

POLYMER ACTION ON ALKALI-SILICA REACTION: FURTHER RESEARCH

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Abstract

Polymer modification of mortar and concrete can lead to improved transport and mechanical properties and thus its potential for an inhibiting effect on ASR or on resulting damage was investigated. An accelerated mortar bar test in a NaOH solution bath at 80 °C had already been established as inadequate to assess the behaviour of polymer-cement mortars (PCMs) under ASR, but compared to that of an unmodified mortar, the cement paste of PCMs had shown a higher resistance to microcracking resulting from ASR. In the present study, unmodified and styrene-butadiene and acrylic-styrene modified mortar bars were subjected to a moist 38 °C environment and their $\text{Na}_2\text{O}_{\text{eq}}$ content previously raised to 1.25%. These test conditions promoted ASR development more consistently between mortars with significant differences in moisture transport properties. It was confirmed that despite the previously observed higher resistance to damage resulting from ASR, higher expansion is expected in PCMs compared to unmodified mortar. Even though a strong correlation was observed between expansion and the volume of open, interconnected porosity, it's likely that closed porosity and significant differences in elastic modulus between PCMs and unmodified mortar are also responsible for the higher expansion of PCMs.

1. INTRODUCTION

The alkali-silica reaction (ASR) is a deleterious phenomenon affecting concrete, resulting from the chemical reaction between the hydroxyl (OH^-), sodium (Na^+), potassium (K^+) and calcium (Ca^{2+}) ions present in the highly alkaline pore solution of concrete and poorly crystallized silica minerals present in some reactive aggregates. This reaction progressively transforms silica minerals into an alkali-silica gel with hygroscopic properties, which expands due to hydration and may crack reactive aggregate particles and surrounding cement paste.

The authors believed that due to the improvement of concrete properties that influence the ASR expansion mechanism, polymer modification could lead to a potential reducing effect on ASR expansion and resulting damage. Mortar and concrete modification with redispersible polymer powders and liquid polymer dispersions lead to lower water absorption and can

reduce ionic mobility [1], thus leading to a potential inhibiting effect on ASR. Higher tensile strength and higher resistance to microcracking [2-5] may also be achieved, particularly for polymer to cement ratios (P/C) in excess of 10%, for which a continuous polymer network starts to form [1,6,7], resulting in an effective polymer-cement co-matrix. On their turn, the improved mechanical properties were believed to have a potential reducing effect on the damage resulting from ASR related expansion.

Ohama et al. [8] and Saccani and Motori [9] addressed the influence of styrene-butadiene and epoxy polymers respectively on ASR. However, distinct test methods were used and conclusions on the influence of the respective polymers on expansion due to ASR were conflicting.

More recently, the present authors studied the behaviour of unmodified and epoxy, styrene-butadiene and acrylic-styrene modified cement mortar bars in a 1 N NaOH solution bath at 80 °C [10], as described in the ASTM C 1260 alkali reactivity test method. It was observed that, despite their water absorption being lower than that of the unmodified cement mortar under standard laboratory temperature, both expansion and mass increase of the polymer-modified test specimens were higher in the aggressive alkali reactivity test conditions. As the mass increase was due to absorption of NaOH solution, which provides both alkali and hydroxyl ions and water necessary for ASR expansion development, ASR was more aggressively promoted in the polymer-modified specimens, as confirmed in SEM observations. Accordingly, expansion of polymer-modified specimens was higher than that of unmodified cement mortar specimens, but significant differences in properties such as porosity and modulus of elasticity between mortars were also identified as potential influencing variables on the observed expansion.

To properly assess the influence of those variables on the ASR-related expansion results, the studied mortars were subjected to a slower alkali reactivity test in which it was believed their transport properties would more closely resemble those under field conditions or standard laboratory climate, thus providing a more accurate assessment of their respective performances and behaviour. This test consisted of expansion monitoring of mortar bars with a $\text{Na}_2\text{O}_{\text{eq}}$ content artificially raised to 1.25% of the mass of cement in a moist 38 °C environment.

The present paper discusses the results of these tests and provides additional data from the previous study [10].

2. MATERIALS

To allow comparison between the previous and the present study, both the materials and the mortar compositions used remained the same and are described below.

