EFFECT OF DEICING SALT AND SEA WATER ON ASR: NEW CONSIDERATIONS BASED ON EXPERIMENTAL DATA

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ABSTRACT

Mortar bars made with a very alkali-silica reactive limestone were stored at 38°C in air at 100% RH, as well as in 1M NaOH and NaCl solutions. The expansion of bars and the chemistry of the mortar pore water were measured up to 18 months. The samples immersed in 1M NaOH presented much more expansion than samples stored at 100% RH or in 1M NaCl. Chemical equilibrium always established in the long term between the mortar pore water and the immersion solution, and the OH^- concentration or the pH significantly decreased in the pore water of mortar bars immersed in 1M NaCl, thus minimizing ASR expansion. SEM observations and microprobe analyses suggest that the bonding of chloride ions in calcium-chloroaluminates, accompanied by the release of OH^- ions to equilibrate alkali cations, is a slow process, however a little faster with a higher initial alkali content. The results obtained suggest that low-alkali concretes should remain protected against ASR even when exposed to deicing salt or sea water. However, exposure to NaCl should promote map-cracking at the surface of concretes that are already affected by ASR, due to the possible formation of a pH gradient in the concrete skin.

Keywords: Alkali-silica reaction, Chloroaluminates, Mortar, NaCl, Pore water chemistry.

INTRODUCTION

It is a common belief that exposure to deicing salt or sea water promotes an ASR reaction and expansion by supplying additional alkalies to the exposed concrete. However, measurements on field concrete usually indicate that chloride does not penetrate more than a few centimeters inside the concrete exposed to NaCl, while ASR affected concrete members are expanding in their all mass. Moreover, one must remember that OH^- ions, which control the pH, are the aggressive ions in regards to ASR, and that NaCl should not contribute to the increase of their concentration as long as the chloride ions do not transform to calcium chloroaluminates, thus forcing the portlandite to release OH^- ions to balance the alkali cations in the pore water. In a recent study conducted in France, measurements on cores from sea-shore concrete posts supporting gaz reservoirs and exposed for more than 20 years to sea water sprinkling effectively indicate that penetration of sodium and chloride ions in concrete is limited to 6 to 7 centimeters, while more than 90% of chloride is still water-soluble, e.g. as NaCl rather than chloroaluminates (Escadeillas, INSA of Toulouse, pers. comm. 1995). This study was conducted to clarify the effect of deicing salt and sea water on ASR.

MATERIALS AND METHODS

Materials

The aggregate selected was a very alkali-silica reactive limestone from the Spratt Quarry in Ottawa (Ontario, Canada). Two ordinary portland cements (ASTM type I), a high-alkali containing 0.89% Na_2O_{eq} and a low-alkali with 0.54% Na_2O_{eq} were used for making mortar bars. The NaOH and NaCl immersion solutions were prepared from reagent grade material.

Sample preparation

Mortar bars were made in accordance with ASTM C 227 using a water/cement ratio of 0.5. Ten bars were made from each type of cement. The alkali content of the bars made with the high-alkali cement was increased to 1.25% Na_2O_{eq} of the cement mass by adding NaOH to the water mixture. In addition to mortar bars, four mortar samples of each kind of cement were poured into sealed plastic bottles in order to evaluate the difference in the amount of alkalies leached from the mortar bars during the testing period.

