Pergamon

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 33 (2003) 1263–1268

CEMENT AND CONCRETE RESEARCH

The effect of the silica content of silica fume on its ability to control alkali–silica reaction

A.M. Boddy, R.D. Hooton*, M.D.A. Thomas

Department of Civil Engineering, University of Toronto, 35 St. George Street, Toronto, Ontario, Canada M5S 1A4

Received 29 March 2000; accepted 3 February 2003

Abstract

The use of silica fume (SF) has been instrumental in the development and utilization of high-strength and high-performance concrete. In the interests of economics, questions have been raised regarding the possible use and effectiveness of "lower grade" SFs with SiO_2 contents less than 85%. Such materials do not meet current CSA and ASTM standards for SF. In this study, the performance of two SFs from the same U.S. plant but with different silica contents (68% and 88% SiO_2) were compared by examining the effect of the materials on the expansion due to alkali–silica reaction (ASR) and the composition of the pore solution. The mixtures tested with these procedures included 0%, 4%, 8%, and 12% SF replacement by mass of cement. Results show that the SF with lower than standard silica contents cannot control ASR at the levels of replacement examined in this program.

Keywords: Silica fume; Alkali–silica reaction; Silica content

1. Introduction

Research has continued to prove that low-water-content, silica fume (SF) concrete can be stronger and more durable than concrete made solely with Portland cement [1]. As such, the market for SF in concrete applications has increased greatly. In fact, the ability of SF to increase both strength and durability properties of concrete has resulted in SF becoming almost synonymous with high-strength or high-performance concrete.

SF is a by-product resulting from the reduction of high-purity quartz with coal in electric-arc furnaces in the manufacture of ferrosilicon alloys and silicon metal [2]. It is a highly reactive pozzolan due to three of its most notable characteristics, namely [3]:

- an average particle diameter of 0.1 μm (approximately 100 times smaller than average Portland cement particles),
- a high amorphous silica composition (typically >90% SiO_2), and
- a very high surface area of 20,000 m^2/kg (as compared to Portland cement values of 300–500 m^2/kg).

The product is referred to as silica fume because of how it is formed. During the process, SiO gas oxidizes and condenses to form extremely fine spherical particles of SiO_2 (amorphous or glassy silica), which are highly reactive. Table 1 summarizes data from Aitcin [4] and explains the relationship between the alloy being produced and the silica content of the resulting SF.

It is evident that the higher the silicon content in the alloy, the higher the silica content in the resulting SF. Aitcin [4] also mentions that it is important to know the origin of any SF to be used in concrete because the same furnace can produce different alloys. However, steady production of a given alloy will result in an SF with consistent properties.

Three chemical requirements of SF are specified by the CSA A23.5 standard for supplementary cementing materials (SCMs) [5], namely: (1) SiO_2 content, (2) SO_3 content, and (3) loss of ignition. Isabelle [6] noted that the most important of these requirements is the minimum SiO_2 content. Currently, both CSA A23.5 and ASTM C1240 require minimum silica content of 85%. In addition, the CSA A23.5 limits the use of SF in Canada to materials recovered from the production of silicon or ferrosilicon alloys containing at least 75%

---

* Corresponding author. Tel.: +1-416-978-5912; fax: +1-416-978-7046.

E-mail address: hooton@civ.utoronto.ca (R.D. Hooton).

0008-8846/03/$ – see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0008-8846(03)00058-9

Table 1
Typical silica content for various alloys [4]

Nominal silicon content of alloy (%)	Typical silica content of resulting SF (%)
>98	94–98
90	90–96
75	86–90
50	≈ 80

silicon. The ACI *Guide for the Use of Silica Fume in Concrete* [3] further states the following regarding the amorphous silica content of SF: "It is sometimes assumed that the higher the SiO_2 content of a silica fume, the more reactive the silica fume will be in concrete. However, the committee does not have data to relate performance directly to SiO_2 content." It is also of interest to note that SFs from current Canadian sources generally have SiO_2 contents well in excess of the specified 85% minimum [6].

Investigation of the performance of SFs with lower than normal SiO_2 contents is of interest both in terms of economics and efficiency, and only limited information is available relating the durability of SF concrete mixtures to the amorphous silica content of the SF used.

