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S252

THE CHEMISTRY OF ALKALI-AGGREGATE REACTIONS

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SYNOPSIS

In an alkali-rich Portland cement clinker, some of the silicate, aluminate or sulphate ions are balanced by Na^+ or K^+ instead of Ca^{2+}. This can be undesirable, because the pH of the pore fluids in pastes made from such clinkers tends to be abnormally high. The hydroxyl ions produced react with certain types of aggregate, those containing ill-crystallised silica being particularly vulnerable:

$$Na^+, K^+ + OH^- + silica \rightarrow amorphous\ alkali\ silicate\ ('gel')$$
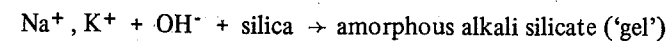
The breaking of bonds in the silica reduces its rigidity, and the presence of the alkali ions sets up an imbibition pressure: the result may be a 'swelling gel', whose presence can disrupt the concrete. To throw more light on these processes, and to clarify ideas concerning the 'quick chemical test' for reactive aggregates, the reaction between sodium hydroxide and various forms of silica has been studied. Variations with time in the sodium, hydroxyl and silicate concentrations in solution have been followed. If the silica is an absorbent and reactive form, such as silica gel, there is a rapid drop in the sodium ion content of the solution immediately after mixing. If the sodium hydroxide is present in excess, this is later reversed as the gel dissolves. Less reactive forms of silica, such as quartz, behave quite differently. The practical significance of these observations will be discussed.

SAMEVATTING

In 'n alkali-ryke Portlandsementklinker word sommige van die silikaat-, aluminaat- of sulfaatione deur Na^+ of K^+ in plaas van Ca^{2+} gebalanseer. Dit kan ongewens wees aangesien die pH van die porieëvloeistof in bry wat van sulke klinkers gemaak word, geneig is om abnormaal hoog te wees. Die hidroksielione, wat geproduseer word, reageer met sekere tipes aggregate en dié wat swak-gekristalliseerde silika bevat is besonder kwesbaar:

$$Na^+, K^+ + OH^- + silika \rightarrow amorfe\ alkalisilikaat\ ('jel')$$
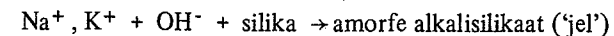
Deur die bindings van die silika te breek, word die onbuigsaamheid verminder en die teenwoordigheid van die alkali-ione begin 'n imbibisiedruk: die resultaat kan 'n 'swellende jel' wees wat die beton kan kraak. Die reaksie tussen natriumhidroksied en verskillende vorms van silika is bestudeer om meer lig op hierdie prosesse te werp en om idees met betrekking tot die 'vinnige chemiese toets' vir reaktiewe aggregate op te klaar. Variasies met verloop van tyd in die natrium-, hidroksiel- en silikaatkonsentrasies in oplossing is gevolg. Indien die silika 'n absorberende en reaktiewe vorm het, soos silikajel, vind 'n vinnige verlaging van die natriumiooninhoud onmiddellik ná vermenging plaas. Indien oortollige natriumhidroksied voorkom vind 'n omkering later plaas namate die jel oplos. Die gedrag van minder reaktiewe vorms van silika soos kwarts, is totaal verskillend. Die praktiese belangrikheid van hierdie waarnemings sal bespreek word.

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1.   INTRODUCTION

In the forty or so years since deterioration due to alkali-aggregate reaction was first recognized, research into and understanding of the process have both made impressive strides: some excellent recent reviews are available[1]. We propose to summarise here what seems to be current thinking on the problem, and to present some data that support these views. Our contribution begins with a general account of the phenomena associated with expansion or swelling, reserving the latter term for processes that involve uptake or intake of additional material. We then discuss the structure and chemistry of solids that can undergo swelling, and apply these ideas to the formation of 'swelling gels' in concrete. Finally we present evidence concerning the probable pressures that could be generated in this way.