Testing conditions and measurements

After 24 hours in their moulds at 23°C and 100% RH, the bars were demoulded. One bar of each mixture was moist cured for 7 days and then used for pore water expression using the high-pressure method (Longuet *et al.* 1973). The other bars were placed in sealed plastic containers under various conditions. The first group of bars was immersed in 1M NaCl solution to simulate exposure to sea water and deicing salt. The second was immersed in 1M NaOH solution which is largely used in ASR testing to generate high pH conditions. The last group was stored in air at 100% RH above water along with the mortar samples sealed in plastic bottles. The containers were then immediately placed inside a room kept at 38°C. The next day, the bars were measured for the first time and periodical measurements were performed afterwards up to 18 months. One bar and one sealed mortar sample of each mixture were removed from the tests after 7 days, 3, 6, and 18 months, and pore waters were expressed. Immediately after being removed from the hot room, the corresponding mortar samples were crushed, then enough representative fragments to obtain at least 1 ml of solution were placed inside the cylindrical chamber of the expression apparatus. A maximum load pressure of 560 MPa (81 500 psi) was applied for expression. Chemical analysis of K^+, Na^+, Cl^-, and SO_4^- ions was carried out on the solutions, shortly after expression, using atomic absorption for cations and ionic chromatography for anions. Mortar samples from each mixture were examined under the scanning electron microscope (SEM) and the electron probe microanalyser (EPMA) was used to determine Cl, Al, Na, and Ca concentration profiles on polished thin sections.

RESULTS AND DISCUSSION

Mortar bar expansion

Figure 1 shows that the mortar bars immersed in 1M NaOH solution present much more expansion than samples stored at 100% RH or immersed in 1M NaCl solution. The low expansion obtained for samples immersed in 1M NaCl agrees with results obtained by Hooton & Rogers (1989) but disagrees with those of Chatterji *et al.* (1986) who used, however, a saturated NaCl solution. Bérubé & Frenette (1994) obtained more expansion for concrete prism samples immersed in NaCl than for those cured in NaOH, but only for samples made with a high alkali cement (1.25% Na_2O_{eq}). This was partly attributed to the formation of chloroaluminate crystals

Figure 1 also shows that the alkali content of the mortar mixture has no significant effect on expansion of samples immersed in 1M NaOH solution, as also observed by Fournier & Bérubé (1991), but affected those stored in air at 100% RH and in 1M NaCl.

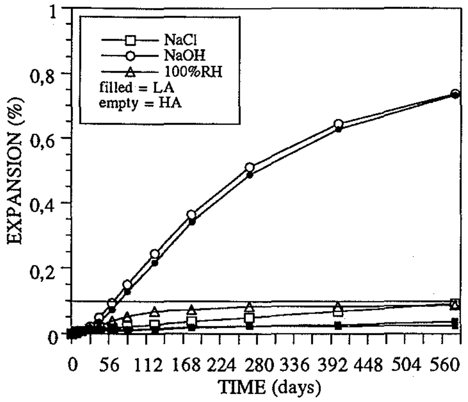

Fig. 1 Expansion results obtained for mortar bars cured at 100%RH, in 1M NaOH and in 1M NaCl solutions, at 38°C.

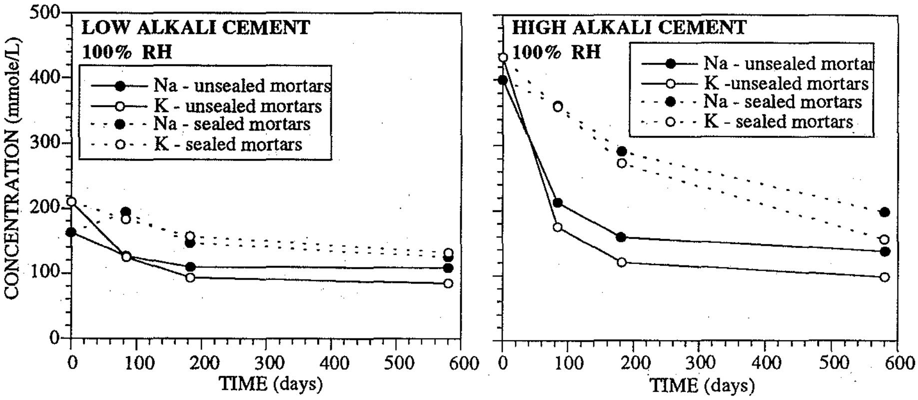

Fig.2 Alkali concentration in the pore water for unsealed mortar bars cured in air at 100% RH and for mortar samples in sealed plastic bottles.

