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Effect of the cement chemistry and the sample size on ASR expansion of concrete exposed to salt

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Abstract

Mortar bars and concrete prisms made with a very alkali–silica reactive limestone were stored at 38 °C in 1 M NaOH and NaCl solutions. A high-alkali (HA) cement and a low-alkali (LA) cement were used in order to evaluate the cement chemical composition on the expansion and on the chemistry of the pore water. The mortar bars immersed in 1 M NaOH presented much more expansion than mortar bars stored at 100% RH or in 1 M NaCl. The behaviour of the concrete prisms was completely different. Low expansion was obtained for concrete prisms made with the LA cement immersed for more than 5 years in 1 M NaCl solution, while the expansion was over 0.45% for concrete prisms made with the HA cement. Chemical equilibrium between the pore waters and the immersion solution was much longer to obtain for the concrete prisms (near 3 years) than for the mortar bars (less than 3 months). The results obtained in this study show that the type of sample used (mortar bars or concrete prisms) and the cement composition strongly influence the harmful effects of ASR in concrete exposed to salt.

Keywords: Alkali–silica reaction; Chloride; Concrete; Mortar; Pore water chemistry

1. Introduction

It is a common belief that exposure to de-icing salt or sea water promotes alkali–silica reaction (ASR) and expansion by supplying additional alkalis to the exposed concrete. However, measurements on field concrete usually indicate that chloride does not penetrate more than a few centimetres into good quality concrete exposed to NaCl, while ASR affected concrete members are expanding in their all mass. Stark [1] states that an average chloride content at a depth of 25 mm was only 0.6 kg/m^3 after 830 daily salt applications on a concrete with a water/cement ratio of 0.4. Jensen et al. [2] have measured by electron probe microanalyser Cl migration at a depth of 1 mm in a high performance concrete made with 20% silica fume at a water/cement ratio of 0.3 after 1 month of salt immersion. In an other hand, many studies suggest that exposure to de-icing salt or sea water can initiate or accelerate alkali–silica reactivity [3–6].

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 chloroaluminate (or Friedel's salt), thus, forcing the portlandite to release OH^- ions to balance the alkali cations in the pore water. Some authors have shown that exposure to de-icing salt causes a pH increase in the concrete pore solution [4,7], while others [5,8] have observed a significant $[OH^-]$ decrease in the pore solution of mortar bars stored in NaCl solution compared with control bars immersed in distilled water or stored at 100%RH. In a study conducted in France [9], measurements on cores from sea-shore concrete posts supporting gas 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 6–7 cm, while more than 90% of chloride is still water-soluble, e.g., as NaCl rather than calcium chloroaluminate. The role of exposure to de-icing salt and sea water on the ASR is unclear, and this study was undertaken in order to clarify this effect.

2. Materials and methods

2.1. Materials

The aggregate selected in this study was a very alkali–silica reactive siliceous limestone from the Spratt Quarry in

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Table 1
Chemical composition of cements (%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Alc Na_2O_e	C_3S	C_2S	C_3A	C_4AF	C_3A+C_4AF
LA	22.13	4.24	3.24	64.28	1.49	3.03	0.18	0.48	0.50	51.7	24.4	5.8	9.9	15.7
HA	20.91	5.09	2.36	63.07	2.64	2.92	0.29	1.04	0.97	51.9	20.7	9.5	7.2	16.7

Ottawa (Ontario, Canada). Two ASTM type 1 cements were selected based on their alkali contents. Cement HA is a high-alkali cement (0.97% Na_2O_{eq}), while cement LA is a low-alkali cement (0.50% Na_2O_{eq}). The chemical compositions of cements are given in Table 1. NaOH and NaCl immersion solutions were prepared from reagent grade material.

2.2. Sample preparation

Mortar bars (2.5 × 2.5 × 25 cm) 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 HA cement was increased to 1.25% Na_2O_{eq} of the cement mass by adding NaOH to the water mixture.

Concrete prism specimens (7.5 × 7.5 × 30 cm) were made according to the CAN/CSA-A23.2-14A Concrete Prism Method with a cement content of 420 kg/m^3 and a fixed water/cement ratio of 0.47. Thirteen prisms were made from each type of cement. The alkali content of the prisms made with the HA cement was increased to 1.25% Na_2O_{eq} of the mass of cement by adding NaOH to the mixture water.

