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PHYSICAL AND CHEMICAL PRINCIPLES IN ALKALI SILICA REACTIONS

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* A S R is used as an abbreviation of Alkali Silica Reactions

PREFACE

In 1983, at the Division of Building Materials of the Lund Institute of Technology, Lars-Olof Nilsson reported "Alkali-silica Reactions in Scania, Sweden". The work commenced in 1978.

Five international conferences regarding the effects of alkalis in cement and concrete have taken place, the last one in Copenhagen in 1983. Even so, it seemed difficult to obtain a reasonably accurate picture of the chemical and physical conditions for alkali-silica reactions, and in particular for such mechanical consequences as pop-outs.

In the following paper, I have tried to collect essential chemical and physical facts, concerning alkali-silica reactions. After several discussions with Lars-Olof Nilsson, I have tried to accommodate the chemical part of the contents to the world picture of an intelligent civil engineer.

Britt Andersson has prepared the end-papers and the diagrams, completed the two-dimensional chemical formulas, and framed the tables.

SUMMARY

Properties of silica, which may have an effect upon its sensitivity to attack by alkaline solutions, are discussed. The chemistry of the transformation of the silica to different silicates is explained. It is proposed that the transformation may start by an attack on acid hydroxide groups, bound to silicon atoms ("silanol groups", -Si-OH), when this silicon atom is still part of a solid lattice.

Principally, the silicate ions may form calcium silicate hydrates with low solubility, or solutions of an alkaline metal (sodium or potassium) silicate, if the concentration of calcium ions is low enough.

The properties of pure water solutions of sodium and potassium silicates are accounted for, regarding pH value, size and composition of silicate ion, and viscosity.

The properties are treated in relation to the molar ratio between silica and alkaline metal oxide in the silicate. In a fresh reaction mixture, where this ratio is still low, the solution always contains considerable amounts of alkaline metal hydroxides, together with the silicate.

It is interesting that the viscosity is very much influenced by the concentration of the silicate in the solution, but only to a very moderate degree by the ratio.

With increasing concentration, the liquid gradually turns into a gel, and the gel into a solid.

In concrete, the alkaline metal hydroxides may originate from the cement. The development of silicate gel is discussed, and some chemical analyses are given.

Other sources, such as de-icing salts (sodium chloride), are also potential risks in concrete, but the mechanism of the reaction is not clear in detail.

The conditions in concrete are complicated by the possibility that "composite gels" may be formed. The solid component may be a calcium silicate hydrate, residual reactive silica, or inert mineral grains. The importance of composite gels regarding its capacity to damage concrete is still under discussion.

Calcium silicate hydrates may be formed when so much of the hydroxide ions has become consumed for silicate formation that the pH value has decreased to a level of about 12. This makes the solid calcium hydroxide soluble to quite a normal degree, thus increasing the concentration of calcium ions.

The physical conditions for imbibition of water are discussed. They are related to the conditions for osmotic pressure, and probably the ability of silicic acid and soluble silicates to absorb water is a main factor.

1. THE SILICA

Silica, or silicon dioxide (SiO_2), is one of the most important of the chemical components of concrete aggregates.

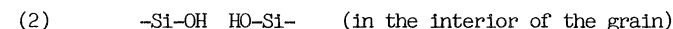
Well crystallized silica, such as quartz, resists the chemical influence of strongly alkaline solutions very well, as do, according to most Swedish experience hitherto, many well crystallized silicates, e. g. most feldspars. Van Aardt and Visser (1977) have, however, reported that alkaline feldspars, under certain conditions, may liberate hydroxide of sodium or potassium, or alkaline metal silicates.

In some types of rock, the silica lattice is less stable than in quartz. Strong mechanical stress can also make quartz insufficiently stable.

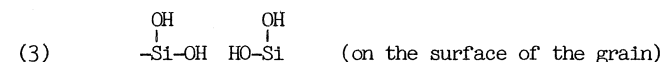
Opal is an extremely unstable form of silica. Instead of a stable oxygen bridge between two adjacent silicon atoms, as in quartz:



many of the silicon atoms may separately bind a hydroxide group:



or



Two OH-groups contain the same quantity of oxygen and hydrogen atoms as one molecule of water, H_2O , and one atom of oxygen, O. Thus, in opal the silica is chemically bound to some water. On the surface, quartz also contains a small amount of water, bound as hydroxide groups, $-\text{OH}$, to the silicon atoms.

Though silica is the main component of quartz as well as of opal, the latter mineral is far more exposed to chemical attack because of the less dense and less stable lattice. Also "silica-fume", with a glassy structure, has an essentially lower density than quartz:

Quartz	2635 - 2660 kg/m ³
Opal	2170 - 2200 "-
Silica-fume	2190 "-

Experience has proved that the density cannot be used for selecting reactive grains from a mixture of reactive and non-reactive grains in a gravel. Grains of fairly stable rocks may contain closed air cells, which makes the density of the grain lower than that which could be expected from the densities of each mineral in the rock.

Where the reaction rate is concerned, the porosity of the silica grains is important. A dense grain can only be attacked from the surface, but a grain with open porosity may also be attacked from internal surfaces.

2. THE TRANSFORMATION OF SILICA TO A SILICATE

A grain of silica, for having the ability to cause a "pop-out" or a "wet spot" on a concrete surface, must be possible to dissolve by reaction with an alkaline water solution. For this to take place, two reaction steps must occur:

1. A sufficient amount of "hydrated silica", -Si-OH , must be changed to a silicate .
2. A sufficient number of silicon atoms, forming silicate groups, must break away from the silica lattice to form a rather concentrated silicate solution in water (a silicate "gel").

2.1 The "silanol group"

In modern chemical literature, the -Si-OH group is sometimes called a "silanol group", perhaps because of its formal similarity to the alcohol groups.

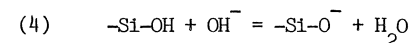
The -OH group reminds the reader of sodium hydroxide, NaOH , or calcium hydroxide, Ca(OH)_2 . However, this comparison is false. There does not exist a molecule of NaOH (or Ca(OH)_2), either as a solid crystal or as a solution, but only ions of sodium, Na^+ , and hydroxide, OH^- .

The same is true for calcium hydroxide. Since this compound is built from calcium ions, Ca^{2+} , and twice as many hydroxide ions, OH^- , it is not true that calcium hydroxide is less alkaline than sodium hydroxide, because all hydroxide ions are equally strong. However, the lattice of crystallized calcium hydroxide is so stable in water that a saturated solution of calcium hydroxide in water only contains a limited amount of hydroxide ions for each liter of solution. Thus, the solution has to be compared with an equally dilute solution of sodium hydroxide.