Findings are reported by Wolsiefer et al. [7], on a study involving SFs with SiO_2 contents ranging from 79% to 95%. Mixtures were made at water/cementitious material (w/cm) ratios of 0.40, 0.35, 0.30, and 0.22 and were tested for compressive and flexural strengths, drying shrinkage, and rapid chloride permeability. There was no significant difference in performance, and lower SiO_2 levels did not require higher SF dosages for comparable performance by these measures.

Another deterioration mechanism, which affects concrete durability, is alkali–silica reaction (ASR), a reaction between the thermodynamically unstable silica in some aggregates and the alkali hydroxides in the pore solution. SCMs, such as SF, have been proven to improve ASR resistance of concrete through the production of a dense and impermeable matrix that will inhibit the movement of water and alkalis [8], and by binding free alkalis in calcium silica hydrates or by adsorption on their large specific surface area, thereby, reducing the hydroxyl ion concentration of the pore solution. A review of the literature on the ability of SF to control ASR expansion is available [9].

The majority of the information found relating the ability of SF to control ASR to its silica content involved work performed by Duchesne and Berube [10]. Included in the SCMs examined in the study were a high-silica (HS), low-alkali SF and a low-silica (LS), high-alkali SF. They found that 10% of the LS, high-alkali SF was not sufficient to control ASR expansion in concrete containing high-alkali cement and Spratt aggregate (siliceous limestone) when tested by the CSA-A23.2-14A Concrete Prism Method (similar to ASTM C1293). In the paste pore solution analysis work performed by the same authors, it was found that 5% of an LS, high-alkali SF paste did not reduce the alkalinity of the pore solution in pastes made with high-alkali cement, even at 545 days of age. Reductions were observed at a 10% level of replacement when compared to neat cement paste, but these reductions were very similar to those observed with 5% of an HS, low-alkali SF. It is important to note that the SF with LS content also had a very high alkali content, and as such, it is not possible to ascribe its poor performance solely to the LS content.

This report will discuss the method, results, and analysis of a research program carried out to investigate the effect of amorphous silica content on the efficacy of SF in controlling ASR.

2. Experimental test program

2.1. Materials

All specimens tested in this program were made with high-alkali, CSA Type 10 cement (similar to ASTM Type I). The equivalent alkali content of this cement is 0.98% Na_2O_{eq}, and a complete chemical analysis is provided in Table 2. This cement met the requirements for use in the accelerated mortar bar test (CSA A23.2-25A), that being a Type 10 cement with an alkali equivalent of 0.8% to 1.0%.

It should be mentioned that the LS SF does not meet the 85% minimum silica content required by CSA A23.5 or ASTM 1240, and as such, is not currently marketed for use in ready-mixed concrete. The chemical analyses for the LS SF and normal-silica (NS) SF are presented in Table 2. These SFs both came from the same U.S. plant. It is important to note that although the silica content of these SFs differ significantly (LS SF has SiO_2 of 68.21%, NS SF has SiO_2 of 88.40%), they have about the same alkali content (LS SF has Na_2O_{eq} of 1.16%, NS SF has Na_2O_{eq} of 0.98%).

There is currently no standard method for measuring the loose bulk density of SF. For this study, this was determined by filling and weighing a calibrated 400-ml brass cup with SF. The cup was always filled in two layers, with four tamps per layer, and extra material was struck off. This procedure was performed five times for each fume to obtain an average loose bulk density for the material. The bulk densities of the LS SF and NS SF were found to be 233 and 218 kg/m^3, respectively.

Similar to the work of Berube and Duchesne [10], deleteriously reactive aggregate from the Spratt quarry near Ottawa, Ontario, was used in the mortar and concrete test specimens. This is crushed, siliceous limestone, which is deleteriously alkali–silica reactive and often employed as a standard aggregate for ASR tests (CSA A23.1-94, Appendix

Table 2
Chemical analyses for cementitious materials

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Na_2O_{eq}
OPC	19.82	5.13	2.2	62.72	2.64	3.15	1.08	0.27	0.98
LS	68.21	1.55	12.27	4.57	1.16	1.02	1.37	0.26	1.16
NS	88.40	0.60	5.42	0.84	0.73	0.71	1.12	0.24	0.98

B). It should be noted that it is the siliceous component of this aggregate that is reactive.

