

**Preventive Effects
of
Mineral Admixtures
on
Alkali-Aggregate Reaction**

EVOLUTION OF CHEMICAL AND PHYSICAL PARAMETERS OF BLENDED CEMENT MORTARS SUBJECTED TO THE NaOH BATH TEST

M. Berra*, G. De Casa°, T. Mangialardi°

*ENEL SpA-CRIS, Via Ornato 90/14 - 20162 Milan (Italy)

°Faculty of Engineering, University of Rome "La Sapienza", Via Eudossiana, 18
00184 Rome (Italy)

ABSTRACT

Mortar bars incorporating two different alkali-reactive aggregates and containing various amounts of two different supplementary cementing materials (SCMs) were subjected to the NaOH bath test. Measurements of expansion, water permeability, pore liquid composition, and $\text{Ca}(\text{OH})_2$ content were performed periodically on the specimens. Expansion data showed the ability of SCMs (condensed silica fume and pulverised fuel ash) to reduce mortar bar expansion. Furthermore, the SCMs were able to hydrate in a short time so that they were capable of reducing the OH^- ion concentration in the pore solution within the mortar specimens as a result of a reduced permeability of mortar and an incorporation of alkalis by pozzolanic reaction products. These results prove the suitability of the NaOH bath test method as a means for evaluating the effectiveness of SCMs against alkali-silica reaction.

Keywords: NaOH bath test, pozzolanic reaction, supplementary cementing materials

INTRODUCTION

Since 1986, the accelerated mortar-bar expansion test in a 1M NaOH solution at 80°C, also formerly known as South African NBRI test (Oberholster & Davies, 1986; Davies & Oberholster, 1987a), has largely been used for predicting the potential alkali-reactivity of concrete aggregates. Published work has also shown the good potential of this test for evaluating the effectiveness of supplementary cementing materials (SCMs) against alkali-silica reaction (ASR) (Davies & Oberholster, 1987b; Bérubé & Duchesne, 1992a; Shayan, 1992).

However, in the ASTM version of the NaOH bath test (Test Method C1260-94), no mention is made about the use of this test for assessing the performance of SCMs against ASR, probably because it was thought unlikely that, after the short (two days) curing period prior to immersion in the hot sodium hydroxide solution, the SCMs have sufficiently hydrated to become so impermeable as to prevent NaOH from penetrating the small cross section of the mortar bars (Hooton & Rogers, 1992).

This hypothesis did not appear to be supported by the results of more recent studies dealing with the effect of SCMs on the pore liquid composition within alkali-reactive mortar specimens immersed in NaOH solution (Berra *et al.*, 1994a; Bérubé *et al.*, 1995).

The aim of this paper is to search thoroughly into this subject. The behaviour of two types of SCMs, one condensed silica fume (CSF) and one pulverised fuel ash (PFA), is discussed with respect to the time evolution of the expansion, water permeability,

portlandite content, and pore liquid composition in mortar bars made with siliceous aggregates of high or moderate alkali-reactivity when subjected to the NaOH bath test.

MATERIALS AND METHODS

Table 1 gives the chemical and physical characteristics of the Portland cement (PC) and SCMs used in this study.

In addition to the control (0% SCM), various SCM contents were used as replacement by mass of cement: 5%, 10%, 15% and 20% for CSF, 5%, 15%, 25% and 35% for PFA.

The effectiveness of the two SCMs were tested in the presence of a natural italian siliceous aggregate (designated NSA) of known moderate reactivity in service or an artificial very reactive siliceous aggregate such as fused quartz (FQ) (density = 2.20 g/cm³; SiO₂ content = 99.2%; alkali content = 0.01% Na₂O equivalent). The natural aggregate consisted of rhyolite rocks with large amounts of strained quartz as the main reactive component and was used in the standard gradation (0.15-4.75 mm) as specified in ASTM C1260-94. The fused quartz was used in the 150-300 µm size fraction and was combined with a natural non-reactive quartzitic sand (density = 2.64 g/cm³; water absorption = 1.0%) having the ASTM gradation. Fused quartz replaced the corresponding fraction of natural sand by an amount equal to 4% by mass of the total aggregate (Berra *et al.*, 1994b).

