cement hydration. Since the amounts in Equation 2.2.1 are expressed in percentages of cement weight, this increase of available alkali is expressed as:

$$Na_2O\% \text{ from fly ash} = + 0.30(p/c)(Na_2O_{eq})_{fa}\% \qquad (2.2.4)$$

3) Pozzolanic reactions between fly ash, calcium hydroxide, and additional alkalies in the pore solution are assumed to produce a product similar to the nonswelling component of ASR gels. In the next section this is shown to have a composition of about $N_{0.16}C_{1.4}SH_x$. We assume that the remaining 70% of alkali in the fly ash is released from the percentage reacted, and that each mole of SiO_2 from the fly ash reacts initially with the alkali released, $0.7(Na_2O_{eq})$, calcium hydroxide, and water to produce:

$$0.7yNa_2O + SiO_2 + 1.4Ca(OH)_2 + (x-1)\,H_2O \rightarrow$$
$$(NaO)_{0.7y}(CaO)_{1.4}SiO_2x\,H_2O \qquad (2.2.5)$$
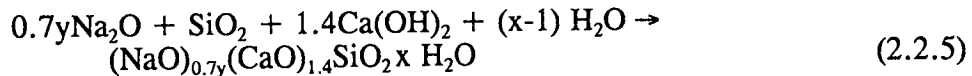
where:

$$y = (Na_2O\%/62)/(SiO_2\%/60) \text{ moles of alkali/mole of silica} \qquad (2.2.6)$$
in the fly ash

4) Then the amount of alkali removed from the pore soluton to complete the pozzolanic reaction is:

$$N_r = (0.16\text{-}0.7y) \text{ mole } Na_2O_{eq}/\text{mole } SiO_2 \text{ reacted}$$

or:

$$N_r = (0.16\text{-}0.7y)(62/60)(SiO_2\%/100)(p/c)(p\%/100) \qquad (2.2.7)$$

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in terms of grams of alkali removed/gram of cement, in which p% is the percentage of fly ash reacted. The increase in alkali content given by Equation 2.2.4 then needs to be reduced by $100N_r$:

$$Na_2O\% = (Na_2O_{eq})_{pc}\% + 0.30(p/c)(Na_2O_{eq})_{fa}\% - 100N_r \qquad (2.2.8)$$

5) The effect of evaporable water content reduction by hydration of the portland cement has been included by our use of Equation 2.2.1. The pozzolanic reaction further reduces the water content. The value of x in the product is not known, but is assumed to be similar to that of lower C/S ratio products of C_2S and C_3S hydration, about 3.0 (27b). If w_{np} is the reduction of w/c by pozzolanic reaction in grams of water per gram of cement, then:

$$w/c = [w/(c+p)](c+p)/c - w_{np} \qquad (2.2.9)$$

where:

$$w_{np} = (3-1)(18/60)(SiO_2\%/100)(p/c)(p\%/100) \qquad (2.2.10)$$

Equations 2.2.8, 2.2.7, 2.2.9, and 2.2.10, are then substituted into Equation 2.1.1:

$$[OH^-] = 0.339(Na_2O\%)/(w/c) + 0.022 \qquad (2.2.1)$$

to calculate hydroxyl ion concentrations when pozzolanic fly ashes are used.

Appendix B. Compositions of Alkali-Silica Reaction Gels

The following analysis of the EPMA data shows that ASR gels containing calcium appear to be simple two component mixtures, in which the swelling component is an alkali silicate gel (or sol) of low and nearly constant alkali-silica ratio, which should have nearly constant swelling characteristics. These ASR gel compositions have been compared with CaO-Na_2O-SiO_2-H_2O gels prepared by Kalousek (16). Plots of CaO content data, shown in Figure 2.3.1 as anhydrous weight percentages of $CaO + SiO_2 + Na_2O + K_2O$ contents (as 100%), were well represented by the straight line:

$$CaO\% = 103 - 1.24\ SiO_2\%$$

(2.3.1)

On the same diagram the 100% line is given by:

$$CaO\% + Na_2O\% + K_2O\% = 100 - SiO_2\%$$

(2.3.2)

which is a line of slope -1 intersecting the SiO_2 axis at 100%. The CaO% line has a slope of -1.24 and reaches 0% CaO at 83% SiO_2 and 17% ($Na_2O + K_2O$). These are the highest alkali content and lowest CaO content gels, and are apparently in near equilibrium with high alkali content solutions and calcium hydroxide. At lower silica and alkali contents, CaO contents increase linearly as SiO_2 decreases.

The equations were solved for the C/S and (N+K)/S (weight) ratios at various alkali contents over the range of data 50 to 83% SiO_2, with the results given in Table B-1.

Table B-1. Compositions of ASR Gels (in mass percent) in Concrete (36) and Synthetic Gels Prepared by Kalousek(16)

$Na_2O\% + K_2O\%$	C/S	C/S Molar	(N+K)/S
11	0.524	0.56	0.188
12	0.408	0.44	0.192
13	0.304	0.33	0.195
14	0.213	0.23	0.197
15	0.130	0.14	0.200
16.92	0.000	0.00	0.204

These (N+K)/S weight ratios are all very close to the Glasser and Kataoka (3,10) value of 0.196 for sodium silicate gels before dissolution, calculated from the molar Na_2O/SiO_2 ratio of 0.19 (see Equation 2.1.1). They also observed that reactive silica produced both gel and C-S-H (containing some alkali) in the presence of calcium hydroxide in solution.

Equations 2.3.1 and 2.3.2 can be simply explained if it is assumed that the ASR gels are composed of N+K-S-H gel which is 83% SiO_2 and 17% (Na_2O + K_2O), and an amount of C-N+K-S-H required to account for the calcium content. Mass balance calculations can be done at any point over the data range since these equations are linear but, if the C/S and (N+K)/S ratios of the C-N+K-S-H are allowed to vary, an additional assumption is required to calculate phase compositions and proportions. Trial calculations made at the opposite end of the data range (50% SiO_2) with different assumed (N+K)/S weight ratios in the C-N+K-S-H show that a good fit to the data and reasonable values are obtained over only a narrow range of (N+K)/S. Over the (N+K)/S weight ratio range from 0.16 to 0.17, calculated molar C/S ratios in the C-N+K-S-H range from 1.23 to 1.58, and weight fractions of N+K-S-H range from 0.17 to 0.27. This is greatly reduced from 1.00 at 83% SiO_2 with 0% CaO.