2.3. Testing conditions and measurements

After 24 h in their moulds at 23 °C and 100% RH, the samples were demoulded. One mortar bar and one concrete prism of each mixture was moist cured for 7 days and then used for pore water expression using the high-pressure method [10]. The other samples were placed in sealed plastic containers under various conditions. The first group of samples was immersed in 1 M NaCl solution to simulate exposure to sea water and de-icing salt. The second was immersed in 1 M NaOH solution, which is largely used in ASR testing to generate high pH conditions. Some mortar bars were stored in air at 100% RH above water. The containers were then immediately placed inside a room kept at 38 °C. The next day, the samples were measured for the first time and periodical measurements were performed afterwards up to 18 months for mortar bars and 5 years for the concrete prisms. One mortar bar of each mixture was removed from the tests after 7 days, 3, 6 and 18 months, and pore waters were expressed. Pore solution from concrete was expressed after 1, 12 days, 1, 3, 6, 12 and 36 months. For the last two curing times, the interstitial solution coming from the border and the centre of the concrete prisms were expressed separately. Immediately after being removed from the hot room, the corresponding mortar or concrete 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^{2-} ions was carried out on the solutions, shortly after expression, using atomic absorption for cations and ionic chromatography for anions.

3. Results

3.1. Expansion of mortar bars and concrete prisms

Fig. 1 shows that the mortar bars immersed in 1 M NaOH solution present much more expansion than samples stored at 100% RH or immersed in 1 M NaCl solution. The low expansion obtained for samples immersed in 1 M NaCl agrees with results obtained by Hooton and Rogers [11] showing no expansion exceeding 0.1% in the Danish salt test where mortar bars are immersed in saturated NaCl solution at 50 °C for 8 and 20 weeks. These authors studied 12 aggregates among which 6 were recognised reactive including Spratt limestone. Results obtained in this study disagree with those of Chatterji et al. [3] who used, however, a saturated NaCl solution. Fig. 1 also shows that the alkali content of the mortar mixture has no significant effect on expansion of samples immersed in 1 M NaOH solution, as also observed by Fournier and Bérubé [12], but affected those stored in air at 100% RH and in 1 M NaCl.

Fig. 2 presents the short term expansion of concrete prisms cured at 38 °C under different conditions. Fig. 2 shows that

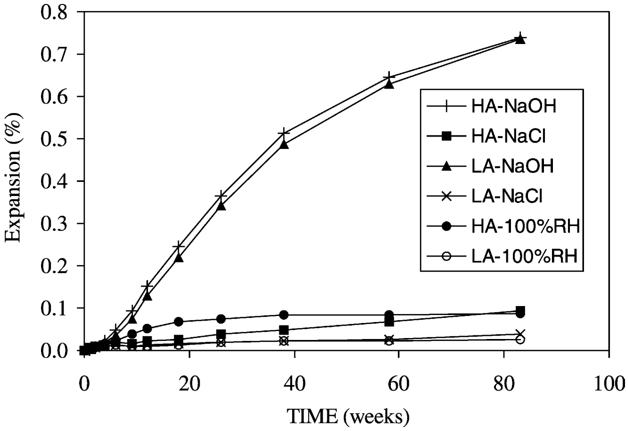

Fig. 1. Expansion of mortar bars cured at 38 °C in 1 M NaOH, 1 M NaCl and at 100% RH 38 °C.

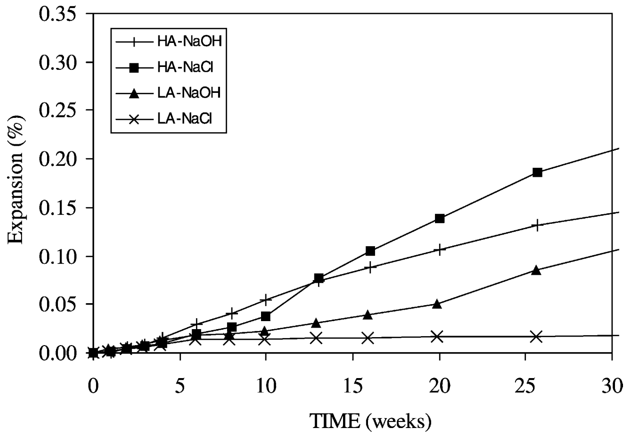

Fig. 2. Short-term expansion of concrete prisms cured at 38 °C in 1 M NaOH and 1 M NaCl.

concrete prisms stored in 1 M NaOH solution start early to expand. The rate of expansion of samples made with the HA cement immersed in 1 M NaCl solution increases and after around 13 weeks of testing, the expansion of those samples are the most important. Fig. 3 presents the long-term expansion for the same samples. This figure shows that the alkali content of the concrete mixture has no influence on expansion of samples immersed in 1 M NaOH solution. However, the composition of cement is really important for samples immersed in NaCl solution. Fig. 3 shows low expansion for samples made with a LA cement immersed for more than 5 years in 1 M NaCl solution, while the expansion is over 0.45% for samples made with a HA cement.