2.   FUNDAMENTAL CONSIDERATIONS

The generation of pressure through physical expansion or restraint of physical expansion is a familiar phenomenon: burst water pipes, steam engines, bimetallic strips, are examples that spring to mind. Thermal expansion, change of phase and piezo-electric effects have all been used to generate pressure in this way. Although dictionaries do not differentiate precisely between 'expansion' and 'swelling', common usage generally equates swelling with an increase in the total quantity of material (as in the *swelling* of the tissues at the site of an injury, or a river *swollen* by flood water). This seems a useful distinction, and where the uptake or intake of extra material is the result of spontaneous imbibition (often producing a change in chemical composition) the resultant swelling might be considered to be 'chemical expansion'.

Mere expansion, or swelling, does not in itself create pressure; to create pressure, the material must be restrained in some way. For fluids, this restriction must be total, or virtually so, and the pressure produced is isotropic. Solids, because of their rigidity and definite shape, can produce pressure even if only partially confined, as in a bimetallic strip, or the distortion of girders in a fire. Moreover some solids, such as clay minerals, expand or swell anisotropically, although gels and other amorphous solids exhibit only isotropic expansive properties.

It is worth noting that from one substance to another there is no direct correlation between the amount of free expansion (expansion at constant pressure) and the pressure generated at constant volume by the same conditions, because compressibility varies enormously. A freely expanding gas undergoes a large volume change with rise in temperature, but if restricted to constant volume produces only a relatively low pressure compared with a metal, whose much lower compressibility more than compensates for its lower coefficient of expansion.

Perhaps all of the above seems rather obvious: we restate it here to point out that those expansive aggregates that produce the greatest free swell are not necessarily those with the greatest potential for destruction.

3.   THE PHENOMENON OF SWELLING

Swelling, in the sense used here, implies expansion through taking up or forcing in additional matter, and this requires a driving force to accomplish the movement of material. We will leave out of the discussion those cases where this force is purely physical (eg blowing up a balloon), and confine our attention to those in which the driving force is chemical in origin.

A substance moves - if it can - from a region where its chemical potential is high to one where it is low. Such a variation in chemical potential implies that free mixing is in some way prevented, or at least is relatively slow. In the familiar example of osmosis, free mixing of the solutions is prevented by a membrane permeable to the solvent and (ideally) impermeable to the solute(s). The solvent moves spontaneously into the solution in which its chemical potential is the lowest - that is the one containing the highest concentration of solute. A similar effect is found with some solids or semi-solids, and is generally termed imbibition; fluid moves into the interior of the solid, where its chemical potential is low. Rubber, for example, swells in this way when placed in benzene, or dry gelatine when placed in water. No semi-permeable membrane is necessary in such systems, because the relative rigidity of the solid prevents free mixing; provided that the solid is not too rigid, swelling results.

What then are the requirements for a solid to swell when placed in water? It must in the first place be sufficiently polar to exert some attraction on the surrounding water molecules: metals or polythene do not imbibe water. Neither do sand or salt, despite being polar: in order to swell, our solid must be neither too rigid nor too soluble. In addition to attracting water, therefore, it must be relatively insoluble and capable of expanding in at least one dimension, perhaps through rupturing weak bonds or distending a partially collapsed structure.

Substances with layer structures are often able to absorb additional molecules between their layers, and so swell in the perpendicular direction, increasing the inter-layer or basal spacing. Examples are graphite intercalation compounds or, more relevant to our problem, clay minerals. Uptake of water by clay minerals can produce sufficient pressure to cause serious engineering problems[2]. High-ratio sodium silicates such as magadiite also exhibit basal spacings that vary with water content[3]; although there have so far been no reports of the formation of such compounds during alkali-aggregate reactions, the possibility should be borne in mind. The authors will be delighted to examine any potential specimens.