2.1 Aggregate

Crushed pebblestone with original minimum (d) and maximum (D) dimensions of respectively 5.6 mm and 11.2 mm was used. The aggregate was crushed again to obtain the grading specified in both ASTM C 1260 and C 227 alkali reactivity tests. After crushing and combining the different grades in the required proportions, the properties of the resulting aggregate were determined according to EN 933-1:1997/A1:2005 and an ASTM C 1260 test was conducted to assess its alkali reactivity. The results of these tests are shown in Table 1. The alkali reactivity of the crushed pebblestone was confirmed, as the expansion at 14 days was higher than the 0.20% lower limit for reactive aggregates specified in ASTM C 1260.

Table 1: Aggregate properties

Nature	d (mm)	D (mm)	Fineness Modulus	Expansion due to alkali reactivity (%)
Pebblestone	0.125	4	3.99	0.22

2.2 Cement

A CEM I 42.5 R Portland cement was used in this study. The chemical and mechanical properties of this cement are listed in Table 2. Compressive and flexural strengths were determined according to EN 12190 and EN 196-1 respectively.

Table 2: Cement properties

Chemical composition (%)								Mechanical strength at 28 days (MPa)	
C ₃ S	C ₂ S	C ₃ A	C ₄ AF	SO ₃	Na ₂ O	K ₂ O	Na ₂ O _{eq}	Compressive	Flexural
64.7	3.2	9.9	9.3	2.7	0.1	1.1	0.82	49.6	7.9

2.3 Polymer additions

Commercially available styrene-butadiene (SB 1 and SB 2) and acrylic-styrene (AS) dispersions were selected for cement mortar modification in this study and their properties are shown in Table 3. The glass transition temperature (T_g) represents the midpoint of the glass transition region observed in differential scanning calorimetry tests of polymer films. The specific mass was determined with a hydrometer and the pH was determined with a pH meter according to ISO 4316. The listed pH of AS 1 polymer addition was taken from the manufacturer's technical sheet, as this particular addition was significantly more viscous and stable pH readings were difficult to achieve.

A two-component (diglycidil ether of bisphenol-A and an aliphatic amine hardener) aqueous epoxy (EP) used in the previous study was also considered, but due to the artificially raised Na₂O_{eq} content of the mixing water, reticulation of the epoxy polymer started abruptly from the moment it was added to the mixing water.

Table 3: Polymer properties

Polymer addition	Specific mass (g/cm ³)	pH at 20 °C	T _g (°C)
AS 1	1.014	9 - 11	27.5
SB 1	1.026	9.59	0.8
SB 2	1.022	9.74	20.3

2.3 Mix design and curing method

Mortar composition is expressed in Table 4 and followed the mix proportions used in the previous study to assure comparable results.

A constant flow between the PCMs and an unmodified CM was sought. While the unmodified CM's mix followed the design specified in the ASTM C 1260 alkali reactivity test used in the previous study, the W/C ratio of PCM mixes was adjusted so that their flow fell in a $\pm 7.5\%$ range relative to the unmodified CM. The $\pm 7.5\%$ acceptable range was adopted

from the ASTM C 1567 alkali reactivity test for combinations of cementitious materials and aggregates.

Table 4 lists the total water to cement ratio (W_{tot}/C), comprising both the added water and the liquid content of the polymer addition used, and the water to cement ratio (W/C), which comprises only the added water. Flow and air content in the fresh state according to the procedure described in ASTM C 1437 and C 231 (type B meter) respectively are also listed. Additionally, NaOH was added to the mixing water in the amount required to increase the Na_2O_{eq} content of mortars to 1.25% of the mass of cement.

Test specimens were cured for a 28-day period according to the process specified in the test methods of EN 1504-3. Specimens were demoulded after 24 h and wrapped in film for 48 h to allow cement hydration, and subsequently unwrapped and cured for 25 days in standard laboratory climate to allow coalescence of polymer in PCMs. The test specimens of the AS PCM, however, required a curing period of 7 days before demoulding was possible. It was thought that the artificially increased Na_2O_{eq} of mortar further delayed cement hydration with this type of polymer, as this problem was not observed in previous experience with this specific polymer addition.

