

## ALKALI SILICA REACTIVITY MECHANISMS OF GEL FORMATION AND EXPANSION

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A series of well characterised samples of hydrous siliceous materials ranging from cherts to CT opal have been treated with sodium, potassium and mixed hydroxides under a range of conditions. The OH groups are attached only as monomeric groups at surfaces or within the open structure in all samples. Degradation of these materials and reaction products produced have been examined using  $^{29}\text{Si}$  NMR, scanning electron microscopy and microanalysis. On treatment with alkalis discrete alkali-silica gels only formed if solutions were very concentrated or if calcium ions were also present. Degradation is dependant on surface area but increases rapidly as the hydration state of the sample increases.  $^{29}\text{Si}$  NMR studies the transient presence of monomer, dimer and trimer OH groupings. A model of the reaction mechanism and the formation of gel product which takes account of the experimental observations is proposed.

### INTRODUCTION

The simple view of deleterious alkali-aggregate reaction being the reaction between silicious aggregate and alkalis from the cement is in detail much more complex. Even the view suggested by Diamond (1), Jones & Poole (2), and numerous others that the reaction takes place in two main stages, reaction followed by swelling of the gel produced does not take account of various other factors such as the nature of the gel produced and its change in composition and change in physical properties with time as it moves away from the reaction site.

It is a common observation that the deleterious expansion of the gel reaction product which leads to cracking of the concrete surrounding it varies considerably from case to case as does the rate at which the expansion progresses and the volume of gel that is produced. In at least one example, the Kambura Dam concrete two gels were produced, a voluminous one which does not cause deleterious expansion and a resinous small volume gel from an opaline material which appears to be the principal cause of the expansion (Hammersley, Pers.Comm).

#### The Deleterious Expansion of Concrete

Expansion of concrete due to alkali-aggregate reaction has been clearly shown by Hobbs (3) and others to result from the development of microfractures within the fabric of the concrete. Initiation of such a fracture and its subsequent propagation is dependant on the gel developing at a reaction site producing sufficient swelling pressure to overcome the tensile strength of the surrounding concrete.

In a thorough study of synthetic alkali-silica gels by Krogh (4), it was suggested that gel viscosity was of prime importance in crack development. Factors influencing gel viscosity including gel structure and composition, temperature and water content were investigated, but the modification of the gel with time as the reaction continues were not considered in the study. More recently French (5), has shown that gel composition changes as it moves away from the reaction site, becoming richer in calcium and poorer in alkalis. This progressive compositional change has been suggested as a mechanism whereby alkalis are regenerated within the cement paste to allow continued alkali-aggregate reaction. This process will also modify the viscosity of the gel initially formed by the reaction as it develops

### Reactive Silica

A large number of siliceous materials have been shown to be alkali-silica reactive, these include opals, fused silica, volcanic glass and some cherts and chalcedonies. In an extensive study of 28 materials of this sort Adams, Hawkes and Curzon (6) were able to demonstrate that they all contained at least a small amount of water ranging from 15.31% for one Australian opal down to 0.26% for calcined flint but more typically between 1 and 8%. Using solid state  $^{29}\text{Si}$  NMR they were also able to show that silanol monomer groups  $\equiv\text{Si}-\text{OH}$  were present in each case. This finding confirms the presence of single OH groups attached to the silica network as indicated in the Glasser Kataoka model (6). However, it was not possible to differentiate between 'surface' and internal OH groups.

In a scanning electron microscope study samples of gels from alkali-silica affected concrete were examined to provide a direct comparison with gels produced from a selection of reactive siliceous materials treated with alkali hydroxides. These materials included greywacke and chert taken from concrete coarse aggregate, volcanic glass, fused silica, calcined flint, CT and AG varieties of opal and chert.

These materials were subjected to attack by strong alkali solutions (1 to 4 M), KOH, NaOH and mixed potassium and sodium hydroxides. Some of the materials were held at 20°C while others were held at temperatures of 38°C and 80°C during reaction. The storage periods ranged from 30 minutes to 4 weeks.