If 0.165 is taken as the approximate value for (N+K)/S for the C-N+K-S-H in these ASR gels, and 0.23 as the weight fraction of N+K-S-H at 50% SiO_2, the linear relationships indicate that at 40% SiO_2 the ASR gel would consist entirely of C-N+K-S-H of a composition (by weight) of 6.6% (Na_2O+K_2O), 52.6% CaO, and 40% SiO_2 (exclusive of water). On a molar basis, assuming the only alkali is Na_2O, as in Kalousek's data, this composition is $N_{0.16}$ $C_{1.4} SH_x$. The weight percentage of this alkali calcium silicate hydrate in the ASR gel between 40% and 83% SiO_2 is then given by:

$$(C\text{-}N+K\text{-}S\text{-}H)\ \% = 2.32\ (83 - SiO_2\%).\tag{2.3.3}$$

Figure 2.3.2 shows the percentages of both the C-N+K-S-H and N+K-S-H gels for ASR gels calculated, with these assumptions, over the range of SiO_2 contents from 40 to 83%. There were no data at higher SiO_2 contents because all alkali-silica gels contained 17% (Na_2O+K_2O).

The important result of this analysis, on an anhydrous basis, is that for such ASR gels to be free of the swelling component the CaO content must be more than about 53% and the SiO_2 content must be less than 40%.

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Part II: Gaps in our Knowledge of Alkali-Silica Reactions in Concrete

1 Introduction

Gaps in our knowledge of the mechanisms of damage to concrete by ASR limit our ability to predict accurately or to control:

1. the effects of different reactive aggregates in concrete and

2. environmental effects on aggregate reactivity and effects in different concretes in different applications.

This lack of predictability limits our ability to relate chemical tests or other characteristics of aggregates, or mortar test results, to performance of potentially reactive aggregates in field concrete. It stems from the wide ranges of aggregate reactivity, chemical environments, rates of reaction, and reaction product compositions as well as the response of the concrete structure to expansive stress and environmental changes. The mechanisms of damage include not only the reaction chemistry and expansion processes, but also how the concrete dries, shrinks, and creeps under expansive stresses and external restraint in various applications. ASR cracking and disintegration of concretes depend on the nature of the reaction products and rates of reaction of the reactive particles, relative to the rates of stress relief processes, and how environmental factors and stress relief affect the rates of reaction. Our ability to control such processes improves with our knowledge of how they work.

In section 6 of Part I of this report, seven areas of needed research on mechanisms were identified:

1. The role of calcium in the reaction chemistry

2. The compositions and properties of ASR gels as two-component systems

3. Volume changes of real reactive aggregates at stages of swelling and reaction that cause initial cracking

4. Swelling pressures of ASR gels of representative compositions brought to equilibrium RH before exposure to a higher RH, and their response to stress under known conditions

5. The effects of mechanical restraint of concrete on ASR and expansions under known moisture and temperature conditions, analysis of structural element behavior with aggregates of different reactivities, and probable effects of remedial measures

6. Direct examination of Powers and Steinour's model for the effects of different pozzolans on ASR control in terms of pore solution chemistry may be very difficult, but requirements for safe reactions can probably be established by SEM-EDX and empirical relationships

7. "Safe" reactions with pozzolans in accelerated tests in salt solutions, and the relationship of these test results to the effects of different pozzolans and reactive aggregates under a variety of field conditions must be examined with respect to concrete properties

Results of such studies should be synthesized in practical predictive models for concrete performance.

2 Rapid and Reliable Test Methods to Identify Potentially Reactive Aggregates in Concrete

Since the first recognition by Stanton (1) of ASR in the late 1930s, a need has existed for rapid and reliable test procedures to identify susceptibility of aggregates to expansive ASR. The early test procedures, which are still widely used today, are ASTM C 289, Potential Reactivity of Aggregates (Chemical Method), and ASTM C 227, Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar-Bar Method).

Early researchers concluded that excessive expansion due to ASR could be avoided with the use of cements with alkali levels not greater than 0.6% as equivalent Na_2O. Until about 1980, it was believed that the necessary information and testing techniques were available to avoid distress associated with ASR in field structures (2). However, it was recognized even at that time that certain volcanic materials may produce abnormal expansions with low-alkali cements in ASTM C 227 tests. Nevertheless, the belief persists that low alkali cement would alleviate ASR problems in field structures. It persists primarily because test periods greater than 12 months were required to reach the expansion criteria identified in the ASTM standards.

Neither the ASTM standard specifications for concrete aggregates, C 33, nor for portland cement, C 150, specify maximum ASR expansions in C 227 or by any other test, although an Appendix in C 33 provides nonmandatory information. It explains that the line of demarcation between nonreactive and reactive combinations is not clearly defined, but that expansion is generally considered excessive if it exceeds 0.05% at 3 months or 0.1% at 6 months. Specifications for pozzolans, C 618, and blended cements, C 595, contain specific expansion limits at specified ages.

Although these tests have been fairly successful in identifying materials that react rapidly with high alkali cements, such as opal, glassy to cryptocrystalline volcanics, chalcedony-bearing aggregate, and certain phyllites, they fail to adequately identify slowly reactive aggregates such as granite gneisses, metagraywackes, and quartzites, or those that react with low alkali cements (3).

In short, it was believed that the ASTM C 227 mortar bar test was an accelerated procedure that would identify most, if not all, potentially reactive cement-aggregate combinations when, in fact, it allowed numerous potentially reactive aggregates to appear innocuous.

A further complicating factor has been the discovery that the storage of test specimens over water in sealed containers at 100°F (38°C), and cooling to about 73°F (23°C) for measurements, leads to leaching of alkalies from the mortar bars, thereby reducing potentials for expansive ASR in the test (3). Slowly reacting aggregates therefore are more liable to escape detection.