Chemically, the silanol group -Si-OH should preferably be compared with the acid group -S-OH in sulphuric acid, H_2SO_4 , and with the somewhat less acid group -P-OH in phosphoric acid, H_3PO_4 .

The slightly acid silanol group -Si-OH is different from the metal hydroxides and does not contain a hydroxide ion, OH^- .

On the contrary, it may consume one, making the solution less alkaline:



In this paper, I shall call the residual group -Si-O^- a "silicate group".

During the reaction (4) the silanol group -Si-OH breaks at the O-H bond, and the hydrogen atom H leaves its single electron to the oxygen atom O, giving the silicate group a negative charge. The hydrogen ion without its electron is called a hydrogen ion or a proton, H^+ .

The hydrogen ion immediately accepts the surplus electron from the hydroxide ion, OH^- , thus forming water, HOH or H_2O .

The reaction (4) is reversible as in all acid-base reactions, and it will reach an equilibrium when the hydroxide ion concentration, or the pH value, has decreased to a certain level.

It may seem strange that the OH group behaves so differently:

- * as a hydroxide ion, OH^- , adding strong alkalinity to a solution
- * as a more or less acid group, which may detach a positively charged hydrogen ion, H^+ , from a negatively charged residue, A-O^- .

Here, A may be, e. g., silicon, phosphorus, or sulphur.

Typical for metal atoms such as sodium, potassium or calcium, is that the outmost electron shell contains one or two electrons, which are easily able to leave the atom. A positively charged metal ion is formed, the electron arrangement of which is similar to that of a noble gas (neon for sodium, argon for potassium or calcium), and energy is liberated.

The oxygen atom in the hydroxide group readily takes up one electron from the metal atom, thus forming a hydroxide ion.

The other type of atoms, the oxide of which has an acid character, has a greater number of valence electrons: Silicon 4, Phosphorus 5, and Sulphur 6.

In silicon dioxide, SiO_2 , the silicon atom shares two electrons with each of the two oxygen atoms. In a complete lattice with oxygen in four directions, the silicon atom shares one electron from each of the four oxygen atoms.

The result is that the silicon atom has its valence electron shell "completed" to a noble gas (argon) shell by sharing with a number of electrons from oxygen atoms in the same molecule.

The stronger acid the oxide is, the more the shared electrons are displaced towards the central atom. If the second valence of the oxygen atom is bound to a hydrogen atom, as in a hydroxide group, the two shared electrons in the O:H bond will also be displaced towards the central atom, and towards the oxygen atom.

In a strong acid, such as sulphuric acid, this displacement is strong enough for the hydrogen atom to be liberated as a hydrogen ion, H^+ ,

from the oxygen atom, unless the solution is very acid, leaving the oxygen atom with an surplus electron.

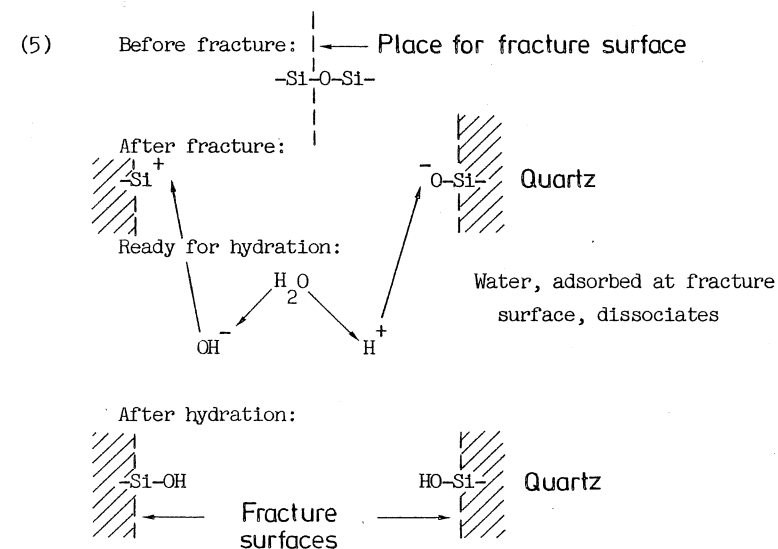
In a weak acid group, such as the silanol group, $-\text{Si-O:H}$, the displacement of the electrons is not so strong, and the hydrogen ion will only be liberated if the solution is rather strongly alkaline.

2.2 The alkaline attack on quartz or opal

In the interior of well crystallized quartz, almost every silicon atom, Si, is bound to four oxygen atoms, O. Normally, an oxygen atom has two valence bonds, and the second bond belongs to a second silicon atom. In this way, a large piece, or "crystal", of quartz, may be considered as being one giant molecule. Thus, it is difficult to dissolve such a good quartz in alkaline solutions at a temperature below 100°C .

The oxygen atoms on the surface of a quartz crystal have no "second" silicon atoms to bind. During the formation of the crystal from a hot alkaline water solution (perhaps 200°C), the surface silicon atoms were bound to hydroxide groups, OH, from the solution.

A fresh fracture surface of a quartz crystal is demonstrated below:



If such a perfect crystal of quartz becomes exposed to an alkaline solution, the silanol groups on the surface may very well be transformed into silicate groups according to the reaction (4).

It is unlikely that the bonds between the oxygen atoms and the silicon atoms in the lattice will be broken, and this would be necessary for bringing the quartz into solution.

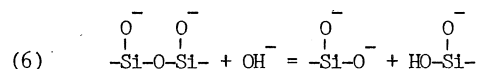
The surface of a grain of the opal is also covered with silanol groups, $-\text{Si}-\text{OH}$, and they may change to silicate groups in alkaline solutions, just as in the case of silanol groups on a quartz surface.

The opal has a much less dense lattice structure than quartz. There are two possible explanations for this:

1. The grain of opal is more porous and consequently contains a greater amount of external or internal surfaces.
2. The opal contains silanol groups, $-\text{Si}-\text{OH}$, not only at surfaces (external and internal), but also in the solid material. Thus, the system of oxygen links is not as stable in solid opal as in quartz.

The oxygen links between adjacent silicon atoms in opal are essentially more exposed and consequently more easy to attack than the oxygen links in quartz.