Table 1 Chemical and physical characteristics of Portland cement and supplementary cementing materials used.

Oxide (%)	Cement	PFA	CSF	Oxide (%)	Cement	PFA	CSF
SiO ₂	22.11	56.02	96.20	Na ₂ O equivalent			
Fe ₂ O ₃	4.76	7.45	0.40	Total	0.43	1.96	0.41
Al ₂ O ₃	3.62	29.14	0.35	Available	0.29	0.43	0.13
CaO	65.93	0.04	0.43	Water-Soluble	0.13	0.03	0.13
Free CaO	0.14			L.O.I. (%)	0.72	3.03	0.98
MgO	0.57	0.40	0.20	Density (kg/m ³)	3160	2330	2200
SO ₃	1.51	0.40		Surface Area, Blaine (m ² /kg)	306	446	25,000**
Mn ₂ O ₃	0.04	0.07		Autoclave Expansion (%)	-0.01		
TiO ₂	0.08	0.30		Bogue Compounds (%)			
P ₂ O ₅	0.11	0.15		C ₃ S	64.67		
SrO	0.04			C ₂ S	14.67		
Na ₂ O				C ₃ A	1.56		
Total	0.11	0.73	0.18	C ₄ AF	14.47		
Available	0.08	0.14	0.04				
Water-Soluble	0.02	0.03	0.04				
K ₂ O							
Total	0.49	1.87	0.35				
Available	0.32	0.44	0.14				
Water-Soluble	0.16	0.003	0.14				

**BET method

The mortar bars (water/cement weight ratio = 0.47; aggregate/cement weight ratio = 2.25; bar dimensions = 25x25x285 mm) were cast and stored in accordance with the ASTM C1260-94 test procedure.

The length of the bars was periodically measured using a comparator with a sensitivity of 0.001 mm.

The OH⁻ ion concentration in the pore solution and the portlandite content within the cementitious matrix were determined after the 1-day storage of the bars in the water bath at 80°C and during their period of immersion in a 1M NaOH solution at 80°C.

The OH⁻ ion concentration was measured by a pH-meter with a Radiometer type G202 A electrode and a calomel reference electrode (Dent Glasser & Kataoka, 1981) on the pore solution expressed from each bar through the use of a high pressure apparatus (550 MPa).

The portlandite content was determined by thermogravimetric analysis (30-950°C at 10°C/min under N₂ atmosphere) on powdered, dried (through acetone and ethyl ether treatment) mortar samples obtained from a portion of each bar.

For the permeability measurements, cylindrical specimens (38 mm in diameter and 76 mm in height) were used instead of prismatic ones. However, the storage conditions were the same.

Water permeability was measured at room temperature (about 20°C) using de-aired water and a tri-axial permeability cell in which driving and confining pressures were 0.67 and 1.34 MPa, respectively. Before testing, each cylindrical specimen was vacuum saturated using a standard test procedure (AASHTO T227-83, 1988). The permeability coefficient, K, was calculated according to Darcy's law.

TEST RESULTS AND DISCUSSION

Expansion

Figures 1a and 1b show the effect of replacing various amounts of Portland cement by PFA or CSF on the expansion of mortar bars incorporating FQ or NSA aggregate at varying times of immersion in the NaOH bath.