The experiments were of three types. The siliceous component ground flat and held in the surface of a cement 'pat' or disc, as crushed and washed powder, (between 212µm and 500µm grain size) and as individual grains mounted in epoxy resin and polished ready for immediate examination in the scanning electron microscope.

Some observations concerning the production of gel and the corrosion of the siliceous specimens are of interest and have relevance to models of the reaction process. The strong 4M alkali solutions produced gel in almost every case at 20°C though amounts varied considerably. Opals produced the largest quantities of gel. With 1M solutions and specimens mounted in epoxy resin only two opal specimens and fused silica showed any evidence of gel development within a 76 hour time period though most specimens had etched and degraded surfaces which could often be associated with crystallite or compositional boundaries within the specimen. (Fig. 1A). This corrosion of the surface without visible gel being present was also noted after 192 hours storage at 40°C for the epoxy mounted specimens. (Fig. 1B). One epoxy mounted CT opal specimen produced gel within 24 hours storage in 1M sodium or potassium hydroxide solutions at 20°C. SEM examination of the vacuum dried gel at 76 hours showed that small calcium rich crystallites had formed on its surface presumably precipitated from the interstitial fluid within the gel network as it dried under vacuo (Fig. 1C). This opal contained 0.07% CaO and 9.28% water.

An Australian opal which contained 15.31% water produced copious gel after only 30 minutes storage at 20°C and small specimens mounted in epoxy for SEM examination had almost entirely dissolved after 24 hours in 1M alkali solution at 20°C. It is perhaps important to note that this opal also contained a small amount of calcium (CaO = 0.09 wt %). These two opals were the two most highly hydrated samples examined. Most specimens contained a small amount of calcium the highest being calcined flint (CaO = 0.26 wt%) though this material only contained 0.26 water.

In a separate series of experiments samples mounted epoxy resin were stored in 1M NaOH and KOH solutions which were saturated with calcium hydroxide. After 72 hours storage at 40° visible gel had formed on the surfaces of all the specimens (Fig. 1D). With the stronger alkali solutions, and with higher storage temperatures volumes of gel produced increased suggesting reaction rate in terms of formation of gel reaction product increased with both increase in reactant concentration and with reaction temperature. No clear distinction could be drawn between reactions with the sodium as against potassium hydroxide solutions. However, in a separate experiment using LiOH considerably more gel was produced than with the other hydroxides under similar conditions.

Compositions of Akali-Silica Gels

A detailed examination and analysis of gels produced as a result of the reactions between calcium hydroxide saturated solutions of mixed 1M KOH and reactive siliceous materials was undertaken. Some of the gel analyses are given in Tables 1 and 2.

TABLE 1 - Analyses of gels taken from particles mounted in cement pats (Normalised weight %)

Storage Temperature °C		SiO <sub>2</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
20	Greywacke B	35	42	7	13
20	Greywacke D	38	32	6	13
20	Greywacke J	22	59	5	4
20	Chert E	33	26	20	19
20	Chert H	17	54	19	4
20	Wood Opal X	44	33	10	13
38	Greywacke C	36	24	19	20
38	Greywacke G	36	35	7	18
38	Greywacke Y	38	19	19	14
38	Wood Opal	37	25	18	10

TABLE 2 - Analyses of gels from wood opal mounted in a cement pat (Average results Normalised weight %)

Storage Temperature	Number of Analyses	SiO <sub>2</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
20°C	8	45	34	8	10
38°C	7	56	14	13	17
80°C	5	57	1	25	16

If account is taken of the simplified chemistry of these experimental gels the similarity of the analyses to published analyses of gels extracted from alkali-silica reacted concretes is striking. Direct comparison may also be made with the three new analyses of concrete gels given in Table 3.

TABLE 3 - Analyses of alkali-silica gels extracted from concrete cores (Normalised weight %).

Sample	number of Analyses	SiO <sub>2</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
1	8	66	11	8	14
2	1	68	12	9	11
20	2	60	27	2	10

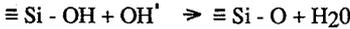
This similarity between the experimental and 'natural' alkali-silica gels from concretes supports the suggestion that inferences drawn from the artificial gels may reasonably be extrapolated to gels produced in structural concrete.