Fig. 4 shows the weight change of saturated surface dry concrete prisms cured at 38 °C in 1 M NaOH and 1 M NaCl as a function of time. This figure supports expansion results because ASR expansion is accompanied by a weight increase. Bérubé and Frenette [13] obtained similar expansion results. However, Sibbick and Page [6] reported that the effects of NaCl ingress on ASR development in hardened concrete made from certain UK aggregates are strongly dependent on the initial alkali content of the concrete concerned, the tendency of the salt to promote enhanced expansion being more noticeable in relatively low-alkali concretes than in high-alkali concretes.

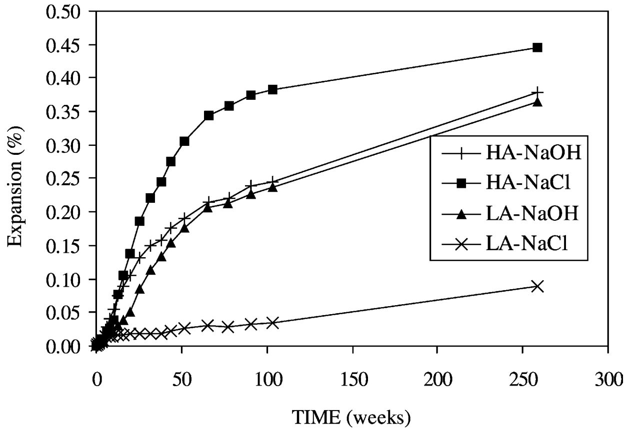

Fig. 3. Long-term expansion of concrete prisms cured at 38 °C in 1 M NaOH and 1 M NaCl.

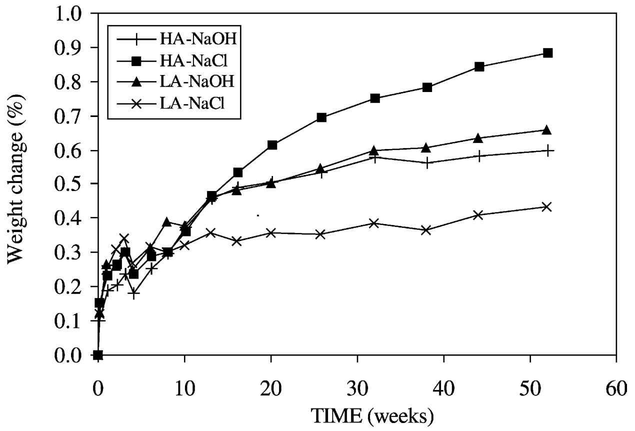

Fig. 4. Weight change of concrete prisms cured at 38 °C in 1 M NaOH and 1 M NaCl.

3.2. Pore water chemistry

3.2.1. Pore water chemistry of mortar bars

Measurements of the pore water composition were performed to explain the above variations in expansion. Table 2 presents pore water chemistry of mortar bars. All pore water composition are in mmol/l units. After 7 days of curing, the alkali concentrations of the pore water were 0.83 and 0.37 M [(Na,K)OH] for the HA and LA cements, respectively. These values are similar to those measured by Diamond [7]. The hydroxide concentration in the pore water can be calculated using a charge balance equation. Indeed, $[\mathrm{Na}^{+}]+[\mathrm{K}^{+}]\approx 2[\mathrm{SO}_4^{-2}]+[\mathrm{Cl}^{-}]+[\mathrm{OH}^{-}]$ in the pore water because the concentration of other ions are negligible.

Table 2 presents the results obtained from the mortar bars cured in air at 100% RH. These samples, especially those made with the HA cement, showed a drop in alkali concentration with time, and hydroxide as well, which is attributed to alkali leaching [14], 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 between sealed and unsealed mortar bars. Duchesne and Bérubé [15] showed that the amount of alkali lost due to leaching and humidity uptake was important.

