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Long-term effectiveness of supplementary cementing materials against alkali–silica reaction

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Abstract

The long-term effectiveness of six supplementary cementing materials (SCM) were tested according to the CSA-A23.2-14A Concrete Prism Method in the presence of two very alkali–silica reactive aggregates from Canada. Three fly ashes, two silica fumes, and one ground granulated blast furnace slag (GGBFS) were selected based on their elemental composition in order to represent a wide range of composition. The performance of SCMs in suppressing expansion due to alkali–silica reaction was compared with that obtained by a low-alkali cement. Pore solution composition of the mixtures was also determined. Results show that expansion curves flatten out after 2 years of curing. This phenomenon was due to alkali leaching from the concrete prisms and alkali binding by the alkali aggregate reaction products in the presence of the very reactive aggregates used, which was supported by very low alkali ion concentrations measured on concrete samples at the end of the experiment. A 2-year expansion limit is then suggested when using the CAN/CSA-A23.2-14A method to evaluate mixtures containing SCM. The proportion of SCM and total alkali content of the concrete are very significant factors controlling concrete expansion. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Alkali–aggregate reaction; Durability; Fly ash; Granulated blast-furnace slag; Silica fume

1. Introduction

The utilization of supplementary cementing materials (SCM) is one of the most popular ways to minimize the deleterious expansion due to alkali–silica reaction (ASR). However, the long-term effectiveness and the behavior of these materials are not well understood. Alkali contribution from SCMs seems to be a key factor. According to Berra et al. [1], a dilution effect cannot be invoked to explain the reduced concentration of the OH^- ions in the pore solution because the total alkali content of the SCM used was comparable to or above that of the Portland cement. Shayan et al. [2] state that generally low-alkali SCMs are more effective than high-alkali ones in reducing pore solution alkalinity and expansion caused by AAR, and that their effect is greater than a mere dilution of high-alkali cements. This view was supported by Oberholster and Westra [3] and many other authors.

Concerning the long-term effectiveness of SCMs against ASR, Durand [4] reported that no deleterious expansion has been observed at the Lower Notch dam, Northern Ontario (Canada), built with a reactive argillite and 20% fly ash, after more than 20 years. Thomas et al. [5] state that in Britain, some dams built more than 50 years ago with reactive aggregates and SCM are still in excellent condition. According to Gudmundsson and Möller [6], silica fume has extensively been used in Iceland since 1979, and after almost 20 years of service there are no signs of alkali–silica reaction. During the same time, some restriction were applied on aggregates used in Iceland such that aggregates must present a mortar bar expansion lower than 0.1% after 12 months when tested according to ASTM C227. Shayan et al. [2] concluded after 6 years of laboratory testing that the effectiveness of the fly ash in preventing deleterious AAR expansion depended on the alkali content of the concrete. At high alkali content of the order of 12.5 kg/m^3 Na_2O_{eq}, the fly ashes only had a delaying effect.

The objective of this study was to understand the behavior of various types of SCM against ASR and to evaluate their effectiveness in the long term. This study is the follow-up of results published by Duchesne and Bérubé

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[7]. The chemistry of the pore solution was determined for each mixture and compared with expansions obtained with two very reactive aggregates in a modified version of the CAN/CSA-A23.2-14A Concrete Prism Method, using 350 kg/m^3 of cementitious materials and a fixed 0.5 water/cementitious material ratio.

2. Materials and methods

2.1. Materials

The long-term effectiveness of six SCMs was tested in the presence of two very alkali-reactive aggregates from Canada, one siliceous limestone (Spratt Quarry) and one rhyolitic tuff (Beauceville Quarry). The SCMs were chosen based on their elemental composition in order to represent a wide range of composition. Three fly ashes (FA) were selected. Fly ash A has low calcium and low alkali contents, B has moderate calcium and low alkali contents while C has high calcium and high alkali contents. Two silica fumes (SF) containing different alkali and silica contents were chosen along with one ground granulated blast furnace slag (GGBFS). Two Type 1 cements were selected based on their alkali contents. Cement HA is a high-alkali cement while cement LA is a low-alkali cement. The chemical compositions of SCMs and cements are given in Table 1.

