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CHEMISTRY AND OTHER CHARACTERISTICS OF ASR GELS

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ABSTRACT

ASR gels are almost (but not quite) universally considered to be responsible for expansion and the resulting damage due to ASR in concrete. Some of their characteristics are reviewed. Chemical composition of gels varies extremely widely, and there is little unanimity on whether high-calcium content gels and low-calcium, high alkali content content gels should be treated as distinct phases. In a model derived by Helmuth and Stark, gels in concrete are treated as intimate mixtures of two end member phases of well-defined composition. In a brief study of ASR development in high alkali cement mortars containing opal-bearing natural sand, it was found that the opal grains had completely reacted and much or most of each sand grain had dissolved. Analyses of the residual reaction product were made and interpreted according to the Helmuth and Stark model. Surprisingly, residual material was neither uniformly low-calcium gel or high-calcium gel, but varied from one individual grain to another; different grains spanned almost the full range of compositions.

Keywords: Alkali-silica reactions, gel compositions, opal, gel phases, dissolution, ASR models

INTRODUCTION

Since the discovery of ASR it has been the prevailing view that (a) the damage produced in concrete is due to expansion, and (b) that the expansion in turn is a consequence of (1) the formation of amorphous ASR gel by reaction between pore solution alkali hydroxide and susceptible components in the aggregate, followed by (2) osmotic imbibition of water (or additional pore solution) and consequent swelling. While this continues to be the general view held by most workers, there are indications that other mechanisms may be also be at work.

In particular, a challenge to idea that ASR expansion is induced by the swelling of ASR gel has recently been mounted by Wieker and associates (Wieker et al.,1994; Wieker et al. 1998). These authors have suggested that ASR expansion may be due to a reaction between certain crystalline alkali silicates having a transitory existence in concrete and the reactive siliceous aggregate to form a hydrous layer-structure alkali silicate. The postulated starting compounds are δ-$Na_2Si_2O_5$ and its potassium analog; the reaction product is $Na(HSi_2O_5)\cdot 3H_2O$, or kanemite. Kanemite is stable under high humidity conditions, and should persist; however, its potassium analog is not. Wieker et al. (1998) demonstrated that both δ-$Na_2Si_2O_5$ and its potassium analog generate strong expansions if mixed with opal, compacted in the form of pressed pellets, and then exposed to high relative humidity. Similar expansions were also observed if "siliceous chalk" or silica gel were used instead of opal, but not if powdered quartz was used.

Despite these (and possibly other) concerns, it appears incontestable that ASR gel does form in ASR attack, and it that it often plays a major (if not necessarily exclusive) role in the ASR damage process. Many details of the relation of its composition to its structure and properties remain of current concern, and studies continue. This paper provides some of the background to these studies, and provides some new observations which may be of interest.

THE NATURE OF ASR GEL

ASR gel is usually amorphous to X-rays and optically isotropic, although some gel exhibiting modest birefringence has been reported by various workers (St. John et al., 1998, p. 296). Refractive indices are typically low, of the order of 1.45 to 1.51. Crystallization of older gel into various compounds can take place. Crystalline phases having ~ 10Å, 12Å, 13Å and 15Å X-ray diffraction basal spacings have been found in concrete by various authors; these findings were reviewed by Way and Shayan (1993), who have prepared synthetic analogs of some of them. None of these is kanemite, which has its smallest angle x-ray diffraction peak at about 5.2Å according to the x-ray pattern provided by Wieker et al. (1998).

It is commonly reported that ASR gels in concrete tend to change composition over time, usually accumulating calcium from the surrounding cement paste.

A very wide range of gel chemical compositions has been reported, varying especially in CaO content. Much current research suggests that ASR gel is not a single substance. Some authors suggest that there are distinct low calcium and high calcium ASR gels. Indeed, Scrivener and Monteiro (1994), in their study of ASR on a large disc of opal, record the presence of not two, but three different forms of gel types: a low calcium content gel of high

alkali content, a high calcium gel with similar total calcium plus alkali content but a lower water content, and a third type with a still higher calcium content. Some authors, for example Helmuth and Stark (1992) suggest that ASR gels are typically intimate mixtures of two phases of different chemical characteristics on a very fine scale. Generally gels rich in calcium are considered non-swelling, but this is disputed by some authors, including Thomas (1998) and Kawamura et al. (1998). Indeed, Thomas emphasized the point that some Ca is necessary for the formation of gel; otherwise silica simply dissolves in high alkali solutions.