Table 4: Mix proportions, flow and fresh air content of the studied mortars

Mortar mixes	P/C (%)	A:C	W/C	W_{tot}/C	Flow (%)	Air content (%)
Ref CM	0	2.25:1	0.47	0.47	124	7.6
SB 1 PCM	15	2.25:1	0.11	0.32	125	10.1
SB 2 PCM	15	2.25:1	0.08	0.32	129	6.5
AS PCM	15	2.25:1	0.16	0.42	130	14.8

3. TEST METHODS

3.1 SEM/EDX

Scanning electron microscopy (SEM) observations were conducted on a JEOL JSM-6400 research grade SEM after the alkali reactivity tests to confirm expansion due to ASR. Samples for observation were obtained by impregnation of sections of mortar specimens with low-viscosity epoxy resin under vacuum, after which they were polished and coated with gold. Line profiles were possible with the energy dispersive X-ray (EDX) microanalysis capability provided by an Oxford Instruments INCAx-sight detector and used a livetime of 50 s and a distance between point analyses of 10 μ m.

3.2 Water vapour permeability

Water vapour permeability was tested according to the EN 1015-19 test method for plastering mortars. Circular specimens (\varnothing 200 mm and 20 mm thick) were set on a circular test cup approximately 10 mm above the free surface of the volume of demineralised water contained in the test cup. Test results were based on frequent monitoring of the mass of the test cup.

3.2 Alkali reactivity test

An alkali reactivity test under conditions similar to those specified in ASTM C 227 was used, but a curing period was required before testing to assure proper formation of a polymer-cement co-matrix. After the 28-day curing period, mortar bars (25 x 25 x 285 mm) were

vertically stored over water inside a stainless steel container kept in an oven at 38 ± 2 °C, which assured a moist, warm environment to accelerate ASR. To further increase ASR expansion rates, the $\text{Na}_2\text{O}_{\text{eq}}$ content of mortars was increased to 1.25% of the mass of cement, as described in subsection 2.3.

4. RESULTS AND DISCUSSION

4.1 Additional results from the previous alkali reactivity test in NaOH solution bath at 80 °C

In a previous paper, the authors assessed the polymer action on ASR through an accelerated alkali reactivity test procedure similar to that described in ASTM C 1260 [10] on a set of mortars using the same mix proportions used in the present study and listed in Table 4. Under those specific conditions, consisting of mortar bar test specimens immersed in a NaOH solution at 80 °C, expansion was generally higher in PCMs compared to the unmodified Ref CM, as shown in Figure 1. The epoxy modified mortar (EP PCM) listed in Figure 1 was incompatible with a raised $\text{Na}_2\text{O}_{\text{eq}}$, as explained in section 2.3, and thus was not used in the present study.

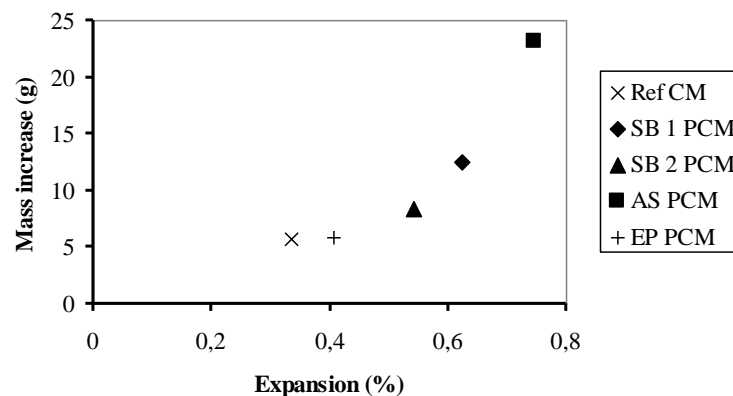


Figure 1: Expansion versus mass increase after 28 days of a previous alkali reactivity test [10] of mortar bars immersed in a NaOH solution bath at 80 °C

Figure 1 also shows that there were significant differences in mass increase of test specimens due to absorption of NaOH solution between the different mortars studied. As in that specific test method the NaOH solution bath is responsible for acceleration of ASR expansion rates, supplying water and both OH^- and Na^+ ions, ASR was more aggressively promoted in the test specimens with higher absorption of NaOH solution. This was confirmed by SEM observations [10], which revealed that aggregate particles in the test specimens of PCMs were more damaged due to silica dissolution.