2.2. CAN/CSA-A23.2-14A Concrete Prism Method

Concrete prism specimens were made according to the CAN/CSA-A23.2-14A Concrete Prism Method with the two aggregates and various SCM contents as cement replacement by mass. SCM contents were 0%, 20%, and 40% for fly ashes; 0%, 5%, and 10% for silica fumes; and 0%, 35%, and 50% for GGBFS. The SCMs were tested with a high-alkali cement (HA). The cement alkali content was increased to 1.25% Na_2O_{eq} of the mass of cement by adding NaOH to the mixture water. The cementitious material content was 350 kg/m^3 with a fixed water/cementitious material ratio of 0.5. The performance of SCMs in suppressing expansion due to alkali–silica reaction was compared with that obtained with a low-alkali cement (LA). Concrete prisms were also made with mixtures having the highest cement replacement (FA-A 40%, FA-B 40%, SF-A 10%, and GGBFS-A 50%) with the alkali content increased to 3.0% Na_2O_{eq} of the mass of cement by adding more NaOH to the mixture water. These samples were made to determine the influence of the alkali content on expansion.

Table 1
Chemical composition of SCMs and cements

	FA			SF		GGBFS	Cement	
	A	B	C	A	B[a]	A	HA	LA
SiO_2	42.20	53.90	32.59	94.17	74.60	36.60	20.47	20.05
Al_2O_3	21.60	20.90	17.93	0.21	0.59	8.00	5.51	4.78
Fe_2O_3	27.60	3.52	5.94	0.32	6.54	0.67	2.45	3.38
TiO_2	–	–	1.17	0.00	0.00	–	0.24	0.26
MnO	–	–	0.03	0.07	0.38	–	0.05	0.04
MgO	0.92	1.11	4.12	0.47	1.56	13.70	2.82	2.32
CaO	1.87	12.00	20.70	0.50	0.40	37.20	63.12	62.94
Na_2O	0.66	2.74	8.08	0.00	1.68	0.44	0.29	0.26
K_2O	2.55	0.50	0.72	1.17	2.97	0.31	1.16	0.42
P_2O_5	–	–	0.59	0.04	0.00	–	0.13	0.06
Cr_2O_3	–	–	0.01	0.00	0.03	–	0.00	0.07
SO_3	1.10	0.09	1.48	0.12	0.81	3.97	2.60	2.75
LOI	1.85	0.57	0.96	2.77	7.34		0.81	3.00
Total	100.35	95.33	94.32	99.84	96.90	100.89	99.65	100.33
Alkali (Na_2O_{eq})	2.3	3.07	8.55	0.77	3.63	0.64	1.05	0.54

[a] SF-B does not meet CSA-A23.5 or ASTM C1240 standards (SiO_2 < 85%).

2.3. Pore solution extraction method

During the cement hydration reactions a certain amount of alkali ions can be released from the SCMs and carried into the pore solution of concrete. These alkali ions become available for potential alkali–silica reaction. To measure this alkali content we used the high-pressure pore solution extraction method [8]. Paste samples were made in a mortar mixer with the same cement/SCM proportions as above, and the same water/cementitious material ratio (0.5), cast into plastic bottles and stored at 38°C. After 7, 28, 84, 182, 364, and 545 days of curing, pore solutions were extracted by the high-pressure method first described by Longuet et al. [8] with an applied maximum load pressure of 560 MPa (81 500 psi). Shortly after extraction, chemical analyses were carried out on the solutions, and Na^+ and K^+ cations were determined by atomic absorption. After 3270 days (more than 9 years) of curing over water at 38°C, pore solutions were extracted directly from concrete prisms made with the Spratt aggregate for expansion measurements, using a larger apparatus.

