

Mechanisms of Accelerating Effects of NaCl and Ca(OH)₂ on Alkali-Silica Reaction

S. Chatterji, N. Thaulow, A.D. Jensen, and P. Christensen

*Teknologisk Institut
Taastrup, Denmark*

ABSTRACT

The physico-chemical modes of action of NaCl and Ca(OH)₂ in the alkali-silica reaction have been investigated. Mechanisms have been proposed to explain the accelerating action of NaCl and roles of Ca(OH)₂ in the alkali-silica reaction. Practical implications of these mechanisms have been stressed.

INTRODUCTION

Recently it has been shown that a saturated solution of NaCl accelerates the alkali-silica reaction (Chatterji, 1978) and the presence of free Ca(OH)₂ is a pre-requisite of the expansion (Chatterji, 1979). Supporting evidence of the above claims have been reported (Chatterji et al 1983, 1984). This paper reports work carried out to clarify the situation.

MATERIALS AND EXPERIMENTAL TECHNIQUES

In this work Portland-moler blended cements containing 0, 10, 20 and 25% moler were used. A single batch of reactive sand, containing carbonate free opaline flint as reactive component, was used.

From each of the blended cements 1:3::cement:sand mortars were made. Water/cement ratio was 0.5. From each of these mortars a number of 40x40x160 mm prisms were cast and cured following a previously described method (Chatterji, 1978). On the 28th day half of the prisms of each series were transferred to a saturated NaCl bath and the other half to a water bath; both were maintained at 50°C. The length of the prisms were measured regularly. After 45 weeks in these baths, one prism of each mortar type from each bath was removed for X-ray diffraction and petrographic examinations. During the petrographic examination of a section, reactive grains were marked for subsequent electron-probe micro-analysis of these grains and their surrounding paste.

RESULTS AND DISCUSSION

Expansion Measurements: Prisms stored in the water bath did not expand irrespective of the type of "cement". This is consistent with previous studies (Chatterji, 1978, Chatterji et al, 1983).

Expansions of prisms, stored in NaCl bath, depended on the type of "cement". From the results of expansion measurements (Fig. 1) it can be seen that expansion decreases with increasing moler content.

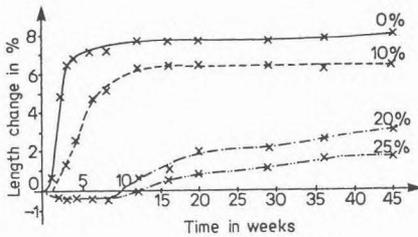


Fig. 1. Expansion characteristics of prisms stored in NaCl. Figures indicate moler contents.

X-Ray Diffraction Analyses:

Results of the whole series are shown in Table 1. Table 1 shows that Ca(OH)_2 contents of the water bath stored prisms are higher than those of NaCl bath stored ones. This indicates that NaCl accelerates the reaction between Ca(OH)_2 and reactive silica. Table 1 further shows that calcium mono-chloro-aluminate crystals are present in all the prisms stored in NaCl bath. The formation of calcium mono-chloro-aluminate indicates that NaCl penetrated all these prisms and the difference in expansions between different series could not be attributed to a lack of NaCl in the prisms.

Petrographic Examination: Results are shown in Table 2. From Table 2 it can be seen that (i) water bath stored prisms show either traces of or no alkali-silica reaction, (ii) prisms stored in NaCl bath show varied degree of reaction which decreases with increasing moler content, (iii) extensive reaction is always accompanied by formation of gel in and around reactive grains. The gel formation indicates penetration of water in the reactive grains, (iv) Ca(OH)_2 contents of different series substantiate the results of X-ray diffraction analyses. During petrographic examination it was observed that each reacted grain is surrounded by an area which is devoid of crystalline Ca(OH)_2 . Width of this Ca(OH)_2 -free zone tends to increase with moler content. This will mean that either some silica diffused out of the grains and reacted with Ca(OH)_2 or/ and Ca(OH)_2 dissolved and migrated into the reacted grains. From the petrographic examination alone it is not possible to distinguish between these two possibilities.