A striking feature illustrated by Table 2 is the reduction in the calcium content of the gels with increasing temperature and reaction rate.

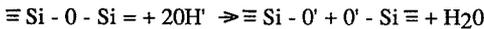
The Detailed Reaction Mechanism

It is generally recognised that reaction between reactive silica and the alkalis in the cement paste form the first stage in the process which produces a gel reaction product which then swells by absorbing water.

Dent Glasser and Katoaka (7), propose a two stage model for the attack by alkali on a hydrous disordered silica. In this model the reaction is envisaged as proceeding by an acid-base reaction in which OH<sup>-</sup> groups from the alkali solution react with the acid silanol groups.



The charge on the terminal oxygens are balanced by Na<sup>+</sup> ions which diffuse into the structure. Further OH<sup>-</sup> groups may be dispersed on the silica in two different sites the first within the "holes" in the open structure while the second lie on the outer surfaces of the structure. Access by OH<sup>-</sup> and Na<sup>+</sup> ions to the inner sites would be limited by the size of the 'holes' and by the distance they are from the particle surface. The surface sites will be dependant on surface area considerations. In the second stage further OH<sup>-</sup> attack the siloxane (Si-O-Si) bridges within the structure.



This process is thought to loosen and break up the structure leading to the formation of an alkali-silica gel polymer.

Silica is slightly soluble in water to the extent of 6PPM at 25° but solubility increases with temperature, pressure and with increasing pH of the solution. Experiments with quartz by Morey et al. (8) suggest that the solubility of silica is dependant on the rate of diffusion of dissolved silica away from parental material and this in turn will be controlled by the mobility of fluids close to the reaction site. The alkali concentration, the effective surface area of the siliceous component and the nature and stability of its structure, will also be important in dissolution of the silica

The mechanisms of migration of Na<sup>+</sup> and OH<sup>-</sup> ions through the surrounding cement paste have been discussed by French (9). He suggests that the migration of water and alkalis to reacting aggregate particles is a function of the 'hygroscopic' nature of the silicon ions produced by the reaction. These silicon ions remain within or close to the reacting material to form gel which will not migrate away until it has become fluid enough through absorption of water into the gel network.

The alkali ions can be readily exchanged in these gels by simple washing suggesting that these ions are not firmly attached to the gel structure. This feature is exploited by methods of staining alkali-silica gels for ease of identification (10).

<sup>29</sup>Si NMR studies of gels forming from alkali reaction with opaline materials indicate the transient development of monomer, dimer and trimer OH<sup>-</sup> groupings which eventually all revert to monomeric groupings in the sols formed when reaction is complete.

#### A Reaction Model

The evidence presented above suggests that reaction proceeds by the rupture of the siloxane bridges as indicated in Fig. 2. The terminal oxygens may be balanced by alkali cations with the adjacent silicon gaining an OH<sup>-</sup> group. The system will be dynamic depending on interatomic forces and thermal motion. It is further complicated in that the alkali cation's will normally be surrounded by a number of water molecules. The average number of molecules associated with the relevant cations are shown in Table 4 below.

TABLE 4 - Comparison of ionic radii and average hydration values for various ions.

Cation	Ionic Radius A°	Coordination	Average number of H <sub>2</sub> O Molecules per ion
K <sup>+</sup>	1.38	VI	5.4
Na <sup>+</sup>	1.02	VI	8.4
Li <sup>+</sup>	0.74	VI	14.0
Ca <sup>2+</sup>	1.70	VI	24.0

If account is taken of the size of each ion with its envelope of water molecules a clearer explanation of their reactivities and behaviour emerges. In particular it may be inferred that the calcium ions will tend to remain near the surface of the developing silica gel until the voids in the gel network become large enough for them to enter displacing the smaller alkali ions.

The model suggested in Fig. 2. envisages the breakdown of the siloxane (Si-O-Si) bridges in the silica structure adjacent to the Si-OH groups which will distort and reduce the local stability of the network. The system is dynamic in that the siloxane bonds break and reform as water and alkali cations penetrate the structure. The more open the structure and the greater its hydration state the more rapidly it is attacked.