3. Results and discussion

3.1. Concrete prism expansion

Fig. 1 presents the expansion of concrete prisms containing silica fume A and B at 5% and 10% cement replacement by mass. The high-alkali control is labeled 0% while the low-alkali control LA-0%. The 10%++ label is for the concrete prisms made with 10% SF-A and a cement alkali content increased to 3.0% Na_2O_{eq}.

In general, Fig. 1 shows that after 2 years of curing the rate of expansion decreases significantly and most expansion curves flatten. The low-alkali controls expanded by 0.047% with the rhyolitic tuff aggregate and 0.070% for the Spratt limestone after 9 years of curing. The utilization of 5% SF was not sufficient to control concrete expansion,

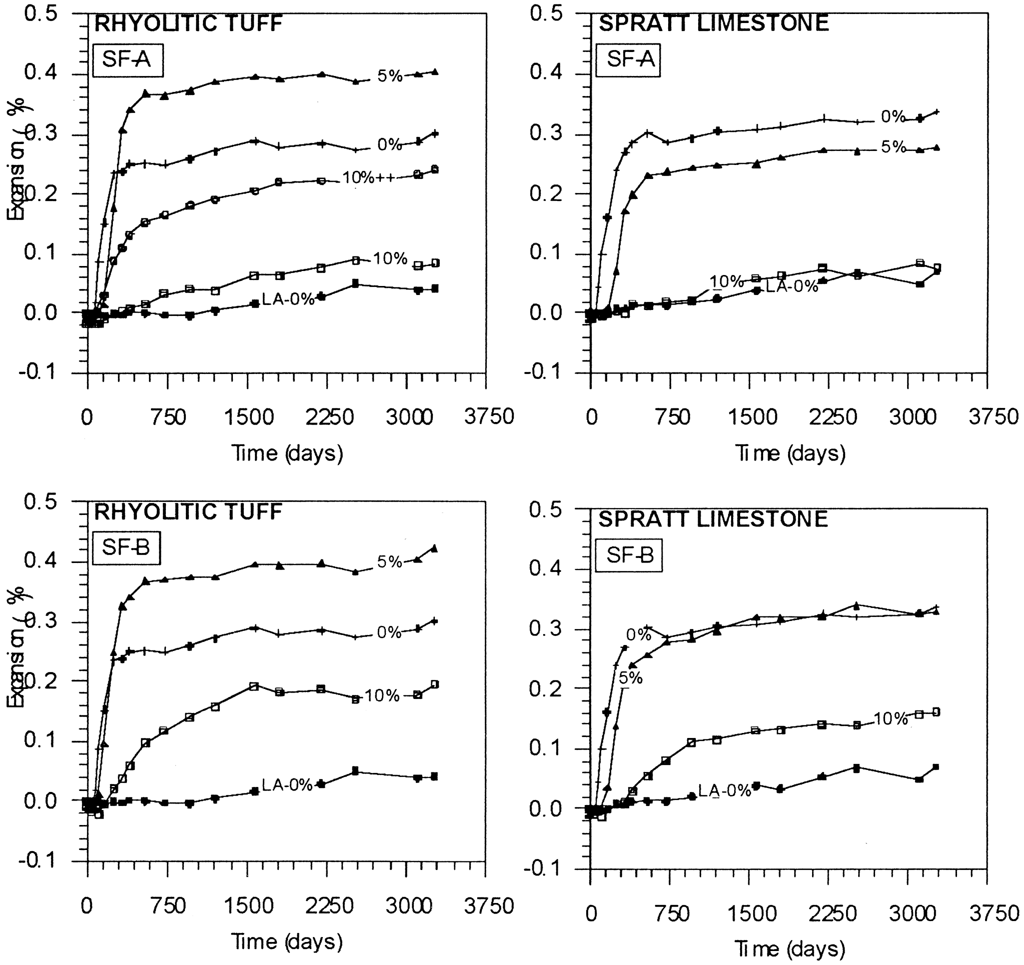

Fig. 1. Expansion of concrete prisms (CSA-A23.2-14A) made with two reactive aggregates and various amounts of two SF, cured at 100% RH and 38°C.

even producing more expansion than the high-alkali control with the rhyolitic tuff. Only the use of 10% SF-A was able to restrict expansion to the level obtained by the low-alkali control. By comparing samples 10%++ and 10% SF-A we can see that increasing the cement alkali content also increases the expansion level. SF-A is more efficient in reducing concrete expansion than SF-B. Table 1 shows that SF-A contains more silica and less alkali than SF-B.

