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Fundamentals of alkali-silica gel formation and swelling: Condensation under influence of dissolved salts

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ABSTRACT

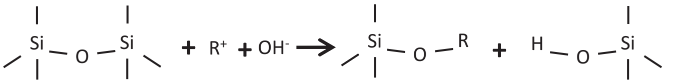
The current theory of ASR gel formation in concrete between silicic acid anions with cations and is unable to explain the differences in concentration required for gel formation between e.g. potassium and sodium or the effect of calcium on the gel formation. In this paper, a new gelation mechanism is explained by means of a condensation between silicic acid anions. The role of salts on the ASR gel formation and gel time is described by their charge screening capacity of the silicic acid, resulting in the decreasing concentration range for gelation: Ca < Mg < Cs < Rb < K < Na < Li. A Cation Gelling Strength (CGS) is defined to assess the cation strength when different cations are present. Silica gel formation will moreover in many cases form a calcium silica precipitate rather than a gel that will be difficult to distinguish from CSH formed during hydration.

1. Introduction

Alkali-Silica Reaction (ASR) in concrete is, as its name implies, the reaction between alkalis (mostly sodium and potassium) and silica in solution. The resulting product is a gel that can swell considerably by taking up water. This gel expansion produces a pressure within concrete that may lead to extensive damage of concrete structures (e.g. [1–4]).

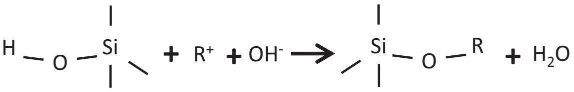
A first concise attempt to model the damage mechanism due to ASR in term of the chemical reaction mechanisms underlying it, was made by Powers and Steinour [5]. They described the expansion of ASR gel in terms of safe and unsafe reactions in concrete with reactive opal as aggregate. They concluded that reactions could be safe or unsafe depending on the relative amounts of calcium and alkalis in the reaction products. If a high calcium concentration was present in the pore water, a non-expansive gel was formed containing a high amount of calcium. However, if the calcium concentration in the pore water was low, alkali-rich swelling gels were formed. Ever since their first postulation of this importance of the composition of the gel, much evidence has been found that affirmed their conclusions. An amendment came from Helmuth et al. [6], who concluded on the basis of their review of the research done until 1993, that the 'rule' for safe and unsafe reaction seemed to break down only for very high alkali/silica ratios.

Powers and Steinour's model includes a two-step chemical reaction mechanism on the formation of a gel (see also [7,8]) which is based on the view that siloxane (Si—O) bonds within the aggregates are attacked by the hydroxide ions (accompanied by an opposite charged cation R = Na or K) according to:



(1)

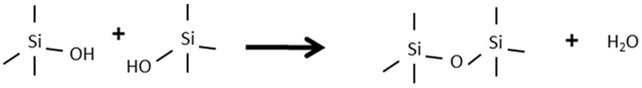
As the silicic acid is a weak acid, it immediately reacts further with hydroxyl ions, liberating water according to:



(2)

The model of Powers and Steinour [5] is still used today [9–14], although often a third step is added that takes into account the water uptake in the gel [15,16]. In addition, exchange mechanisms are sometimes included, e.g. by exchanging the alkalis with calcium [8].

The alkali-silicagel as defined in Eq. (2) is based on the assumption that binding of the silicic acid ions by cations in the pore fluid is sufficiently strong to form a gel. However, in a fundamental study on the chemistry of silica, Iler [17] concluded that the binding between the silicic acid anions and these cations is too weak to serve as major binding mechanism of the gel, on the conclusion that these bonds are formed mostly by Van der Waals forces. Instead, Iler [17] proved that the major reaction mechanism in gel formation is the reaction between the silicic acid anions (and its related dissociates) themselves, e.g.:



(3)

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This is a condensation reaction, as two (more or less similar) species join under formation of water. In the condensed reaction product, the cations form mostly a (weakly attached) charge compensating absorbed layer on the gel.

Iler [17] could explain many effects on the formation of the gels that are also observed for alkali silica gels in concrete, although many details remained unclear, especially with respect to the structure of the silica gel itself [18–20]. However, no attempt has been made to investigate the suitability of the condensation theory to ASR in concrete. In this study, the fundamental mechanism of the alkali silica reactions, gel formation and gel swelling potential are (further) developed, by making use of the pioneering work of Iler [17] on sol-gel techniques and knowledge on gel formation in other scientific fields, especially on colloids and clays. No attempt has been made to come to a concise overview on all literature that may have bearing to this discussion, only that literature that illustrates the hypothesis best is referred to.

In the following, first a brief overview on the dissolution and hydrolysis of silica will be given insofar it is of relevance for the mechanism of gel formation and the gel structure that are explained next. Then, a new mechanism for ASR formation will be presented. It will be shown that ASR-formation can be fully explained by condensation of dissolved and hydrolysed silica under addition of charge-neutralizing effect of dissolved, hydrated cations.

2. Dissolution and hydrolysis

The first step in the Alkali-Silica Reaction process is the dissolution of silicon atoms (Si) from some form of solid silica (SiO_2) (also called depolymerisation of silica). There is quite some debate in the literature on the exact specie(s) that dissolve(s). According to Crundwell [21], silicon-oxygen bonds are broken at the surface of a silicate solid and produce a range of hydrolysed silicon-oxygen products in the double layer, e.g. Si^{4+} with $SiO_4{}^{4-}$ (to maintain charge equilibrium) or any other combination of anions/cations that maintain stoichiometry and charge balance. Beyond the double layer, species form according to the equilibrium condition in the bulk solution. Following Iler [17], another view of the dissolution mechanisms is that is due to a gradual breakage of the oxygen bonds in the solid silica by 'water attack': if sufficient charge differences exist at the interface, silicon ions will be or become hydrolyzed. A further increase in water adsorption due to charge inequality (Fig. 1) will lead to more broken bonds, until full dissolution of the silicic acid anion $Si(OH)_4$. The net effect of either model is the same: only water is consumed for dissolution at neutral pH.