The mass increase of test specimens also did not agree with either the water absorption under atmospheric pressure (Table 5) or the coefficient of capillary sorption coefficient [10], both determined at a standard laboratory temperature of 20 °C. This further established this type of alkali reactivity test as inadequate to assess the performance of PCMs, as they showed

reduced water absorption at 20 °C compared to the unmodified Ref CM, but higher mass increase in the NaOH solution bath at 80 °C.

Further confirmation was observed on EDX line profiles of the interfacial transition zone (ITZ) of unmodified Ref CM and AS PCM. The cumulative distribution of the relevant elements detected in the available line profiles is plotted on Figure 2. While the sodium (Na) content at the ITZ of AS PCM is mainly above 1% of the total detected elements (Figure 2 b), its content in Ref CM is clearly under 1% (Figure 2 a). The higher content of Na at the ITZ, along with the occurrence of potassium (K) and detection of Na inside the boundary of aggregate particles of AS PCM, agrees with both the higher absorption of NaOH solution and the higher dissolution of aggregate particles previously observed in PCMs compared to the unmodified Ref CM.

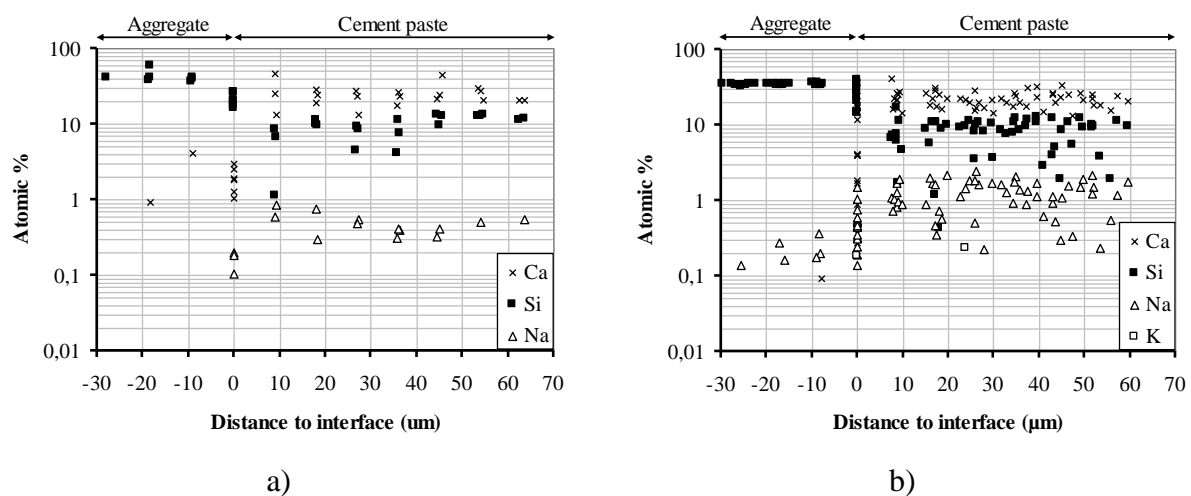


Figure 2: Silica (Si), alkalis (sodium, Na and potassium, K) and calcium (Ca) distribution at the ITZ; a) unmodified Ref CM; b) AS PCM

Figure 1 also shows that although mortars with higher mass increase due to NaOH solution absorption also expanded more, no clearly defined correlation exists. Other significant differences in relevant properties besides absorption, such as porosity or elastic modulus, were thus expected to have had influence on expansion rates.

4.2 Alkali reactivity test of 1.25% $\text{Na}_2\text{O}_{\text{eq}}$ specimens in moist 38 °C environment

By increasing the $\text{Na}_2\text{O}_{\text{eq}}$ content of all mortars to 1.25% of the mass of cement and subjecting mortar bar test specimens to a moist 38 °C environment, it was expected that, compared to the previous NaOH solution bath test at 80 °C, the influence of significant porosity or sorptivity differences on expansion would be minimized. Not only the moisture transport properties would more closely resemble those under field conditions or standard laboratory climate due to the lower temperature, but their influence on ASR related expansion would be less critical, as NaOH was added during mortar mixing instead of being added to an immersion bath.

