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MECHANISMS OF ALKALI–SILICA REACTION AND EXPANSION

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1. ABSTRACT

In the recent years the author and his co-workers have carried out an extensive investigation on different aspects of alkali-silica reaction and expansion. Basing on these investigations detailed mechanisms for alkali-silica reaction and the associated expansion have been developed. These mechanisms are substantially different from the generally accepted mechanism of Powers and Steinour. These mechanisms and their implications will be presented and discussed. It will be shown that the new mechanisms explain better the roles of $Ca(OH)_2$, alkali salts, the varying activities of Li, Na and K ions and effect of pozzolans.

2. INTRODUCTION

Alkali-silica reaction in concrete and its associated expansion are both industrially important as well as intellectually fascinating subjects. Until recently the only mechanism which explained these two aspects of concrete durability was that proposed by Powers and Steinour in the 1950's (1). Since 1972 the present author and his co-workers have carried out an extensive series of investigations on different aspects of alkali-silica reaction and basing on the results of these investigations have proposed alternative reaction mechanisms to explain the occurrence of alkali-silica reaction and its associated expansion (2). The object of the present paper is to compare the two reaction mechanisms.

3. SALIENT POINTS OF THE TWO HYPOTHESES AND SOME COMMENTS ON THEM

3.1 Hypothesis of Powers and Steinour

This hypothesis draws heavily on a paper by Carman on the properties of colloidal silica (3). The salient features of this hypothesis are (1):

(i) Reactive silica grain-water interface is covered with a layer of silanol groups

(ii) When a reactive grain is exposed to a dilute alkali hydroxide solution, these silanol groups are first neutralized according to the following equation:

$$\equiv Si{-}OH + Na^{+} + OH^{-} = \equiv Si{-}O^{-}Na^{+} + H_2O \quad [1]$$

At a <u>higher caustic concentration</u> the underlying siloxane groups are also attacked:

$$\equiv Si{-}O{-}Si\equiv + 2NaOH = 2 \equiv Si{-}O^{-}Na + H_2O \quad [2]$$

By this attack, amorphous silica is reduced to colloidal particles; higher hydroxide concentrations produce smaller sol particles. The alkali-silica complex thus produced imbibe water causing swelling.

(iii) In a reactive silica-cement-water system, the initial reaction produces thin layers of non-swelling lime-alkali-silica complex on the grains. During further reaction lime and/or alkali is transported through these layers from the environment to the grains.

(iv) The relative amounts of lime or alkali transported through the layer is determined by the caustic content of the solution external to the layer.

(v) If more lime is transported then a non-swelling lime-alkali-silica gel is produced; if more caustic is transported then a swelling alkali-silica complex is produced which causes expansion.

(vi) During non-swelling reaction parts of silica diffuse out of the grains.

(vii) Effective pozzolans, by reacting with caustic, reduce the caustic concentration of the liquid phase so that safe reaction can then proceed on larger reactive silica grains.

3.1.1 <u>Some comments</u>: It is to be noted that in the formation of alkali complex only alkali hydroxides take part and neutral alkali salts can not take part in the reaction, i.e. alkali salts can not accelerate alkali-silica reaction or expansion. The expanding gel is expected to have no or low lime content. Furthermore, pozzolanic additions will only be effective when a reactive grain-high alkali cement system does not receive any significant alkali from an outside source.

3.2 Hypothesis of Chatterji et al

Although this hypothesis was originally proposed without any knowledge of the paper by Bolt (4), its further development was influenced by it and that of Tadros and Lyklema (5). The salient features are (2):

(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. pH and ionic strength remaining constant, the absorption of OH^- ion decreases with the increasing size of the hydrated cation i.e. decreases in the series K^+ to Na^+ to Li^+ and Ca^{++}.

(ii) In a mixed electrolyte environment eg $Ca(OH)_2$ and NaCl, more of the smaller ions i.e. Na^+ will follow the penetrating OH^- ions than the larger ions i.e. Ca^{++}, although both the cations will penetrate reactive silica grains.

(iii) OH^- ions hydrolyses siloxane bonds according to the following equation:

$$\equiv Si-O-Si\equiv + OH^- = \equiv Si-OH + Si-O^- \quad [3]$$

This reaction opens up the reactive grains for furhter attack and liberates some silica enabling them to diffuse out of their original sites.

(iv) Diffusion of silica out of the grains is controlled by Ca^{++} concentration of the environment. Higher Ca^{++} ion concentration lowers diffusion.

(v) An expansion occurs when more materials i.e. Na^-, Ca^{++}, OH^{--} and water enter a grain than silica diffuses out.

3.2.1 Some comments: It is to be noted that the items (i) and (ii) together indicates that alkali-silica reaction will occur, even in the absence of alkali hydroxide, provided a OH^- ion source and alkali salt are present in the system. Item (i) states that alkali-silica reaction will be accelerated by concentrated solutions of alkali salts due to increased ionic strength of solutions. Item (i) also indicate that the rate of alkali-silica reaction will decrease from potassium to lithium salt.

4. INTERPRETATION OF OBSERVATIONS

4.1 Effect of alkali salt concentration on alkali-silica reaction

It has recently been shown that at 50°C storage of mortar prisms in alkali salt solutions alkali-silica reaction increases with increasing concentration of alkali salts (6). As alkali hydroxide concentration is only marginally increased by alkali salt solutions, the above observation is difficult to explain on the basis of Powers and Steinour hypothesis. The above observation is, however, easily explained by the hypothesis of Chatterji et al as due to the increased ionic strength of alkali salt solutions.

4.2 Higher aggressivity of potassium ions compared to sodium

It is a general belief that a cement containing potassium is more aggressive than a cement containing equivalent sodium. This belief though difficult to explain on the basis of Powers-Steinour hypothesis, is easily explained on the basis of the ionic sizes of hydrated potassium and sodium ions. Ineffectivity of lithium salts in producing alkali-silica reaction could also be attributed to large size of hydrated Li^+ ion.

4.3 The role of calcium in alkali-silica expansion

According to Powers-Steinour hypothesis expanding alkali-silica complex should be poor in calcium; calcium rich complex being harmless. In the hypothesis of Chatterji et al no such distinction has been made. Recent electron probe analyses of alkali-silica gels show that expanding gels contain substantial amounts of calcium (7) thereby lending support to the new hypothesis.

4.4 The role of pozzolanic addition

In the Powers-Steinour hypothesis, the role of pozzolan is to fix and reduce alkali hydroxide concentration at the initial stage so that safe calcium rich alkali-silica complex may form on larger reactive aggregates. A pozzolan to function in the above fashion alkali content has to be limited i.e. if alkali content is unlimited a pozzolan will not be very effective.

In the hypothesis of Chatterji et al the role of a pozzolan is to combine with $Ca(OH)_2$ thereby lowering OH^- and Ca^{++} ion concentration; both these factors decrease alkali-silica reaction and expansion. Note that according to the above a pozzolan will be effective even when alkali is unlimited. Recent demonstration of the effectivity of pozzolanic addition even in the presence of unlimited alkali lends support for the hypotheses of Chatterji et al (8).

5. CONCLUSION

From the above comparison it will appear that many aspects of alkali-silica reaction are more easily explained on the basis of reaction mechanisms proposed by Chatterji et al.

6. REFERENCES

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