Calcium ions because of their double charge and large envelope of water molecules tend to remain near the surface of the developing gel as a CSH phase, (11) which is less soluble in alkali solution than sodium or potassium gels.

In a real concrete, pore fluids are principally composed of strong sodium or potassium hydroxide solutions but calcium ions are also freely available. Thus as the gel swells on absorption of water the network opens sufficiently to allow calcium ions to penetrate into the gel where they can replace the alkali ions thus regenerating the alkali pore fluids which allow the reaction to continue while the gel gradually becomes increasingly calcium rich and loses its capacity to produce swelling pressures.

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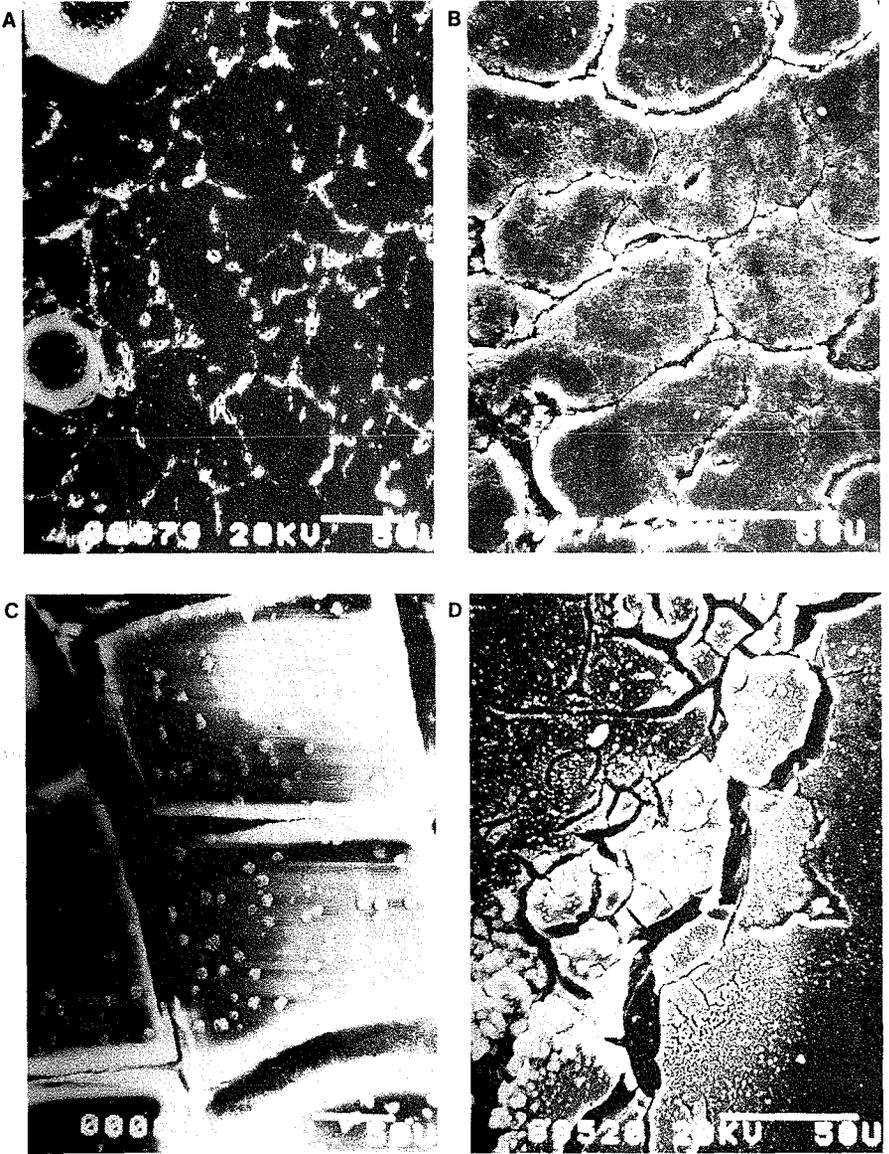


Fig. 1 Scanning electron micrographs of alkali attacked siliceous materials A) damage at grain boundaries in a fused silica surface (1M NaOH for 76 hours at 20°C). B) AG opal surface after 1M KOH attack for 192 hours at 40°C. C) Gel with calcium rich exudations after CT opal had been treated for 76 hours (1M,NaOH at 20°C). D) carbonated alkali-silica gel on the surface of Chalcedony (72 hours with 1M,NaOH at 40°C).