2.2. Accelerated mortar bar test

The accelerated mortar bar test used was CSA A23.2-25A-M94 (similar to ASTM C 1260-94). Questions have been raised as to whether this test is appropriate for evaluating the effectiveness of SCMs against ASR. Recent work has shown that the specified curing conditions (24 h in water after demoulding at 1 day of age) are suitable to accelerate the pozzolanic reactions of SCMs, thus helping to ensure that this test is a reasonable evaluation method [11–13]. As such, the accelerated mortar bar test has been included in the *Canadian Standard for Supplementary Cementing Materials*, CSA A23.5-98, as an optional requirement to assess the ability of SCMs such as SF to control expansion due to ASR. The test method requires that the SCM in question be tested at various replacement levels and that the reactive aggregate used produce an expansion of at least 0.30% after 14 days in a high-alkali Portland cement mixture. The Spratt aggregate used in this study meets this requirement. It should also be noted that the test conditions are quite severe. However, combinations of materials that expand less than 0.10% at 14 days in this accelerated test are also likely to perform satisfactorily in concrete prism tests, generally producing less than 0.04% at 2 years [12,14–18].

The grading and proportioning of the Spratt aggregate was carried out according to the CSA standard and all aggregate was washed before use. The mortars were mixed following ASTM C305-94. A water/cement/aggregate ratio of 0.50:1.00:2.25 was used. After demoulding at 1 day, bars were heated in water to 80 °C and initial length measurements were made at 2 days of age. The specimens were then stored in a standard 1 M NaOH host solution, preheated to 80 °C, for 28 days, during which time length measurements were taken periodically. It should be noted that to maintain flow, 2.5 and 3 g of a naphthalene-sulfonate-based, liquid superplasticizer were added to the 8% and 12% SF replacement mortar bar mixtures, respectively.

2.3. Pore solution composition

For each SF type, pastes were prepared at 4%, 8%, and 12% mass replacement at a w/cm of 0.5. A 100% ordinary Portland cement mixture was also cast for control purposes. The paste specimens were mixed in a high shear blender (Waring stainless steel, 3.81 capacity) under vacuum with the following mixing sequence to minimize heat build up:

1. 15 s low-speed setting—45 s medium-speed setting—release vacuum—stir with plastic spatula
2. 15 s low-speed setting—45 s high-speed setting—release vacuum—stir with plastic spatula
3. 15 s low-speed setting—45 s high-speed setting—release vacuum—stir with plastic spatula.

No superplasticizers or water reducers were included in the mixtures to be tested for pore solution. Eight cylinders (50 mm diameter × 100 mm high) were filled in two layers and sealed with plastic wrap and a plastic lid. After casting, the specimens were slowly rotated about their ends at 12 rpm for 24 h to avoid bleeding and segregation prior to set.

The samples remained sealed in their molds until test. Pore solution was extracted from the specimens at 1, 3, 7, 28, 90, and 365 days of age and analysed for chemical composition. The pore solution was expressed from the samples using a high-pressure apparatus, originally described by Longuet et al. [19], and more recently by Barneyback and Diamond [20]. It should be noted that Duchesne and Berube [21] have shown that the alkali concentration of the pore solution is not affected by the pressure at which a sample is expressed. Further analysis will be performed on specimens at 2 years of age. The sealed paste specimens were stored at 23 °C and 100% RH to help prevent moisture loss until they were tested. Once the pore solution was collected, it was immediately tested for OH^- ion concentration using automatic titration against H_2SO_4 and for Na^+ and K^+ ion concentrations using flame photometry.

3. Results and discussion

3.1. Accelerated expansion of mortar bars due to ASR

Although this is traditionally a 14-day test, to obtain additional information length changes were monitored up to 28 days.