Pore water chemistry

Measurements of the pore water were performed to explain the above variations in expansion. After 7 days of curing, the alkali concentrations of the pore water were 0,83 and 0,37M [(Na,K)OH] for the high and low alkali cements, respectively. These values are similar to those measured by Diamond (1983).

Figure 2 demonstrates the results obtained from the mortar bars cured in air at 100% RH. These samples, especially those made with the high alkali cement, showed a drop in alkali concentration with time, and hydroxide as well, which is attributed to alkali leaching (Rogers & Hooton 1989), humidity uptake (dilution), and also to a lesser extent to alkali trapping by ASR reaction products. The alkali leaching and humidity uptake can be estimated by the alkali concentration differences on figure 2 between the sealed mortar samples and the unsealed mortar bars.

The hydroxide concentration in the pore water can be calculated using a charge balance equation. Indeed, $[Na^+] + [K^+] \sim 2[SO_4^{-2}] + [Cl^-] + [OH^-]$ in the pore water because the concentration of other ions are negligible.

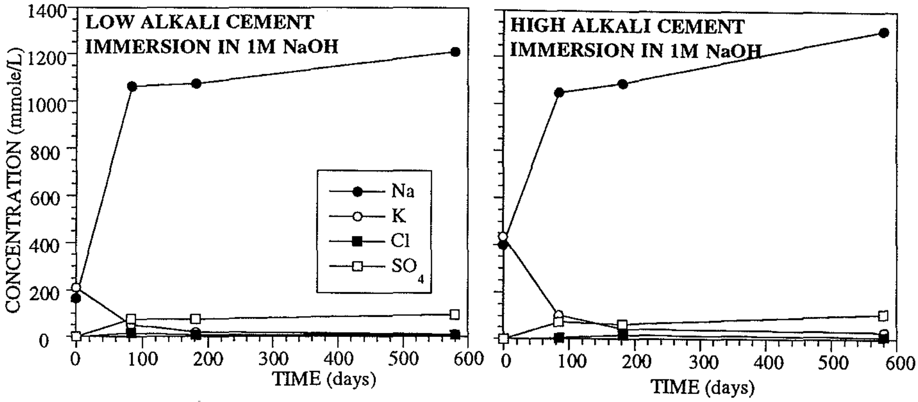

Fig. 3 Concentration of ions in the pore water for mortar samples immersed in 1M NaOH solution.

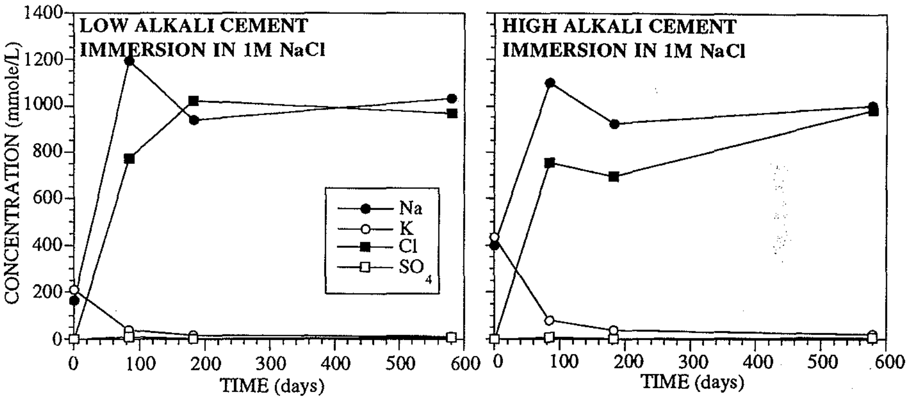

Fig. 4 Concentration of ions in the pore water of mortar samples immersed in 1M NaCl solution.

Figure 3 shows a Na^+ increase and a K^+ decrease in the pore water of samples immersed in 1M NaOH solution, with the total NaOH content reaching relative equilibrium with the immersion solution, e.g. ~ 1M. The sulphate concentration in the pore water increases when the pH increases, which is related to the increase of the solubility of ettringite with pH.