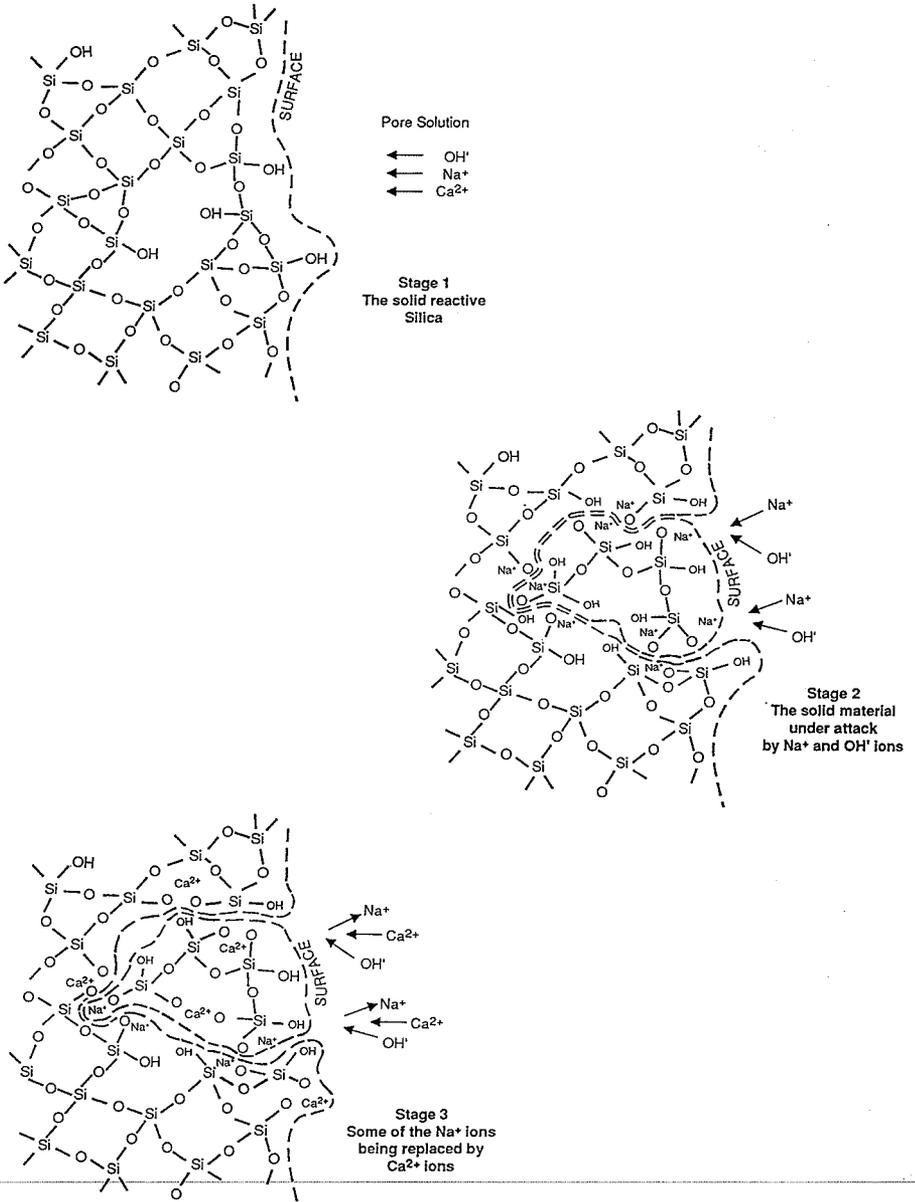


Fig. 2 Two dimensional diagrammatic representation of a reactive hydrous siliceous materials breaking down to form a swelling alkali-silica gel as a result of attack by alkali hydroxides in solution.