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SOME FUNDAMENTAL ASPECTS OF ALKALI-SILICA REACTION

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ABSTRACT

Two somewhat contrasting mechanisms, those of Powers-Steinour and Chatterji et al., have been proposed for the alkali-silica reaction and its accompanying expansion. These two mechanisms have then been compared. Though the two mechanisms share some common elements they differ significantly in other aspects e.g. the role of calcium ion. Recently a third mechanism has been proposed which depends on the electrostatic repulsion between the electrical double layers that form around silica grains. However, none of these mechanisms have addressed some fundamental aspects of alkali-silica reaction. These are (i) the mode of transport of alkali and calcium ions from low concentration pore solution to the reactive grains, (ii) the accelerating effect of ionic strength of the ambient solution, and (iii) the effects of anions.

In an alkaline medium reactive silica grains acquire negative charges by ionization of the surface Si-OH groups and by the breakage of Si-O-Si bonds. The charge density increases with the ionic strength of the ambient solution. This explains the effect of ionic strength. Due to the presence of negative charges on the reactive silica grains positive ions migrate in electric double layers that form around the grains. The concentration of positive charges, both calcium and alkali ions, in these double layers is much higher than that in the ambient solution. These positive ions then penetrate the reactive grains. This explains the ion transport process. Calcium/alkali ion ratio in the double layers depends on a number of factors; anion type is one of these fators. This ion ratio determins the rates of inflow and outflow of materials in the reactive grains and the expansion.

Keywords: Alkali-silica reaction, mechanism, ion transport, pore solution, ionic strength, electrochemistry.

INTRODUCTION

Two somewhat contrasting mechanisms have been proposed for alkali-silica reaction and its accompanying expansion (Powers and Steinour 1955), (Chatterji et al. 1986). In the Kvoto symposium these two mechanisms have been compared (Chatterji 1989). Later Helmuth reviewed the two mechanisms (Helmuth and Stark 1992). These reviews showed that though these two mechanisms have some common elements they differ significantly in other respects e g the role of calcium ions. It also appears that the mechanism proposed by Chatterij et al. explains a wider range of observations than that of Powers-Steinour. Very recently a third mechanism has been proposed to explain the alkali-silica expansion (Rodrigues et al. 1999). The first two mechanisms depend on the alkali-silica reaction products for the generation of destructive pressure. The third mechanism, on the other hand, depends on the electrostatic repulsion between the electrical double layers that form around electrically charged silica particles for the generation of the destructive pressure. There are some unusual characteristics of this third mechanism e.g. an implicit assumption of less than 10nm separation between silica grains, the absence of calcium in the near vicinity of the reactive grains, which are improbable to be satisfied in real life concrete mixtures (Chatterji 1999 a). However, there are a number of aspects of alkali-silica reaction which have not been discussed by any of the mechanisms. In this paper some of them will be discussed.

THE DESCRIPTIONS OF THE PROBLEMS

The problems associated with the aspects to be dealt with in this paper may be described as follows.

Movement of Ions

Early workers noticed that the alkali-silica reaction involves a movement to and concentrating of ions in the reactive grains. These became very apparent with the introduction of the electron- probe micro-analytical technique to the analyses of reaction products (Knudsen and Thaulow 1975), (Chatterji et al. 1986), (Regourd-Moranville 1989). These analyses showed that the alkali ion concentration could be 50% in alkali-silica gel whereas in the cement paste itself it is of the order of 1-2%. This means that alkali ions are moving toward the reactive grains against an apparent concentration gradient. However, no explanation has been put forward for this unexpected movement of alkali ions. Furthermore, there is a general belief that in the absence of any alkali ingress from the environment and/or localized up-concentration of alkali, no alkali-silica reaction occurs if the alkali content of the cement is below a critical value. Here again no explanation is available.

The electron-probe micro-analytical results also showed that calcium ions migrate inside the reactive grains and the gels can have a CaO concentration of 15-20%. These results indicate an extensive and rapid movement of calcium ions to the reactive grains. This is in spite of a very low i.e. 0.001 to 0.003 N concentration of calcium in expressed pore liquids (Diamond 1983). The rapid movement of calcium ions to the reactive grains should reduce the repulsion pressure due to the overlap of their electrical double layer. This rapid movement of calcium ions toward the reactive grains also needs an explanation.

The Effect of Ionic Strength on the Reaction and Expansion

It has been shown that alkali-silica reaction and expansion can be hastened by increasing the ionic strength of the ambient solution (Chatterji et al. 1990). This acceleration occurs even in a saturated NaCl solution, a concentration far beyond the electrolytic stabilization range of colloidal dispersions. At this high concentration the mechanism proposed by Rodrigues et al (1999) is not expected to be operative. This acceleration also needs an explanation.