Storage conditions and reliability of the ASTM C 227 mortar bar test and CSA.A.23.2.14A concrete prism test have been improved (4). New container and reactor designs reduce relative humidity gradients and maintain the temperature constant at 100°F (38°C), so that

leaching of alkalies is avoided in C 227. In CSA.A.23.2.14A, the alkali level as equiv. Na_2O is 1.25%. With slowly reactive aggregates, a higher cement content is used, i.e., 691 lb/yd^3 (410 kg/m^3). The time required for the expansion limit of 0.04% is 2 months for a highly reactive aggregate and 6 months for a slowly reactive aggregate. With 523 lb/yd^3 (310 kg/m^3) of cement, an expansion of 0.046% was measured after 10 months for the slowly reactive aggregate. Although this result was an improvement in the time required for identifying slowly reactive aggregates, these tests remain time-consuming.

The ASTM C 289 "quick chemical" test also was found to identify the more highly reactive aggregates but, subsequently, it was found not to be capable of identifying slowly reactive materials (5). Furthermore, it did not identify, by itself, potentially reactive or nonreactive cement-aggregate combinations.

ASTM procedures C 227 and C 289 are recommended to be used in conjunction with a third procedure, ASTM C 295, Petrographic Examination of Aggregates for Concrete, to determine potential for expansive ASR in highway structures. The latter is tedious, subjective to a major extent, and fully dependent on the capabilities of the petrographer. It is, however, rapid relative to the other procedures.

Service record is a fourth method recommended for assessing potential of an aggregate for expansive ASR. Although seemingly the most definitive of the four methods noted, all of the required background information, such as cement alkali level, are usually not available. Thus, one must assess whether the aggregate used with another cement in a different concrete will perform in similar fashion to that with the service record.

In summary, the cumulative effect of utilizing the four procedures noted above leaves a serious need to develop a single rapid and reliable test procedure to identify potential for expansive ASR of cement-aggregate combinations. Existing methods are tedious, inaccurate, and may require extended periods of time before assurance is obtained that a particular cement-aggregate combination is innocuous.

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3 Moisture Conditions of Concrete in Highway Structures

One of the three requirements for expansive ASR to occur in concrete is sufficient moisture for absorption by gel reaction products. It is well known that large expansions can be developed by mortar bars and concrete prisms stored at 100% relative humidity conditions, particularly at elevated temperatures. It also has been observed in laboratory investigations that expanded test specimens may not exhibit abnormal cracking until partial drying occurs (1). Whether one is dealing with expansion due to ASR, or distress associated with ASR, the moisture condition of the concrete in question is of fundamental importance in understanding the effects of ASR in highway structures.

The moisture condition of concrete under which ASR and associated distress may or may not develop appears to be best defined in terms of relative humidity (RH) of the concrete in question. Recent work at CTL has shown that expansive ASR occurs when RH values of concrete exceed about 80%, referenced to 70 to 75°F (21 to 24°C)(2). However, little or no data have been available for RH levels and gradients in highway structures.

CTL has developed a method of determining the RH of samples of concrete from specified depths and locations in highway pavements, bridge decks, columns, etc. Application of the method would appear to fill a major gap, not only in our knowledge of development of ASR in field structures, but also in our knowledge of environmental or climatic effects on highway performance, including shrinkage, warping, curling, and creep.

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4 Effects of Salts and Direct Participation of Chloride Ions in Alkali-Silica Reactivity

It has been considered that the specific chemical agent initiating ASR and most responsible for the effects is the OH^- ion. In the usual explanations of the ASR reaction it is considered that OH^- ion "depolymerizes" the reactive silica, i.e., breaks some of the covalent bonds connecting adjacent silica tetrahedra in the reactive aggregate thus permitting "mobilization" of the silica and subsequent precipitation of alkali silica reaction product gel, as discussed in Section 2.1 of Part I. That this idea is fundamentally sound has been demonstrated in recent studies at Purdue University and the University of Illinois, where magic angle Si^{29} NMR has been used to study the process of formation of reaction product. The results obtained in these studies reveal that the original "Q_4" configuration of the reactive aggregate (indicative of covalent Si-0-Si bonding between adjacent tetrahedra) for all the four apices is transformed to a "Q_2" configuration indicative of only two such covalent bonds, i.e. linear chains or rings of tetrahedra, in the reaction product gel.

According to this picture, the effect of the specific alkali cation on the reaction is incidental; that is, the alkali merely balances the resulting excess negative charge. Of course the specific alkali ion incorporated into the gel may make a difference with respect to its sorptive or other physical properties.

Since most researchers have assumed that the OH^- ion is the only anion that plays any role in ASR attack, the influence of added salt (e.g., NaCl) was assumed to be confined to the effect of increased OH^- ion concentration resulting from the conversion of NaCl to NaOH in the cement paste pore solution. Incorporating NaCl in the mix water causes formation of Friedel's salt ($C_3A \cdot CaCl_2 \cdot 10H_2O$) and increases pH, as discussed in Section 4.1.4 of Part I. The phenomenon has been specifically studied by Nixon et al. (1), who concluded on the basis of extensive studies that:

> "Introduction of sodium chloride or synthetic seawater to a cement paste, mortar, or concrete at the mixing stage results in an elevation of the hydroxyl ion concentration of the pore solution to a level similar to that produced by a portland cement with an equivalent alkali level. This in turn can increase the likelihood and severity of damage from alkali-silica reaction if the mortar or concrete contains reactive aggregate. The extent of the effect is in line with that produced by an equivalent amount of alkali in the cement."

However, there have been indications and experiments reported by Chatterji and co-workers in Denmark, that the presence of chloride has a major effect on ASR, independent of any possible conversion to alkali hydroxide in the pore solution. Sections 4.1.4 and 5.3 of Part I provide background.

In 1978, Chatterji (2) developed an accelerated test method for ASR involving placing mortar prisms in saturated NaCl solution at 50°C (122°F). Significant expansion occurred with

reactive aggregates; in contrast, similar mortar bars placed in water did not expand, but leaching of cement alkalies prevent valid comparisons. In 1983 Thaulow and Olafsson (3) evaluated this test method against the standard ASTM mortar bar method and others, and found reasonably good agreement. Jensen et al. (4) compared the salt mortar bar method with a non-standard German test method and found the salt method superior.

