SESSION 1

Mechanisms of Alkali–Silica Reaction

Keynote Lecture
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1. INTRODUCTION

This paper represents an attempt by the writer to provide some current concepts and a framework for discussion concerning the mechanisms of alkali silica reaction (ASR) in concrete. It does not purport to be a balanced presentation of the current state of the art, but it is offered in the hope that it may stimulate further discussion and focussed investigation on what has become a global, rather than a regional problem.

Among the aspects ASR receiving more attention are the variation in responses found with different reactive aggregates, and concern with the actual details of damage found in individual concrete structures. In part this has been stimulated by litigation stemming from major cases of ASR in the United Kingdom, Canada, the United States and elsewhere. It appears that a new speciality of forensic alkali aggregate reaction investigation is rapidly developing.

A large number of publications, quasi-official committee reports and guidelines, and at least one book [1] have appeared in the last few years, attesting to the growth of activity in the field.

2. SOME GENERAL PRINCIPLES

2.1 Distinction Between Reaction and Damage

Alkali-silica reaction is a chemical phenomenon which can occur in field concrete and is readily reproduced on demand in laboratory investigations. Visible or measurable distress arises as a result of physicochemical responses subsequent to ASR reaction, not necessarily as a result of the reaction itself. In the writer's opinion the term "deleterious reaction", commonly used in early American literature, has resulted in much confusion; ASR reactions can take place without damage to the concrete.

2.2 Status Of Alkali-Silica Reaction As A Solid-Liquid Reaction

Chemical reactions are classified as homogeneous, if taking place within a single phase such as a solution, or heterogeneous, if involving two or more phases. Alkali-silica reaction processes clearly involve a solid (the reactive aggregate) and a liquid (the pore solution) and are properly classed as
heterogeneous solid-liquid chemical reactions. ASR is unusual in that the liquid is constrained in the pores of the solid, and the reacting solid constitutes only a small and irregularly distributed part of the constraining total solid. This complicates the study of the reaction.

2.3 Association of Damage With Osmotically-Induced Local Expansion

Damage to concrete affected by ASR, when it occurs, arises primarily from irregular and localized internal expansion. Despite differences from the usual membrane-limited nature of most classical osmotic systems, the driving force for the expansion is clearly osmotic. The distinction between swelling induced by "imbibition pressure" and by "osmotic pressure" as discussed by Dent Glasser [2] is purely formal. Water (or more properly, pore solution) is induced to flow into the reaction product gel because the water already in the gel has a lower free energy than the water in the pore solution surrounding it. As Dent Glasser pointed out, no membrane is required to separate the regions of differing chemical potentials; the separation is automatically achieved by the gel simply through its insolubility in the liquid.

That cement paste can act as a classical constraining osmotic membrane separating solution and gel is demonstrated in the osmotic cell test for aggregates reactivity. In this laboratory test a membrane of cement paste is artificially provided to separate a cell containing alkali hydroxide from an adjacent cell containing gel generated by ASR attack on the aggregate under test. The velocity of the osmotic flow between the cells is taken as an index of the susceptibility of the aggregate to reaction.

The fact that the ASR swelling mechanism is osmotic in character permits at least approximate calculation of the local stresses that can be generated, as will be discussed later.

2.4 Distinction Between Damage to Functioning of Structures and Concrete Damage

Damage may occur to the functioning of certain structures purely as a result of expansion, without any visible cracking or other deterioration. Geometrically sensitive massive structures such as locks and turbine pedestals may be rendered non-functional by small expansive strains exhibited over large concrete masses. On the other hand, even when concrete appears to be severely cracked and visibly deteriorated, the structural effects, according to many recent investigations, may be negligible. Thus in assessing the consequence of ASR, a distinction between effects on the concrete properties and effects on the structure must be maintained.

3. SEQUENCE OF THE DEVELOPMENT OF ASR DISTRESS

While different stages of the overall ASR response may be present simultaneously in different portions of a given structure, at any one location a definite sequence of responses must take place. Accordingly, it is useful to frame the discussion of mechanisms in terms of such a sequence. The following stages are specifically recognized here:

(1) Development of high concentrations of alkali hydroxides in the pore solution.

(2) Reaction with aggregate and formation of reaction product gel.
(3) Expansion arising from fluid flow into the gel.
(4) Cracking and subsequent deterioration.

These stages are generalizations. Different concretes affected with ASR under different conditions respond quite differently from one another in detail, reflecting differences in aggregates, cement alkali contents, incorporation of supplementary cementing materials, temperature and humidity exposure, mechanical restraint, and a host of other variables.