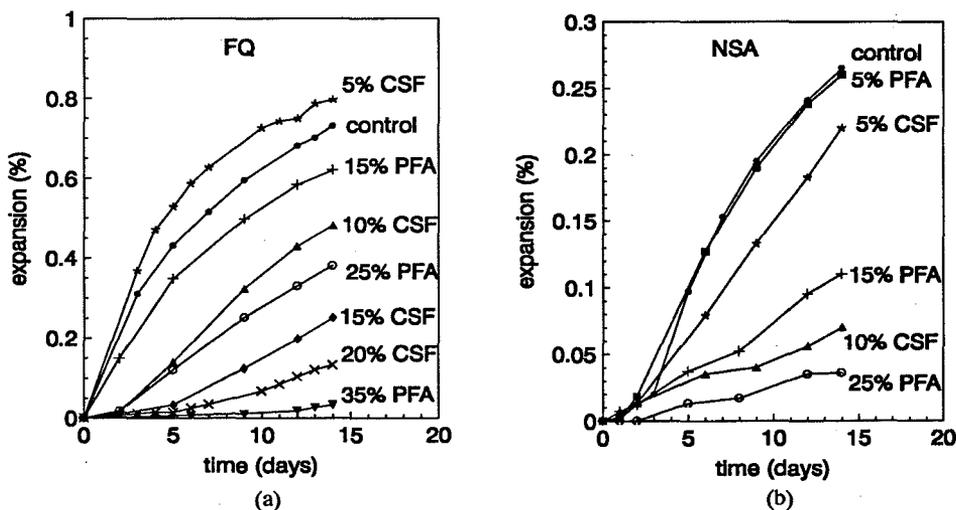


Fig. 1 Effect of replacing various amounts of Portland cement by PFA or CSF on the expansion of mortar bars incorporating FQ or NSA aggregate.

As expected, in the absence of SCMs (control specimens), mortar bars incorporating either FQ or NSA showed 14-day expansions above 0.10%, that is the value reported in the Appendix of ASTM C1260 as indicative of innocuous behaviour of aggregates. SCM addition always reduced the expansion of mortar bars except for the specimens containing aggregate FQ and 5% CSF, which showed larger expansion than the control (pessimum effect). However, in most cases 14-day expansion was still above 0.10%.

The effect of SCM content on the 14-day expansion of mortar bars is shown in Figure 2.

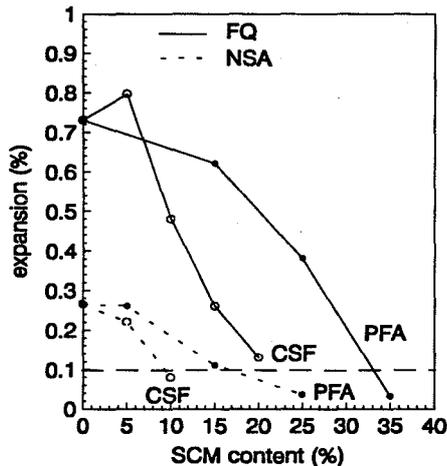


Fig. 2 Effect of SCM content on the 14-day expansion of mortar bars.

With aggregate NSA, dosages of about 10% for CSF and 17% for PFA are sufficient to reduce the expansion level below 0.10%. With aggregate FQ, due to its higher alkali-reactivity, dosages of about 33% for PFA and higher than 20% for CSF are needed.

Water permeability

Figures 3a and 3b show the values of the coefficient of water permeability, K , for some representative mortar specimens at different times of immersion in the NaOH bath at 80°C. The K value at the time zero (initial permeability) is that measured after the 1-day storage of the specimens in the water bath at 80°C.

With aggregate FQ (Fig. 3a), at a given time, the permeability of blended cement mortars was always lower than that of the control specimen. Furthermore, the change in the permeability with increasing immersion time in NaOH solution was very different for the two types of mortars. The permeability curve exhibited a maximum for control specimen and a minimum for mortar containing 15% CSF. No appreciable variation of permeability with time was observed for mortar containing 35% PFA.

With aggregate NSA (Fig. 3b), the initial permeability of blended cement mortars was comparable to that of the control specimen (about $6 \cdot 10^{-11}$ m/s). During the period of immersion in the NaOH solution, the permeability coefficient decreased for all the

mortars down to about $0.1 \cdot 10^{-11}$ m/s. However, this permeability decrease was slower for the control specimen.