Effect of Anion

It has been shown that at equivalent concentration of 3 N solution the alkali-silica expansion is highest with alkali nitrates and lowest with alkali hydroxide. Alkali chlorides occupy an intermediate position (Chatterji et al. 1987). If alkali-silica expansion is due to the attack of alkali hydroxide on reactive particles then alkali hydroxides are expected to give highest expansion. It is not obvious how different anions can affect the repulsion pressure due to electrical double layer overlap. None of the mechanisms, as they stand, offers an explanation to this observation.

COLLOID ELECTROCHEMISTRY OF PORTLAND CEMENT PASTE-AGGREGATE ASSEMBLY

An exchange of electrical charges occurs whenever two dissimilar materials are brought in contact. The extent of this exchange depends on the subdivision of the materials and their nature. In the assembly under consideration the cement hydration products are of submicroscopic sizes, the reactive silica grains are large and both of them are immersed in a common electrolyte (pore) solution which is mainly an alkali hydroxide solution with traces of $Ca(OH)_2$. In this assembly, cement hydration products are negatively charged (Chatterji and Kawamura 1992); so also are the silica grains (Bolt 1957) (Tadros and Lyklema 1968) (Rodrigues et al. 1999). Due to their charged states the cement hydration products and silica grains are surrounded by positively charged electrical double layers (Fig. 1).



Distance from the solid surface

Fig. 1: A schematic distribution of excess ions in a double layer.

The "thickness" (of the order of a few nm) of these double layers can be calculated from the ionic strength of the pore electrolyte. These double layers not only determine the type of and concentration of the positive ions in them they also affect the ion transport to the reactive

silica grains. It is therefore necessary to examine the nature of the double layers round both the cement hydration products as well as those round the silica grains.

Portland Cement Paste-Electrolyte Assembly

The average surface charge density of the cement hydration products has not yet been measured although it has been estimated to be -50 mColoumbs /m² in a 0.5 NaOH solution. A corresponding amount of positive ions collects in the double layer. From a knowledge of the average surface charge density, the ionic strength of the pore solution and the thickness of the double layer it is possible to calculate the average ion concentration in the double layers which is much higher than that of the pore solution (Chatterji 1998). Nearly one half of the total positive ions are in the strongly held Stern layer and the rest is in the Gouy-Chapman diffuse layer. Any divalent ion, e.g., Ca2+, present in the pore solution, preferentially collects in the double-layer. It is difficult to calculate theoretically the divalent/monovalent ion ratio in the double layers. However, it has recently been shown that the divalent/monovalent ion ratio in the Gouy-Chapman layer could be estimated from the diffusion data of alkali salts through cement pastes in a diffusion-cell set up (Chatterji and Kawamura 1992, Chatterji 1998). Analyses of such results show that more Ca^{2+} ions diffuse to the downstream side than alkali ions along with anions. This Ca²⁺ ion diffusion indicates that somewhere in Portland cement paste there is a highly concentrated solution of Ca^{2+} Since the pore solution is very low in Ca2' ion concentration, the postulated highly concentrated solution can be identified with the double layer solution. This high Ca²⁺ concentration in the double layer is consistent with (Collis-George and Bozeman 1970). The high Ca²⁺ concentration in the double laver is maintained by continued dissolution of Ca(OH)2 from Portland cement paste. In cements like blast furnace slag-Portland cement (with a minimum slag content of 65%) where there is no free Ca(OH)₂ in its paste (Clausson-Kaas and Chatterji 1984) no or very little Ca²⁺ diffuses to the downstream side. Table 1 shows some estimated Ca^{2+}/R^{1+} mol. ratios in the double layer at different concentrations of alkali salt diffusant (Chatterji and Kawamura 1992) (Chatterji 1994) (Chatterii 1999 b). Table 1 shows that Ca^{2+}/R^{1+} ratio depends on the type of cement, at the same concentration on the type of diffusing salt and the diffusant concentration. Most informative results are those with Danish white cement which is very low in alkali and low in Al₂O₃ It is of interest to note that with this cement Ca^{2+}/R^{1+} ratio decreases with increasing diffusant concentration. These results indicate that with increasing content of alkali in a cement paste the ratio decreases i.e. the alkali ion concentration increases in the immediate vicinity of cement hydration products.

Diffusant	Molality	Ca/R	Cement, origin
NaCl	1	2	OPC, Japan
NaCl	1	100	Low-alkali, white, Danish
NaCl	3	17	Do
KCl	1	30	Do
KCl	2	8	Do
KC1	3	4	Type III, USA
KNO ₃	3	15	Do

TABLE 1: Estimated Ca/R Mol. Ratio in the Double Layer Soln.