In 1986 Chatterji et al. (5) attempted to explain ASR effect brought about by exposure to NaCl on the basis that Na^+ from the salt and Ca^{2+} from $Ca(OH)_2$ in the cement paste were simultaneously penetrating the reactive aggregate. This mechanism does *not* require the conversion of the sodium chloride to sodium hydroxide. Nor does the proposed mechanism involve penetration of Cl^- ions into the reactive aggregate, which Chatterji et al. showed did not occur to a significant extent in their tests.

These authors considered that this mechanism would explain expansion taking place in systems of calcium hydroxide, sodium chloride salt, reactive silica, and water, presumably irrespective of the conversion of some or all of the dissolved chloride to dissolved hydroxide ions.

In line with this idea, Chatterji, Thaulow, and Jensen (6) studied expansions in mortar bars made with reactive aggregate and low alkali cement immersed in various alkali salt solutions of the corresponding hydroxides. Expansion recorded in a given kind of salt solution increased with increasing concentration of the salt. Although these authors recognized that some conversion of the alkali salts to alkali hydroxides in the solution had undoubtedly occurred, they considered the evidence indicated that alkali salts, rather than any possible alkali hydroxide, were the actual attacking components in these ASR responses. Later, the same authors called attention to some practical implications of this proposed mechanism (7).

Kawamura and associates in Japan proposed a perspective on chloride effects different from either the "conversion to alkali hydroxide" school or the "alkali salt attack" school. In a 1989 paper, Kawamura, Takemoto, and Ichise (8) studied the effect of various concentrations of NaCl added to the mix water in the presence of reactive aggregate containing mortars in which steel was embedded. They found both Cl^- and OH^- were removed from the pore solution, but that the uptake of Cl^- was less than that of OH^-. This led to a net increase in the Cl^-/OH^- ratio in the pore solution, and consequent acceleration of the corrosion on the steel.

In a 1990 paper, Kawamura and Ichise (9) reported that expansion of Beltane opal-containing mortar bars increases with content of either sodium or calcium chloride added in the mix water. Marked concentration changes were found for the chloride ions in the pore solution, especially for NaCl between 12 and 24 hours. These changes were taken to indicate that some chloride ions entered into very rapidly-forming ASR reaction product, in addition to that used to form Friedel's salt. A major acceleration of the ASR apparently accompanies the uptake of the Cl^- ions as hydroxyl ions were released by both cement hydration and chloroaluminate formation. There was a somewhat slower uptake of Cl^- ions from pore solutions of $CaCl_2$ bearing reactive mortars but even with $CaCl_2$, there was a distinct acceleration of ASR over the corresponding chloride-free reactive mortar. Indeed, as Kawamura and Ichise pointed out, this ASR acceleration occurs with $CaCl_2$ despite the fact that addition of $CaCl_2$ actually reduces the OH^- ion concentration in the pore solution.

Unfortunately, these data were flawed by leaching of ions from the specimens made with reactive aggregate. The evidence for direct participation by chloride ions is not strong, but the strong effects of chloride salts on expansions are well documented.

In 1989, Chatterji (10) called attention to the importance of ionic strength of the solutions; stating that "OH⁻ ions penetrate reactive silica...in amounts increasing with pH and ionic strength of the solution." This salt effect on activity coefficients (11) and solubilities (12) is well known in physical chemistry but is not commonly considered in research on ASR. It needs to be systematically investigated especially with respect to chloride salts.

The consequences of these ideas on our perceptions of the hazards involved when chlorides enter concretes are of the greatest importance. There are obvious implications with respect to highway concrete practice. All of our concrete bridges in the frost zone are being subjected to major dosages of applied chloride salt each winter. Many highway structures in states like Florida are exposed to salt spray. The necessity for protection of steel against corrosion is well appreciated, but it seems one must seriously consider the effects on ASR as well as the effects on steel corrosion. The use of pozzolans to control ASR may also aggravate the steel corrosion problem.

Even worse, in current generation "fast track" pavement construction practices in many states, very liberal dosages of $CaCl_2$ containing accelerators are used to get the desired fast-tracking effect. In the light of the preliminary and as yet imperfectly understood information available on the effects of chloride on ASR, this might turn out to be a very dangerous practice.

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5 Role of Sulfate Reactions Accompanying Expansion Caused by Reactivity

In most modern cements, the alkali present is mostly in the form of potassium sulfate or potassium calcium sulfate, although smaller amounts of sodium sulfate and of both alkalies substituted in C_3A and C_2S may also be present. Most of the alkali and alkali-calcium sulfates are quickly dissolved in concrete mix water.

Diamond and Penko (1) recently detailed the mechanism by which alkali sulfates are converted to the corresponding alkali hydroxides in the pore solution. Conversion takes place rapidly after the interground gypsum has been completely dissolved. The gypsum does not dissolve passively, but only in response to removal of SO_4^{2-} ions from solution by ettringite formation from C_3A reactions. Gypsum dissolved to maintain an almost constant level of solution sulfate concentration. The start of conversion to hydroxide was triggered by exhaustion of the gypsum, i.e., inability to continue feeding sulfate ions to the solution. Rapidly afterward, sulfate ion concentration declined and hydroxyl ion concentration increased on a mole-for mole basis until the sulfate was essentially exhausted from the pore solution.

In 1989 Wieker et al.(2) showed that if concrete was steam cured (exposure to 194°F (90°C) for 13 hours), this sulfate for hydroxyl ion conversion did not occur. On cooling to room temperature, the sulfate ion concentration actually increased for some days, then slowly and incompletely declined over a period of months. Hydroxyl ion increase was thus delayed and the long-term concentration substantially reduced.

This effect is implicated in late cracking found in steam cured concretes by various workers. This late cracking is apparently due to the delay in ettringite formation, which in turn is a consequence of the early steam curing treatment. However, it is possible that both ASR and late ettringite formation are jointly responsible.

In reviewing the older literature on interactions between sulfate, especially alkali-bearing sulfates and ASR, one is struck by the interrelationships exhibited. For example Mehta (3) in 1978 investigated the effects of additions of various salts added to the mix water of reactive aggregate-containing mortars made with low alkali cement. He found that sodium sulfate had the greatest influence, increasing the expansion from negligible (about 0.02%) to almost 0.60% by 28 days. Lesser effects were observed with sodium chloride and carbonate and with the potassium salts of these anions.