Electron-Probe Micro-Analyses: Normalised major oxide analyses of reacted grains and their surrounding areas have been plotted in Figs. 2-5. Only the two extreme "cement" compositions have been shown; results of other mixes fall in between these two. The figures show that (i) reactive grains have higher Na_2O contents when stored in NaCl bath than in water bath, (ii) of the prisms stored in NaCl bath, Na_2O content of the reactive grain is higher in moler free prisms than in prisms containing 25% moler, (iii) Na_2O content in the paste is always lower than in grains, (iv) Cl contents of reacted grains were very low, i.e. high Na_2O values were not due to NaCl, (v) CaO penetrates reactive grains irrespective of the bath type. However, more CaO penetrates reactive grains if prism is stored in NaCl bath than in water bath, (vi) a comparison of Figs. 2-5 show that in samples free of moler, SiO_2 concentration drops sharply near the grain/paste boundary; whereas in prisms with moler SiO_2 concentration decreases slowly. This gives an impression that in moler containing prisms SiO_2 , from reactive grains, could diffuse out.

TABLE 1.
Hydration products identified by X-ray
diffraction in mortar prisms.

% MOLER	STORAGE BATH AT 50°C	ETTRINGITE	MONOCARBO-ALUMINATE-HYDRATE	MONOCHLORO-ALUMINATE-HYDRATE	CALCIUM-HYDROXIDE
0	WATER	2	-	-	5
10	WATER	2	-	-	5
20	WATER	1	TRACE	-	2
25	WATER	1	1	-	1
0	SATD. NaCl	1	-	5	4
10	SATD. NaCl	1	-	5	2
20	SATD. NaCl	1	-	4	1
25	SATD. NaCl	1	-	4	0.5

NOS. 1, 2, 3 ETC. ARE THE RELATIVE X-RAY LINE INTENSITIES

TABLE 2.
Results of petrographic examination of
prisms.

% MOLER IN CEMENT	STORAGE BATH AT 50°C	DEGREE OF AFR REACTION*	CALCIUM HYDROXIDE CONTENT	STATE OF THE SAMPLE
0	WATER	SLIGHT	HIGH	UNDAMAGED
	NaCl	HIGH	MEDIUM	HEAVILY CRACKED
10	WATER	TRACE	HIGH	UNDAMAGED
	NaCl	HIGH	MEDIUM	HEAVILY CRACKED
20	WATER	TRACE	MEDIUM	UNDAMAGED
	NaCl	MEDIUM	LOW	CRACKED
25	WATER	TRACE	LOW	UNDAMAGED
	NaCl	LOW	VERY LOW	LOW DEGREE OF CRACKING

*) AS FRACTION OF TOTAL POTENTIALLY REACTIVE GRAINS

This is expected from general chemistry. In the presence of an excess of $\text{Ca}(\text{OH})_2$, any SiO_2 diffusing out of a reacting grain will quickly encounter $\text{Ca}(\text{OH})_2$ and will be precipitated out as calcium silicate hydrate. In a paste low in free calcium hydroxide, SiO_2 will be able to diffuse long distance before encountering $\text{Ca}(\text{OH})_2$ and consequent precipitation.

It is obvious that calcium, sodium and silicon must have moved in or out in the form of Ca^{2+} , Na^+ and Si^{4+} ions. Ca^{2+} and Na^+ ions must have been accompanied by OH^- ions so as to maintain electroneutrality of the grain. These ions must have carried water molecules with them, as solvated layer.

From the results it can be seen that expansion of mortar prisms, extent of reaction, and penetration of Na^+ , Ca^{2+} , OH^- and H_2O decreased with the decrease in free $\text{Ca}(\text{OH})_2$ content of surrounding paste. However, diffusion of Si^{4+} out of a reactive grain increased with the decrease in free $\text{Ca}(\text{OH})_2$ of its surrounding paste.