Fig. 2 shows the expansion of concrete prisms containing GGBFS at 35% and 50% cement replacement by mass.

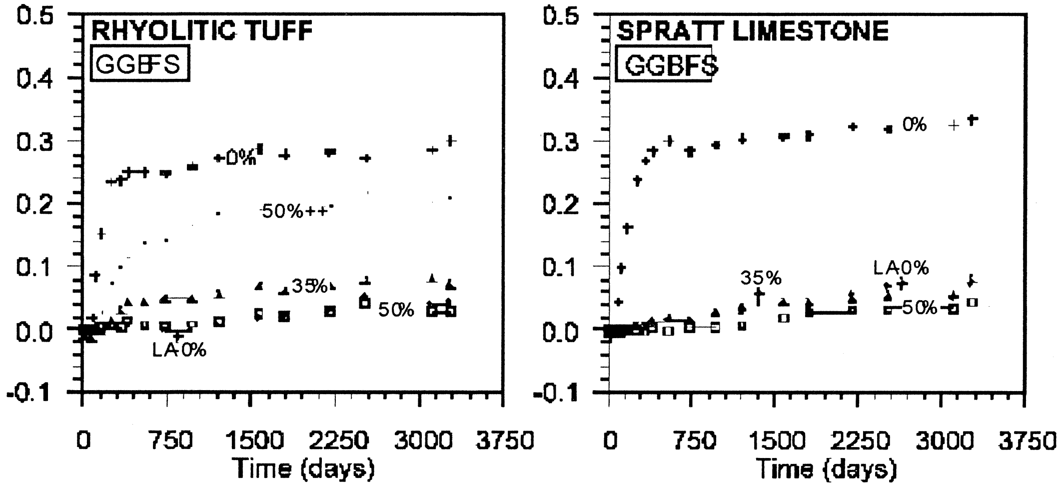

Fig. 2. Expansion of concrete prisms (CSA-A23.2-14A) made with two reactive aggregates and various amounts of GGBFS, cured at 100% RH and 38°C.

Samples containing 50% GGBFS present expansion of 0.044% in the presence of the Spratt limestone and 0.029% with the rhyolitic tuff aggregate after more than 9 years of curing. These values are lower than those obtained by low-alkali control. Expansions in the order of 0.07% were obtained with 35% cement replacement by GGBFS. The cement alkali level is an important factor governing concrete expansion. Sample 50%++ corresponding to concrete prisms made with 50% GGBFS and a cement with alkali content increased to 3.0% Na_2O_{eq} presents expansion of 0.207%, which is 10 times more than that of the sample made with the 1.25% Na_2O_{eq} cement. These results suggest good long-term behavior for blended slag cements that contain less alkali than 1.25% Na_2O_{eq}. All prisms containing GGBFS reached their maximum expansion value after 2 years of curing. After this time period, the rate of expansion decreased and remained constant.

Fig. 3 presents the expansion of concrete prisms containing 20% and 40% FA. Shrinkage is often observed in the short term when using high levels of FA. Fig. 3 shows that the high-alkali FA-C is totally ineffective, even at 40% cement replacement. With the two low-alkali fly ashes FA-A and FA-B, concrete expansions were under the values obtained by the low-alkali controls when used at a replacement level of 40%. Samples containing 20% of FA-A and FA-B show expansions equivalent to or less than those obtained for the low-alkali controls. Samples 40%++ showed that increasing the alkali level in samples containing FA-A and FA-B intensifies the concrete expansion even when using 40% FA. These results are in agreement with those of the other investigations mentioned earlier. The same as for SF and GGBFS, after less than 2 years of curing concrete expansions reached a pseudo-plateau.