ASR gel as produced in concrete has long been accorded the status of a colloidal substance capable of imbibing water and swelling (Hansen, 1944). It has been generally understood that the potassium and sodium cations are only loosely associated with the covalent siliceous framework and may be exchanged and replaced by other cations (Lombardi et al., 1996); the status of calcium ions is more ambiguous, as will be discussed later. The well-accepted uranyl acetate technique for exposing the presence and location of gel in concrete by fluorescence is thought to be based on cation exchange of uranyl (UO_2^{++}) cations for previously held alkali (and calcium?) cations (Natesaiyer and Hover, 1988).

The appearance of ASR gels has been described many times. Macroscopically gels have been described as "transparent and resinous in appearance" with variable viscosity; on exposure they are said to alter in appearance, "becoming white and hard, with dessication cracks similar to those observed in layers of dried mud" (Poole, 1992).

At lower magnifications in secondary SEM observations, ASR gel usually shows relatively smooth featureless surfaces except for the characteristic shrinkage cracks. At high magnifications (ca. 10,000x) gels generally appear to be composed of very fine nodules; the dried mass appears to be finely porous and it displays a characteristically spongy texture (Diamond, 1978). Fig. 1, taken from that publication, shows the appearance of ASR gel formed in a Beltane opal-bearing mortar at 700x and at 10,000x.
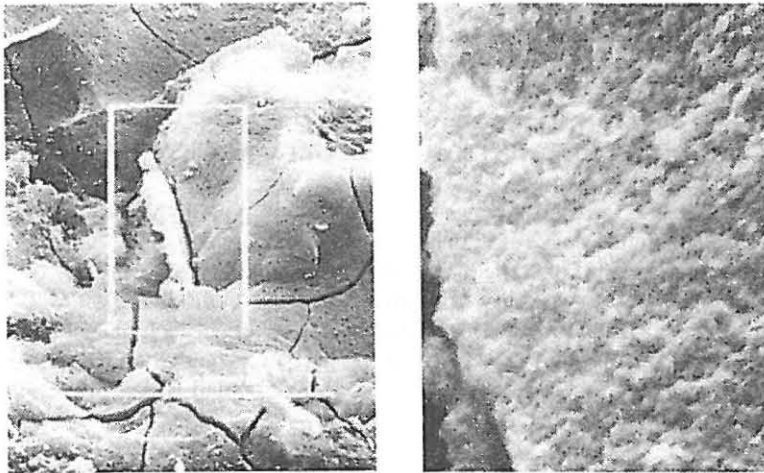

Fig. 1. Appearance of ASR gel in SEM. Original magnifications: left: 700x; right:10,000x.

"MOLECULAR" SCALE STRUCTURE BY NMR

Some years ago the writer prepared several series of 'simulated' ASR mortars in such a way that the reaction products could be studied by NMR. The simulated mortars were mixtures of an ASR- reactive sand and either an appropriate volume of a 1 N KOH solution, or a mixture of the solution and finely divided (precipitated) reagent grade $Ca(OH)_2$. Three types of reactive sand were used: opal from Nevada, Beltane opal, and cristobalite (calcined flint). No cement was used, the idea being to track NMR signals reflecting the conversion to ASR gel without the complication of NMR signals from cement hydration products. Exposure was at room temperature in sealed containers for periods up to 10 months. The products were washed several times in acetone to remove uncombined KOH and $Ca(OH)_2$ prior to analysis. ^{29}Si magic angle spinning NMR spectroscopy and ^{1}H - ^{29}Si cross polarization measurements were carried out at intervals on these preparations by Xian-Dong Cong and R. James Kirkpatrick, and the results were subsequently published (Cong et al. (1993).

The starting materials all showed primarily (but not entirely) Q^4 peaks indicative of fully cross-linked silica tetrahedra. As the reaction proceeded, the Q^4 peaks gave way progressively to a variety of other peaks characteristic of the reaction products. With both Nevada opal and Beltane opal, in the $KOH-Ca(OH)_2$ bearing preparations, the relative intensity of the starting Q^4 peak dropped rapidly, and only about 20% of the original intensity was left after 60 days. The predominant reaction product peak was attributed to Q^2 sites; some evidence for Q^1 sites and other, less well definable peaks were also encountered. It is well established that Q^2 and Q^1 sites are also characteristic of C-S-H gels, suggesting some similarity between these reaction product gels and C-S-H.