Fibrous substances, such as cotton or wood, exhibit two-dimensional swelling perpendicular to the fibres, and we can at present think of no example of this likely to be concerned in the alkali-aggregate reaction. It is the third case - substances such as gels and similar non-rigid three-dimensional frameworks - that interests us most.
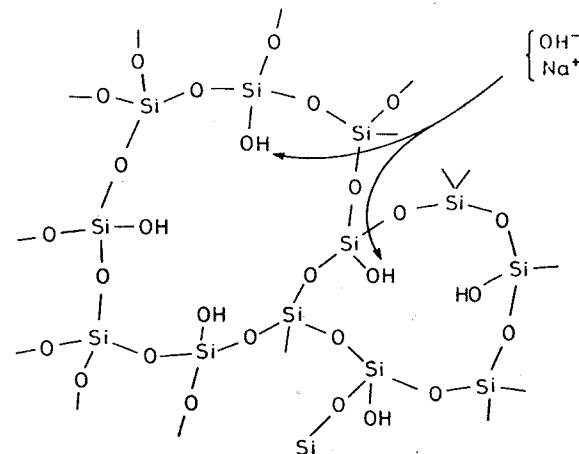
If such a substance is to swell and produce pressure, its framework must be permeable to water, and, although sufficiently strongly bonded to maintain solidity, not completely rigid. Thus felspars are too impermeable to imbibe water at all, while zeolites (of similar composition) are porous enough to imbibe water but because they have relatively rigid frameworks do not swell appreciably. In contrast, partially decomposed silicas and sodium silicate gels formed from them can exert sufficient imbibition pressure to disrupt concrete[1,4].

Such a swelling solid, although harmless while the concrete remains plastic, may well be the most disruptive item that a set concrete could contain[5], since it can exert pressure on any neighbouring rigid bodies, such as other aggregate particles, irrespective of whether it is completely contained or restricted (Figure 1a). If decomposition proceeds further, so that the semi-solid is converted into a viscous liquid that can ooze, pressure is exerted only if all of the surrounding pore spaces are completely filled (Figure 1b)[6], or if imbibition of water is more rapid than movement of the gel (for example, following a sudden influx of water into the concrete). Cracks filled with gel (Figure 1c) are a common feature of concretes disrupted through reactive aggregate, but it is very difficult to say whether they are the cause or the effect of the problem.

4. REACTION OF ILL-CRYSTALLISED SILICA WITH ALKALI

With the aim of gaining insight into the mechanism of alkali-aggregate reaction, the model system of silica gel and sodium hydroxide has been studied. Some kinetic and other results have already been reported[7]. Although the gel used is very much more reactive than even the most deleterious aggregates normally encountered, it appears from these

KEY

SOUND AGGREGATE

REACTIVE AGGREGATE

SEMI FLUID REACTION PRODUCT

CEMENT MATRIX

Figure 1a: A swelling solid exerts pressure on all neighbouring solid material.

Figure 1b: A viscous fluid exerts pressure only after all available pore space is filled.

Figure 1c: Cracks produced by the expanding material are filled by further supplies of gel. These may contribute further to the disintegration under, for example, cyclic conditions of wetting and drying.

FIGURE 1: Effect of a reactive aggregate particle on concrete. (The size of the pores in the matrix is greatly exaggerated).

studies to act as a reasonably good model; the advantages in using it are that its homogeneity and well defined particle size simplify the interpretation of results.

The structure of a typical ill-crystallised hydrous silica is represented diagrammatically in Figure 2a; the more open the structure, the more reactive it is likely to be. Titration methods[8] showed that the sample used here contained about 0,38 moles of OH per mole of SiO_2; if these are assumed to be more or less uniformly distributed, rather more than one third of the silicon atoms carry silanol groups. Some molecular water is also present, but for simplicity is not shown in Figure 2a; it seems reasonable to assume that it would be hydrogen bonded to the silanol groups.

When such a material is placed in NaOH solution, two reactions occur. Initially, there is a straight acid-base reaction, in which the hydroxyl groups of the alkali solution react with the acidic silanol groups:

Figure 2a: Acidic silanol groups in the gel are neutralised by the alkali. ...
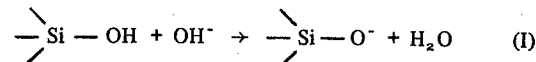
Figure 2b: Further supplies of alkali attack siloxane bridges.