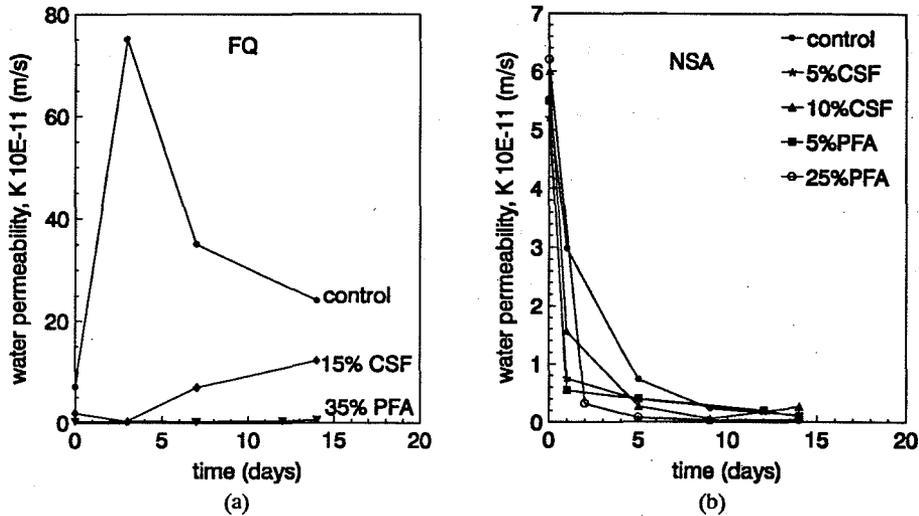


Fig. 3 Effect of replacing various amounts of Portland cement by PFA or CSF on the water permeability of mortars incorporating FQ or NSA aggregate.

The results in Figures 3a and 3b may be explained taking in mind that alkali-silica reaction may lead to an increase of the mortar permeability, while a reduction in the permeability may occur as a result of a progressive reduction of the porosity of the cementitious matrix due to cement hydration, pozzolanic reaction, and ASR gel formation.

However, blended cement mortars characterized by similar values of permeability (Fig. 3b) showed very different expansion levels (Fig. 1b). This suggests that permeability alone cannot explain the effectiveness of SCMs against ASR.

Pore liquid composition

Figures 4a and 4b show the OH⁻ ion concentration in the pore liquid within the same mortars as those of Figs. 3a and 3b at different times of immersion in NaOH solution.

After the 1-day storage of mortars in the water bath at 80°C, the OH⁻ ion concentration in the pore solution was always very low because of a significant leaching of alkali ions out of the specimens (Berra *et al.*, 1994b).

During the period of immersion in the NaOH bath, the OH⁻ ion concentration within control specimens increased rapidly, because the relatively high permeability of these specimens promoted the penetration of the NaOH from the surrounding solution.

Conversely, for blended cement mortars a slower increase in the OH⁻ ion concentration or a plateau was observed during a certain period of immersion, depending on the reactivity of the aggregate and the type and amount of SCM used.

During this immersion period, all the mortars, except 15% CSF, exhibited no appreciable change in the permeability (Figs. 3a and 3b), thus suggesting that the

reduced concentration of the OH^- ions within blended cement mortars is largely related to the incorporation of alkali hydroxides into the supplementary, low CaO/SiO_2 CSH gel produced by pozzolanic reaction.

The larger the amount of a given SCM, the lower will be the OH^- ion concentration in the pore liquid and the longer the time period for which a relatively low OH^- ion concentration will be maintained.

For CSF and PFA tested, a diluent effect cannot be invoked to explain the reduced concentration of the OH^- ions in the pore solution, because the total alkali content of these SCMs was comparable (CSF) or above (PFA) to that of the Portland cement used (Table 1).

After 14 days of immersion in a 1M NaOH solution, the OH^- ion concentrations within mortars made with aggregate FQ and 35% PFA (Fig. 4a) or with aggregate NSA and 10% CSF or 25% PFA (Fig. 4b) were still far from having reached the equilibrium concentration. Accordingly, the 14-day expansions of these mortars were very low (Figs. 1a and 1b).

In the other cases examined, the amount of SCM used and, consequently, the OH^- ion consumption by pozzolanic reaction was insufficient to counteract the alkali-reactivity of the aggregate tested, so relatively high expansion levels were recorded.