Figure 4 presents the pore water composition of samples cured in 1M NaCl. The Na^+ and Cl^- concentrations in the pore water increase to reach equilibrium with the immersion solution. The $[K^+]$ and the $[SO_4^{-2}]$ decrease to almost nothing. The charge balance calculations give hydroxide concentrations of around 0,84M and 0,37M for the high and low alkali cements, respectively, before immersion in the NaCl solution. The hydroxide concentrations drop afterwards to around 0,4M at 3 months, 0,2M at 6 months and lower than 0,1M at 18 months for both cements. The immersion solution was analysed at the end of the experiment and its hydroxide concentration of 0,11M is another indication that equilibrium is effectively reached in the long term between the mortar pore water and the immersion solution.

Relationship between pore water chemistry and mortar bar expansion

The hydroxide concentration of mortar pore solution correlates well with the expansion results (figure 5). Data presented on figure 5 correspond to mortar bars cured in air at 100% RH, in 1M NaCl and in 1M NaOH after 3, 6 and 18 months of curing. High concentration values are for samples immersed in 1M NaOH solution. A minimum hydroxide concentration in the pore solution is necessary to develop and sustain alkali silica expansion. The threshold value of 0,65M after 1.5 years observed by the same authors for concrete prisms (38°C, in air at 100% RH; Duchesne & Bérubé 1994) and mortar bars (80°C, in 1M NaOH; Bérubé *et al.* 1995), still applies in the present study.

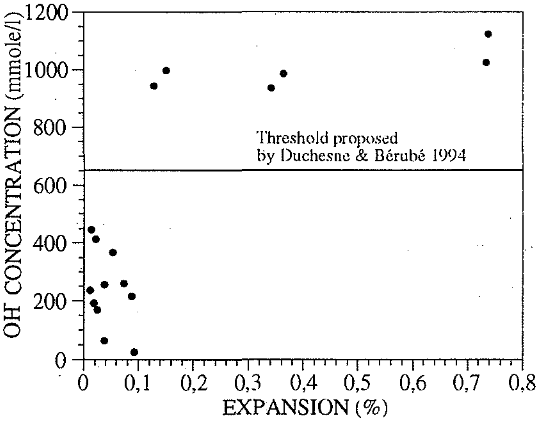

Fig. 5 Expansion of mortar bars stored in different conditions as a function of pore solution chemistry.

SEM and EPMA examinations

The potential removal of chloride ions by incorporation into calcium chloroaluminate is a way to increase hydroxide concentration in the system. Indeed, the electroneutrality of the solution must be maintained and OH^- ions are released by portlandite to compen-sate for the incorporation of Cl^- ions into solid phase. To verify the presence of calcium chloroaluminates samples, SEM observations and EPMA analyses were carried out.

Mortar samples were examined under the SEM to determine the reaction products formed during the 580 days of curing. All samples made with the high alkali cement, and those made with the low alkali cement and immersed in the NaOH solution, contained ASR reaction products. A few calcium chloroaluminate euhedral crystals were found in mortar bars immersed in 1M NaCl, however mostly in the air voids at the border of the mortar bars, along with NaCl crystals. Chloride was also detected in the hydrated paste by EDAX, but this method cannot tell us under which form we may find chloride. EPMA was then performed on polished thin sections of mortar samples to analyse the amount of Cl, Al, Ca, and Na along cross sections through the mortar bars and to determine the existing types of chloride phases, NaCl and/or calcium chloroaluminate. Figure 6 presents Cl, Al and Ca concentration profiles for samples immersed in 1M NaCl. Chloride concentrations were generally higher close to the surface of the mortar bars, 25 mm thick, than at a depth inside the samples. Aluminium and calcium concentrations vary from point to point without any trend from the border to the core of the mortar samples. It is difficult to determine the types of chloride phases on figure 6.