The observed higher Na_2O contents of NaCl bath stored prisms compared to those in water bath indicates a reaction of the type shown in Fig. 6 was occurring during alkali-silica reaction. During accelerated alkali-silica reaction, Na^+ ion from NaCl and OH^- from $\text{Ca}(\text{OH})_2$ along with water molecules preferentially enter reactive silica grains and corresponding amounts of Ca^{2+} and Cl^- ions are left behind in the liquid phase of the paste.

The last point deserves further consideration. Figs. 2-5 show that reactive grains contain little Al_2O_3 , i.e. the reactive grains originally contained very little Al_2O_3 and very little Al_2O_3 has penetrated the reacted grains. As Al_2O_3 belongs only to the paste, the ratios $\text{CaO}/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the paste near a reactive grain provide information about diffusion of CaO and SiO_2 .

Detailed calculation indicates that some SiO_2 has diffused out of the grain to increase the $\text{SiO}/\text{Al}_2\text{O}_3$ ratio near the interface; similarly some CaO has diffused into the grain decreasing thereby the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio near the interface. A similar analysis shows that SiO_2 enriched and CaO depleted zone is wider in the case of NaCl bath stored prism than in corresponding water bath stored prisms. The SiO_2 enriched zone round a reacted grain is wider in the prism containing moler than in the prisms without moler.

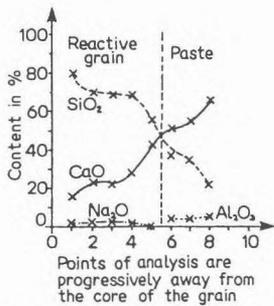


Fig. 2. Shows distribution of oxides in and around a reactive grain. Prism stored in a water bath. No moler in cement.

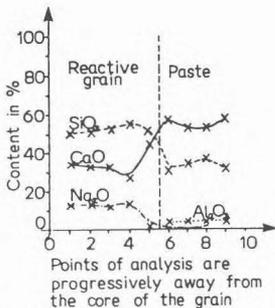


Fig. 3. Shows distribution of oxides in and around a reactive grain. Prism stored in NaCl bath. No moler in cement.

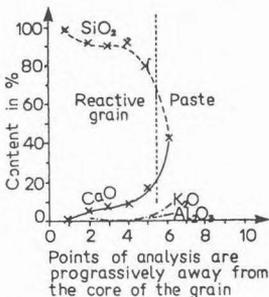


Fig. 4. Shows distribution of oxides in and around a reactive grain. Prism stored in water bath. "Cement" contains 25% moler.

Availability of Ca(OH)_2 near a reactive grain is the controlling factor in the penetration of Na^+ and OH^- ions in reactive grains. Above reaction occurs concurrently with independent penetration of Ca^{2+} , OH^- and H_2O in reactive grains. It is obvious that free Ca(OH)_2 is essential for above Na^+ penetration to occur. The above reaction explains how NaCl bath accelerates alkali-silica reaction and the role of Ca(OH)_2 in this acceleration. Above hypothetical reaction implies that sodium salts will accelerate alkali-silica reaction and that alkali-silica reaction could be simulated in a Ca(OH)_2 -reactive silica-NaCl- H_2O system. These expectations have been found to be valid.

In alkali-silica reaction Ca(OH)_2 plays at least a three-fold role. It accelerates penetration of Na^+ , Ca^{2+} , OH^- , and H_2O molecules in a reactive grain. It promotes preferential penetration of Na^+ , OH^- , and H_2O in a reactive grain in the presence of NaCl solution. It hampers diffusion of Si^{4+} ions out of reactive grains.

In a cement paste environment Ca^{2+} , Na^+ , OH^- , and H_2O are pumped in reactive grains; at the same time Si^{4+} ions diffuse (leak) out. Whether an expansion will occur or not depends on the relative rates of pumping and leakage. If the alkali content of the paste is low, only a limited amount of Ca^{2+} , OH^- , and H_2O can penetrate a reactive grain. This is due to the large size of hydrated Ca^{2+} ion and precipitation of C-S-H which hinders further penetration of Ca^{2+} ions.