The attack may be described in the following way:



The higher content of silanol groups, $-\text{Si}-\text{OH}$, and the greater availability for attack on the oxygen links make it far easier for opal to dissolve in alkaline water than for well crystallized quartz.

A volume of silica (opal or another silica mineral) on a surface is dissolved when its silicon atoms are no longer bound by oxygen links to the central mass of the original grain.

Very often a damage may be observed on a concrete surface before all the silica in the reactive grain is dissolved.

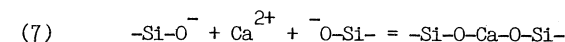
At the Fifth International Conference on Alkali-Aggregate Reaction in Concrete, held in Cape Town in 1981, L S Dent-Glasser described the dissolution of a reactive form of silica in an alkaline solution in a similar way.

2.3 The effect of the metal ions in cement paste

When Portland cement hydrates, calcium hydroxide is formed. If the concrete does not contain other soluble hydroxides, the maximal concentration of hydroxide ions will be about 0.04 moles per liter, and the corresponding calcium ion concentration is 0.02 moles per liter.

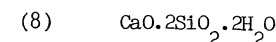
If the aggregate contains silica of a type, which is sufficiently reactive to be attacked by a hydroxide solution of such a low concentration, silicate ions will be formed, which contain about one silicate group, $-\text{Si}-\text{O}^-$, for each atom of silicon.

This solution contains calcium ions, the concentration of which is sufficient to form solid silicates with the silicate ions, and as a first step, the following reaction seems reasonable:



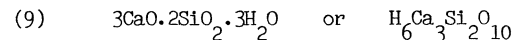
The three free bonds for each silicon atom (Si) are assumed to be occupied by OH groups

A calcium silicate phase called okenite exists and looks similar to this hypothetical reaction product:



The phase sometimes occurs in old concrete.

In freshly hardened concrete, which still contains crystals of calcium hydroxide, other calcium silicate hydrates form, which are similar to the formulas:



which is of great importance to the strength of hardened Portland cement concrete.

In concrete with an extra addition of highly reactive silica (pozzolanes) there may exist calcium silicate hydrates with less calcium.

Though calcium hydroxide in solid state is always present in a Portland cement concrete, the concentration of calcium ions in the pore liquid may diminish considerably. This will happen if the concentration of hydroxide ions is much higher than in a saturated water solution of calcium hydroxide, i. e. 0.04 moles per liter (pH value about 12.6).

If the cement contains an average percentage of sodium or potassium, the concentration of hydroxide ions in the pore liquid of concrete may very well, during the hardening, increase to e. g., 0.8 moles of potassium or sodium hydroxide per liter. This concentration corresponds to a pH value of about 13.9.

In such a strong hydroxide solution, a saturated solution of calcium hydroxide will not contain as much as 0.02 moles of calcium ions (Ca^{2+}) per liter.

Normally, the solubility product of calcium hydroxide would be helpful in calculating a reasonable value for the calcium ion concentration:

$$(10) \quad (\text{Ca}^{2+}) \times (\text{OH}^-)^2 = L$$

With the figures above, the solubility product L would be equal to

$$(11) \quad 0.02 \times 0.04^2 = 32 \times 10^{-6} \text{ mol}^3 \times \text{liter}^{-3}$$

The hydroxide ion concentration of 0.8 mol per liter would accept a calcium ion concentration of

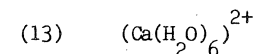
$$(12) \quad 32/0.8^2 \times 10^{-6} = 50 \times 10^{-6} \text{ mol per liter}$$

Practical analyses of concrete fluid with a hydroxide ion concentration of about 0.7 mol per liter have resulted in a calcium ion concentration of 2000×10^{-6} mol per liter.

This figure is 40 times greater than that calculated from the solubility product, but is still only about a tenth of the concentration in a saturated solution of calcium hydroxide in pure water.

An error of 40 times the calculated value seems to imply that the solubility product for calcium hydroxide is invalid.

A reasonable explanation is that calcium ions easily form complexes with other ions. Only calcium ions complexed with water:



are valid in the solubility product (10).

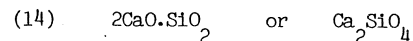
In a strongly alkaline solution, one or more hydroxide ions may replace water molecules, and the calcium ion in such a complex ion is not valid in the solubility product, but will still be comprised in a chemical analysis. There are also other sources of error in concentrated solutions, but these are not of such great importance.

The conclusion is that the presence of calcium hydroxide in hardened concrete does not influence the types of silicates, formed from silica, as long as the hydroxide ion concentration is high.

Later on, most of the hydroxide ions have become consumed by silicate formation. Now, the solubility product allows the concentration of calcium ions to increase, and different types of calcium silicate hydrates may be formed, alone or together with alkaline metal silicates.

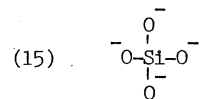
2.4 The influence of basicity on the type of silicate ions

In a silicate, all four bonds of the silicon atom may be used for forming silicate groups. The clinker mineral dicalcium silicate,



may serve as an example.

However, the "ortho silicate" ion in this mineral:



does not form unless the conditions are extremely basic, as in a clinker kiln with a raw mixture, partially converted to calcium oxide. In water solutions, the conditions are essentially less basic, even in a cement paste with a high alkali content.

The silica under reaction should be looked upon as a "silicic acid", quite comparable with other acids with OH groups, e. g. sulphuric acid and phosphoric acid. The fact that the silicon atom may be part of a large lattice does not alter this fact.

Since one of the hydroxide groups of a silicon atom, $-\text{Si}-\text{OH}$, has been attacked by an alkaline solution according to the formula (4) and transformed to a silicate group, $-\text{Si}-\text{O}^-$, and since subsequently one or more oxygen links to the main lattice have been split according to (6), then the silicon atom may have one, two, or three hydroxide groups in addition to the silicate group.

The transformation of the first hydroxide group changes the distribution of charges in the remaining hydroxide groups so that a higher concentration of hydroxide ions, or a higher pH value, is needed for shaping the second silicate group, and a still higher one for shaping the third silicate group.

This is quite in analogy with the conditions for other acids, capable of generating more than one hydrogen ion.

The basicity of water in a cement paste may be strong enough to change the first hydroxide group, or silanol group, to a silicate group. Sometimes the basicity is also sufficient to change the second hydroxide group to a silicate group.