The pH of the solution strongly influences the rate of dissolution. As reported in Rajabipour et al. [8], the solubility of amorphous silica (in glass) is fairly low at a neutral pH but increases strongly from about pH 9 onwards (Fig. 2). Crundwell [21] showed that the dissolution rate increases (as the square root of the OH-concentration), with the lowest dissolution rate at a pH of 7. Hence, hydroxides ions can be viewed as catalysts as they accelerate the dissolution. Their accelerating effect is thought to be due to their adsorption on the silica surface, in proportion to the concentration (i.e. pH). This reduces the surface energy, making it easier for the silicon atoms to leave the surface [17].

The dissolution rate of silica depends on quite a few parameters, for instance on the form of the silica (e.g. quartz, amorphous silica), the presence of impurities (most notably foreign ion inclusions) and particle size. In general, reactivity (and thus dissolution rate) follows the trend $Q^1 > Q^2 > Q^3 > Q^4$ where the Q notation refers to the number of bridging oxygens around the silicon ion and with an oxygen atom that connects two silicon atoms (Si—O—Si) being a bridging oxygen while the oxygen atoms that connect a silicon atom and either a hydrogen ion or another cation is called a nonbridging oxygen atom. As the Si—O bond is very strong, Q^4 is thus the strongest bond type of the silicon atom by four bridging oxygen atoms, while Q^1 is the weakest bond type by just one bridging oxygen atom. Hence, also the degree of hydroxylation of the surface is important, especially for small particles that have a large surface to volume ratio. Experiments described in Iler [17] on acid cleaning of hydroxylated surfaces of silica minerals show that the dissolution rate of the hydroxylated silica decreases to that of non-hydroxylated silica after cleaning.

The total amount of silica that can be dissolved in a solution is determined by the chemical balance between the solid silica and the solution. Fig. 3 gives as example the dissolution of various types of silica in a similar solution, showing that each mineral dissolves at its own rate as well as has its own solubility (the maximum amount of dissolved silica). Iler [17] reports for massive amorphous silica at 25 °C (mostly Q^4-bonded silica) a solubility constant of 70 ppm SiO_2, while for powders and gels (less well bounded, mostly Q^2 and Q^3), the solubility of 100–130 ppm SiO_2. In general, the presence of other species, especially salts like NaCl, not only increases the dissolution rate but also the solubility [23,24,25]. Icenhower and Dove [26] and Dove [27] found that the accelerating effect of salt on the dissolution became smaller for higher salt concentrations. Ultimately a further increase in NaCl no longer had any effect on the dissolution rate. The enhanced solubility of quartz by sodium chloride is thought to occur because of the $Si—O^-Na^+$ surface complex is weaker than the Si—OH complex ([28]).

Fig. 2 shows that in addition to an increase in total silica dissolving with the pH, also the dominant species of the various dissociates changes. Another view of the exact species formed is shown in Fig. 4. The predominant mononuclear species in the solution changes according to the pH from 100% $Si(OH)_4$ at a pH of about 6 to 50% $SiO(OH)_3{}^-$ and 50% $SiO_2(OH)_4{}^{2-}$ at a pH of 12.6 (Fig. 4a). With an increase in concentration, also higher order particles like $[(SiO_2)_2(OH)_3]^{3-}$ are formed (Fig. 4b).

There are conflicting opinions in the literature whether dissolution of silica is an acidifying or neutral process, but this depends on the pH at which dissolution takes place. The most simple view on this is expressed by Eq. (4) showing that at a neutral pH, dissolution results in

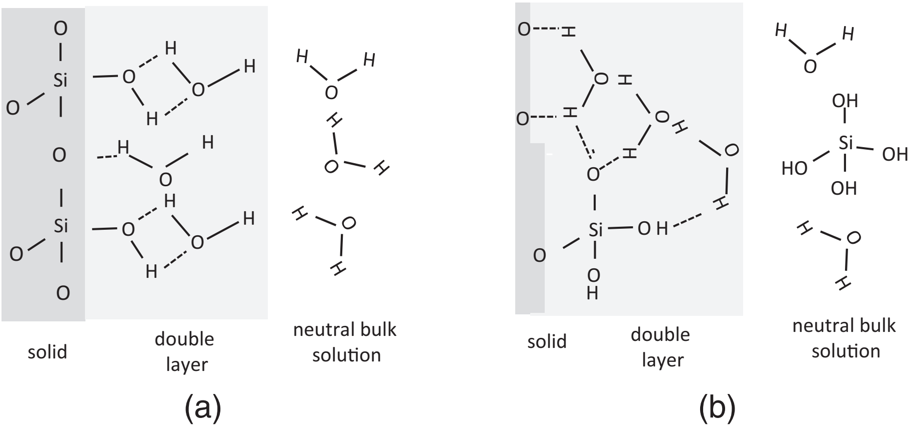

Fig. 1. Visualization of the dissolution process: 'water attack' of the hydroxylated surface, dotted connector = weak polar bond, solid connector = ion bond (a) and further breakage of Si—O leading to weakening of the silicon bonding and finally dissolution after which the silicic acid molecule will enter the bulk solution (b), for readability not all bonds are shown.