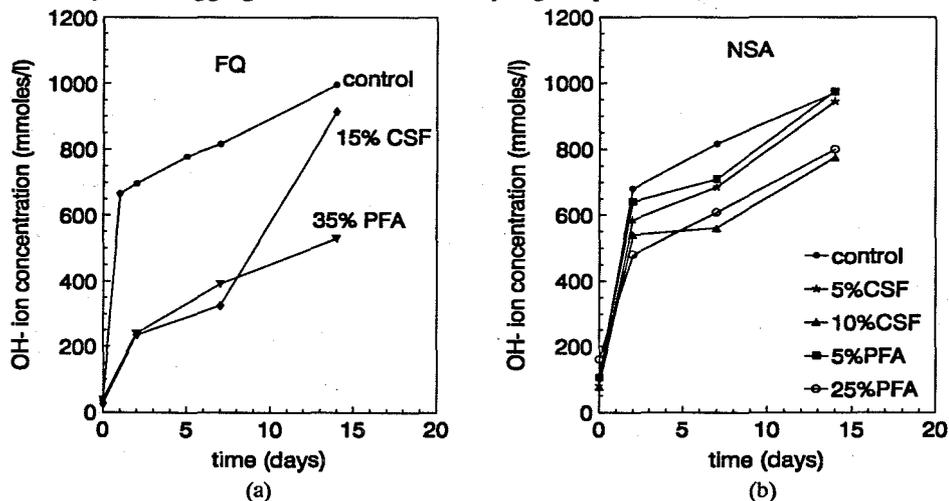


Fig. 4 Effect of replacing various amounts of Portland cement by PFA or CSF on the OH^- ion concentration in the pore liquid within mortar bars incorporating FQ or NSA aggregate.

These results are in very close agreement with those of Bérubé *et al.* (1995), who observed that, similarly to more realistic expansion tests performed in air at 100% R.H., the most critical mechanisms involved when testing SCMs by the NaOH bath test are still alkali reduction (by dilution and/or incorporation) and consequent pH decrease in the mortar pore solution.

Portlandite content

Figure 5 shows the portlandite content of some representative mortar specimens as a function of their immersion time in the NaOH bath.

In the absence of SCMs, the portlandite content of control specimens was virtually independent of the aggregate type and immersion time up to about 4 days of immersion in the NaOH solution. Thereafter, a reduction of portlandite content was observed, particularly in the mortars incorporating FQ aggregate (more reactive mortars), because of the formation of a diphasic gel system consisting of CSH and siliceous gel, the latter being responsible for expansion (Wei & Glasser, 1989).

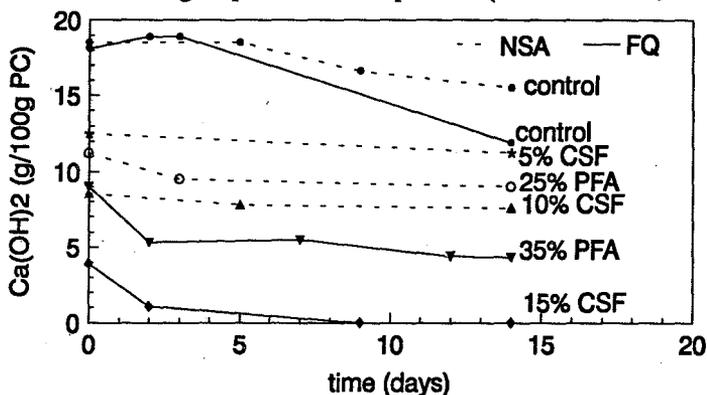


Fig. 5 Time evolution of portlandite content of mortars.

Blended cement mortars generally contained less portlandite than control specimens because of the diluent effect and pozzolanic activity of SCMs. However, at a given immersion time, the differences between the $\text{Ca}(\text{OH})_2$ contents of the control and blended cement specimens shown in Figure 5 are indicative of the pozzolanic activity of SCMs, the portlandite content being expressed as g $\text{Ca}(\text{OH})_2/100$ g Portland cement.

In most cases, these differences were very high just after the 1-day storage of the specimens in the water bath at 80°C , thus indicating that the storage conditions were suitable to accelerate the pozzolanic reaction of the SCMs tested. This was particularly evident for CSF which proves to be a more pozzolanic material compared to PFA.

As can be calculated from the data in Figure 5, the portlandite consumption varied from 1.14 to 0.80 g $\text{Ca}(\text{OH})_2/\text{g}$ CSF and from 0.22 to 0.18 g $\text{Ca}(\text{OH})_2/\text{g}$ PFA when the content of CSF and PFA in the mortars was varied from 5% to 15% and from 25% to 35%, respectively.

Based on the data in Table 1 and Figure 5, and assuming a CaO/SiO_2 mole ratio of 1:1 for pozzolanic CSH (Bérubé & Duchesne, 1992b), it can be calculated that, after the 1-day water storage, about 96%, 76%, and 68% of silica contained in the CSF would be transformed to pozzolanic CSH when the CSF content is 5%, 10%, and 15%, respectively. With 25% and 35% PFA, the percentage of silica transformed was about 32% and 24%, respectively.