Fig. 1 presents the expansion results up to 28 days for the mortar bars cast with 4%, 8%, and 12% levels of replacement for both the LS and NS SFs. In general, it was found that the degree of expansion decreased as the level of SF

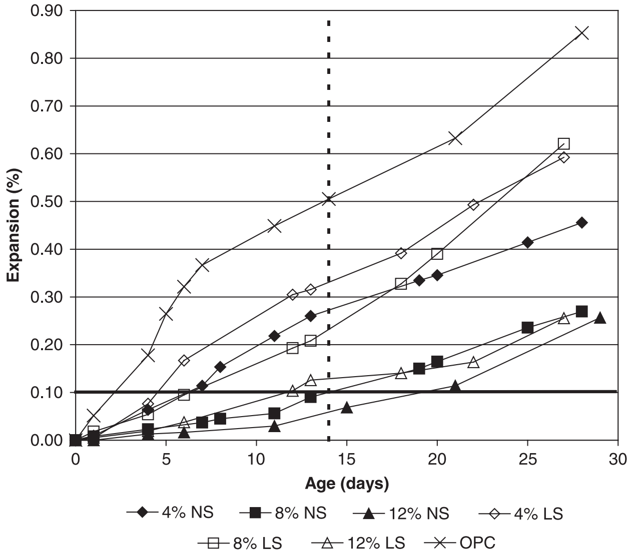

Fig. 1. Effect of SiO_2 of SF on accelerated mortar bar expansion with time at various levels of replacement.

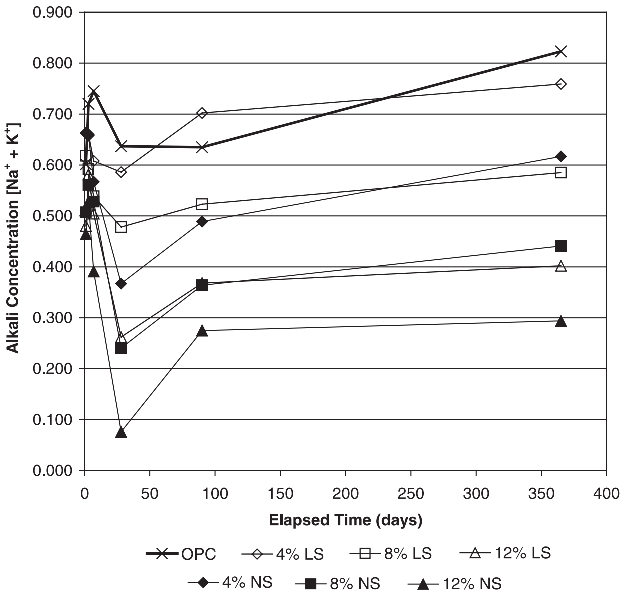

Fig. 2. Effect of SiO_2 of SF on pore solution alkalinity with time at all levels of replacement.

increased. It is evident from Fig. 1 that the mortar bars containing the LS SF experienced no delay in onset of expansion. At all three levels of replacement, the LS SF mortar bars expanded at a faster rate and to a higher ultimate expansion than did the bars containing NS SF. Also, even the 12% LS SF mortar bars failed the expansion limit of 0.010% after 14 days. In the case of the bars made with the NS SF, the mortar mixtures with 4% replacement failed the limit criterion after 7 days, and with 8% replacement was just below the limit at 14 days. The mortar bars made with 12% NS passed the expansion criterion.

Based on the results of the accelerated mortar bar test, it appears that the lower silica content does affect the ability of the SF to control mortar bar expansion. It should be noted, however, that the test conditions are very severe in this procedure, and as such, these results should not fully discount the possible effectiveness of LS SFs at controlling ASR expansion. More research is required. Also, it would be of great interest to test mortar bars made with higher replacement levels (i.e., >12%) of the LS SF to see if that level of replacement of Portland cement would be sufficient for the mixture to pass the 0.10% ASTM expansion limit criterion. Investigation of the effectiveness of LS SFs at controlling ASR when used in combination with fly ash and/or slag in ternary blends would also be worthwhile.

3.2. Paste specimen pore solution composition

Fig. 2 presents the pore solution analysis results comparing the 4%, 8%, and 12% replacement mixtures for both SFs.