FIGURE 2 : Structure of a silica gel or ill-crystallised silica, and the effect of NaOH.

$$-Si-OH + OH^- \rightarrow -Si-O^- + H_2O \qquad (I)$$

The charge on the terminal oxygen atoms so produced is balanced by the Na$^+$ ions that simultaneously diffuse into the structure. At the completion of this step, the structure is as shown in Figure 2b (again, the H_2O produced is omitted from the diagram; it may be hydrogen bonded to the terminal oxygen atoms or form part of the hydration sphere of a Na$^+$ ion or both). The overall reaction could be represented as::

$$H_{0,38}SiO_{2,19} + 0,38\,NaOH \rightarrow$$
$$Na_{0,38}SiO_{2,19} + 0,38\,H_2O \qquad (Ia)$$
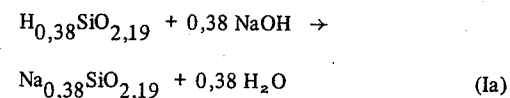
As far as the internal structure of the silica gel is concerned, this can be regarded as exchange of Na$^+$ for protons, without rupture of any Si - O - Si (siloxane) bridges.

As further hydroxyl ions diffuse into the structure, attack on the siloxane bridges begins:

$$-Si-O-Si- + 2OH^- \rightarrow$$
$$-Si-O^- + {}^-O-Si- + H_2O \qquad (II)$$
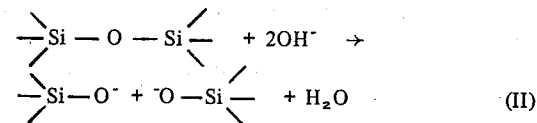
This simultaneously loosens the structure and increases its capacity to absorb Na$^+$ and H_2O (Figure 2b); a similar effect has been observed for flint[9]. In the limit, the structure disintegrates completely, and the silica passes into solution as silicate ions. The overall reaction could be written, approximately:

$$Na_{0,38}SiO_{2,19} + 1,62\,NaOH \rightarrow$$
$$2Na^+ + H_2SiO_4^- \qquad (IIa)$$
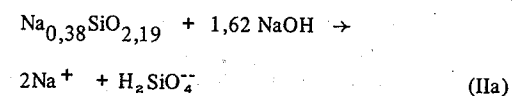
although the formula of the silicate species depends on the concentration and pH of the solution produced. In general, silicate solutions contain a mixture of monomeric and more highly polymerised species, so that the average size of anion would be larger than the monomer used, for simplicity, in (IIa).