Reactive Silica Grains-Pore Solution Assembly

Surface charge density on silica grains suspended in different types of electrolyte solutions of different concentrations and pH has been studied by many workers (for example Bolt 1957, Tadros and Lyklema 1968, Rodrigues et al. 1999). Bolt studied the surface charge development over wide range of NaCl concentrations and pH values. Results of other workers are in broad agreement with those of Bolt. Bolt showed that the charge density on silica increases with increasing pH and NaCl solution concentration. The charge density on silica could be higher than -240 mCoulombs/ m². The negative charges were originally thought to reside only on the outer surface as ionized -SiOH groups. However, it was subsequently shown that in an alkaline solution a part of the charges is due to the cleavage and ionization of inner Si-O-Si groups (Tadros and Lyklema 1968). This cleavage of inner Si-O-Si groups is much facilitated if a small ion like hydrated Na¹⁺ accompanies OH⁻ ion than by a large ion like hydrated Ca^{2+} or Ba^{2+} . It appears that about one half of the measured surface charge on reactive silica lies within the grains (Chatterii and Kawamura 1992). The last point is particularly important for silicas with disordered, or metastable or porous structures, e.g., tridymite. One has to remember that reactive silicas have disordered structures. Very few, if any, of the inner Si-O-Si groups of crystalline quartz are cleaved.

The pH range studied by the above workers was up to about 10; above that pH the formation of silicate ion increases rapidly making the charge measurement uncertain. In cement pore solutions, with OH ion concentrations above 0.5 M, this silicate ion formation assumes much importance. It has also been reported that increasing concentration of NaCl increases the rate of solution of quartz in water (Van Lier 1965). Other alkali salt solutions are expected to increase the rate of quartz solution in water. It is also expected that this higher dissolution rate will be still higher with disordered silicas.

In this case also electrical double layers, that form on the negatively charged silica grains, have high ionic strength and preferentially collect Ca^{2+} ions from pore solution. When a reactive silica grain is incorporated in a cement paste, the double layer on it is more concentrated than that on a cement hydration product. This is due to much higher surface charge density on the silica grain compared to the average charge density on cement hydration products.

SALIENT FEATURES OF THE MECHANISM OF CHATTERJI ET AL.

Though some of the questions raised in the Introduction could be answered without a reference to any alkali-silica expansion mechanism others need to refer to an expansioncausing mechanism. In the following the salient features of the mechanism proposed by Chatterji et al. (1986,1989) are recapitulated.

i) OH ions penetrate reactive silica, when placed in an environment of pH 7 or above, in amounts increasing with pH and ionic strength of the solution. At a constant pH and ionic strength the absorption of OH decreases with the increasing size of the hydrated cation, i.e., decreases in the series K¹ to Na¹ to Li¹ and Ca².

- ii) In a mixed electrolyte environment, e.g., Ca(OH)₂ and NaCl, more of the smaller ions, i.e., hydrated Na¹ follows the penetrating OH ions than larger hydrated Ca²⁺; although both the cations penetrate reactive silica grains.
- iii) The penetrating OH ions hydrolyses inner siloxane bonds according to the following equation:

Si-O-Si + OH = Si-OH + Si-O [1]

This reaction opens up the reactive grains for further attack and liberates some silica ions from their original sites. This liberation then enables them to diffuse out of the silica grains.

- iv) Diffusion of silica out of the reacting grains is controlled by Ca²⁺ in the immediate environment. A high Ca²⁺ ion concentration lowers silica diffusion.
- v) In alkali-silica reaction Ca(OH)₂ plays at least three roles. Firstly it accelerates penetrations of Na¹⁺, Ca²⁺, OH, and H₂O molecules in a reactive grain. Secondly it promotes preferential penetration of Na¹⁺, OH, and H₂O molecules in a reactive grain in the presence of NaCl solutions. Thirdly it hampers the diffusion of silicate ions from the reactive grains.
- vi) An expansion occurs when more materials, i.e., Na¹⁺, Ca²⁺, OH and water enter a reacting grain than silica diffuses out. In contrast to the osmotic pressure theory, in this mechanism the hydrated ions are moving from the low concentration to the high concentration regions.

EXPLANATION OF THE QUESTIONS RAISED IN THE INTRODUCTION

With the above background information, it is now possible to put forward explanations of the questions raised in the Introduction.