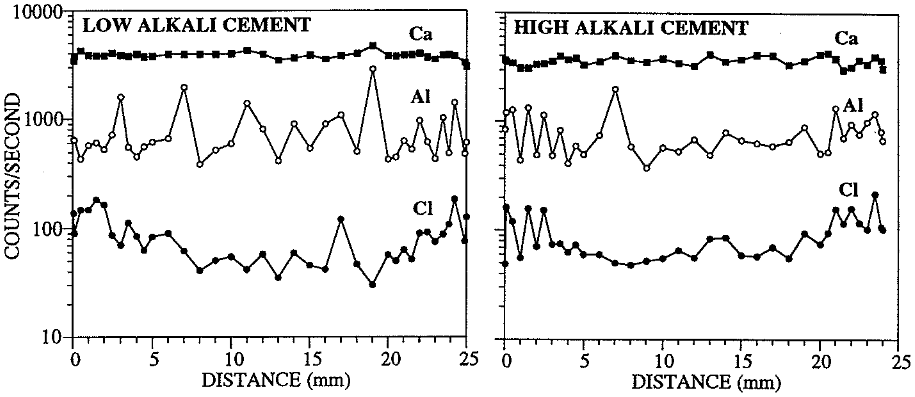

Fig.6 Cl, Ca and Al concentrations measured by EPMA through the mortar bars immersed in NaCl solution.

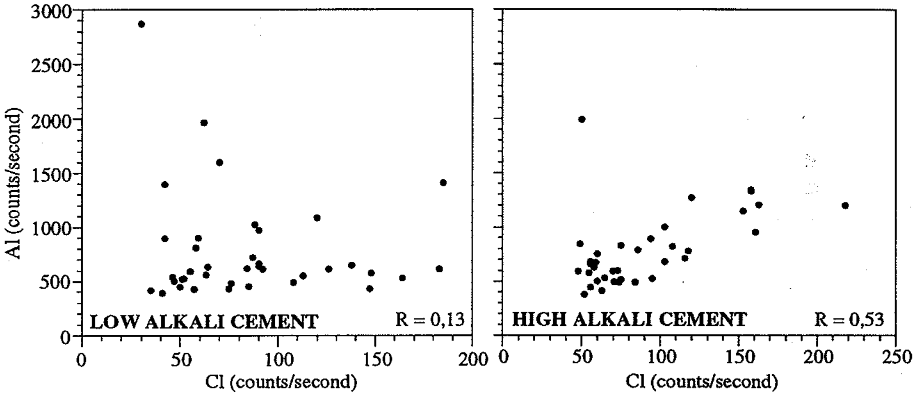

Fig. 7 Al concentration as a function of Cl concentration for punctual measurements by EPMA in mortar samples immersed in NaCl solution.

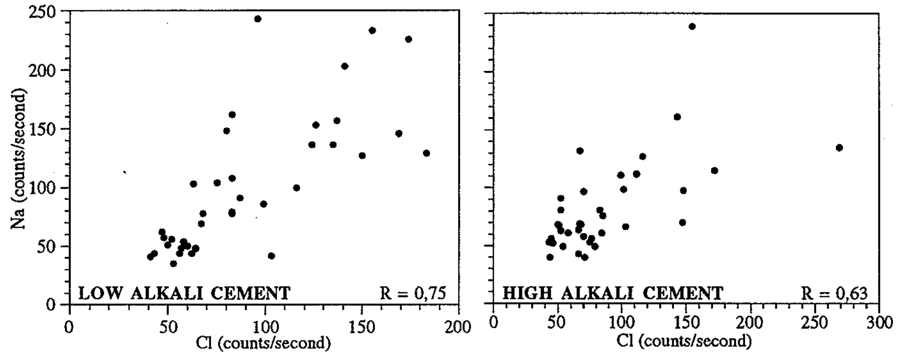

Fig. 8 Na concentration as a function of Cl concentration for punctual measurements by EPMA in mortar samples immersed in NaCl solution.