The sequence of events within any given silica particle depends on factors such as the rate of diffusion of ions through the structure. Figure 3 shows some possible results of placing such a particle in NaOH solution (a). Initially, a concentration gradient of Na$^+$ within the particle will undoubtedly form (b), reaction (I) having proceeded to completion in the outer parts. If diffusion is rapid, or
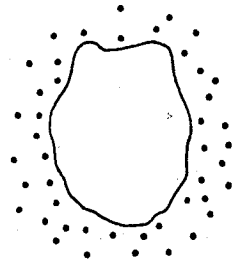
Figure 3a: A silica gel particle surrounded by sodium hydroxide solution; only the sodium ions are shown.
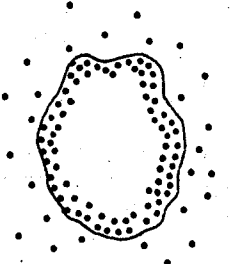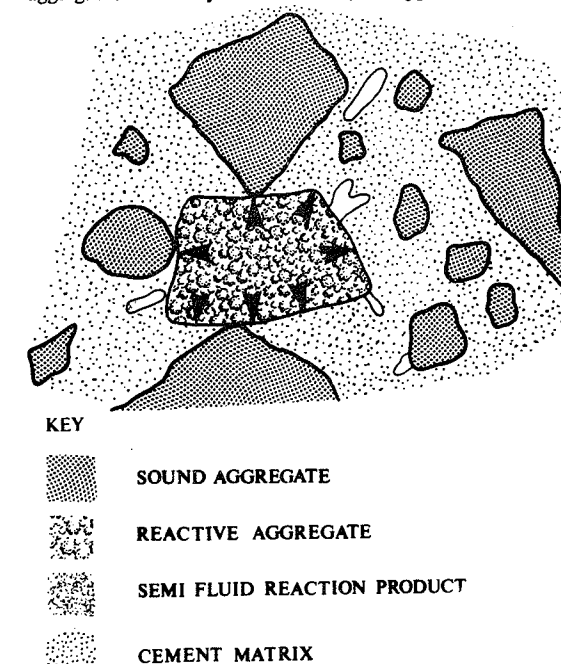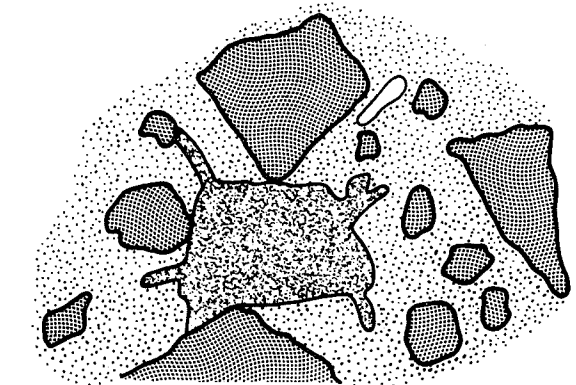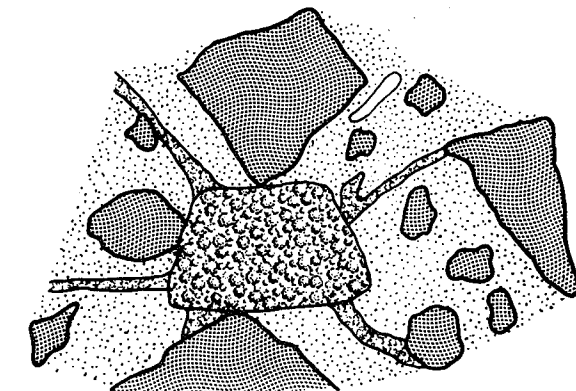
Figure 3b: Sodium ions begin to diffuse into the gel.

TABLE 1 : Initial and final compositions of silica gel in contact with alkali solution. Only solutions that reached at least quasi-equilibrium with solid are included. The osmotic pressure π was calculated assuming all the silica in solution to be present as monomer. For solutions more concentrated than 0,1 M this is unlikely to be true, and values for these solutions are probably too high.

| Initial mixtures (200 mℓ NaOH) | | Composition of final solution (M) | | | SiO_2/Na_2O for solid remaining | π |
NaOH (M)	SiO_2 gel* (g)	[OH⁻]	[SiO_2]	[Na⁺]		kg cm⁻²
0,01	1,2	,0001	,0080	,0053	35,7	0,33
0,05	1,2	,0008	,0551	,0474	27,4	2,6
0,05	2	,0006	,0487	,0424	27,6	2,3
0,05	5	,0003	,0280	,0252	28,7	1,4
0,05	10	,0003	,0117	,0150	41,3	0,68
0,05	10	,0001	,0080	,0064	34,8	0,38
0,05	10	,0001	,0075	,0076	35,7	0,38
0,05	10	,0001	,0068	,0068	35,2	0,35
0,10	10	,0003	,0275	,0272	20,3	1,4
0,10	10	,0007	,0429	,0324	21,4	1,9
0,20	4	,0021	,2911	,1964	8,72	12,4
0,50	10	,0030	,7076	,4640	3,39	26,7
0,70	20	,0016	1,5076	,692	6,55	55,8
0,70	30	,0016	1,0125	,4961	12,6	38,2
0,70	50	,0013	,4043	,2116	14,0	15,7