3.1 Development of High Concentrations of Alkali Hydroxides

That concrete pore solutions are all very high pH fluids containing mostly dissolved alkali hydroxides has been known for a number of years. This generalization may be verified empirically for any given structure by coring it and subjecting the cores to the by the now widely available procedure of pore solution expression and analysis. It is also widely appreciated that (a) alkali hydroxide concentration is not necessarily uniform in different parts of a structure and that concentration gradients may develop; that (b) in special circumstances a significant part of the dissolved alkali hydroxide may be derived from sources other than the original cement, including salt, admixtures, and even aggregate; and that (c) that as ASR reaction proceeds and insoluble gel forms, the residual concentration of alkali hydroxide is reduced. Some discussions of these effects are provided below.

3.1.1 Pore Solution Effects As Related to Cements

The relationship between cement alkalies and pore solution alkali hydroxide concentrations can be studied conveniently in closed systems in the laboratory where other possible effects in field concrete can be avoided.

The sequence of early (ca. 1-day) changes in pore solution compositions has been studied by various authors, including the writer [3] and can be briefly summarized for present purposes as follows: soluble alkali components in the cement go into solution quickly; OH⁻ ion concentration levels quickly rise to the order of 0.2 or 0.3M, and the solution is immediately supersaturated with respect to calcium hydroxide. After a few hours sulfate concentrations begin declining progressively to low levels and OH⁻ ion concentrations concomitantly increase. Calcium is reduced to almost negligible concentrations. After 1 day these processes are essentially complete and the solution consists primarily of dissolved potassium and sodium hydroxide, with only minor amounts of other components. The concentrations of alkali hydroxides may increase slightly over the course of the next few weeks as additional alkalies are liberated from solid solution in cement components and as solvent water is removed by hydration. After a month or so, further changes in alkali hydroxide concentrations in cement paste pore solutions are irregular and usually negligible; some slight reduction may occur, but basically by a month or so the pore solutions are at equilibrium with the paste.

Struble [4] recently completed an extensive study of the relationship between alkali type and location in cements and the resulting development of equilibrium pore solutions in mortars. A suite of eight different cements were specifically selected to cover the widest possible range of alkali types and locations in cement. Mortars were prepared at water:cement ratio 0.5, sealed, allowed to hydrate for various periods, and pore solutions were expressed and analyzed at intervals.
The writer has combined these results with those of a number of earlier ones, including data from Kollek et al. [5], Page and Vennesland [6], Diamond [7], Barneyback [8], Longuet et al. [9], and Diamond [10], and plotted the results shown in Fig. 1. The data include determinations for 19 different cements, ranging in Na\textsubscript{2}O equivalent from 0.34 to 1.31. The set includes both pastes and mortars, but all specimens were cast at a water:cement ratio of 0.50. All were made with purely portland cement, i.e. without any supplementary cementitious addition.

The plot is that of OH\textsuperscript{-} ion concentration at "equilibrium" vs. the alkali content of the cement, expressed as equivalent percent Na\textsubscript{2}O. To arrive at the OH\textsuperscript{-} ion concentration at equilibrium, the results of all successive analyses of age 30 days or longer reported by the investigator were averaged; in some cases the results extended to several years.

The result clearly confirms that at the state of equilibrium represented by hydration in sealed systems, the concentration of alkali hydroxide found in the pore solution is a linear function of the total alkali content of the particular cement used.

\[ Y = 0.017 + 0.699 \times \]
\[ R = 0.977 \]

![Fig. 1. Relation between equilibrium OH\textsuperscript{-} ion concentrations of pore solution and alkali content of cement, for w:c 0.50 pastes and mortars.](image)

The linear regression coefficient \( r \) is 0.977, attesting to the close fit of the data. The relationship essentially goes through zero (statistical intercept \( = 0.017 \)), and the slope is almost exactly 0.7 moles/liter of OH\textsuperscript{-} ion concentration per percent Na\textsubscript{2}O equivalent in the cement.
Thus one can now predict, at least water:cement ratio 0.5 concretes, what the OH- ion concentration ought to be at equilibrium. Since the OH-ion concentration is usually equal to the sum of the concentrations of the alkali ions (within experimental error), this gives us the expected alkali hydroxide concentration level, i.e., the driving force for ASR, in a given concrete.

The few available data for pastes and mortars of other water:cement ratios suggest that the Fig. 1 relationship can be used to estimate their alkali hydroxide concentrations as well, if allowance is made for the appropriate effect of dilution or concentration. The results of Diamond [11] for a paste at water:cement ratio 0.4, and of Glasser and Marr [12] for two pastes at water:cement ratio 0.6, all fit the Fig. 1 relationship reasonably well if the concentrations found are linearly adjusted for the differences in water:cement ratio.