3.2. Pore solution extraction results

Table 2 presents the alkali concentrations in the pore solution of various mixtures ($Na^+ + K^+$) as a function of time. Data obtained after 7, 28, 84, 364, and 545 days of curing correspond to equivalent paste samples sealed in plastic bottles until the appropriate time for pore solution extraction. Values at 3270 days of curing relate to concrete samples used for expansion measurements. These concrete prisms were stored over water in sealed plastic containers with wicks in order to achieve about 100% RH. When the pH is high, $[Na]+[K] \sim [OH]$ because other species are insignificant compared with alkali ions. The relation between the alkalinity measured and the summation of $Na^+ + K^+$ is a straight line for this pH range. The SO_4^{2-} ion concentrations are also insignificant compared with OH^- concentrations. The alkali ion concentrations given in Table 2 are very high with values of 0.920 M for the high-alkali control at 545 days compared to 0.689, 0.669, 0.646, and 0.857 M at 7, 28, 84, and 365 days of curing. With time, a larger proportion of the cement becomes hydrated and less pore solution remains, which may explain the increase in alkali concentration. After 149 days of curing under sealed conditions, Diamond [9] obtained 0.83 N (Na + K) with a high-alkali cement (0.91% Na_2O_{eq}).

The paste containing 5% of SF-B presents higher alkali concentrations in pore solution than the high-alkali control at 84 days of curing. In the presence of this silica fume, the alkali content tends to increase with time due to the high alkali content of SF-B. The alkali concentration is a function of the amount of SCMs in the mixture. For most samples, a larger cement replacement ratio implies lower alkali concentration in the pore solution. Table 2 shows that all SCMs (except FA-C) reduced at 1 year the alkali (and hydroxide) ion in the pore solution compared to the control, even though some of SCM containing much more alkali than the control (SF-B, FA-A, FA-B). This suggests that significant amounts of alkali ions are incorporated in CSH in presence of SCM. Duchesne and Bérubé [10] presented an extensive study on alkali incorporation in hydration products in the presence of SCM. These results also agree with the previous investigations which stated that the effect of SCM is more than a mere dilution effect. The effect of alkali on expansion cannot be completely explained by alkali content. For example, cement with 5% SF has a similar or lower alkali concentration in pore solutions compared with the control, yet they produced a significantly higher expansion in the presence of the rhyolitic tuff. Similarly, the alkali concentration of pore solutions of 10% SF systems is about the same as that of fly ash A and B, whereas the expansion of 10% SF specimens are higher.

Samples containing 40% FA-C are the only ones with 40% cement replacement that lead to higher alkali concentration values than samples with 20%. The pulverized fly ash C is rich in alkali (FA-C, 8.55% Na_2O_{eq}) and contains thenardite (Na_2SO_4), which is easily soluble contributing alkali to the pore solution. This explains why short-term values in the presence of FA-C are higher than those obtained in the long term and also why unlike other cases the 40% FA-C presents higher alkali contribution. The alkali concentration measured on samples containing FA-C are higher than values obtained by the high-alkali control for all curing times. More alkali ions are available from FA-C than the amount trapped in reaction products, as a result of its relatively low silica content.

Alkali concentration values obtained by extraction of pore solution directly from concrete prisms after 3270 days of curing are an order of magnitude less than concentrations from sealed pastes. A part of the alkali ions in the concrete pore solution can be trapped in ASR reaction products. However, even specimens showing small expansion showed an important drop in alkali ion concentration between sealed (paste) and unsealed (concrete) samples. This implies that the storage conditions used in most laboratories (concrete prisms stored over water in sealed plastic containers with wicks) allow leaching of a large proportion of alkali ions initially present in the specimens. According to Shayan [11], reactive aggregates are very effective in reducing the alkali