The calcium-free KOH mixes produced reaction products (i.e."pure" potassium silica gels) showing rather different NMR characteristics. Various broad bands were generated, indicative of Q^3 and Q^2 configurations in a variety of local environments, rather than the relatively sharp Q^2 and Q^1 peaks noted earlier. It would appear that the internal structures of the "pure" potassium-bearing ASR gels generated were different and less well organized than those of the gels produced with $Ca(OH)_2$ present.

THE CHEMISTRY OF ASR GEL – ARE THERE TWO PHASES?

The NMR results cited above appear to be in conformity with the idea frequently espoused in recent ASR literature suggesting that there are at least two distinct ASR products or phases, one relatively rich in Ca and perhaps trending toward an alkali-bearing C-S-H of limited (or non-existent) swelling capacity, the other being the traditional "swelling gel" composed primarily of potassium (or sodium) silicate hydrate with only a little calcium. Conclusions to this effect harken back to the classic work of Powers and Steinour (1955); more recent observations include those of Liang et al. (1992), Dron and Brivot (1996), and Kurtis et al. (1998), among others.

Other views of the influence of calcium in ASR gels have been have been suggested by several authors. For example, Monteiro et al. (1997) considered that the influence of calcium content on swelling is not due to formation of a separate phase, but to the fact that the divalent calcium ions reduce swelling (of the alkali silica gel component) by being inactive in the formation of the diffuse double layers responsible for swelling. Lombardi et al. (1996)

did not consider separate phases, but concluded that ASR gels formed a series defined structurally only by $CaO:SiO_2$ ratios; the alkalis present were said by these authors to be "simply the result of the trapping of the solution of precipitation into the texture of the gels".

The variation in calcium content (whether or not associated with the formation of a distinct second phase) is often related to physical location of the ASR gel in concrete, and perhaps to its age. Knudsen and Thaulow (1975) observed that gel close to a reacting grain showed low calcium contents (a few percent CaO); gels that had moved progressively further along cracks away from the grain showed progressively higher CaO contents. It was assumed that the gel movement was progressive, and that the gel furthest away was oldest, and had the longest exposure to calcium from the surrounding cement paste. Similar observations were recorded by Liang et al. (1992), but these authors specifically concluded that two distinct gel phases existed.

Much of the published literature on gel compositions was summed up by Helmuth and Stark (1992). These authors concluded that ASR gels of different compositions "may be regarded as mixtures of different proportions of (1) an alkali silicate hydrate sol or gel and (2) poorly crystalline calcium silicate hydrates containing some alkali (as well as variable water content)".

Specifically, Helmuth and Stark (1992) concluded that (1) the published ASR gel analyses were entirely consistent with the phase equilibrium results of Kalousek (1944) for gel compositions in the CaO-Na_2O-SiO_2-H_2O system, (2) that the published analyses could be expressed as being due to combinations in the same location of mixtures of a specific alkali silicate hydrate phase and a specific calcium alkali silicate hydrate phase, (3) that the compositions of the two phases (on a water free basis) are 17% $(Na_2O + K_2O)$ and 83% SiO_2 for the alkali silicate hydrate and approximately 6.6% $(Na_2O + K_2O)$, 52.6% CaO and 40% SiO_2 for the calcium alkali silicate hydrate, and (4) that accordingly, the percentage of the calcium-bearing phase in any given ASR gel could be calculated as being 2.32 times (83 – % SiO_2).

EXPERIMENTAL

Small amounts of laboratory mortars were prepared using a high alkali ASTM Type I cement ($Na_2O_{equiv.}$ 1.31%, K_2O 1.57%) and two opal-bearing natural sands kindly provided by N. Whiting of the Minnesota Department of Transportation. Both sands were known to have participated in ASR in pavements (Whiting and Peterson, 1998). The sand:cement ratio used was 1.0; the water:cement ratio used was 0.5. Some mixes incorporated additional alkali in the form of 1% sodium sulfate by weight of cement predissolved in the mix water.