At all ages tested to date, the addition of the NS SF lowered the pore solution alkalinity when compared to that of the neat cement paste. Also, an increased level of SF replacement of Portland cement caused an even greater decrease in the alkali level of the pore solution. In all cases, there was a significant reduction in alkalinity between 1 and 28 days. This reduction was more pronounced for the paste specimens made with NS SF. The reduction also increased with increased SF replacement level. However, beyond 28 days, for all mixtures tested, the alkalinity increased with time. Similar trends have been reported by other investigators for cement pastes containing SF stored at 38 °C [22] and, to a lesser extent, at 23 °C [23]. The implication of this trend in terms of the long-term control of ASR using SF is not clear, but it definitely warrants further investigation.

The results of the pore solution analysis of the LS SF pastes were not as clear. An increase in the replacement level of LS SF resulted in a larger decrease in the alkali concentration for the pastes analyzed at 28 days and later ages. However, at 90 days, the alkali concentration of the pore solution from the 4% LS SF mixture was higher than the sample from the OPC sample at the same age.

It is evident from Fig. 2 that a change in amorphous silica content of the SF does affect the resulting pore solution alkalinity. This effect is much more dramatic at the 4% level of replacement, but there is still a significant difference even with the 12% SF samples. It is possible that the SF with the lower SiO_2 does not have the capacity to bind as much of the alkalies in the formation of supplementary C-S-H as does the SF with the higher amorphous silica content or simply that there is less supplementary C-S-H formed with a similar alkali content for the lower SiO_2 SF.

There may be some point of equivalency between a higher replacement level of SF with lower SiO_2 and lower replacement level of SF with higher SiO_2. Some evidence of this can be seen in Fig. 3. The 12% LS SF paste have almost the same alkalinity as the 8% NS SF paste at 90 days of age. Similarities in performance are not as evident by examining the effect of SF level of replacement and SiO_2 content on mortar bar expansion at 14 days, as shown in Fig. 4. However, interpolation of the data would seem to indicate that a replacement level of 6% LS SF would result in a

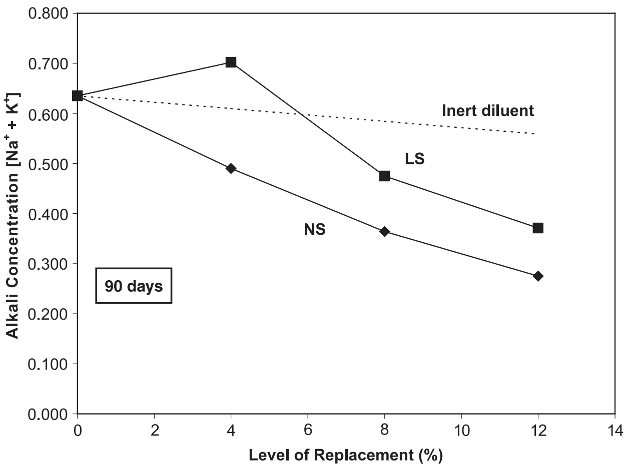

Fig. 3. Effect of SF level of replacement and SiO_2 content on pore solution alkalinity at 90 days.

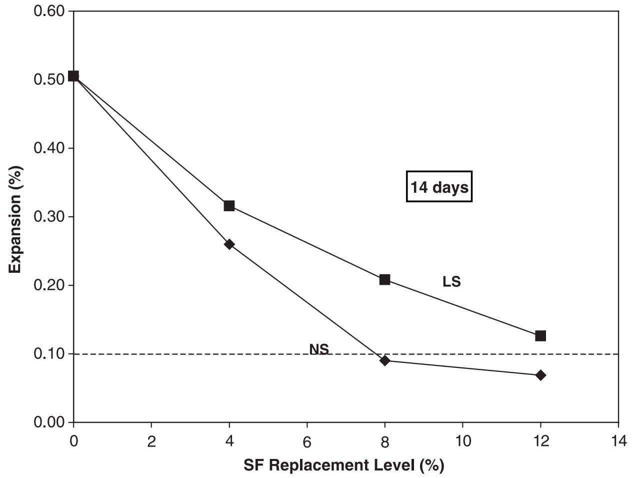

Fig. 4. Effect of SF level of replacement and SiO_2 content on mortar bar expansion at 14 days.

similar expansion to the 4% NS SF replacement. The same statement could be made corresponding to 10% LS SF replacement compared to 6% NS SF replacement and 14% LS SF replacement compared to 8% NS SF replacement. Work should be performed to further investigate this trend and its possible implications.