Table 2 shows a Na^{+} increase and a K^{+} decrease in the pore water of samples immersed in 1 M NaOH solution over time, with the total NaOH content reaching relative equilibrium with the immersion solution, e.g., ~ 1 M. 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.

The pore water composition of mortar samples cured in 1 M NaCl shows an increase of Na^{+} and Cl^{-} ions to reach

Table 2
Pore water chemistry of mortar bars (values are in mmol/l)

Curing time	100% RH				Immersion in 1 M NaOH						Immersion in 1 M NaCl					
	LA		HA		LA			HA			LA			HA		
	Na	K	Na	K	Na	K	SO$_4$	Na	K	SO$_4$	Na	K	Cl	Na	K	Cl
7 days	160	210	400	430	160	210	0	400	430	0	160	210	0	400	430	0
3 months	125	125	220	175	1050	50	100	1050	125	75	1200	75	780	1100	100	780
6 months	120	100	160	130	1100	50	100	1100	75	75	950	50	1000	900	25	700
18 months	120	90	140	120	1250	0	100	1250	125	125	1025	25	975	985	25	785

equilibrium with the immersion solution. The concentrations of K$^+$ and SO$_4^{2-}$ ions decrease to almost nothing. The charge balance calculations give hydroxide concentrations of around 0.83 and 0.37 M for the HA and LA cements, respectively, before immersion in the NaCl solution. The hydroxide concentrations drop afterwards to around 0.4 M at 3 months, 0.2 M at 6 months and lower than 0.1 M at 18 months for both cements. The immersion solution was analysed at the end of the experiment and its hydroxide concentration of 0.11 M is another indication that equilibrium is effectively reached in the long-term between the mortar pore water and the immersion solution.

3.2.2. Pore water chemistry of concrete prisms

Table 3 presents pore water chemistry of concrete prisms. After 1 day of curing, the alkali concentrations of the pore waters were around 0.2 and 0.7 M for concrete prisms made with low and HA cements, respectively. Table 3 shows a Na$^+$ increase and a K$^+$ decrease in the pore water of concrete immersed in 1 M NaOH solution. For those samples, calcium concentrations were always low ranging from 0.04 to 3 mmol/l. After 1 year of curing, the borders of the concrete prisms have reached equilibrium with the NaOH solution. It took about 3 years for the centre of the LA cement sample to reach equilibrium and equilibrium was not attained in the case of the high-alkali sample.

The pore water composition of samples cured in 1 M NaCl solution shows an increase of Na$^+$ ions to reach equilibrium in the border of the samples after a curing time of a year. It was necessary to wait 3 years in order to obtain equilibrium in the centre of the prisms made with the LA cement. Even after 3 years of curing, the centre of the samples made with the HA cement did not reach equilibrium. Measurements of the chloride contents support these data.

These results show that obtaining chemical balance between the pore waters and the immersion solution requires much longer exposure for the concrete prisms (near 3 years) than for the mortar bars (less than 3 months). These last are much more porous having a more significant cement/aggregate ratio and a higher water/cement ratio. The results on the pore water expression separating the

Table 3
Pore water chemistry of concrete prisms (values are in mmol/l)

Curing time	LA-immersion in 1 M NaCl						LA-immersion in 1 M NaOH					
	Na	K	Ca	SO$_4$	Cl	OH	Na	K	Ca	SO$_4$	Cl	OH
1 day	80	110	0.04	17			80	110	0.04	1		
12 days	410	60	0.6	140			330	135	0.4	10		
1 month	700	110	4	135			335	135	3	15		
3 months	610	65	5	70			500	40	2	30		
6 months	825	100	9	5			850	45	1	55		
12 months—border	1150	25	13	50			1050	20	2	75		
12 months—centre	780	110	10	70			600	50	2	45		
36 months—border	1225	30		10	1225		1070	15		90	15	900
36 months—centre	1050	40		9	1025	100	1090	15		90	20	740

Curing time	HA-immersion in 1 M NaCl						HA-immersion in 1 M NaOH					
	Na	K	Ca	SO$_4$	Cl	OH	Na	K	Ca	SO$_4$	Cl	OH
1 day	310	370	0.2	15			310	370	0.2	15		
12 days	410	135	0.7	30			510	150	0.6	45		
1 month	510	20	4	30			470	270	1	55		
3 months	500	100	1	15			510	60	1	35		
6 months	775	140	2	20			670	125	2	55		
12 months—border	1090	70	4	15			880	45	1	70		
12 months—centre	540	135	2	30			610	15	2	50		
36 months—border	1080	70		15	1005	165	825	40		60	10	800
36 months—centre	740	90		25	625	210	610	45		50	15	610

border from the centre of the concretes show that even after 3 years of total immersion at 38°C, the centre of the prisms, which is located at 5 cm from the border, did not reach balance. This shows that the migration of salt inside good quality concrete is a slow phenomenon, which affects mainly the first centimetres of the concrete.