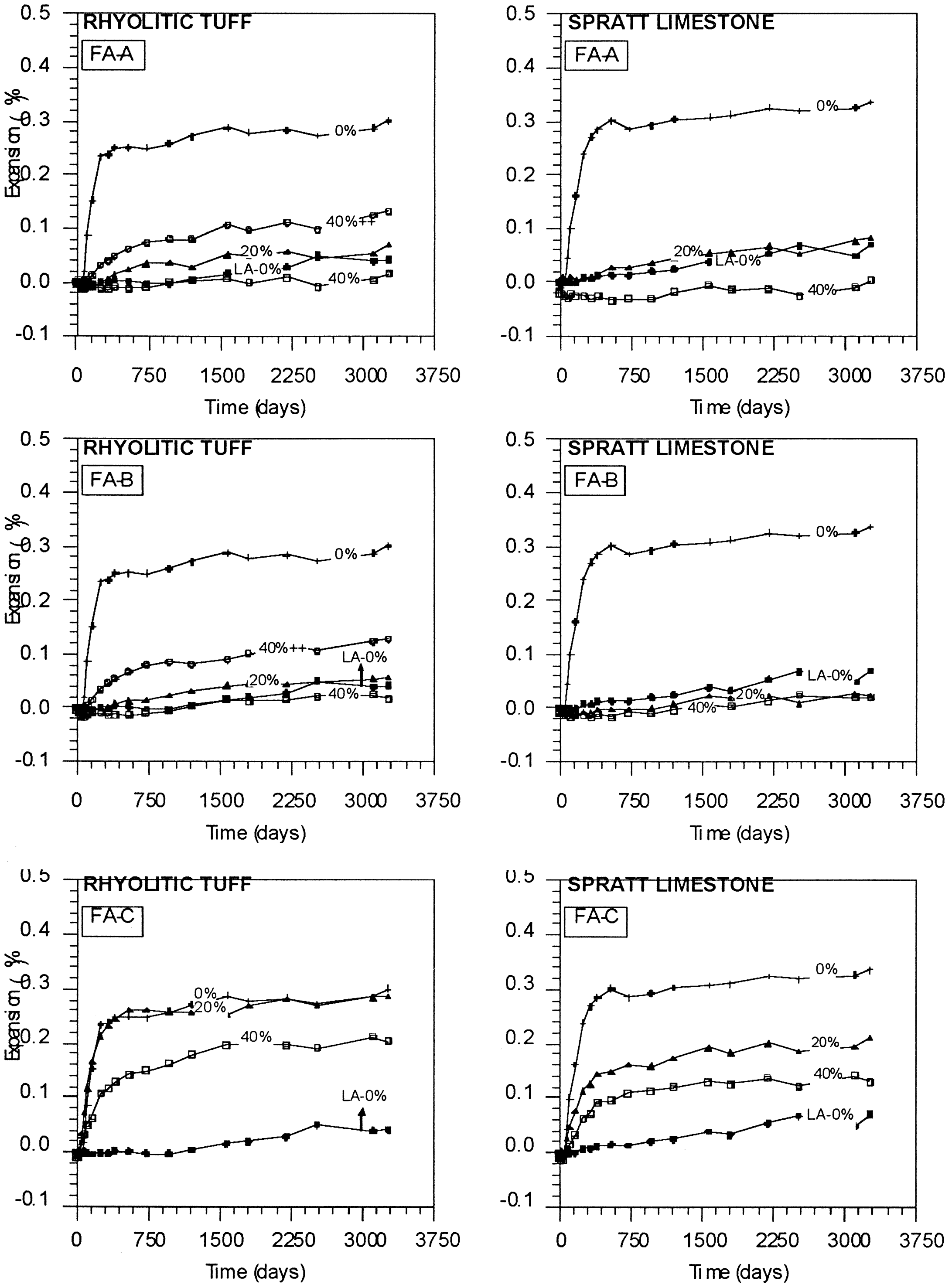

Fig. 3. Expansion of concrete prisms (CSA-A23.2-14A) made with two reactive aggregates and various amounts of FA, cured at 100% RH and 38°C.