Compared to the previous test (Figure 1), PCMs still expanded more than the unmodified Ref CM, although the relative order amongst PCMs changed (Figure 3 a). During the first 28 days (dashed line in Figure 3 a), the SB 2 PCM was mistakenly subjected to an approximately

10 °C higher temperature than the targeted 38 °C, thus it is possible that its expansion during this period would be slightly lower if the target temperature had been met.

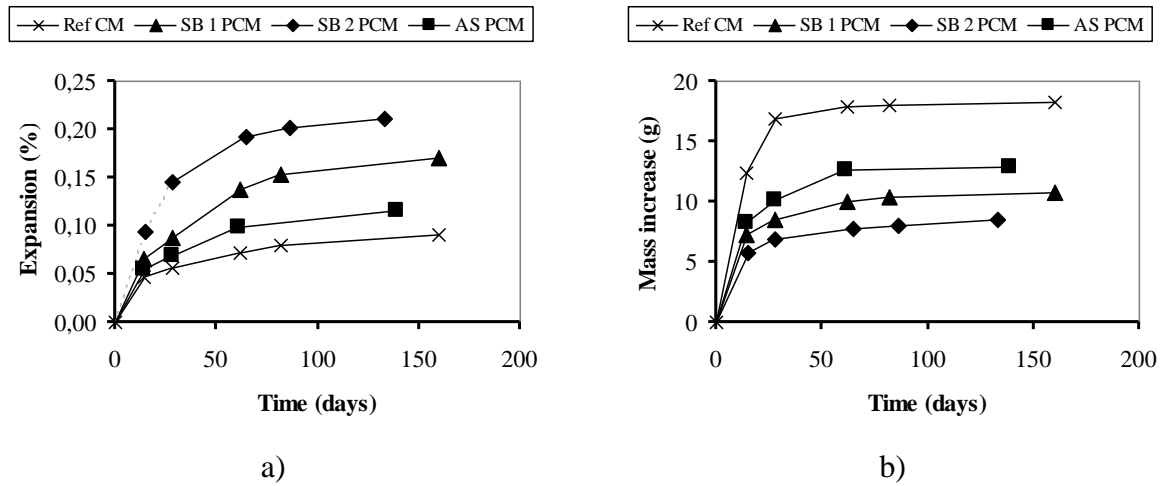


Figure 3: Alkali reactivity test results of 1.25% $\text{Na}_2\text{O}_{\text{eq}}$ specimens in moist 38 °C environment; a) expansion; b) mass increase

Compared to the previous alkali reactivity test, in the moist 38 °C conditions the mass increase of the different mortars studied (Figure 3 b) still didn't completely agree with their respective characteristic values of the relevant moisture transport property in the said test environment, which was considered to be the water vapour permeability (Table 5). Despite having slightly higher water vapour permeability than Ref CM (Table 5), AS PCM had higher mass increase during the alkali reactivity test (Figure 3 b).

However, SB PCMs had both lower water vapour permeability and lower mass increase in the alkali reactivity test compared to the unmodified Ref CM. Relative differences between the relevant moisture transport properties determined at 20 °C and the mass increase in the alkali reactivity test were thus smaller, but also with less influence on expansion in moist 38 °C environment than in the NaOH solution bath at 80 °C, as the $\text{Na}_2\text{O}_{\text{eq}}$ of mortars was artificially raised to an equal amount from the start and their alkali content did not depend on absorption. Compared to the 80 °C NaOH solution bath, the current test was thus confirmed as the preferred method to assess the performance of PCMs and to identify the mechanisms responsible for any differences in expansion.

Table 5: Properties of hardened mortars

	Ref CM	SB 1 PCM	SB 2 PCM	AS PCM
Elastic modulus at 28 days (GPa) [10]	27.2	11.8	18.8	10.0
Water absorption under atmospheric pressure (%) [10]	11.5	5.8	4.3	8.9
Water vapour permeability (kg/Pa·m·s)	8.80	3.44	1.11	8.99
$(W_{\text{tot}} + V_{\text{air}})/C$	0.61	0.51	0.44	0.72

The significant differences in elastic modulus (Table 5) and porosity between the unmodified Ref CM and PCMs had been previously identified as properties with potential influence on ASR related expansion. It was expected that under the internal stress developed due to ASR, significantly lower elastic modulus could lead to higher expansion. Recently developed ASR numerical models consider this influence [11-12]. On the other hand, higher volume of porosity could accommodate a higher amount of expanding ASR products, thus relieving expansive pressure and reducing expansion due to ASR, as acknowledged by other authors [9,13]. The ratio of the water (including the liquid portion of polymer additions in the case of PCMs) plus entrained air content to the cement content (Table 5) has been reported to improve the correlation coefficients for Abrams' law [14] and was additionally used to qualitatively assess the total (open and closed) porosity due to differences in both W/C ratio and entrained air content.