It should be emphasized that the relationship above is for pastes, mortars, or concretes without supplementary cementing components, e.g., fly ash, silica fume, or slag. The influence of such supplementary components on alkali hydroxide concentrations has been discussed previously by the writer [10], Glasser and Marr [12], and Glasser, et al. [13], among others. Fly ash, with few exceptions, lowers the OH- ion concentration, but mostly by dilution. Silica fume actively removes alkalis (and OH- ions) from the solution by reaction; recently Tenoutasse [14] isolated and identified alkali-bearing gel and crystalline reaction products formed in such processes. Slag lowers the OH- ion concentration to the order of pH 12 level (about 0.01M) if used in the usual high proportion [13].

The predicted alkali hydroxide concentration may of course underestimate the actual concentration if the concrete has dried out significantly. Also, gross departures from the calculated value may be expected from various other perturbing effects, such as addition of alkali from some other source than the cement, leaching, previous formation of ASR reaction gel, etc. These complications are considered in the following section.

3.1.2 Pore Solutions in Concretes

With pore expression devices of appropriate design it is possible to express sufficient fluid from most concretes to carry out solution analyses. Thus laboratory concrete cast into specimens of appropriate size and shape may be studied in the same way as cement pastes or mortars.

However, the more interesting and important potential applications of the technology are to field concrete, with its variable conditions of exposure. Cores of appropriate size may substitute readily for laboratory-cast concrete specimens.

Unfortunately, interpretations of concentration measurements from uncontrolled field concretes are not necessarily straightforward because of the various perturbing effects that may occur in field exposure. The concentration determined will reflect changes in both level of dissolved alkali hydroxides and degree of saturation of the pores. If a gradient in the degree of saturation extends inward from a dry outside zone, cores taken from the outside will provide average values over the depth of the core taken.

Where concrete permeability (and diffusivity) is sufficiently high to
permit easy equilibration of pore solution concentrations in a core, it may be desirable in practical cases to bring all cores taken from a given structure to a uniform reference state of moisture equilibrium. The obvious reference state of choice is that of saturation. However, in resaturating partially dry concrete it is important to minimize and monitor any loss in alkali hydroxide, and to adjust the observed concentrations for such effects. Such techniques have been used in field investigations for several years.

One indication of the potential applicability of such techniques in practice are the laboratory paste results reported recently by Nixon et al. [15] on the effects of salt (NaCl). These authors confirmed that NaCl added to cement paste rapidly converts to alkali hydroxide and exacerbates ensuing alkali silica reaction. The degree to which concrete in a given structure exposed to salt water or salt spray has undergone such alkali hydroxide enhancement could readily be monitored by pore solution analyses of cores taken from various locations in the structure.

Other perturbing influences may modify the alkali hydroxide concentration of concrete pore solutions. Pavements in relatively dry areas may accumulate locally high concentrations of alkali hydroxides near the evaporation front some distance below the level of the top surface of the pavement, leading to ASR distress [16]. Certain alkali-bearing feldspars and other rock components may react in concrete to liberate appreciable amounts of alkalis [17, 18]. On the other hand, prolonged leaching of thin section concrete members may lower the concentrations of alkali hydroxides in the pore solution, especially in permeable lean concretes.

3.2 Reaction and Formation of Reaction Products.

Few actual measurements of alkali silica reaction rates exist, given the inhomogeneity of the solid components in concrete; comparative reaction speeds are usually inferred either from expansion measurements. At one extreme, opals and cristobalites are well known to react quickly; graywackes, argillites, and strained quartz to react slowly, and most other aggregate types to be in between.

Many of the details of the reaction process continue to remain obscure.

Several authors, for example Jones and Poole [19] have emphasized the idea of active transport of alkalis to the reaction front, i.e. surface of the reacting grain. Active (non-diffusive) transport is seen to represent a side effect of the imbibition (or osmotic uptake) by previously-formed gel; as the solution is drawn into the gel it carries additional dissolved alkali hydroxide to the reaction front. To some extent such a mechanism couples reaction rates to expansion, suggesting they may not be quite independent of each other.

In the past few years, considerable new information has been developed on the role of calcium in the formation of expansive gels, and on the development of crystalline ASR reaction products. Each of these topics is discussed below.