content of pore solution. This binding of alkali by aggregate does not necessarily cause very high expansions, but may still be high enough to cause minor cracking, depending on the amount of alkali available. Alkali leaching and alkali binding in ASR reaction products during storage explain the plateau of the expansion curves after around 2 years of experiment. It is clear after these long-term experiments that an expansion criterion after 2 years of curing is realistic for the evaluation of the expansion behavior of concrete containing SCM. Bérubé et al. [12] measured in detail the alkali leaching of mortar bars tested at 100% RH by comparing pore solution composition, mortar expansions, and quantity

Table 2
Alkali ion concentration in pore solution of sealed pastes[a]

	$Na^{+} + K^{+} \approx OH^{-}$ (mol/l)					
Time	7 days	28 days	84 days	364 days	545 days	3270 days
0% (control)	0.689	0.669	0.646	0.857	0.920	0.083
LA-0%	–	–	–	–	–	0.107
SF-A 5%	0.475	0.493	0.534	0.681	0.760	–
SF-A 10%	0.261	0.305	0.307	0.420	0.580	0.127
SF-B 5%	0.389	0.426	0.705	0.895	0.940	–
SF-B 10%	0.252	0.214	0.377	0.617	0.720	0.067
GGBFS 35%	0.446	0.411	0.399	0.493	0.560	–
GGBFS 50%	0.348	0.289	0.268	0.362	0.370	0.101
FA-A 20%	0.549	0.459	0.406	0.510	0.570	–
FA-A 40%	0.394	0.290	0.268	0.361	0.370	0.046
FA-B 20%	0.486	0.435	0.377	0.492	0.500	–
A-B 40%	0.385	0.294	0.238	0.310	0.330	0.088
FA-C 20%	1.399	1.498	1.201	1.636	1.670	–
FA-C 40%	1.718	1.525	1.499	1.493	1.640	0.112

[a] In sealed cement paste except at 3270 days (unsealed concrete prisms).

of alkali ions found in the bottom solutions. These authors concluded that leaching is very significant when testing mortar bars stored over water at 38°C. The present study leads to the same conclusion but for concrete prisms. The phenomenon takes more time to show out because concrete prisms are less porous than mortar bars and sections of specimens are larger.

By comparing concrete expansion values and alkali ion concentrations in the pore solution we can note that there exists a good correlation between the drop of alkali ions in pore solution and expansion reduction in concrete for all concrete samples tested. All mixtures of this work capable of reducing the pore solution alkali content by 30% of the control at 2 years were nonexpansive. The mixture with 10% SF-B is just over the limit. This concrete sample presented an expansion of 0.048% in the presence of the rhyolitic tuff and 0.019% with the Spratt limestone after 1 year of curing. However, at 2 years the expansions were 0.117% and 0.082%, respectively, which are significantly high values. The different behavior of the two aggregates can be explained by the possibility that the tuff aggregate liberates alkali ions in pore solution. Samples containing FA-C present very high expansion and also very high alkali ion concentrations in the pore solution. This FA is totally ineffective even at a 40% cement replacement by mass.

Except for the very high-alkali FA-C, increasing the SCM content decreased the amount of alkali ions in pore solution and reduced the expansion. Subsequently, concrete tests were made with those mixtures that showed the best expansion reduction (FA-A 40%, FA-B 40%, SF-A 10%, and GGBFS-A 50%) but with the alkali content increased to 3.0% (Na_2O_{eq}) of the mass of cement by adding more NaOH to the mixture water (samples ++ on Figs. 2 and 3). Results show that increasing the alkali ion content produced deleterious expansion even if great amounts of good SCM were used as observed by Shayan et al. [2].

4. Conclusion

This study presents long-term expansion measurements of concrete prisms tested according to the CAN/CSA-A23.2-14A method. In parallel, high-pressure pore solution extraction method was conducted on paste samples made with different SCM in order to determine the hydroxide ion concentration of the pore solution. After 3270 days of curing, pore solution was recovered directly from the concrete prisms used for expansion measurements. Results show that expansion curves flatten out after around 2 years of curing for all mixtures tested. This phenomenon was due to alkali ions leaching from the concrete prisms stored over water in sealed plastic containers with wicks and alkali binding in the ASR reaction products. This view is supported by very low alkali ion concentrations measured on concrete samples at the end of the experiment. A 2-year limit is thus suggested when using the CAN/CSA-A23.2-14A method to evaluate the expansion potential of mixture containing SCM. It is not pertinent to continue the test to a longer time period.