Movement of Ions

In a reactive silica-Portland cement paste assembly there are two negative potential wells where positive ions like Na¹⁺, Ca²⁺ can concentrate, i.e., in the double layers either on cement hydration products or on reactive silica grains. Of these two negative wells the ones around the reactive silica grains are deeper than those around the cement hydration products. The depth of a potential well is proportional to the surface charge density on the grain. As a result of their depths the wells around the reactive grains attract cations more strongly than the shallower wells around the cement hydration products. This explains the quick and against-gradient movements of Na¹⁺ and Ca²⁺ ions from the paste environment to the reactive grains. Higher Ca²⁺ ion concentration, in these wells, over that of Na¹⁺ ion is due to its double positive charge and its selectivity (Collis-George and Bozeman 1970).

The Effect of Ionic Strength on the Reaction and Expansion

In the absence of any alkali ion in a Portland-cement paste Ca^{2*} , and OH will react with dissolved silica forming a dense layer of calcium-silicate hydrate (Diamond 1989). For further reaction to proceed large hydrated Ca^{2*} ions would have to diffuse to the reactive grain surface through the dense calcium-silicate hydrate layer. In this case due to the low ionic strength of the pore solution the surface charge density is low; so also is the concentration of Ca^{2*} in the double layer. Furthermore due to the low ionic strength the cleaving of the inner Si-O-Si bonds proceeds at a very low rate. The net result will be a virtual stoppage of any further reaction.

In the assembly under consideration the ionic strength of the pore solution can only be increased either by using a alkali containing cement or by the ingress of the ions of an alkali salt from the environment. In either case the following will occur: (a) due to the increasing ionic strength of the pore solution the surface charge on the silica grains increases; so also the rate of cleaving of the inner Si-O-Si bonds, (b) the rate of dissolution of silica grains also increases, (c) in the double layer the Ca²⁺/Na¹⁺ ratio decreases and the lowered Ca²⁺ concentration makes the calcium-silicate layer less dense and more permeable to ions and water molecules. The net result is a higher rate of alkali-silica-lime complex formation, (d) at the same time some silicate ions are able to diffuse out through the porous calcium-silicate layer. However, Diamond's results indicate that so long as the Ca²⁺/Na¹⁺ ratio is high in the double layer the diffusion of silicate ions is very low. Since the expansion is an inter-play between the rate of ingress of materials and out-flow of silicate ions there will be a net expansion with increasing ionic strength. The opposite of this happens in the case of a cement which is free of Ca(OH)₂, e.g., slag-Portland cement. In this case the double layer is free of Ca²⁺ ions and silicate ions are free to diffuse out without any hinderance or pressure generation.

This mechanism also explains the existence of a critical alkali content below which no damage occurs. To cause damage to a structure by an internal pressure generation the magnitude of the pressure needs to be two times the tensile strength of the material composing the structure (Timoshenko and Goodier, 1951). The pressure generation of the required magnitude needs a minimum of ionic strength and / or OH⁻ ion concentration. In the case of Portland cement both of these are supplied by its alkali content.

The Effect of Anion Type

From table 1 it can be seen that at 3N concentrations Ca^{2+}/R^{1+} ratio is higher with KNO₃ solution than with KCl solution. This means that the calcium silicate layer is tighter with KNO₃ solution and the diffusion of silicate ion is slower than with KCl solution. This will explain the higher expansion with 3N KNO₃ solution than with 3N KCl solution. On the other hand 3N KOH solution depresses the solubility of Ca(OH)₂ in the pore liquid so much that the double layer is nearly free of Ca²⁺ ions and silicate ions are free to diffuse out without causing any pressure generation.

A COUPLE OF PRACTICAL CONSIDERATIONS

Most of the practical implications of this mechanism have been discussed earlier (Chatterji et all 1988). However, the following two aspects have not been considered earlier :

The Use of Low-Alkali Cement for the Prevention of Alkali-Silica Damage

It is a very common practice to specify a low-alkali Portland cement if the aggregates are suspected of being reactive. From the above discussion it appears that the use of a low-alkali Portland cement hinders the development of alkali-silica distress so long no alkali ingress occurs from the environment and /or alkali does not concentrate locally due to evaporation of pore solution. If either of the above processes occur during the expected life time of the structure then distress may develop.

Testing of Aggregate for Their Reactivity

In some of the testing methods mortar bars made with the suspected aggregates are exposed to a concentrated alkali hydroxide solution at an elevated temperature. The danger is that both these accelerating steps decreases the Ca^{2+} ion concentration in the double-layer thereby increasing the diffusivity of the silicate ions from the grains. It would be desirable to check this possibility by petrographic examination of the exposed mortar bars at the end of the exposure.

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