During the period of immersion in the NaOH solution, further $\text{Ca}(\text{OH})_2$ consumption was mostly related to the amount of SCM unreacted after water storage. Thus, further portlandite consumption was observed only for mortars containing PFA or high CSF content (Fig. 5).

These considerations coupled with the results of the pore liquid composition suggest that pozzolanic reaction products formed during water storage are able to incorporate alkali hydroxides during the subsequent immersion in the NaOH bath.

CONCLUSIONS

The storage conditions of the accelerated mortar-bar expansion test in NaOH solution (24 hours in a moist room at 20°C, 24 hours in a water bath at 80°C and then 14 days in a 1M NaOH solution at 80°C) are suitable to accelerate the pozzolanic reactions of SCMs such as condensed silica fume and pulverised fuel ash.

Pozzolanic reaction development produces a reduction of the OH⁻ ion concentration in the pore solution within mortar specimens as a result of the reduced permeability of blended cement mortars (compared to control specimens) and the incorporation of alkali hydroxides by pozzolanic reaction products. The lowering of the OH⁻ ion concentration is in turn responsible for the reduced expansivity of alkali-reactive aggregates.

These results prove the suitability of the NaOH bath test method as a means for evaluating the effectiveness of SCMs against alkali-silica reaction.

References

- Berra, M., Mangialardi, T. & Paolini, A.E. 1994a, Application of the NaOH bath test method for assessing the effectiveness of mineral admixtures against reaction of alkali with artificial siliceous aggregate, *Cement and Concrete Composites*, 16 (3), 207-218.
- Berra, M., Mangialardi, T. & Paolini, A.E. 1994b, Influence of Portland cement type on alkali-expansivity of fused quartz in mortars subjected to the NaOH bath test, *II Cemento*, 91 (4), 229-242.
- Bérubé, M.A. & Duchesne, J. 1992a, Evaluation of testing methods used for assessing the effectiveness of mineral admixtures in suppressing expansion due to alkali-aggregate reaction, Proc. 4th CANMET/ACI Int. Conf. on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Istanbul, Turkey, ed. Malhotra, ACI SP-132, 549-575.
- Bérubé, M.A. & Duchesne, J. 1992b, Does silica fume merely postpone expansion due to alkali-aggregate reactivity?, Proc. 9th Int. Conf. on Alkali-Aggregate Reaction in Concrete, London, U.K., 871-880.
- Bérubé, M.A., Duchesne, J. & Chouinard, D. 1995, 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, *Cement Concrete Aggregates*, 17 (1), 26-34.
- Davies, G. & Oberholster, R.E. 1987a, An interlaboratory test program on the NBRI accelerated test to determine the alkali-reactivity of aggregates, CSIR Spec. Rep. BOU 92, National Building Research Institute, Pretoria, South Africa, 16 pp.

Davies, G. & Oberholster, R.E. 1987b, Use of the NBRI accelerated test to evaluate the effectiveness of mineral admixtures in preventing the alkali-silica reaction, *Cement and Concrete Research*, 17 (1), 97-107.

Dent Glasser, L.S. & Kataoka, N. 1981, Some observations on the rapid chemical test for potentially reactive aggregate, *Cement and Concrete Research*, 11 (2), 191-196.

Hooton, R.D. & Rogers, C.A. 1992, Development of the NBRI rapid mortar bar test leading to its use in North America, Proc. 9th Int. Conf. on Alkali-Aggregate Reaction in Concrete, London, U.K., 461-467.

Oberholster, R.E. & Davies, G. 1986, An accelerated method for testing the potential alkali reactivity of siliceous aggregates, *Cement and Concrete Research*, 16 (2), 181-189.

Shayan, A. 1992, Prediction of alkali reactivity potential of some Australian aggregates and correlation with service performance, *ACI Materials Journal*, 89 (1), 13-23.

Wei, X. & Glasser, F.P. 1989, The role of microsilica in the alkali-aggregate reaction, *Advances in Cement Research*, 2 (8), 159-169.