In the same year French and Poole (4) studied petrographic evidences of reaction between certain porous cherty dolomites and cement paste solutions. They found ASR gel rims surrounding the cherts and quartz grains, extensive microcracking in these areas, and gypsum. These authors stressed the importance of a reaction linking calcium hydroxide, gypsum, and dissolved sulfate and hydroxyl ions, viz:

$$Ca(OH)_2 + SO_4^{2-} + 2H_2O = CaSO_4 \cdot 2H_2O + 2OH^-$$
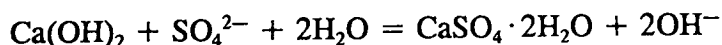
While the reactions taking place with this aggregate were unusually complex, involving dedolomitization of the carbonate and ettringite formation (i.e., sulfate attack) as well as ASR on the silica, the authors indicated that "...the presence of gel-filled cracks linking silicate and sulfate grains suggests that these grains are important in the reactions."

In 1980, the link between ASR and sulfate attack was specifically explored in a paper by Pettifer and Nixon (5), who found a number of cases where both occur simultaneously. These authors suggested that sulfate attack on the concrete by alkali sulfates drawn into the concrete from exterior sources or concentrated locally by drying may promote ASR — the sulfate precipitating to form ettringite (e.g., participating in sulfate attack), and at the same time correspondingly increasing the OH^- ion concentration of the pore solution, thus initiating or facilitating ASR. The field petrographic evidence that this combination of unfortunate circumstances indeed occurred in the concretes examined seems very strong.

The practical importance of conversion of alkali sulfates to alkali hydroxides with respect to possibility of ASR was stressed by Veronelli and Calleja (6). These authors concluded that low alkali cements are not enough in avoiding ASR when external sources of sulfates (and chlorides) are in contact with concrete. Pozzolanic cements are recommended as they are able to take up the alkalies generated.

The intimate interrelation of alkali (and other) sulfates to alkali hydroxides, and the interconversion of the two in solution under some circumstances seems to be clearly established. The clear link between the two are evidence in those cases where ASR and sulfate attack due to late ettringite formation are intertwined. Steam-cured concrete often used on highway structures may be well at risk from such interrelated effects. Detailed study of this gap in our information on ASR seems certainly justified from a purely practical point of view.

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6 Measurement of Aggregate Reactivities Unimpeded by External Diffusion Processes

In order to understand mechanisms of ASR, and to be able to model and predict performance of aggregates in concrete, researchers need data for intrinsic reaction rates of representative aggregates in tests unimpeded by diffusion (1). Reactions between aggregates and pore solutions in mortars and concretes are slowed by diffusion of moisture and ions in the pores in the matrix. Furthermore, initial reaction rates, which may determine the course of further reaction, may be relatively rapid but are not easily measured in mortar, nor are they readily related to mortar expansions or other properties. Nevertheless, the intrinsic reaction rate is probably the most important characteristic of reactive aggregates.

The lack of appropriate data on representative aggregates has been confirmed during the literature review. There are very limited amounts of SEM-EDX data on the progress of ASR as discussed in Sections 4.1 and 5.3 of Part I. It was expected that some usable data from chemical tests would be available, but there seem to be no useful data that include the effects of calcium ions in solution, unless the osmotic cell test is included as such a test. The probable reasons for the lack of such data are that calcium silicate hydrates tend to form films that impede diffusion (2), and the lack of simple methods to measure the degree of reaction.

Early researchers recognized the need for, and value of, chemical methods to characterize aggregates for potential deleterious reaction rates by rapid tests of the intrinsic reactivities (3,4). The early work by Mielenz et al. (3) revealed some of the complexities of chemical methods. Measurements of the effects of alkali solutions on aggregate particles showed no consistent correlations with ASR mortar expansions, nor did measurements of amounts of dissolved silica or reduction of alkalinity, taken separately. It was found however, that if both of these latter measures of reactivity were used, that a measure of deleterious reaction in concrete that had considerable reliability could be obtained quickly. These studies led to the adoption of ASTM C 289-52, Potential Reactivity of Aggregates (Chemical Method). Although many aggregates with good service records fail the test, and some with unsatisfactory records passed the test, it remains the most popular chemical test (5).

At the time of the earlier work it was not clear why the reduction of alkalinity and the dissolution rate were both necessary to indicate deleterious reactivity. In Sections 2.1 and 3.2 of Part I, it was shown that the alkalinity of the solution is reduced by both dissolution of silica and neutralization of OH$^-$ by undissolved silica. Since the initial expansion and cracking of mortars is believed to be caused by expansion of the aggregate particles by swelling of undissolved silica, and that gel formed by dissolved silica can also cause damage, it is to be expected that both measures should be involved. However, it is also clear that there are additional factors that can make chemical test results unreliable predictors of performance in concrete.

One of the reasons for such unreliability is that almost all of the available data on reaction rates of reactive aggregates have been obtained with alkali solutions without solid calcium hydroxide in the mixture. Although the Ca^{++} concentrations in such solutions are quite low,

the availability of large amounts of calcium hydroxide (solids) has major effects on the compositions of reaction products formed both inside and outside of the reactive particles of silica. Formation of C-(N+K)-S-H within the particles, as well as swelling and dissolution of silica, affects the rates of the reactions, as discussed in Sections 4.2 and 5.3 of Part I.

Another reason for unreliability is that the observed chemical effects may vary with the alkali/silica ratios used in the mixtures. The proportions used should be reasonably related to those expected in concrete to establish reaction conditions that occur in concretes. The Na_2O/SiO_2 ratios used in ASTM C 289 are only about 0.04 for aggregates that are mostly reactive silica. The presence of calcium hydroxide increases the effectiveness of the NaOH solutions in reacting the silica by regeneration of the alkalies while generating C-N-S-H gel. Hence that same Na_2O/SiO_2 ratio would be effectively much higher, perhaps about 0.2, with solid calcium hydroxide present.

Early reaction rate data, such as those discussed in Section 2.1 of Part I, obtained for different aggregates with calcium hydroxide in the mixture and expressed in terms of reaction rate per unit area would fill an important gap in our knowledge. It would both help us understand reaction chemistry in realistic pore solutions, and help to improve test methods for aggregates. However, it is not certain that the practical difficulties can be quickly overcome.

Direct observation of the progress of reaction into small aggregate samples by SEM-EDX would not only provide measures of intrinsic reactivity, but also provide important information on the way the reaction is affected by changes in alkali and calcium ion concentrations.