* containing 7 per cent H_2O
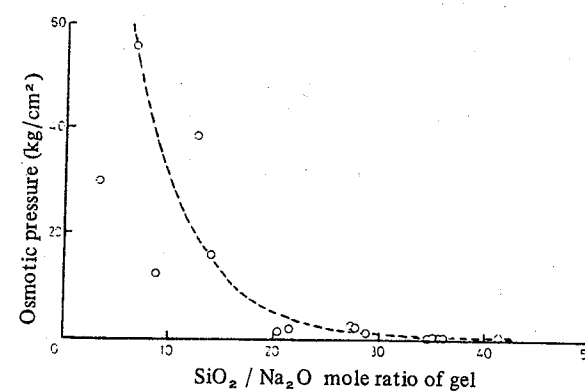
FIGURE 5: Calculated osmotic pressures of solutions from Table 1 plotted against the SiO_2/Na_2O ratios of the remaining solid.

In Figure 6, free swell of various gels, measured as reported earlier[7], is compared with their imbibition pressure calculated as described above. The free swell values were determined after thirty minutes of contact between gel and solution, while the imbibition pressures are calculated for equilibrium, where attained; nevertheless the way in which both vary with the ratio of the starting mixture is similar. Of particular importance from the practical viewpoint are the maxima that occur in all curves at an overall mole ratio of between about three and five, confirming the idea of a 'pessimum' concentration of reactive aggregate[12,13]. This ratio is rather lower than that calculated from Vivian's[13]
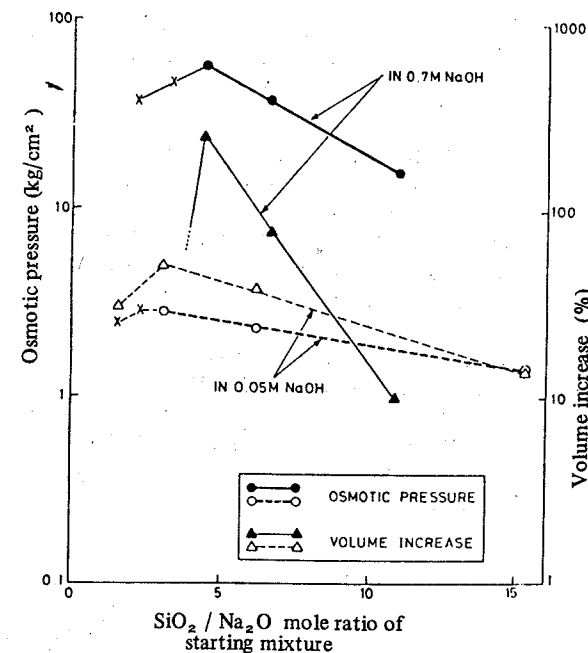

FIGURE 6: Free swell of solids and osmotic pressure of solutions plotted against SiO_2/Na_2O ratios of the starting mixtures. The volume increase of the solid was measured as described in[7], after 30 minutes in contact with NaOH solution. The osmotic pressure was calculated from the final composition of the solution (see Table 1); crosses correspond to solutions in which no solid remained.
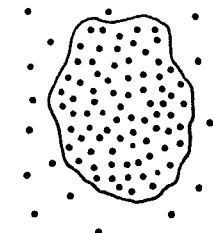

Figure 3c: Rapid diffusion leads to an even distribution of sodium throughout the particle (reaction I complete before reaction II begins).
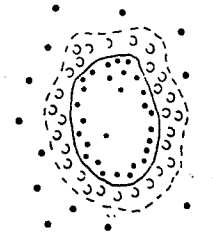

Figure 3d: If diffusion is slower, the surface begins to disintegrate before any sodium ions reach the centre of the particle (reactions I and II occur simultaneously).

if the particle is sufficiently small, reaction (I) may proceed to completion throughout the particle before any further events occur, leading to a uniform concentration of Na⁺ throughout the particle (c). However, experimental evidence from kinetic studies suggests that, with silica gel at any rate, disintegration and dissolution of the outer layers begins before ion exchange is complete in the centre of the particle (d); studies on the distribution of elements in aggregate particles[10] confirm that the Na⁺ is not uniformly distributed. Although the reaction may proceed stepwise at the atomic level, studies on the bulk material are complicated by the overlapping of the two steps.