The mortars were mixed by hand and were compacted into small plastic containers under vibration, and then exposed to 100% RH in a fog room maintained at 24°C, with loosely-fitted caps through which holes were drilled to insure contact with the water-vapor saturated air. After approximately four months the specimens were demolded and vertical slices cut using a saw lubricated with propylene glycol; these slices were dried, impregnated with low viscosity epoxy resin, then polished and coated for backscatter SEM observation and EDS analysis.

It was found that individual opaline sand grains showed strong evidences of ASR reaction. The sand grains affected had undergone extensive dissolution and showed significant cracking through the grains and in many cases into the surrounding paste. In contrast, the sand grains composed of various non-opaline components showed no signs of reaction. Many of the ASR cracks were seen to extend to the upper surfaces of the relatively thin specimens.

Despite the extensive reaction no ASR gel was found in any of the cracks. Alkaline solutions several mm in depth were found above the mortars within the specimen containers after the fog-room exposure. It appears likely that the mobile gel had been dissolved and drawn into these solutions through the cracks; unfortunately, these solutions had been discarded without analysis.

Typical illustrations of the appearance of the reacted sand grains are provided in Fig. 2.
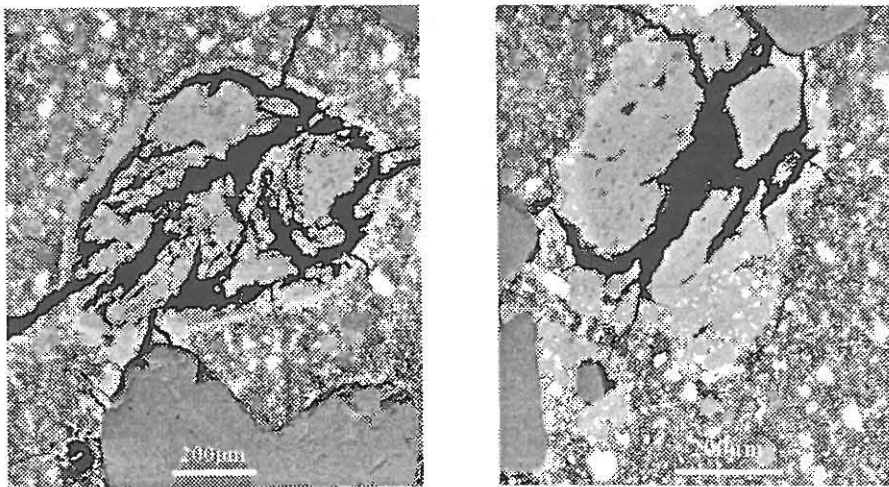

Fig. 2. Appearance of reacted opaline sand grains.

Qualitative EDS examination of the residual solid material within the affected grains disclosed the presence of potassium and calcium in all areas. There was some variation from place to place within a given reacted sand grain, and much greater variation between different grains. It was thought that each affected opaline sand grain had fully reacted, and the reaction product had been self-partitioned into "mobile" ASR gel which was lost, and immobile ASR gel which remained. Naturally there could be no assurance that the partitioning was complete, but after four months of reaction with a very high alkali cement in wet environment the author would expect this to be so. In this view, according to the picture developed in the proceeding discussions, the 'mobile' component should have been largely K-N-S-H gel (in the terminology of Helmuth and Stark (1992)), and the immobile component the Ca-rich phase, (C-K-N-S-H). This proved not to be the case.

The analyzed compositions (on a water-free basis) of residual material in the nine reacted sand grains as analyzed by EDS are provided in Table 1. The "other" chemical components include substantial contents of Al_2O_3 in all but two of the grains, substantial contents of

Fe_2O_3 in several grains, and small contents (< 1%) of MgO, SO_3, MnO_2, and TiO_2 in most of the grains.

It was found that the CaO percentages ranged from as little as 1.5% to as much as 35%. The alkalis (primarily K_2O, as expected) ranged from about 3% to almost 17%, and the SiO_2 contents ranging roughly from just over 50% to about 75%. Two of the grains in the Na_2SO_4-treated mortar had slightly more sodium than usual, but there was no other noticeable effect of Na_2SO_4 treatment.

The range of the SiO_2, alkalis, and CaO compositions in Table 1 essentially span the full range of compositions for the various ASR gels reported in the literature.