As previously mentioned, Fig. 3 shows the effect of the level of SF replacement on the alkali concentration of the paste samples determined at 90 days. It is of interest to note that the 4% LS paste specimen had a higher alkali concentration than that which would be expected to occur with 4% of an inert diluent. The use of lower grade SFs at low replacement levels appears to be very ineffective.

3.3. Summary of results

To summarize the results in terms of the effect of SiO_2 content on the ability of SF to control ASR, the research work performed in this program indicates that mixtures containing lower SiO_2 SFs will be less effective in reducing both ASR expansion and pore solution alkalinity at a given level of replacement. This was true for the three levels of replacement tested in this study, namely 4%, 8%, and 12%. All three levels of replacement of LS SF failed the accelerated mortar bar test expansion criterion. Also, the long-term alkali concentrations in the pore solution of the cement pastes were quite high, even with 12% replacement by LS SF of OPC (0.40 M OH^- after 1 year). It should be noted that evaluation of the pore solution results using the threshold value of 0.60 M OH^- reported by Duschene and Berube [19] indicates that, up to 1 year, the 8% and 12% LS and NS SF mixtures have sufficiently low hydroxyl concentrations to prevent excessive expansion due to ASR. However, given the trend of the data for the 8% LS SF replacement mixture, it is expected that this mixture would be subject to ASR expansion. Both the 4% LS and 4% NS alkali concentrations have exceeded this reported threshold value. It would also be of interest to test lower grade SFs at higher levels of replacement, such as 15%, or in combination with other SCMs such as fly ash or slag; however, even if expansion due to ASR can be controlled by LS SFs at higher levels of replacement, there are several other practical problems that could still prohibit these high levels of replacement from being used in the field. One main problem would be the fact that many organizations have limits on the maximum allowable SF replacement in concrete due to the increased potential for placing problems during construction. In all, more research will have to be done on the use of LS SFs in terms of control of ASR, as well as other durability issues, before it is considered as a preventive measure.

4. Conclusions

1. Mortar bar mixtures containing LS (68% SiO_2) SF at levels of replacement up to 12% failed to control ASR expansion of Spratt aggregate. An NS (88% SiO_2) SF was effective at 12% replacement, and just below the 0.10% expansion limit criterion at 8% replacement.
2. Pore solution alkalinity of paste specimens containing 4% LS SF were comparable to those of the OPC paste specimens at all ages, up to 1 year. In contrast, 4% replacement with NS SF resulted in significantly lower pore solution alkalinities.
3. The long-term alkali concentrations of LS SF paste specimens remained high at both 8% (≅0.600 M OH^- at 1 year) and 12% (≅0.400 M OH^- at 1 year) compared to the HS SF pastes.
4. Based on the results of this study, it appears that at typical rates of replacement, the lower silica content does affect the ability of SF to control expansion due to ASR.

References

[1] R.D. Hooton, Influence of silica fume replacement of cement on physical properties and resistance to sulfate attack, freezing and thawing, and alkali–silica reactivity, ACI Mater. J. 90 (2) (1993) 143–161.
[2] V.M. Malhotra, Fly ash, slag, silica fume, and rice-husk ash in concrete: a review, Concr. Int. 15 (1993) 23–28.
[3] ACI Committee 234, Guide for the Use of Silica Fume in Concrete, American Concrete Institute, Detroit, 1994.
[4] P.C. Aitcin (Ed.), Condensed Silica Fume, Faculte de Sciences Appliquees, Universite de Sherbrooke, Quebec, Canada, 1983.
[5] CAN/CSA A23.5-98, Canadian Standard for Supplementary Cementing Materials, Canadian Standards Association, Toronto, 1998.
[6] H.L. Isabelle, Development of a Canadian specification for silica fume, Proceedings of the 2nd International Conference, Madrid, Spain, ACI SP 91-77, vol. 2, American Concrete Institute, Detroit, 1986, pp. 1577–1587.
[7] J. Wolsiefer, V. Sivasundaram, V.M. Malhotra, G.G. Carette, Performance of concretes incorporating various forms of silica fume, in: V.M. Malhotra (Ed.), Proceedings of the 5th International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, vol. 2, American Concrete Institute, Detroit, 1995, pp. 591–655.
[8] J. Kropp, Relations between transport characteristics and durability, RILEM Rep. 12 (1995) 138.