Nevertheless, useful results can be obtained from such bulk studies. Figure 4 shows estimates of how the number of silanol groups in silica gel varies after treatment with sodium hydroxide solution. Various quantities of silica gel were agitated with 0,7 M NaOH solution; samples of the solid were removed at intervals, washed with water and then with HCℓ to pH 2 (thus replacing any Na⁺ by protons, and restoring all terminal oxygen atoms to silanol groups) and finally filtered and dried at 120° C. The number of silanol groups per mole of silicon were then estimated by titration (Sears' method[8]) and by ignition to 1200 °C. Both methods of estimation show the same trend: treatment with alkali increases the number of silanol groups per mole of silicon, through the rupture of siloxane bridges, and the more alkali that is available (the lower the SiO_2/Na_2O ratio) the more rapidly this disintegration proceeds. The results from ignition are systematically higher than those from titration, suggesting that some molecular water - about one molecule for every eight silanol groups - is retained after drying at 120 °C.

It is of interest to know how great an imbibition pressure could be exerted by sodium silicate gels, but this is not a quantity that is easy to measure directly: a recent study[11]
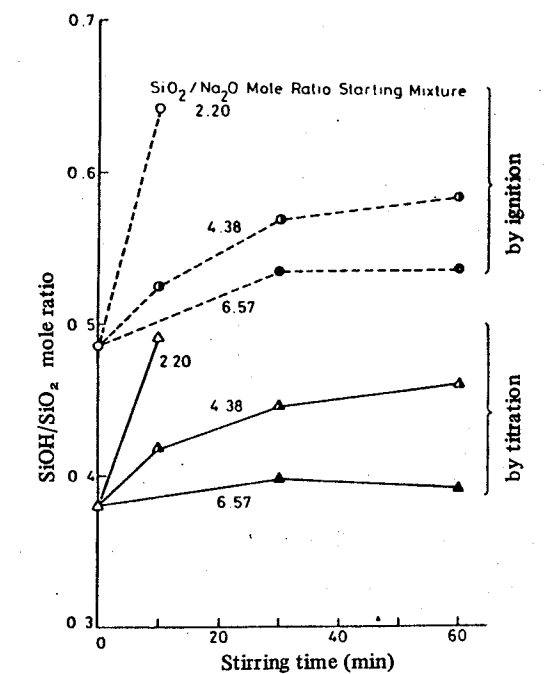

FIGURE 4: Effect of treatment with alkali on the silanol content of silica gel. After stirring with 0,7M NaOH for 10-60 minutes, samples were acidified and dried, as described in the text. The silanol content was estimated by titration[8] and by ignition to 1200 °C. The latter method gives a higher value, presumably because residual water is included.

gives values up to about 100 kg cm⁻², but notes considerable experimental difficulties. It is however possible to estimate it indirectly, from results described elsewhere[7]. Silica gel left in contact with sodium hydroxide solution eventually reaches a state of equilibrium (or at least quasi-equilibrium) at which the composition of any remaining solid and the solution in contact with it ceases to change. (Runs in which all the silica gel dissolved are not included here.) It is assumed that the imbibition pressure of the remaining gel is then equal to the osmotic pressure of the surrounding solution, and the latter can be estimated roughly from the concentration of the various species present. The data used are given in Table 1, and the osmotic pressure of the solution is plotted against the SiO_2/Na_2O mole ratio of the gel in contact with it in Figure 5. Although there is considerable scatter, as might be expected from the rather crude assumptions made and the difference in extent of reaction (Ia), several interesting points emerge. Imbibition pressures of gels increase rapidly as the alkali content increases, and the values reached - up to about 50 kg cm⁻² - are ample to disrupt concrete, whose tensile strength is typically of the order of 30 kg cm⁻² or less. No estimates of imbibition pressures are available for SiO_2/Na_2O mole ratios of less than about three, because fluidity and solubility increase rapidly below this value. It is possible that the curve shown turns downward before this point is reached, but more data would be needed to establish whether this is so.