TABLE 1: EDS Analyses of Residual Gels in Individual Sand Grains

No.	Sand*	1% Na_2SO_4 used?	% SiO_2	% K_2O	% Na_2O	% CaO	% "Other"
1	WS	no	67.4	9.9	0.8	9.5	12.4
2	WS	no	54.5	7.3	0.9	35.3	2.0
3	JS	no	76.3	10.7	1.5	3.3	8.2
4	JS	no	72.7	5.7	0.7	1.5	19.4
5	JS	no	59.5	3.0	0.3	24.1	13.1
6	JS	yes	58.5	13.6	3.0	24.8	0.1
7	JS	yes	69.3	11.6	2.9	8.5	7.7
8	JS	yes	53.4	4.8	0.7	28.5	12.6
9	JS	yes	55.2	7.1	0.9	19.2	17.6

* Code for sands used by Whiting and Peterson (1998)

In order to compare these analyses with the model provided by Helmuth and Stark (1992), it was first necessary to recalculate the analyses on a basis that fixed the sum of the CaO, K_2O, Na_2O, and SiO_2 contents at 100%. This was done, and the recalculated results are provided in Table 2, Table 2 also contains the calculated percentages of the "K-N-S-H" calcium-free component and "C-K-N-S-H" high calcium component according to the model.

One analysis (No. 4) showed so little Ca that it yielded a SiO_2 content of 90%, which was beyond the range attributed to the pure K-Na-S-H component in Helmuth and Stark's model. Presumably it could be considered as 100% of an unusually silica-rich K-Na-Si-H gel. The particular sand grain was nearly completely reacted, possibly 2/3 of its mass being dissolved; accordingly, the high SiO_2 content did seem to not reflect unreacted opal material.

The other eight analyses fell within the range of the model. As indicated in Table 2, the allocations varied from 100% of the supposedly mobile, swelling K-N-S-H gel component to 64 % of the supposedly immobile, non-swelling Ca-K-N-S-H component, i.e. the C-S-H-like phase. This result was quite unexpected.

These values are obviously not in accord with the idea that the ASR product formed within the aggregates is the alkali-rich component, and that the Ca–rich component is produced only

as a result of intimate or prolonged contact of the alkali-rich component with cement paste. If the Helmuth and Stark model calculations are meaningful, all of the reacted sand grains except Nos. 3 and 4 have substantial contents of the Ca-rich component.

The idea that the in these systems the alkali-rich component has been mobilized, dissolved, and removed, leaving *only* the Ca-rich component behind seems to be equally incorrect. The calculations indicate that at least a third of the alkali-rich component is present in the all of the gels analyzed, and the two grains mentioned earlier are entirely composed of this "phase".

Obviously, more work is needed.

TABLE 2: Analyses Normalized to 100% ($SiO_2 + K_2O + Na_2O + CaO$), and the Resulting Partitioning Into the Two Gel Components According to the Model of Helmuth and Stark (1992).

No.	% SiO_2	% K_2O	% Na_2O	% CaO	Calc. % "K-N-S-H"	Calc % "C-K-N-S-H"
1	76.9	11.3	0.9	10.8	86	14
2	55.6	7.4	0.9	36.0	36	64
3	83.1	11.7	1.6	3.6	100	0
4	90.2	7.1	0.9	1.9	--*	--*
5	68.5	3.5	0.3	27.7	66	34
6	58.6	13.6	3.0	24.8	43	57
7	75.1	12.6	3.1	9.2	82	18
8	61.0	5.5	0.8	32.6	49	51
9	67.0	8.6	1.1	23.3	63	37

*Not calculable

Regardless of the validity of the model, it is important to note that with these reactive sands, as with all opaline materials and perhaps others, dissolution (whether or not preceeded or followed by swelling) is a major feature of the ASR reaction process even at 24°C. Various authors have pointed this out in passing, but it seems not to have been emphasized very much in the literature.

CONCLUSIONS

ASR gel remains a complex entity, highly variable in chemical composition and properties. The model of Helmuth and Stark (1992) that postulates that any given ASR gel consists of an intimate mixture of an alkali-rich and a calcium rich phase appears to provide a reasonable basis for considering gels of varying compositions. However, application to analyses of residual undissolved ASR gel in fully reacted natural opal sand grains leads to unexpected results, and it is obvious that further investigation is needed.

ACKNOWLEDGMENTS

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