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7 Effects of Restraint of Expansion on Reaction Kinetics

Field observations of concrete structures damaged by ASR, SHRP laboratory tests, and our review of the literature have each shown various aspects of the effects of mechanical restraint of the expansion and cracking processes. Until this project began, it was widely assumed that ASR reactions could be stopped if sufficient pressure was applied to the reactants, or if swelling pressures developed by the reaction were sufficiently restrained. Indeed, there was considerable evidence for an upper limit for average expansive stresses in concretes of 2 to 4 MPa (300-600 psi) (1). However, study of the reaction and physical chemistry, and the nature of swelling gels and the stresses on the reactants in concrete, have led to a clearer concept of these phenomena: stopping the swelling need not stop the reaction. It may, in fact, accelerate it.

This tentative conclusion is based on the physical chemistry of the dissolution of silica in alkali solutions to form alkali silicate solutions and gels. As discussed in Section 3.1 of Part I, the volume change of amorphous silica and reactive aggregates during dissolution is negative (2,3,4). As a consequence, silica dissolves when the pressure is increased on a solution or gel in equilibrium with undissolved silica. In actual reactions in mortars and concrete the situation is complicated by the fact that:

1. reactive aggregates probably swell before dissolution, as do silica samples (2), as discussed in Section 3.2, Part I, and

2. calcium probably begins to react with the swollen silica before dissolution, as discussed in the last two paragraphs of Section 4.1.2 of Part I.

During these stages of swelling, increasing pressure on the rock may stop the swelling, but not stop the reaction, if the volume change for dissolution is negative with calcium present, as it is with reactive silica in alkali solutions and for cement hydration reactions.

The effect of the restraint of ASR expansions on the stress at the reaction sites in mortars and concretes depends on the fraction of the cross sectional area of the concrete that is reactive aggregate (5), as discussed in Section 4.7 of Part I. If that reactive fraction is only 0.1, observed maximum restraint stresses of ASR in the range 2 to 4 MPa (300 to 600 psi) should not be taken to indicate stress concentrations of 20 to 40 MPa if cracking has occurred. Such stress concentrations could not be the cause of cracking, which would have occurred at much lower stresses. The measurements must instead indicate that swelling gels have increased the effective area of the aggregate by filling of cracks.

Maximum compressive stresses on expanding particles before cracking of the concrete should be more appropriately estimated from calculations based on elastic theory (6), as shown in Figure 4.3.1, and modified for creep. For a small volume fraction ($\sim$0.1) of reactive aggregate, and in the absence of external restraint, compressive stresses on the particles should be only perhaps five times the tensile stress in the matrix at the particle surface, which is

higher than the average tensile stress. If the maximum tensile stress in the concrete before cracking is taken to be about 4 MPa, the maximum compressive stress should be about 20 MPa (3000 psi). Such stresses are high enough to have a significant effect on reaction rates and swelling of gels. When external restraint is introduced, in addition to the internal elastic restraint, it is also amplified by the ratio of cross sectional areas. If cracking and gel flow is prevented by restraint, very high stress concentrations (e.g., 20 to 40 MPa) could be effected by rigid confinement measuring only 2 to 4 MPa.

However, as we have seen in Section 5.2 of Part I, such estimated stresses are strongly affected by drying and shrinkage (7) Creep of the concrete tends to relax stresses around reacting aggregate particles, as well as internal stresses developed in concrete in which the surface has partly dried (8). The uncertainties caused by such complexities become so large that it becomes impractical to attempt to use data from concrete tests alone to determine the effects of restraint of expansion on ASR reaction kinetics. Procurement of such data will require careful experimental work similar to that discussed in Part II, Section 6.

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8 Mechanisms by Which Pozzolans Inhibit Expansion

For many years, concrete technologists have been reasonably confident that high-quality pozzolans assured protection against damage to ASR when used in most concretes made with marginal aggregates (1). Increases in cement alkali contents, the use of deicing salts, and aggregates which release alkalies during reaction have aggravated ASR problems. In addition, recent research has challenged our understanding of the mechanism of the reaction at the aggregate-paste interface, especially the interaction between pozzolans and soluble salts e.g. NaCl and $CaCl_2$, as discussed in Section 4.1.4 and 5.3 of Part I. Although the assertions made by Chatterji et al.(2,3) may not be completely correct, it is apparent that there is a substantial gap in our knowledge concerning reaction chemistry at the particle interfaces, and specific requirements for pozzolans to assure protection against damage by ASR, under both ordinary and accelerated testing conditions.

Under the ordinary conditions considered by Powers and Steinour, pozzolans were considered to be effective because they consumed alkalies and rapidly reduced the concentration of alkalies and hydroxyl ions in pore solutions in mortars and concretes. Reduction of alkalies was believed to slow the attack on reactive aggregates, increase calcium ion concentration, and permit more rapid diffusion of calcium ions into the reaction zone to form non-swelling product, while sufficient silica diffused out from the reacting aggregate to prevent expansion.

In Section 4.1 of Part I, recent work by Kawamura, et al. (4,5) was presented that showed by SEM-EDX measurements that the effect of some pozzolans (e.g., fly ash) was to *increase* the rate of ASR rather than slow the reaction, as with calcined kaolin. Similar results have been obtained by Chatterji et al. in accelerated tests in salt solutions (6). Kawamura, et al., speculated that reduced expansions in mortars made with pozzolan replacements for cement resulted from reduction of mobility of water through the paste matrix, and/or the formation of gels of "high" calcium content (although the CaO/SiO_2 ratios were less than 0.3), but provided no convincing evidence. Reduced pH of the pore solutions was found in mortars made with some pozzolans, but not with granulated slag, which also reduced expansions.

Chatterji, et al., argued that expansions of mortars tested in salt solutions occurred because calcium reaction products that formed in the reaction rim blocked the escape of dissolved silica from the reacting particle (3). In order for pozzolans to be effective in the presence of unlimited alkalies from soluble salts, he argued that calcium hydroxide in the paste matrix has to be leached or reacted to insoluble products in the paste to limit Ca^{++} ions from diffusion into the silica. Safe reactions by this method must depend completely on escape of all excess silica from the reactive particle to prevent expansion, rather than partly on the formation of non-swelling product in the particle interior.