3. STUDIES ON WATER GLASS SOLUTIONS

At the Symposium on Alkali-aggregate Reaction, Reykjavik 1975, Hanne Krogh referred to a work by Weldes and Lange (1969) about soluble silicates, like water glass. There are two essential differences, however, between alkaline metal silicates developing in concrete, and water glass:

- * Water glass is normally in equilibrium.
- * Water glass is normally free from lime.

From Welde and Lange (1969), I have used the following subjects:

1. The basicity of water glass solutions with different compositions.
2. The occurrence of silicate ions with more than one silicon atom.
3. The viscosity of water glass solutions.

3.1 The hydroxide ion concentration (the pH value)

In their study of soluble silicates, H H Weldes and K R Lange measured pH values of different sodium water glasses, dissolved in water. In Table 1 below, one of the authors' diagrams is evaluated at the sodium concentration of 1 per cent by weight, given as sodium oxide, Na_2O . 1 per cent is 10 grammes per kilogram solution. The molar weight of sodium oxide is 61.98, and each molecule contributes two ions of sodium. Thus, all solutions in Table 1 have a total concentration of sodium ions, running to:

$$(16) \quad 10 \times 2/61.98 = 0.32 \text{ moles per liter}$$

The concentration is less than the alkalinity in a hardened paste of a cement with normal alkali content.

Theoretically, the pH value of a pure sodium hydroxide solution with a concentration of 0.32 moles per liter would be about 13.5 at 20°C:

$$(17) \quad \log 0.32 = \text{pH} - 14; \quad \text{pH} = 13.5$$

(pH 14 corresponds to a 1.0 molar hydroxide solution)

This calculated pH value is rather close to the value 13.37 given in the top of Column 2 in Table 1.

In Table 1, a series of water glass solutions are presented, all with equal concentrations of sodium ions, but with different molar ratios between silicon dioxide (SiO_2) and disodium oxide (Na_2O). The ratios, given from chemical analyses, are presented in Column 1.

The pH value of each solution is presented in Column 2. In a solution with a low ratio, the pH value is relatively high, which means that the solution is rich in hydroxide ions:

$$(18) \quad \text{OH}^- = 10^{(\text{pH}-14)} \text{ mol per liter}$$

In the first solution, without silica, the pH value is equal to 13.37, and this value corresponds to a concentration of hydroxide ions, and sodium ions, of

$$(19) \quad \text{OH}^- = \text{Na}^+ = 10^{(13.37-14.00)} = 0.24 \text{ mol per liter}$$

In Column 3 and Column 4, the contents of disodium oxide are divided into two fractions, the sum of them is unity (1.0000).

In Table 1, the concentration of sodium ions in all solutions is always the same, 0.24 mol per liter, but the concentration of hydroxide ions follows the pH value according to (18).

Thus, in Column 3, the fraction of disodium oxide corresponding to hydroxide ions is presented as

$$(20) \quad \text{relative Na}_2\text{O}_{\text{OH}}^- = 10^{(\text{pH}-13.37)}$$

In Column 4, the remaining fraction of the disodium oxide is presented, and this fraction corresponds to the contents of silica in the solution:

$$(21) \quad \text{relative Na}_2\text{O}_{\text{sil}}^- = 1.0000 - \text{rel. Na}_2\text{O}_{\text{OH}}^-$$

This number is helpful in transforming the analytical molar ratio in Column 1 into a "silicate molar ratio":

$$(22) \quad (\text{SiO}_2/\text{Na}_2\text{O})_{\text{anal}} / \text{rel Na}_2\text{O}_{\text{sil}}^- = (\text{SiO}_2/\text{Na}_2\text{O})_{\text{sil}}$$

These "corrected" values are presented in Column 5 in Table 1. They are more useful than the analytical values for understanding how the silicate ions in the solution may be built up.

Table 1

Col 1 Col 2 Col 3 Col 4 Col 5

Anal. molar ratio $\text{SiO}_2/\text{Na}_2\text{O}$	pH value measured	Relative values		Silicate molar ratio $(\text{SiO}_2/\text{Na}_2\text{O})_{\text{sil}}$
		$\text{Na}_2\text{O}_{\text{OH}}^-$	$\text{Na}_2\text{O}_{\text{sil}}^-$	
0.00	13.37	1.0000	0.0000	-
0.52	13.12	0.5623	0.4377	1.19
0.77	13.04	0.4677	0.5323	1.45
1.03	12.93	0.3631	0.6369	1.62
1.55	12.51	0.1380	0.8620	1.80
2.06	12.12	0.0562	0.9438	2.18
2.48	11.73	0.0229	0.9771	2.54
3.09	11.45	0.0120	0.9880	3.13
3.40	11.20	0.0068	0.9932	3.42
4.13	11.10	0.0054	0.9946	4.15

In Figure 3.1:1 below, the pH value (Table 1, Column 2) is plotted against the analytical molar ratio (Column 1), and against the "silicate" molar ratio (Column 5).

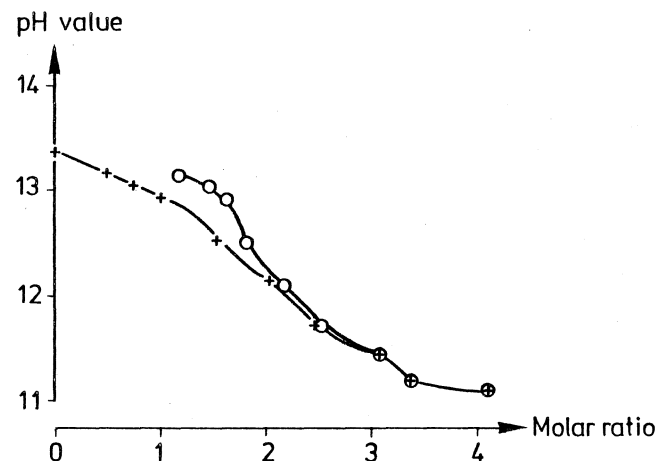


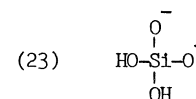
FIG 3.1:1 pH value in sodium silicate solutions, all with a sodium ion concentration of 0.24 mol per liter, plotted against
 + analytical molar ratio, $\text{SiO}_2/\text{Na}_2\text{O}$
 o silicate molar ratio, $(\text{SiO}_2/\text{Na}_2\text{O})_{\text{sil}}$

At any pH value, there is a difference between the two ratios, the analytical one and the ratio which is counted only with disodium oxide which corresponds to the sodium silicate.