3.2.1 The Role of Calcium

It has long been recognized that calcium is universally found in the analysis of gels in situ. Nevertheless, the calcium has often been considered
as incidental and secondary in origin, with calcium being somehow "dissolved" from the surrounding paste and incorporated into reaction gel on a more or less casual basis. Explanations of gel structure such as that of Dent Glasser [2] have been provided in terms of polymeric silica electrolyte species making up the gel, with no particular role assigned to any calcium that might be present. Struble and the writer [20] devoted an entire experimental program to the study of the swelling behavior of mostly calcium-free synthetic alkali silica gels.

In contrast to this view, Chatterji and his colleagues have maintained that the presence of calcium hydroxide is essential to the ASR process, and that systems lacking calcium hydroxide simply do not undergo distress. Recently Chatterji et al. [21] illustrated that the presence of Ca(OH)₂ seems to be essential for sodium and other ions to penetrate into the reacting grain. They also indicated that Ca(OH)₂ is needed to "seal off" the reacting grain from leakage of dissolved silica.

That this idea is fundamentally correct has been conclusively established in results obtained in recent Ph. D. theses of Struble [4] and of Kilgour [22].

Struble [4] prepared "model" reactive mortars of opal and limestone sand placed in solutions duplicating the range of alkali hydroxide compositions found in studies of actual mortars of several cements. These model systems duplicated the size distributions and proportions of reactive-to-inert aggregate used in the mortars, and contained the same proportions of aggregate and solution as used in them. Only the cement was missing.

It was found that by several weeks the opal-bearing model systems had developed dissolved silica contents of the order of 2M or more, and the silica concentrations were increasing with time. This level of dissolved silica is in stark contrast to that found in actual cement mortars, which is typically much less than 0.001M. Furthermore, the model systems showed no evidence of gel formation. It is evident that in the absence of cement hydration products, the opal simply dissolves in the alkali hydroxide solution and does not form gel.

In ordinary concrete, the highly alkaline pore solution restricts the calcium that can remain in solution to negligible concentrations. Thus it is easy to see the need for calcium hydroxide as a source of calcium necessary for gel to form.

This concept is supported by the results of Kilgour [22], who studied the effect of simulated pore solutions on two different low-calcium fly ashes. In her experiments, she exposed 1 g. of fly ash to continuous shaking in 100 ml of combined KOH-NaOH solution (total concentration 0.7M), with and without the presence of calcium hydroxide. Where calcium hydroxide was used, it was added at the level of 0.5 g/l of solution.

In the absence of added calcium hydroxide, approximately 20% of the weight of each of the fly ashes was found to have been dissolved by 6 months. Most of the dissolved material was silica, and it all remained dissolved in solution. In contrast, in the presence of calcium hydroxide, there was no net dissolution at all; instead there was an actual increase in the weight of solids present. X-ray diffraction showed that the new material precipitated was amorphous (with an band centered near 29 2θ), and it was soluble in HCl. It is evident that the reaction product formed in the presence of calcium hydroxide
is analogous to ASR reaction product gel, if not necessarily identical with it.

Attention is called at this point to the local deposits of calcium hydroxide ordinarily encountered in the interfacial zones surrounding aggregates in concrete. It would appear that this feature may have something to do with ASR gel formation in practical concretes, a concept that warrants further investigation.

3.2.2 Crystalline Reaction Products

In most general treatments of ASR, the fact that gels may be converted in part to crystalline products is noted, but not stressed. In recent years findings of such crystalline reaction products have been recorded by various authors, for example Regourd and Hornain [23], Davies and Oberholster [24], and Shayan and Lancucki [25]. Various crystal morphologies and at least four different crystalline species seem to have been reported. The significance of these crystalline reaction products in the ASR damage mechanism is unclear, but it would appear that they are secondary products of crystallization from the gel stage, and once formed are unlikely to contribute to further expansion and cracking.

3.3 Expansion

As indicated previously, the driving force for expansion in AAR is osmotically-derived intake or imbibition of solution into the insoluble reaction gel. However, in any given concrete member, the proportion of any section actually undergoing local expansion is small, and the overall expansive force mobilized across a given section is much less than the local stress that may develop around a given reactive aggregate grain.

It is actually quite difficult to calculate the expected osmotic pressure from physical chemical principles. Osmotic pressure derives fundamentally from the difference in the free energy (or activity) of the water in the gel and the water in the pore solution being drawn into the gel. Neither can be approximated by the dilute solution approximation commonly employed in making osmotic pressure calculations.