4. Discussion

The results of the composition of the pore waters do not help us to understand why the mortars made with the HA cement and immersed in NaCl solution do not undergo expansion whereas the concrete prisms made with the same HA cement show the most significant expansion. Let us recall here that the concrete prisms made with the LA cement showed also little expansion. The concrete samples made with the HA cement are the only ones which show a strong expansion during the immersion in NaCl. These tests were duplicated several times on several concrete prisms in order to verify the validity of the results. According to the pore water expression test, these samples are the only ones not to have reached balance in the centre of the prisms after 3 years of cure.

After obtaining these results, we ran mercury porosimetry tests (Hg intrusion) on samples coming from the border and the centre of the prisms in order to compare the size and the quantity of pores of each sample. These tests showed that there was no significant difference in porosity of the samples coming from the border and the centre of the prisms.

If we look a little more closely at the chemical composition of the two cements given in Table 1, we can see that both cements have equivalent sulphate contents but very different alkali content (0.5% for LA and 1.25% for HA). The cement with the low-alkali content has less C_3A than the HA cement. On the other hand, if we consider that the C_4AF acts mainly like the C_3A in long-term exposure, the combined quantity of these two components is about equivalent. According to Birnin-Yauri and Glasser [16], Friedel's salt formation will be limited by the total Al content of the cement, rather than by the Afm content alone, because all aluminate hydrates will convert in a similar concentration range to Friedel's salt.

The potential removal of chloride ions by incorporation into Friedel's salt 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 compensate for the incorporation of Cl^- ions into solid phase. To verify the presence of Friedel's salt in the samples, scanning electron microscope (SEM) observations and X-ray diffraction (XRD) analyses were carried out. SEM observations on mortar samples have shown that all samples made with the HA cement, and those made with the LA cement and immersed in the NaOH solution, contained ASR reaction products. A few calcium chloroaluminate euhedral crystals were found in mortar bars immersed in 1 M NaCl; however, these were 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 the energy dispersive spectrometer (EDS), but this method cannot tell us under which form we may find chloride. Duchesne and Bérubé [15] presented electron probe micro analysis (EPMA) data showing that the mortar made with the HA cement contains more calcium chloroaluminates than the low-alkali mortar, while both samples contain a significant amount of NaCl. XRD analysis done on concrete samples immersed in the NaCl solution showed that Friedel's salt is present both in the border and in the centre of HA prisms. For the LA samples, Friedel's salt was only detected in the border of the prisms. However, XRD is often not sensitive to the development of small, but potentially important, quantities of secondary mineral phases.

5. Conclusion

The curing conditions greatly influence the expansion of mortar bars made with alkali–silica reactive aggregates. The mortar bars immersed in 1 M NaOH present much more expansion than mortar bars stored in air at 100% RH or in 1 M NaCl solution. The initial alkali content of the mortar mixture has no significant effect on expansion for samples immersed in 1 M NaOH, but affects those stored in air at 100% RH or immersed in 1 M NaCl. The behaviour of the concrete prisms was completely different. Low expansion was obtained for concrete prisms made with the LA cement immersed for more than 5 years in 1 M NaCl solution while high expansion occured (over 0.45%) for concrete prisms made with the HA cement. The initial alkali content of the cement was not important for samples stored in the NaOH solution. Indeed, both samples (LA and HA) have reached expansion near 0.35% after 5 years of curing in the hydroxide solution.

It took less than 3 months for the pore water of mortar samples stored in NaOH and NaCl solutions to reach relative equilibrium with the immersion solution. For concrete prisms made with the HA cement, the equilibrium was still not attained after 3 years of curing in the NaCl solution. This shows that the migration of salt inside good quality concrete is a slow phenomenon, which affects mainly the first centimetres of the concrete.