This difference is larger, the greater the concentration of hydroxide ions (or the pH value) of the silicate solution is. For solutions with high ratio, the pH value is low, and consequently the difference is small.

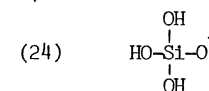
The second solution from the top of Table 1 has the lowest ratio, which almost equals 0.5 (analytical) or 1.2 (silicate).

A silicate molar ratio of 1.0 would correspond to a silicate ion with two of a total of four silanol groups transformed to silicate groups:

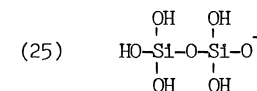


In FIG 3.1:1 it is shown that a pH value of about 13.2 is necessary for shaping two silicate groups around a silicon atom.

Further down in Table 1, the silicate molar ratio passes the value 2.0. If the silicate ions still contain only one silicon atom, only one of a total of four silanol groups will have been transformed to a silicate group:



Still lower down in the Table, the levels 3.0 and 4.0 for molar ratios (analytical or silicate) are passed. The silicate ions in such solutions must contain more than one silicon atom. A ratio of 4.0 would correspond to an ion composition, e. g.:



Solutions with such high ratios have pH values of 11.5 or lower, according to Figure 3.1:1. The splitting of oxygen bridges between two silicon atoms according to (6) does not take place, and silicate ions with more than one silicon atom are stable.

Sodium silicate solutions with such a high molar ratio and such a low pH value cannot form in fresh concrete, because the solubility of calcium hydroxide allows a calcium ion concentration of 0.02 mol per liter. This is enough for forming calcium silicate hydrates without an essential content of alkaline metal ions. Thus, sodium (or potassium) silicate solutions in reasonably fresh concrete rarely reach a molar ratio higher than 2.5 between silica and disodium oxide.

3.2 Di- and polynuclear silicate ions in water glass solutions

Solutions of sodium silicates and potassium silicates with various molar ratios were studied with light scattering techniques, thus estimating the average molecular weights in the solution.

In Table 2 (for sodium silicate solutions), and Table 3 (for potassium silicate solutions), this ratio was presented in Column 1. The concentrations of the solutions are not reported. The weight average molar weight, determined by light scattering techniques, is presented in Column 4.

The analytically determined values of molar ratio $\text{SiO}_2/(\text{Na or K})_2\text{O}$, from Column 1, are recalculated to atomic ratio $(\text{Na or K})/\text{Si}$, and the values are presented in Column 2.

The total "dry" molar weight of alkaline metal oxide together with the corresponding amount of silicon dioxide, the sum divided by the amount of silicon dioxide, is given in Column 3:

$$(26) \quad (\text{Col. 2}) \times 61.98/2 + 60.08 = (\text{Col. 3}) \quad \text{For sodium silicates}$$

$$(27) \quad (\text{Col. 2}) \times 94.20/2 + 60.08 = (\text{Col. 3}) \quad \text{For potassium silicates}$$

The value from the light scattering estimation, Column 4, is divided by the value from the calculation above, Column 3. The result is presented in Column 5 as an average value of the number of silicon atoms in the silicate ions of the solution.

From Tables 2 and 3, the values from Column 5 are plotted against the values from Column 1, in Figure 3.2:1. Where the two tables can be compared, the average number of silicon atoms in a silicate ion follows the analytical molar ratio $(\text{SiO}_2/(\text{Na, K})_2\text{O})$ in the same way, irrespective of the nature of the alkaline metal ion (Na^+ or K^+).

Table 2Sodium silicate solutions

Col. 1	Col. 2	Col. 3	Col. 4	Col. 5
Anal. molar ratio $\text{SiO}_2/\text{Na}_2\text{O}$	Molar quotient Na/Si	Calcul. mol. weight per Si atom	Estimated	
			Average mol. wght	Number of Si per ion
0.48	4.2	189	60	<1
1.01	1.98	121	90	<1
1.69	1.18	97	120	1.2
2.09	0.96	90	160	1.8
2.62	0.76	84	265	3.15
3.30	0.61	79	320	4.1

Table 3Potassium silicate solutions

Col. 1	Col. 2	Col. 3	Col. 4	Col. 5
Anal. molar ratio $\text{SiO}_2/\text{K}_2\text{O}$	Molar quotient K/Si	Calcul. mol. weight per Si atom	Estimated	
			Average mol. wght	Number of Si per ion
1.00	2.00	154	56	<1
1.75	1.14	114	115	1.0
2.50	0.80	98	295	3.0
2.80	0.71	94	304	3.2
3.31	0.60	89	495	5.6
3.62	0.55	86	628	7.3
3.97	0.50	84	848	10.1

Number of silicon atoms in an average ion

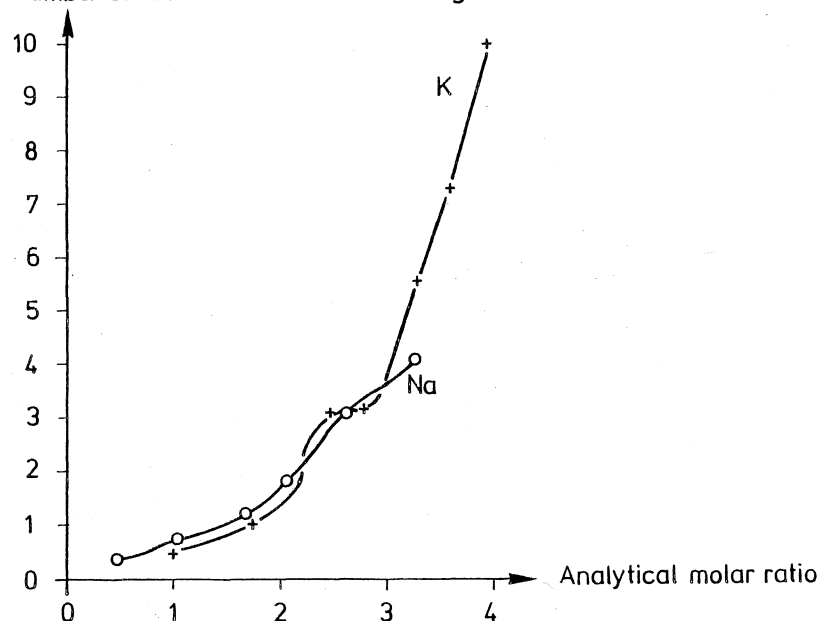
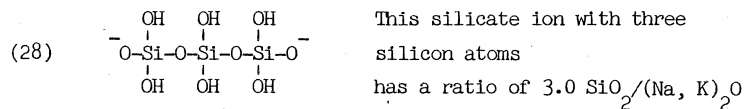


FIG 3.2:1 Average numbers of silicon atoms in silicate ions in (Na,K) silicate solutions with various molar ratios $\text{SiO}_2/(\text{Na}, \text{K})_2\text{O}$.