After 9 years of measurement, the controls made with a low-alkali cement have expansions near 0.04%. The use of 40% FA-A and FA-B as well as the use of 50% GGBFS decreases the expansions to lower than those obtained with low-alkali cement. An excellent correlation was obtained between the drop of alkali ions in pore solution and expansion reduction in concrete. Increasing the alkali ion content produced deleterious expansion even if great amounts of good SCM were used. The total alkali content of the concrete prism and the amount of SCM used are the key factors governing the expansion behavior of concrete containing SCM. The alkali content in the pore solution of sealed paste samples should be near or below 0.6 M at 1 year for safe use. Fly ashes such as FA-C, which is very rich in alkali ions (8.55% Na_2O_{eq}), should not be used for reducing AAR of concrete.

Acknowledgments

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References

[1] M. Berra, G. De Casa, T. Mangialardi, Evolution of chemical and physical parameters of blended cement mortars subjected to the NaOH bath test. in: A. Shayan (Ed.), Proc. of the 10th International Conference on alkali-aggregate reaction in concrete, Melbourne, Australia, 1996, pp. 483.

[2] A. Shayan, R. Diggins, I. Ivanusec, Long-term effectiveness of fly ash in preventing deleterious expansion due to alkali-aggregate reaction in concrete. in: A. Shayan (Ed.), Proc. of the 10th International Confer-

ence on Alkali–Aggregate Reaction in Concrete, Melbourne, Australia, 1996, pp. 538.

[3] R.E. Oberholster, W.B. Westra, The effectiveness of mineral admixtures in reducing expansion due to alkali-aggregate reaction with Malmsbury group aggregates. Proc. of the 5th International Conference on Alkali–Aggregate Reaction in Concrete, Capetown, South Africa, 1981, p. 8 (Paper S252/31).

[4] B. Durand, in: A. Shayan (Ed.), Review of methods used at Hydro-Québec to prevent alkali-aggregate reactions in concrete structures. Proc. of the 10th International Conference on Alkali–Aggregate Reaction in Concrete, Melbourne, Australia, 1996, pp. 522 (August).

[5] M.D.A. Thomas, P.K. Mukherjee, E.J. McColm, M.F. Everitt, Case histories of AAR in hydraulic structures in the U.K. and Canada. Proc. of the International Conference on Alkali–Aggregate Reactions in Hydroelectric Plants and Dams, Fredericton, N.B., Canada, Canadian Electrical Association, 1992, p. 6.

[6] G. Gudmundsson, J.S. Möller, 1998. Silica fume to enhance concrete quality–Icelandic experience concerning alkali-silica reactions. Supplementary papers of the 6th CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Bangkok, Thailand, 1998, pp. 335.

[7] J. Duchesne, M.A. Bérubé, The effectiveness of supplementary cementing materials in suppressing expansion due to ASR: Another look at the reaction mechanisms. Part 2: Pore solution chemistry. Cem. Concr. Res. 24 (1994) 221.

[8] P. Longuet, L. Burglen, A. Zelwer, Rev. Mater. Constr. 1 (1973) 35.

[9] S. Diamond, Alkali reactions in Concrete—pore solution effects. Proc. of the 6th International Conference on Alkalis in Concrete, Copenhagen, Denmark, 1983, pp. 155–166.

[10] J. Duchesne, M.A. Bérubé, ACI Mater. J. 91 (1994) 289.

[11] A. Shayan, Real world concrete, Proc. of R.N. Swamy Symposium, 5th CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Milwaukee, USA, 1995, pp. 35.

[12] M.A. Bérubé, J. Duchesne, D. Chouinard, Cem., Concr., Aggregates (CCAGDP) 17 (1995) 26.