The results obtained in this study show that the type of sample used (mortar bars or concrete prisms) is of the main importance in order to highlight in an accelerated way the harmful effects of the ASR. Moreover, the tests carried out make it possible to highlight the effect of the chemical composition of cement on the phenomenon of expansion. The mechanisms concerned are still not clear. Other tests will have to be set up while varying a chemical element at the time in the composition of cement in order to determine the factor influencing the expansion of concrete prisms immersed in NaCl solution.

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References

[1] D. Stark, Effects of chloride solutions on expansion due to ASR, Concr. Technol. Today, PCA 16 (1995) 2–4.

[2] O.M. Jensen, A.M. Coats, F.P. Glasser, Chloride ingress profiles measured by electron probe micro analysis, Cem. Concr. Res. 26 (1996) 1695–1705.

[3] S. Chatterji, A.D. Jensen, N. Thaulow, P. Christensen, Studies of alkali–silica reaction: Part 3. Mechanisms by which NaCl and $Ca(OH)_2$ affect the reaction, Cem. Concr. Res. 16 (1986) 246–254.

[4] P.J. Nixon, I. Canham, C.L. Page, R. Bollinghause, Sodium chloride and alkali–aggregate reaction, in: P.E. Grattan-Bellew (Ed.), Proc. 7th Int. Conf. on Alkali–Aggregate Reaction in Concrete, Noyes Publications, Ottawa, Canada, 1987, pp. 110–114.

[5] M. Kawamura, K. Takeuchi, Alkali–silica reaction and pore solution composition in mortars in sea water, Cem. Concr. Res. 26 (1996) 1809–1819.

[6] R.G. Sibbick, C.L. Page, Effects of sodium chloride in the alkali–silica reaction in hardened concrete, in: A. Shayan (Ed.), Proc. 10th Int. Conf. on Alkali–Aggregate Reaction in Concrete, CSIRO, Melbourne, Australia, 1996, pp. 822–829.

[7] S. Diamond, Alkali reactions in concrete-pore solution effects, in: G.M. Idorn (Ed.), Proc. 6th Int. Conf. on AAR, Steen Rostam, Copenhagen, Denmark, 1983, pp. 155–167.

[8] M. Kawamura, S. Komatsu, Behavior of various ions in pore solution in NaCl-bearing mortar with and without reactive aggregate at early age, Cem. Concr. Res. 27 (1997) 29–36.

[9] G. Escadillas, INSA-UPS Toulouse, personal communication.

[10] P. Longuet, L. Burglen, A. Zelwer, La phase liquide du ciment hydraté, Rev. Mater. Constr. Trav. Publics 1 (1973) 35–41.

[11] R.D. Hooton, C.A. Rogers, Evaluation of rapid test methods for detecting alkali–reactive aggregates, in: S.N. Okana, M. Kawamura (Eds.), Proc. 8th Int. Conf. on Alkali–Aggregate reaction in concrete, Elsevier, Kyoto, Japan, 1989, pp. 439–444.

[12] B. Fournier, M.A. Bérubé, Application of the NBRI quick mortar bar test to determine the alkali-reactivity potential of the carbonate aggregates produced in the St. Lawrence Lowlands (Quebec, Canada): Part 1. Influence of various parameters on the test results, Cem. Concr. Res. 21 (1991) 853–862.

[13] M.A. Bérubé, J. Frenette, Testing concrete for AAR in NaOH and NaCl solutions at 38 °C and 80 °C, Cem. Concr. Compos. 16 (1994) 189–198.

[14] C.A. Rogers, R.D. Hooton, Leaching of alkalis in alkali–aggregate reaction testing, in: S.N. Okana, M. Kawamura (Eds.), Proc. 8th Int. Conf. on Alkali–Aggregate Reaction in Concrete, Elsevier, Kyoto, Japan, 1989, pp. 327–332.

[15] J. Duchesne, M.A. Bérubé, Effect of deicing salt and sea water on ASR: new considerations based on experimental data, in: A. Shayan (Ed.), Proc. 10th Int. Conf. on Alkali–Aggregate Reaction in Concrete, CSIRO, Melbourne, Australia, 1996, pp. 830–837.

[16] U.A. Birnin-Yauri, F.P. Glasser, Friedel's salt, $Ca_2Al(OH)_6(Cl,OH)$ $2H_2O$: its solid solutions and their role in chloride binding, Cem. Concr. Res. 28 (1998) 1713–1723.