At a ratio of 2.5, the silicate ion, as an average, contains three silicon atoms. According to the authors, an alternative method with trimethyl silylation confirms the results.



3.3 The viscosity, or rigidity, of alkaline metal silicate solutions

Weldes and Lange (1969) have quoted two diagrammes from Vail, J G, (1952), one for sodium silicate solutions, and one for potassium silicate solutions. The diagrammes present the viscosity as a function of the sodium, or potassium, concentration (given as oxides: $(\text{Na}, \text{K})_2\text{O}$) of the solution. One graph is given for each ratio, $\text{SiO}_2/(\text{Na}, \text{K})_2\text{O}$.

In Table 4 (for sodium silicates), and Table 5 (for potassium silicates), the values of the analytical ratio is presented in the two first columns, the molar ratio in Column 1, and the weight ratio (from the diagrams) in Column 2. The molar ratio is obtained from the weight ratio:

Sodium:

$$(29) \quad (\text{weight ratio}) \times 61.98/60.08 = (\text{molar ratio } \text{SiO}_2/\text{Na}_2\text{O})$$

Potassium:

$$(30) \quad (\text{weight ratio}) \times 94.20/60.08 = (\text{molar ratio } \text{SiO}_2/\text{K}_2\text{O})$$

The concentrations of sodium ions, taken from Vail's diagram, at a viscosity of 1000 poises, are found in Column 3 of Table 4, and the corresponding concentration of silica in Column 4.

For the viscosity of 1 poise, the corresponding two sets of values are to be found in Columns 5 and Column 6.

For potassium, the concentrations for 1000 poises are not given. Thus, for the viscosity of 1 poise, the concentration of potassium is found in Column 3, and for silica in Column 4.

In Figure 3.3:1, the values in Column 4 and Column 6 (concentration of silicon dioxide at two different viscosities), are plotted against the values in Column 1 (molar ratio $\text{SiO}_2/(\text{Na}, \text{K})_2\text{O}$).

Sodium silicate solutions

Table 4

Analytical ratio $\frac{\text{SiO}_2}{\text{Na}_2\text{O}}$		At 1000 poises		At 1 poise	
molar	weight	per cent		per cent	
		Na_2O	SiO_2	Na_2O	SiO_2
Col. 1	Col. 2	Col. 3	Col. 4	Col. 5	Col. 6
4.13	4.0	—	—	5.69	22.76
3.61	3.5	8.34	29.2	7.40	25.9
3.09	3.0	11.33	34.0	9.15	27.45
2.58	2.5	14.60	36.5	11.36	28.4
2.06	2.0	18.18	36.4	13.61	27.22
1.55	1.5	22.11	33.2	15.91	23.87
1.03	1.0	—	—	18.61	18.61

Potassium silicate solutions

Table 5

$\frac{\text{SiO}_2}{\text{K}_2\text{O}}$		No measurements at 1000 poises	K_2O	SiO_2
molar	weight			
Col. 1	Col. 2		Col. 3	Col. 4
4.72	3.01		6.28	18.9
3.95	2.52		8.64	21.8
3.29	2.10		12.31	25.85
3.12	1.99		13.07	26.0
2.35	1.50		19.65	29.5

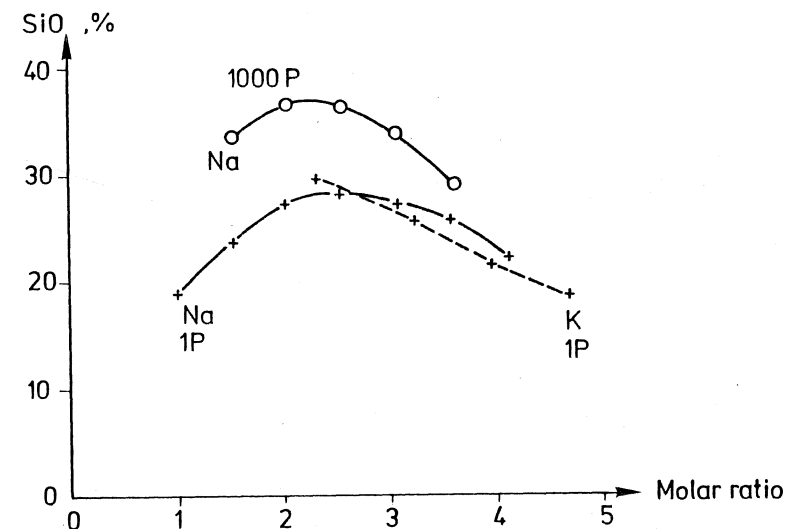


FIG 3.3:1 Concentrations of alkaline metal silicate solutions (expressed in per cent silica by weight). Solutions on the same curve have the same viscosity (1 or 1000 poises), but different molar ratios, $\frac{\text{SiO}_2}{(\text{Na,K})_2\text{O}}$

The Figure shows that the solution (or gel, if the solution is viscous) at a certain viscosity can accept the highest concentration of silica (and silicate, counted as silica):

for sodium silicate solutions (or gels):

1 poise solution, 28.4 % silicon dioxide at the molar ratio 2.6
1000 poises gel, 36.5 % silicon dioxide at the molar ratio 2.3

for potassium silicate solution:

1 poise solution, 29.5 % silicon dioxide at the molar ratio 2.3.

Note: The material does not comprise any potassium silicate solutions with still lower molar ratios. A solution with a higher concentration of silica could possibly, but not probably, exist.

No values are available for 1000 poises gels of potassium silicates.

Weldes and Lange (1969) quote that the viscosity increases rapidly with increased concentration, especially where potassium silicate solutions are concerned.

It seems surprising that an optimal molar ratio $\text{SiO}_2/(\text{Na,K})_2\text{O}$, not far from 2.5, exists. At this ratio, the concentration of silica is maximal in an alkaline metal silicate solution (or gel) for any viscosity.

It seems reasonable that the permitted silica concentration decreases when the molar ratio is increased, as shown in the right hand part of all graphs.

It may seem surprising that a range of molar ratios exists, where the permitted silica concentration decreases, also when the ratio is decreased, as shown in the left hand parts of the two graphs for sodium silicate solutions.