The activities of the water in the two phases systems can be approached by measuring the vapor pressure of water over them, as suggested some years ago by Moore [26]. The appropriate equation (cited in somewhat cryptic form by Moore) is

$$\pi = \frac{RT \ln \left( \frac{p_2}{p_1} \right)}{V}$$

where \(\pi\) is the osmotic pressure (in Pa), \(R\) is the gas constant 8.314 \(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\), \(T\) is the temperature in °K, \(V\) is the partial molar volume of water transferred to the gel, and \(p_2\) and \(p_1\) are the vapor pressures of water in the gel and in the fluid, respectively. The values are all fixed at a given temperature except for \(V\), \(p_2\), and \(p_1\). Moore took \(V\) as equal to the usual value of \(18 \times 10^{-3} \text{m}^3\), although this is far from certain for the gel.
It can be stated with some confidence that (a) the vapor pressure of water is 17.5 torr at 20°C, and (b) the vapor pressure of say, a 0.8M NaOH solution (which probably adequately represents the pore solution of most concretes undergoing ASR) is approximately 14 torr [27]. What we do not know how to estimate is the vapor pressure of water in a typical ASR gel at the time of its formation.

Assuming V is at least close to its normal value, if the vapor pressure over the gel is as low as 5 torr, the corresponding osmotic pressure is about 140 MPa; if it is as high as 10 torr, the osmotic pressure is approximately 45 MPa. These are high values. However, it should be understood that the expansive process is self-limiting; as more fluid enters the gel the vapor pressure in equilibrium with the gel almost certainly decreases and the driving force for further expansion diminishes.

Experimental swelling pressures measured by Struble and the writer [20] for synthetic hydrous sodium silicate gels rarely exceeded 10 MPa when water was the fluid being imbibed. The few gels tested which contained calcium were not noticeably different from the others in this respect.

More to the point, field observations of the behavior of structures undergoing ASR typically report that expansion is suppressed under high superimposed loadings and the crack pattern is strongly conditioned by the restraint produced by reinforcing steel. The latter will vary somewhat, but in studies of the behavior of ASR affected beams under load, Fujii et al. [28] measured the compressive stresses induced on the concrete by constraint of expansion due to ASR in a series of members, and indicated that it was about 4 MPa for all specimens. The restraint was hardly affected by the steel ratio or arrangement of the bars.

As a practical matter, the overall effective expansive stresses in concrete subject to ASR appear to be limited to modest values, and probably rarely exceed 6 or 7 MPa. This appears to limit the damage that can be done to many concrete structures.

3.4 Cracking

The ultimate expression of the ASR response is of course the development first of microcracks and subsequently of large cracks visible on the surface of the concrete member.

Figg [29] has described the geometry of patterns of local microcracking and of overall crack development in ASR-affected concretes. Microcracking through individual aggregate grains tends to be composed of 3 or more branches meeting at the local center of expansion. French [30] discussed the details of microcracking in concrete from several hundred affected U.K. structures; he emphasized the irregularity of the distribution of reactive aggregate, and indicated that larger, visible cracks start at locations where clusters of reactive grains occur, providing a local center or focus of expansion.

Visible cracking in concrete structures is often constrained by reinforcing steel or by loading so as to take place in specific directions. The actual crack pattern may thus be quite unlike the conventional map-cracking pattern associated with ASR in unrestrained structures [29].
4. CONCLUSIONS

The writer has attempted to summarize recent developments in certain aspects of the mechanism of ASR. Of the subjects discussed, the main points are as follows:

1. It is now possible to estimate the alkali hydroxide concentration in the pore solution of a given concrete from the alkali content of the cement used and the water:cement ratio, at least for water:cement ratios near 0.5. Neither the specific alkali (K or Na) nor its form of occurrence in the cement appear to matter. The estimate necessarily assumes that no alkali is solubilized from the aggregate, or brought into the concrete from outside; that neither leaching nor local concentration effects have occurred; and that the concrete has not dried out appreciably. The concentration predicted provides a basis for estimating the relative potential for ASR among different concretes with the same aggregate.

2. In systems similar to concretes undergoing ASR but lacking a source of calcium, the attacking solution simply dissolves the reacting aggregate, and the silica remains in solution. Gel formation occurs only in the presence of a source of readily mobilizable calcium. Thus ASR attack is conditional on having locally available calcium hydroxide, and the calcium in reaction gels is functional rather than incidental.

3. Despite the fact that ASR expansion is fundamentally osmotic in character, swelling pressures measured in synthetic gels and field observations of the effects of loading and of steel restraint both suggest effective expansive stresses much lower than estimates derived from osmotic theory. The latter relate to local stresses only.

7. REFERENCES