Of these properties with potential influence on expansion due to ASR, the open porosity assessed through a water absorption under atmospheric pressure test (Table 5) was clearly the one more closely related to the expansion results (Figure 4), showing a high correlation which could be further improved considering the mistakenly set temperature during the first 28 days of the alkali reactivity test of SB 2 PCM.

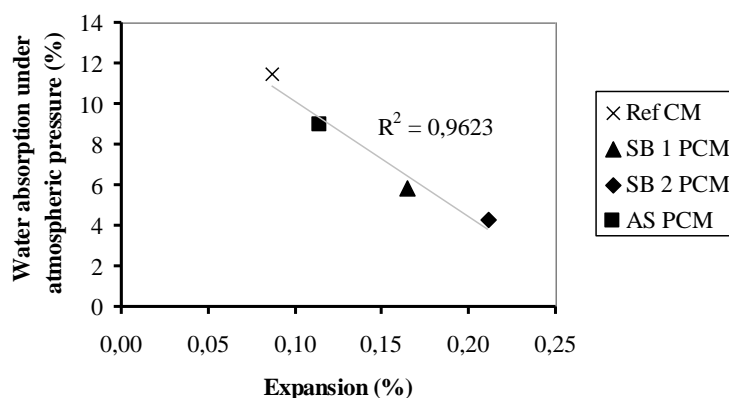


Figure 4: Water absorption at 20 °C versus expansion at 133 days in moist 38 °C environment

Despite the high correlation between expansion due to ASR and open porosity, it's likely that the significant differences in elastic modulus and closed porosity are also responsible for the response of PCMs to ASR, characterized by higher expansion than that of unmodified mortars.

Given the importance of the previously observed higher resistance of PCMs to damage resulting from ASR when compared to unmodified mortar [10], on any further studies on this subject ASR should also be induced through the moist 38 °C moist environment on specimens with raised $\text{Na}_2\text{O}_{\text{eq}}$ content. Compared to the NaOH solution bath at 80 °C and despite resulting in slower expansion rates due to ASR, these conditions seem to establish a more reasonable environment for performance comparison between PCMs and unmodified mortars, whose mechanical and transport properties may be significantly different.

4. CONCLUSIONS

Linear EDX analysis crossing aggregate particle boundaries and the ITZ confirmed that a previous alkali reactivity test in a NaOH solution bath at 80 °C resulted in ASR being more aggressively promoted in PCMs than in the unmodified Ref CM, probably due to higher absorption of NaOH solution. An alkali reactivity test method allowing more adequate assessment of the performance of PCMs was thus sought and its results shown in the present study.

Compared to that occurring in the NaOH solution bath, the mass increase of test specimens in an alkali reactivity test in moist 38 °C environment more closely reflected the relevant water transport properties determined at 20 °C – immersed water absorption in the former and water vapour permeability in the later. Additionally, compared to the previously alkali reactivity test, differences in water transport properties should have less influence on expansion in the moist 38 °C alkali reactivity test, as the alkali content of mortar specimens is artificially raised to an equal amount during mixing and thus do not depend on their absorption. Between the two types of test methods, the moist 38 °C alkali reactivity test on specimens with raised $\text{Na}_2\text{O}_{\text{eq}}$ was thus considered to be the preferred method to induce ASR expansion for performance comparison between unmodified cement mortars and PCMs.

However, PCMs still expanded more than the unmodified Ref CM in the moist 38 °C environment, meaning that the higher expansion of PCMs in the previous alkali reactivity test in a NaOH solution bath at 80 °C may have been the result of their higher absorption of NaOH solution but is also their expected response to ASR. However, it had already been established that higher expansion of PCMs did not necessarily imply higher resulting damage, due to the mechanical differences between polymer-modified and pure cementitious materials.