It seemed natural for me to choose just silica as a measure of the concentration of an alkaline metal silicate solution, because the silica is looked upon as the one source of expansion. Perhaps, this choice provides the explanation.

The molecular weights of dipotassium oxide (94), and disodium oxide (62), are not negligible compared with the one of silicon dioxide (60).

With decreasing molar ratios, the alkaline metal oxides will contribute increasingly to the total content of solids in the solutions, thus reducing the partial solubility of silica.

This explanation might elucidate why the left hand parts of the graphs decrease with decreasing values of the molar ratio.

If this explanation is correct, the range around the value 2.5 happens to be just the optimal molar ratio, where the effect of high contents of alkaline metal oxides (at low ratios), and the effect of long silicate ions (at high ratios) balance each other.

The water glass systems seem to be suitable for studying as a model for the liquid phase in A S R.

During (and after) the reaction, the reactive stone also contains solid materials, e. g. reactive or non-reactive mineral particles.

Later, when much of the hydroxide ions is consumed, particles of different calcium silicate hydrates may become part of this solid content.

The complexity of A S R in real concrete will be dealt with in Chapter 4.

4. INTERACTIONS FROM THE CALCIUM HYDROXIDE IN CONCRETE

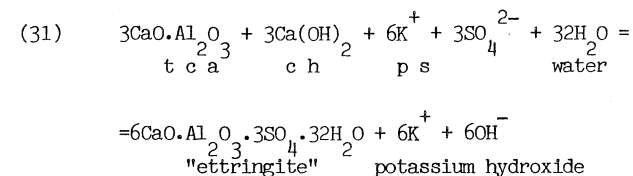
IN THE REACTIONS BETWEEN SILICA, SILICATE IONS, AND HYDROXIDE IONS

All tables and diagrammes hitherto have dealt with pure systems of water and sodium silicate or potassium silicate (or sometimes pure hydroxides). In this chapter, the complicated conditions in concrete will be taken into consideration.

4.1 The range of molar ratios of alkali metal silicates in concrete

During the mixing and moulding of the concrete, the concentration of hydroxide ions in the liquid is not high enough for dissolving silica in the aggregate, even if this has a composition, which makes dissolving in alkaline solutions possible, and even if the cement contains easily soluble sodium and potassium compounds, e. g. sulphates.

After one or two days, the sulphate ions have become bound by calcium aluminates in the hydrating cement. Instead, an amount of hydroxide ions has become liberated, which is equivalent to the total amount of alkaline metal (sodium and potassium) ions:

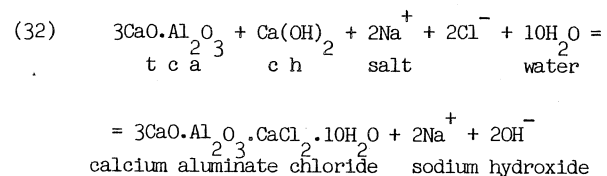


where t c a is tricalcium aluminate
 c h is calcium hydroxide
 p s is potassium sulphate

A lot of water is consumed for hydration reactions, and evaporation. Thus, the concentration of hydroxide ions may approach the level of 0.8 moles per liter.

According to Chatterji, S. (1979), the use of low alkali cement can protect the concrete from damage by A S R, but only in the absence of alkaline metal salts, such as sodium chloride, NaCl. He does not try to explain the mechanism when such a salt gives rise to A S R in concrete.

It is possible that the following reaction may be of importance:



The calcium aluminate chloride has solubility conditions, which probably favour the formation of the sulphate double salts. This may make it difficult to predict the danger of common salt, or sodium chloride, in contact with concrete.

Possibly, reactive forms of silica, such as opal, become in some way sensitized to attack of hydroxide ions in low concentration by sodium chloride, and this is an alternative explanation.

Normally, international experience states that no damage should happen if the contents of alkaline metal oxides in cement (U S A), or concrete (German Federal Republic), are kept below a safe level. However, this is tested for expansion in concrete. There remains a risk for limited damage, such as pop-outs, even at lower levels of alkaline metal oxide contents, because experience of various cements with respect to this type of damage is highly limited.

As soon as the hydroxide ion concentration of the water in the cement paste has increased sufficiently, the reactive silica minerals in the aggregate grains, e. g. opal, start to dissolve as alkaline metal silicates.

During the dissolution, hydroxide ions are consumed according to (4) and (6). In equilibrium, the molar ratio of the solution follows the pH value according to Table 1, and Figure 3.1:1, in Chapter 3.1.

Thus, the liquid very quickly reaches the molar ratio $\text{SiO}_2/(\text{Na}, \text{K})_2\text{O}$ of 0.5. Cleaned from the alkaline metal ions belonging to free hydroxide ions, the "corrected" or net molar ratio would be about 1.0. This means that two of the four silanol groups are transformed into silicate groups.

Later, when more of the hydroxide ions have become consumed, the pH value decreases. At a pH range of 12.0-12.5, the molar ratio will have increased to 2.0 whether the value has been corrected or not.

In this state, the solution has turned to a gel, provided that the concentration of the silicate solution is high enough.

At the decreased pH value the chemical composition of the solution in the cement paste will be modified in accordance to Chapter 2.3. The solubility of calcium hydroxide increases when the pH value decreases to about 12, and so the solid calcium hydroxide of the hydrated cement recovers its normal solubility, which was almost lost in the strong hydroxide solution.

At a calcium ion concentration of about 0.02 mol per liter, the gel may receive contributions of calcium silicate hydrates with very low solubility in the gel. This may make the gel a composite, more rigid than the corresponding pure alkaline metal silicate gel.

It was discussed at the 6th International Conference on ALKALIS IN CONCRETE in Copenhagen 1983, whether the gel with lime is more deleterious to the concrete than pure alkaline metal silicate gel, but more research is needed in this field.

4.2 Some chemical analyses of silicates from A S R

In Table 6 below, chemical analyses are collected from the following samples:

1. Gel drops, which have penetrated joints between ceramic tiles on concrete floors.

The drops totally dissolve, when stored in moist air.

2. White gel, collected from a space between the underside of the ceramic tiles and the cement mortar with which the tiles were fixed.