Addendum

With respect to the diffusion of ions across membranes, and osmotic cells in general, some of our recent results may be of interest. Small blocks of silica gel were prepared, and immersed in a mixed solution of calcium and potassium hydroxides. Rather to our surprise, growths began to form, rather similar to those observed in the so-called 'silicate garden' phenomenon. These were initially translucent, but rapidly became opaque: after about two hours they were completely opaque, and growth ceased. Analysis using an analytical electron microscope (CORA) showed that the translucent growths consisted of silica with a low calcium content and virtually no potassium: as time passed the lime content increased and the growths began to take on the appearance of crumpled foils: after about two hours the lime:silica ratio stabilised at about 1:3. The opaque material thus appears to be a very poorly crystallised C-S-H gel.

The external solution and samples of the solution extracted from inside the growths with a hypodermic syringe were both analysed at intervals; the values obtained are shown in the figure. The values for the internal solution are very rough, because of sampling difficulties. Nevertheless, it seems apparent that any osmotic pressure generated must be due to potassium and silicate ions. Calcium ions appear to penetrate the membrane to an insignificant extent; presumeably they are precipitated and bound in the membrane as C-S-H gel.
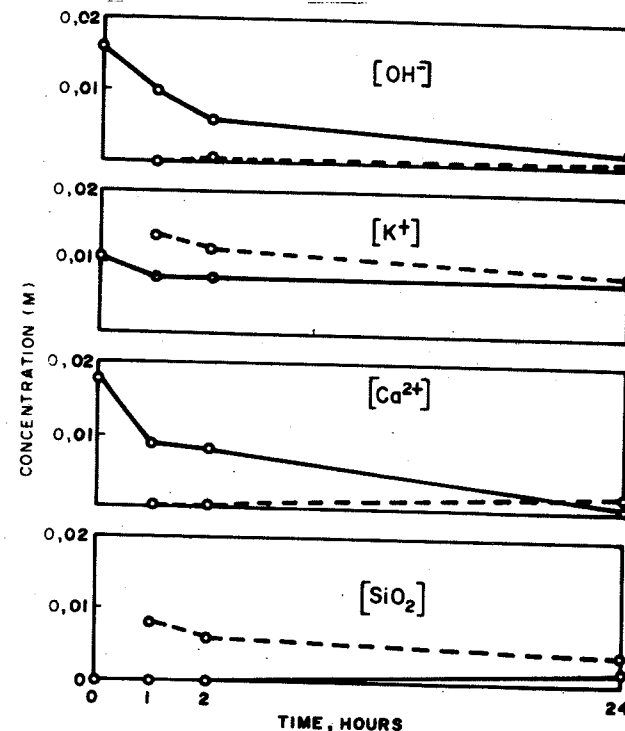

Figure 1: Concentration of species inside (- - -) and outside (———) membraneous growths surrounding a block of silica gel. The horizontal scale is not linear. Initial conditions: 0,06g SiO_2 as very hydrous ($\approx$ 90%H_2O) silica gel; 50 ml of external solution, 0,01 M KOH saturated with $Ca(OH)_2$, but containing no excess solid $Ca(OH)_2$.

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results on mortar bar expansion tests, but this is hardly surprising in view of the very different conditions obtaining in the two studies. The significant fact is that the pessimum concentration has a sound scientific basis.

5. CONCLUSIONS

Model systems using silica gel and sodium hydroxide solutions suggest that the mechanism of alkali-aggregate reaction can be described as follows.

Ill-crystallised and absorbent silicas (or, indeed, silicates) suck in alkali and hydroxyl ions from the pore fluid, and after any silanol groups locally present have been neutralised, the hydroxyl ions attack siloxane bridges, with consequent loosening of the structure. More sodium ions diffuse in, and the resulting polyelectrolyte exerts considerable imbibition pressure. Water is thus absorbed, and the loosened framework of the aggregate particle swells, pushing aside adjacent material in the process. Totally disintegrated material may ooze into any cracks formed, and may further contribute to the disintegration of the concrete; for example if cycles of drying and wetting of the concrete occur such that the dried gel picks up water during the wet cycle more rapidly than it can ooze away.

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