Despite the high correlation between the volume of accessible porosity, assessed through water absorption under atmospheric pressure, and expansion results, it's likely that closed porosity and significant differences in elastic modulus also explain the expected response of PCMs to ASR, characterized by higher expansion than unmodified mortars.

The moist 38 °C alkali reactivity test on specimens with raised $\text{Na}_2\text{O}_{\text{eq}}$ was also established to be the preferred method to induce ASR in future studies on the previously observed higher resistance of PCMs to damage resulting from ASR.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support from FCT - Fundação para a Ciência e a Tecnologia (Portugal) given to the research project PTDC/ECM/101810/2008 - Polymer-modified Cement Mortars for the Repair of Concrete Structures, whose scope included the present study.

REFERENCES

- [1] Yang, Z., Shi, X., Creighton, A.T. and Peterson, M.M., 'Effect of styrene-butadiene rubber latex on the chloride permeability and microstructure of Portland cement mortar', *Constr. Build. Mater.* 23 (6) (2009) 2283-2290.
- [2] Soroushian, P. and Tlili A., 'Effects of latex modification on the failure mechanism and engineering properties of concrete', in 'Polymer-Modified Hydraulic-Cement Mixtures', STP 1176 (ASTM, Philadelphia, 1993) 104-119.

- [3] Pascal, S., Alliche, A. and Pilvin Ph., 'Mechanical behaviour of polymer modified mortars', *Mater. Science Eng. A* 380 (1-2) (2004) 1-8.
- [4] Schorn, H., Butler, M. and Hempel, S., 'Polymers as microcrack stopper in concrete observed in ESEM', in 'Polymers in Concrete', Proceedings of the 11th International Congress (BAM Federal Institute for Materials Research and Testing, Berlin, 2004) 11-18.
- [5] Ribeiro, M.S.S., Gonçalves, A.F. and Branco, F.A.B., 'Styrene-butadiene polymer action on compressive and tensile strengths of cement mortars', *Mater. Struct.* 41 (7) (2008) 1263-1273.
- [6] Afridi, M.U.K., Ohama, Y., Demura, K. and Iqbal, M.Z., 'Development of polymer films by the coalescence of polymer particles in powdered and aqueous polymer-modified mortars', *Cem. Concr. Res.* 33 (11) (2003) 1715-1721.
- [7] Beeldens, A., Van Gemert, D., Schorn, H., Ohama, Y. and Czamecki, L., 'From microstructure to macrostructure: an integrated model of structure formation in polymer-modified concrete', *Mater. Struct.* 38 (6) (2005) 601-607.
- [8] Ohama, Y., Katsunori, D. and Kakegawa, M., 'Inhibiting alkali-aggregate reaction with chemical admixtures', in 'Alkali-Aggregate Reaction', Proceedings of the 8th International Conference (The Society of Materials Science, Kyoto, 1989) 253-258.
- [9] Saccani, A. and Motori, A., 'The effect of polymer addition on alkali silica reactions in cementitious mortars', *Mater. Struct.* 34 (6) (2001) 373-377.
- [10] Feiteira, J. and Ribeiro, M.S.S., 'Polymer action on alkali-silica reaction in cement mortar', submitted for publication in *Cem. Concr. Res.* (2011).
- [11] Multon, S., Sellier, A. and Cyr, M., 'Chemo-mechanical modelling for prediction of alkali silica reaction (ASR) expansion', *Cem. Concr. Res.* 39 (6) (2009) 490-500.
- [12] Dunant, C. and Scrivener, K., 'Micro-mechanical modelling of alkali-silica-reaction-induced degradation using the AMIE framework', *Cem. Concr. Res.* 40 (4) (2010) 517-525.
- [13] Ramachandran, V.S., 'Alkali-aggregate expansion inhibiting admixtures', *Cem. Concr. Compos.* 20 (2-3) (1998) 149-161.
- [14] Sear, L.K.A., Dews, J., Kite, B., Harris, F.C. and Troy, J.F., 'Abrams law, air and high water-to-cement ratios', *Constr. Build. Mater.* 10 (3) (1996) 221-226.