Table 6

Source Mol. wght	SiO_2 60.08	Na_2O 61.98	K_2O 94.20	CaO 56.08	Analytical molar ratio $\text{SiO}_2/\text{Sum metal ox.}$
SKF Göteborg					
Gel drops, % moles/100 g	48.7 0.811	8.5 0.137	27.8 0.295	0.7 0.012	1.83
White gel, % moles/100 g	61.2 1.019	3.0 0.048	12.5 0.133	20.6 0.367	1.86
I. Näslund Höganäs					
Gel drops, % moles/100 g	60.0 0.999	9.7 0.157	25.5 0.271	- -	2.34
William Loe Norcem					
Gel drops, w/w moles/w	168 2.796	43 0.694	30 0.318	1.5 0.027	2.69
White gel, w/w moles/w	37 0.616	3.31 0.053	3.37 0.036	20.3 0.362	(3.2 Al_2O_3) 1.37

The white gel seems to comprise two phases:

one of them is transparent, and dissolves in water when stored in moist air.

The other phase is white and opaque. It does not dissolve in water.

Its ability to swell by imbibition of water seems to be very limited.

The following comments refer to Table 6:

All analyses of gel drops from the different sources indicated that liquid gel does not normally contain much calcium.

The ratio between potassium and sodium follows the sources.

The molar ratio $\text{SiO}_2/(\text{Na}, \text{K})_2\text{O}$ may vary within a wide range, dependent on the reaction conditions. The lowest value, 1.83, corresponds to a pH value of 12.25.

If the water in the cement paste has the same low pH value, it will take up calcium ions (and hydroxide ions) from solid calcium hydroxide. This means that, if more gel is formed, it will contain calcium.

The two samples of calcium rich "gel" are not very similar to each other. The aluminium content in the latter sample, according to William Loe (1983), may indicate that the sample has become polluted with Portland cement.

5. CONDITIONS FOR DAMAGE TO CONCRETE BY A S R

Two conditions have to be complied with, if the concrete is to suffer any damage from gel formation:

1. The gel must imbibe water, thus increasing its volume.

2. The gel must be rigid enough, or it will escape into available pores in the concrete, thus releasing the pressure and preventing it from forming cracks.

5.1 Imbibition of water from the pore liquid

When the alkaline pore liquid starts to dissolve a reactive silica grain, there is no difference in the concentration which may explain any movements of water.

Weldes and Lange (1969) quoted from Iler (1955) that silicon in alkaline metal silicate solutions may have a coordination number of six, and not four as in dicalcium silicate in clinker. As a consequence, some water would be bound to the silicate ions.

In concrete, the silicate ions mainly have one, two, or three silicon atoms in each ion. On an average, they have about one silicate group, $-\text{Si}-\text{O}^-$, for each silicon atom.

A silicon atom has four bonds. In silica and silicates, all the bonds are occupied by oxygen atoms, which may belong to silicate groups, or silanol groups ($-\text{Si}-\text{OH}$). An oxygen atom may also form a link with another silicon atom.

The silanol groups, have the capacity to bind a molecule of water at each hydrogen atom with a "hydrogen bond". A hydrogen bond is weaker than a normal chemical bond, but stronger than a normal van der Waal force of the type we find between two molecules in, e. g., gasoline.

The same capacity to bind water is found in the drying agent for gases, called "silica gel" (without alkalies, i. e. the molar ratio equals 1/0).

The ability of the silanol groups in the gel to bind water molecules reduces the contents of free water in the gel volume, and it is reasonable to presume that the gel-bound water behaves like ice: it has a limited capacity to dissolve salts.

Thus, dissolved matter inside the gel has to concentrate in the free water only, which makes the concentration of, e. g., sodium ions within the gel greater than that of the same type of ions outside the gel.

The border of the gel will act as a semi-permeable membrane: more water molecules will enter the gel than leave it, or a pressure will build up inside the gel.

Sometimes it is discussed, whether a volume of gel, when it expands, takes water from the moist air (above 80-85 per cent relative humidity) or from the cement paste water outside the gel. Feasibly, the answer is that the gel takes water from the surrounding cement paste, but the moisture content of gel and paste are governed (with delay) by the relative humidity of the surrounding air.

If sufficiently concentrated, the gel may have a strength, making it difficult or impossible to calculate the pressure, exerted by a volume of gel upon the surrounding concrete.

5.2 The rigidity of the reaction products from A S R in concrete

In Chapter 3.3, the viscosity of pure alkaline metal silicates was discussed.

In Chapter 4.1 the possible composite action of secondary precipitated calcium silicate hydrates is mentioned. When studying pop-outs, I have frequently observed that the gel solution forms a composite with, e. g., residual mineral grains from the attacked reactive stone, and perhaps non-reactive mineral grains. The visual picture is very similar to crystallized honey.

I do not know any method for analysis of the solid particles.

It is very probable that these liquid-solid composites are more rigid than the pure alkaline metal silicate gel, and have a greater capacity to form cracks in the surrounding concrete.

In the examination of pop-outs, the specimen is usually stored overnight in moist air. Sometimes this treatment provokes a pop-out. Even if it does not, the rigidity of the transformed grain will later be reduced so much that the material can easily be penetrated with a steel probe.

Since most of the pop-outs, which I have studied, looked like crystallized honey, and could be brought to generate more gel liquid in moist air, it seems reasonable to conclude that residual reactive silica is essential for forming a pop-out, or a crack.

If a reacting grain of aggregate contains residual reactive silica and then absorbs a volume of alkaline water, this will diffuse to the particles of silica, thus shaping a fresh quantity of gel. It will be possible for the gel in the reacting grain to keep its rigidity reasonably constant.

If the reacting grain does not contain residual reactive silica, any volume of water that becomes absorbed will dilute the gel liquid, thus reducing its rigidity and increasing its possibility to escape into the pore system of the concrete.

The conclusions above are in good agreement with the paper of H E Vivian (1983).

It seems very probable that the moisture conditions, described by Lars-Olof Nilsson (1983), are more essential regarding the question of damage to concrete than a possible "composite effect". In Chapter 3.3 it is demonstrated that a rather slight increase in the concentration of a silicate solution makes the viscosity of the gel 1000 times greater.

A pop-out or an expansion may require a long time to develop, or they may appear after a short time. The porosity of a reactive grain is essential for allowing the alkaline solution to reach the sensitive minerals, not only on the surface, but also in the interior of the grain.

There may exist differences between the two alkaline metal ions sodium (Na^+) and potassium (K^+) regarding the risk of damage to concrete. Whether the difference depends on the ionic radius, the degree of hydration, or other chemical differences, is not known. More research is needed.

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