[9] M.D.A. Thomas, R.F. Bleszynski, The use of silica fume to control expansion due to alkali–aggregate reactivity in concrete—a review, in: S. Mindess, J. Skalny (Eds.), Materials Science of Concrete, vol. VI, American Ceramic Society, Westerville, OH, 2001, pp. 377–433.

[10] J. Duchesne, M.A. Berube, The effectiveness of supplementary cementing materials in suppressing expansion due to ASR: another look at the reaction mechanisms. Part 1: Concrete expansion and portlandite depletion, Cem. Concr. Res. 24 (1994) 73–82.

[11] 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.), Proceedings of the 10th International Conference on Alkali–Aggregate Reaction in Concrete, Melbourne, Australia, 1996, pp. 483–491.

[12] M.A. Berube, J. Duchesne, D. Chouinard, Why the accelerated mortar bar method ASTM C1260 is reliable for evaluating the effectiveness of supplementary cementing materials in suppressing expansion due to alkali–silica reactivity, Cem., Concr. Aggreg. 17 (1) (1995) 26–34.

[13] M. Berra, T. Mangialardi, A.E. Paolini, Application of the NaOH bath test method for assessing the effectiveness of mineral admixtures against reaction of alkali with artificial siliceous aggregate, Cem. Concr. Compos. 16 (3) (1994) 207–218.

[14] M.D.A. Thomas, F.A. Innis, Use of the accelerated mortar bar test for evaluating the efficacy of mineral admixtures for controlling expansion due to alkali–silica reaction, Cem., Concr. Aggreg. 21 (2) (1999) 157–164.

[15] M.D.A. Thomas, F.A. Innis, Effect of slag on expansion due to alkali–aggregate reaction in concrete, ACI Mater. J. 95 (6) (1998) 716–724.

[16] B. Durand, J. Berard, R. Roux, J. Soles, Alkali–silica reaction: the relation between pore solution characteristics and expansion test results, Cem. Concr. Res. 20 (1990) 419–428.

[17] J. Duchesne, M.A. Berube, An autoclave mortar bar test for assessing the effectiveness of mineral admixtures in suppressing expansion due to AAR, Proceedings of the 9th International Conference on Alkali–Aggregate Reaction in Concrete, Concrete Society, Slough, UK, 1992, pp. 279–286.

[18] B. Fournier, A. Bilodeau, V.M. Malhotra, CANMET/Industry research consortium on alkali–silica reactivity, Proceedings of the 10th International Conference on Alkali–Aggregates Reaction in Concrete, CSIRO, Melbourne, Australia, 1996, pp. 101–108.

[19] P. Longuet, L. Burglen, A. Zelwer, La phase liquide du ciment hydrate, Rev. Mater. 676 (1973) 35–41.

[20] R.S. Barneyback Jr., S. Diamond, Expression and analysis of pore fluids from hardened cement paste and mortars, Cem. Concr. Res. 11 (1981) 279–285.

[21] J. Duchesne, M.A. Berube, Evaluation of the validity of the pore solution expression method from hardened cement pastes and mortars, Cem. Concr. Res. 24 (3) (1994) 456–462.

[22] J. Duchesne, M.A. Berube, 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 (2) (1994) 221–230.

[23] M.A. Berube, J. Duchesne, J. Frenette, Influence of storage conditions and concrete composition on the effectiveness of different silica fumes against ASR, Proceedings of the 6th CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Bangkok, Thailand, SP-178, American Concrete Institute, Detroit, 1998, pp. 1127–1147.