Figures 7 and 8 present the Cl concentration as a function of the Al (Fig. 7) and Na (Fig. 8) concentrations for each of the points measured. A positive correlation between Cl and Al should indicate that the chloride is mainly in the form of calcium chloroaluminate while a correlation between Na and Cl should correspond mainly to NaCl. The results indicate that the sample made with the low alkali cement does not contain much calcium chloroaluminate (figure 7), chloride being mostly linked to Na as NaCl (figure 8). The sample made with the high alkali cement presents a slightly better correlation between Al and Cl but still one between Na and Cl. This implies that the mortar made with the high alkali cement contains more calcium chloroaluminates than the low alkali mortar, while both samples contain a significant amount of NaCl.

CONCLUSION

- The curing conditions greatly influence the expansion of mortar bars made with alkali-silica reactive aggregates. The bars immersed in 1M NaOH present much more expansion than samples stored in air at 100% RH or in 1M NaCl solution.
- The initial alkali content of the mortar mixture has no significant effect on expansion for samples immersed in 1M NaOH, but affects those stored in air at 100% RH or immersed in 1M NaCl.
- The pore water of mortar samples stored in NaOH and NaCl solutions reach relative equilibrium in the long term with the immersion solution. Charge balance calculations give OH^- concentrations of around 0,1M and 1M in the pore water after 580 days of curing for samples stored in 1M NaCl and NaOH, respectively. This explains both the high and low expansions obtained from the corresponding samples. Immersion in 1M NaCl resulted in a considerable pH decrease, through diffusion.
- A minimum hydroxide concentration of around 0,65M in the pore solution which is necessary to develop and sustain alkali-silica expansion in the presence of natural reactive aggregates, had been proposed before by Duchesne & Bérubé 1994. This concentration treshold still holds for the present study.
- Chloride absorbed after 1.5 years by the low-alkali samples immersed in 1M NaCl seems to be mainly in its original form of NaCl rather than transformed into calcium chloroaluminates, while high-alkali samples contain more chloroaluminate, but still a lot of sodium chloride. This suggests that a higher initial pH or alkali content promotes the formation of chloroaluminates.
- The results obtained can be used to predict what can happen in field concrete members containing reactive aggregates and exposed to deicing salt or sea-water:
  - High-alkali concrete already affected by ASR and immersed in sea water (30 g/L NaCl or 0,5M Na). The Na concentration in the pore water decreases in the concrete skin due to diffusion of Na ions out of concrete, then the OH^- concentration and the pH also decrease. This causes differential expansion between the concrete skin and the internal concrete member, thus promoting map cracking on the concrete surface.
  - High-alkali concrete already affected by ASR and exposed to sea water or deicing salt sprinkling. Na and Cl ions may accumulate in the concrete skin by absorption and partial evaporation. Under such conditions, the pH should not increase. It should in fact slightly increase in the concrete skin as chloroaluminates progressively form. ASR should then progress at a similar or sligthly higher rate in the concrete skin than at a greater depth inside the concrete member.
  - Low-alkali concrete immersed in sea water. This concrete should not show any expansion nor surface cracking due to ASR, since the Na concentration in sea water is under the minimum threshold value. However, this excludes other deteriorations such as scaling and corrosion.
  - Low-alkali concrete exposed to sea water or deicing salt sprinkling. Again, Na and Cl ions may accumulate in the concrete skin by absorption and partial evaporation. If they stay in the solution, the pH should not change, then ASR should not take

place. If Cl ions are bonded in calcium chloroaluminates, then the OH^- concentration and the pH will increase to counterbalance the Na cations. ASR expansion could be then initiated in the concrete skin if the hydroxide concentration goes over the minimum threshold value. However, our results as well as measurements on field concrete suggest that chloroaluminates form at a relatively low rate, particularly when the initial concrete alkali content is low.

- In any case, the pore water composition should not be influenced at more than 5 to 10 cm in depth inside the concrete. This implies that exposure to sea water or deicing salt should never initiate an ASR expansion in the entire volume of low-alkali concrete members. However, such exposure conditions should promote map-cracking at the surface of concrete members already affected by ASR.

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