If the alkali concentration is high, smaller hydrated Na^{2+} ions, together with OH^- and H_2O will be able to penetrate in a reactive grain unhindered by precipitation of any insoluble silicate. This penetration of Na^+ , OH^- will cause a breakdown of Si-O-Si bonds thereby opening up of the grains for further penetration of ions.

In the presence of excess Ca(OH)_2 and high alkali ion concentration only a limited amount of Si^{4+} can diffuse out, but more materials are pumped in. This generates an expansive force. In the absence of excess Ca(OH)_2 , the rates of pumping of Na^+ , Ca^{2+} , OH^- and H_2O are lowered and at the same time diffusion of Si^{4+} is increased. This leakage stops the generation of any expansive force.

SIGNIFICANCE OF THE PROPOSED MECHANISMS

Testing of aggregate: Most of the test methods for the detection of alkali-silica reactivity of aggregates are designed to keep the alkali content uniform throughout the test specimens and the alkali content limited by that of cement.

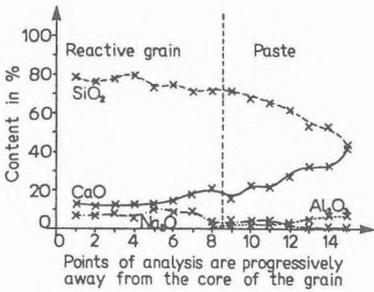


Fig. 5. Shows distribution of oxides in and around a reactive grain. Prism stored in a NaCl bath. "Cement" contains 25% molar.

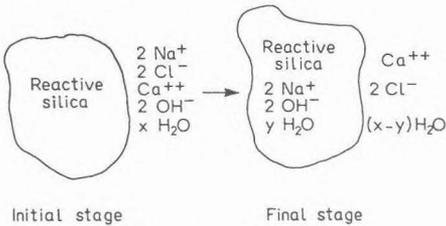


Fig. 6. A hypothetical reaction.

onset of alkali-silica reaction, but may not eliminate the expansion; especially if alkali-salts migrate into the sample from an outside source. It will be of interest to investigate if an addition of a paint quality rutile (TiO_2) will cause a similar delay or not.

If, however, the pozzolanic activity of a mineral admixture is relied on to reduce the expansion, then its reactivity and quantity should be such that the structure should be free, or nearly free, of $\text{Ca}(\text{OH})_2$ throughout. This will mean that the particle size distribution of a pozzolana should be, at least, similar to that of Portland cement. The amount of a pozzolana needed will depend both on its intrinsic $\text{Ca}(\text{OH})_2$ consuming capacity as well as on its rate of reaction with $\text{Ca}(\text{OH})_2$. Ideally, Portland cement/pozzolana ratio should be so adjusted that a structure should remain free or nearly free of $\text{Ca}(\text{OH})_2$ throughout its economic life. A mixture of fine grained inert material such as TiO_2 and a reactive pozzolana will be better. In this case, advantage may be taken of both the two expansion inhibiting processes.

ACKNOWLEDGEMENTS

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In practice, however, concrete structures often absorb alkalis from outside sources, e.g. sea-water spray. Moreover differential drying between parts of a structure often concentrates alkalis in drier parts. In either case there will be more expansion than is expected from the test results. It appears to the present authors that an open-system like NaCl bath method is preferable.

Reduction of expansion: The proposed mechanisms suggest that the expansion due to alkali-silica reaction may be reduced either by reducing the rates of movement of ions and water molecules and/or by a substantial removal of free $\text{Ca}(\text{OH})_2$ from the structure. The addition of micro-silica reduces the rates of movement of ions and water molecules. However, this effect may disappear when micro-silica particles are consumed by free $\text{Ca}(\text{OH})_2$. A small addition of micro-silica will delay the