Powers and Steinour's model appears to account for safe and unsafe ASR in mortars and concretes without salts or pozzolans. However, it is now clear that it does not account for the effectiveness of some pozzolans in controlling ASR expansions and cracking even under ordinary test conditions without salts. Chatterji argues that calcium hydroxide must be

eliminated for safe reactions to occur when reactions are accelerated by soluble salts and temperature. If he is correct, the safe reaction processes are very different for these different conditions, and such accelerated tests may not yield results useful under ordinary conditions. This is a serious gap in our knowledge and is of great practical importance both with respect to possible effects with deicing salts and the use of pozzolans to protect concrete from damage by ASR.

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9 Pozzolan and Mineral Admixture Test Methods and Specifications to Prevent Deleterious Alkali-Silica Reactivity

The need to develop a rapid and reliable test procedure to identify the potential for expansive ASR of cement-aggregate combinations was recognized in Section 2. Similar problems exist with test procedures used to determine the effectiveness of mineral admixtures used to control ASR in concrete. Fly ash, ground granulated blast furnace slag (GGBFS), condensed silica fume (CSF), and natural pozzolans all are used to prevent abnormal expansion caused by ASR (1,2,3). It is recognized that existing test methods for potential reactivity of aggregates (ASTM C 289), ASR of cement-aggregate combinations (C 227), and for the effectiveness of mineral admixtures in preventing excessive ASR expansions (C 441), do not always provide reliable or clearly defined lines of demarcation between "nonreactive" and reactive combinations (3,4,5,6). Reasons for this lack of correlation between test results and concrete performance in practice include:

1. Test mortars are made at specified fixed proportions; concrete proportions vary widely.

2. Tests are done at 100°F (37.8°C) under specified conditions designed to accelerate ASR; concretes are exposed to widely varying conditions.

3. Expansions measured by C 227 are not considered excessive unless they exceed 0.05% at 3 months or 0.10% at 6 months. Such expansions are well above those at which cracking occurs, about 0.03% (7); measurements are of growth of cracks in specimens that have already failed because control of ASR has been inadequate.

4. Reactive aggregates vary in their rates of reaction at different temperatures and pH. They also vary in their threshold pH values for reaction, as shown for phases in Beltane opal in Section 2.1 in Part I, and amounts of alkalies released. Some react rapidly and are readily detected in C 227. Others react so slowly even at 100°F that months may be required to reveal significant reactivity.

In addition, the C 618 specification limit of 1.5% available alkalies for mineral admixtures to be used with reactive aggregates may be an unreliable limit (8).

ASTM C 441

ASTM C 441 is a mortar expansion test, using Pyrex glass as aggregate and cement containing between 0.95 and 1.05% total alkalies as sodium oxide, in which mortars are tested as in C 227. Expansions are determined for mortars made with admixtures as well as those of control mixes made without admixtures. The expansion limit at 14 days specified in ASTM C 618 is 0.020%, which is less than the value found by Hobbs (7) to correspond to cracking in mortars at room temperature, about 0.03%.

This procedure has several shortcomings in addition to those of C 227, including:

1. Pyrex glass reacts with alkalies in solution and expands so rapidly that an accurate assessment of the admixture may not be determined.

2. During reaction, additional alkali is released from Pyrex glass into solution, thereby maintaining higher alkali and hydroxyl ion concentrations in pore solutions than with most natural aggregates.

Factors Influencing Testing

In order to improve or replace C 441 testing for acceptability of mineral admixtures for control of ASR, we need to determine whether such expansion tests are necessary or desirable, or whether chemical tests, such as for reduction of pH, would be superior. The results presented in Part I indicate this not to be the case for several reasons:

1. In Section 4.1.3 it was shown that different pozzolans function by different mechanisms: CSF and calcined kaolin by reduction of pH; fly ashes and GGBFS without much immediate reduction of pH. Reaction with opal was virtually stopped by calcined kaolin. With fly ash the pH was not reduced; the opal reacted and softened and the reaction with calcium was facilitated. Expansions in both cases were greatly reduced.

2. It has also been shown that different fly ashes have different threshold pH values for reaction. In a study of their highly reactive fine fractions, reaction rates for three ashes in alkali hydroxide solutions containing calcium hydroxide varied little from 0.5 to 2.0 mol/L, while one other ash was below its threshold at 0.5 mol/L; it reacted much more rapidly and similar to the other three at 2.0 mol/L (9).

3. Reactive aggregates vary greatly in their reaction rates and other characteristics, as noted above concerning C 227 testing. Mineral admixtures which can control highly reactive rocks can probably also control slowly reacting aggregates, but this is not certain if different mechanisms are involved. In any event testing must yield results for slowly reacting aggregates in a reasonable time.

4. The chemistry of ASR involves all four reactants: water, reactive aggregate, portland cement, and mineral admixture, and depends on the mix proportions and other factors in concrete that are difficult to simulate in chemical tests.

5. There has also been considerable uncertainty concerning the effects of release of alkalies from fly ash (1,8,10,11,12), granulated slag (1,13,14,15), and superplasticizers (1). In Section 2.2 of Part I it was shown that hydroxyl ion concentrations in pastes and mortars depend in complicated ways on the alkali contents of cement and fly ash, and the water-cement ratio, and that cement gel is an alkali-containing buffer that reduces concentration changes. These relationships become even more complex during ASR.

For these reasons it does not seem that chemical tests can adequately assess all those characteristics of mineral admixtures essential for performance. Mortar tests should be able to simulate concrete for this purpose.

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Requirements for Rapid Tests

Two kinds of guidance for use of pozzolans to control ASR need to be improved:

1. Tests and specifications to rate quality of pozzolans, and

2. Tests to determine amounts required with different cement-aggregate combinations.

Recently numerous attempts have been made to devise more rapid mortar test methods that also apply to slowly reacting aggregates. Tests in NaCl and NaOH solutions have been done at 122 to 176°F (50 to 80°C) to accelerate ASR and also simulate situations where concretes are exposed to unlimited amounts of alkali (See Sections 2.3 and 5.3 in Part I). However, these tests also use mortars made at fixed proportions that may be unrelated to use of the materials in practice, and produce alkali/(reactive aggregate) ratios higher than those for pessimum proportions for maximum expansions rarely encountered in practice. We need to know if there is any risk of false negatives in such tests.

What appears to be necessary is a re-examination of the effects of variation of test parameters using a set of real reactive aggregates of differing reactivities and well-defined service records. A testing protocol (not necessarily a single test) needs to be be developed that will define amounts of mineral admixture required in job mixtures of cement, mineral admixture, water, and reactive aggregate that are required to prevent cracking and growth of cracks. Mortar tests are more rapid than concrete tests, permit variations of proportions to simulate alkali/silica ratios in concretes, and are simple and economical, but may require modifications. To be practical the test must be accelerated and yield results, in a reasonably short time (14 or 28 days), that are also valid for very long term periods. Inclusion of Pyrex in the study will provide an objective comparison of those results with those for real aggregate materials, and therefore an assessment of the validity of the current C 441 method.

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10 Inhibiting Expansion Due to Reactivity by Chemical Agents

Chemical agents that reduce or alter the course of ASR in concrete may be either organic or inorganic in nature. They are, however, strictly in the experimental stage, with investigative work having been confined essentially to the laboratory (1). They affect the mechanism of reaction rather than symptoms of the reaction. The details by which they operate, and whether they would be effective in inhibiting ASR in existing concrete, remain obscure. Descriptions of candidate agents are given in the following paragraphs.

Organic Agents

Crown Ethers

Three crown ethers tested in ASTM C 441 mortar bars were found inefficient at all doses (2). Crown ethers were reconsidered in the SHRP C-202 research (3).

The stability of crown ether complexes depends on several factors, including cavity size of the ligand, cation diameter, spatial distribution of ring binding sites, character of heteroatoms, and type of solvent. As water is a polar solvent, the only important constant is the stability constant Ks. In alkaline solution, the dicyclohexyl 18 crown 6 (DCH18C6) was not successful due to the high solvation of Na^+ and K^+ ions in the aqueous solution. However, the chelating power of DCH18C6 is higher in alkaline solutions containing methanol, i.e., log Ks = 16 in water and log Ks = 4.1 in methanol for Na^+ and respectively 2.2 and 6.0 for K^+.

Cryptands

Cryptands are macrobicyclic molecules with spherical cavities. A cryptand is characterized by three numerals, m, n, and p, corresponding to the number of oxygen atoms in each link. Electrons in cavities can complex Na^+ and K^+ ions, forming a cryptate. Cryptands 112, 221, 222, 223, 332, and 333 are able to complex Na^+ and K^+, i.e., log Ks between 1.6 and 5.4 for Na^+, 1.0 and 5.3 for K^+. However, cryptands also complex Ca^{++} ions (log Ks between 2.0 and 6.95). Cryptand 222 appears the most efficient but its ionic selectivity has to be evaluated in concrete pore solution.

Amines

TDA-1, or Tri Dioxa 3-6 Amine, is stable in KOH or NaOH solutions. The degree of complexation for K^+ and Na^+ has been evaluated in an aqueous alkaline solution and in a solution containing 50% methanol. Determination of non-complexed Na^+ or K^+ ions was done by potentiometry using selective electrodes. In K^+ solutions of ionic strength I = 0.6, close to that of concrete pore solution, TDA-1 complexed 88% of K^+ ions. In the 50%

alkaline solution, 50% methanol, 98% of K$^+$ ions were complexed. These first results, although promising, need to be confirmed on ASR- altered concretes still able to expand.

Alkyl-Alkoxy-Silane

Alkyl-alkoxy-silane, (AAS) used as a chemical admixture (0.5 to 1.0% cement replacement, by weight) reduced the expansion of mortars containing reactive aggregates, twenty times (48×10^{-4} to 2.5×10^{-4}). This reduction in expansion has been attributed to the formation of water repellent layers at the surface of aggregates (4). It also may act as an air entraining agent, which has been reported as a reducer of ASR expansion (1).

Inorganic Agents

Phosphate

ASR can be considered as a surface reaction with Na$^+$ or K$^+$ cations first "surface sorbed", then chemisorbed. The active surface of silica possesses a negative charge able to attract positive cations which are themselves able to attract hydroxyl ions. If a "sandwich" of cations and anions is considered, its modification or destruction will inhibit or eliminate ASR. As the phosphate ion is large and strongly negative, it is expected to bind alkalies and to displace OH$^-$ ions (5). A solution of monocalcium phosphate monohydrate was tested in concretes combining reactive Putnam chert and Sudbury aggregate. A precipitate of calcium phosphate was formed which prevented the formation of ASR gel.

Lithium Compounds

Lithium hydroxide, lithium carbonate, and lithium nitrite were found effective in inhibiting ASR expansion (6). This expansion was retarded or reduced by impregnating mortar bars and concrete prisms which had already expanded, more particularly, with the lithium nitrite. The inhibiting effect was attributed to the formation of a lithium silicate which prevented the formation of an expansive gel.

Sodium Silicofluoride

Compared with lithium carbonate, lithium fluoride, and lithium hydroxide, sodium silicofluoride (Na_2SiF_6) was most effective in reducing expansion (4). The ASR expansive gel was transformed into an insoluble compound with strong siloxane bridges, as in water glass. Moreover, the addition of Na_2SiF_6 corresponded to an increase in compressive strength, i.e. 50% for 1% Na_2SiF_6. This has been attributed to hardening of the silica gel. The optimum content of Na_2SiF_6 has been found to be between 0.7 and 1% by weight of cement.

Polymer Cements

Polymer cement with the cement modifier styrene-butadiene-rubber latex (SBRL) was found to increase ASR expansion for polymer-cement ratios up to 10% (4). Then expansion decreased. Polymer cement was used more successfully as an aeration type of coating (7) and behaved better than polyurethane and epoxy resin, both selected as waterproof types of coatings.

Conclusion

As reported at the Kyoto conference (1) and according to Mailvaganan (8) the requirements of a suitable admixture to control ASR in concrete are as follows:

1. It should form a relatively soluble hydroxide.

2. It should react to produce an insoluble silicate.

3. The ions must not interfere with, or modify, cement hydration reactions.

4. The ions should not take part in alkali silica reaction to form other expansive material.

5. It should be of reasonable cost and harmless.

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