

POLYMER ACTION ON ALKALI-SILICA REACTION IN CEMENT MORTAR

João L. Feiteira^{*}, Maria S. Ribeiro[†]

^{*}Concrete Division of Materials Department, LNEC - Laboratório Nacional de Engenharia Civil
Avenida do Brasil 101, 1700-066 Lisboa, Portugal
e-mail: jfeiteira@lneec.pt, web page: <http://www.lneec.pt>

[†]Concrete Division of Materials Department, LNEC
e-mail: sribeiro@lneec.pt

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Summary. *Polymer modification of mortar and concrete leads to reduced water absorption, lower ionic mobility, reduced thickness of the interfacial transition zone, lower availability of $\text{Ca}(\text{OH})_2$ and higher tensile strength and ductility and thus may have an inhibiting effect on alkali-silica reaction (ASR) and related damage. However, the existing studies are inconclusive and cover only a limited range of polymers. In this study, polymer-cement mortars (PCMs) based on styrene-butadiene, acrylic and epoxy polymer additions were subjected to an accelerated alkali reactivity test and their expansion compared with that of an unmodified cement mortar (CM). Despite their lower capillary water absorption in standard laboratory climate, the weight increase of PCMs during exposure to the 80 °C NaOH solution bath of the alkali reactivity test was higher than that of the unmodified CM, promoting higher expansion due to ASR in PCMs. Even though SEM observations confirmed the existence of more extensive ASR in PCMs, microcracking in the cement paste of the unmodified CM was widespread, while little evidence of microcracking was present in the cement paste of PCMs. The potential for polymers to inhibit ASR and reduce related damage may be further evidenced through a more suitable alkali reactivity test at a temperature closer to field temperature, under which PCMs have been shown to have lower water absorption than unmodified CMs.*

1 INTRODUCTION

The alkali-silica reaction (ASR) has been responsible for premature concrete degradation in more than 40 countries all over the world [1]. This phenomenon consists of a 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 aggregates. This reaction progressively transforms silica minerals into an alkali-silica gel with hygroscopic properties, which can expand due to hydration and crack the aggregate and surrounding cement paste [2].

Preventing measures have been studied and used whenever potentially reactive aggregates

cannot be avoided. Besides limiting the alkali content in concrete, supplementary cementitious materials (SCMs) and lithium compounds have been shown to have a reducing effect on ASR-related expansion.

The main inhibiting mechanism of SCMs is the reduction of Na^+ , K^+ and OH^- ions concentration in the pore solution [3], which can be partially justified by the alkali dilution in concrete as result of the replacement of part of the cement with SCMs of lower alkali content. However, other inhibiting mechanisms exist, as even SCMs with higher alkali content than the replaced cement can lead to the reduction of ASR-related expansion [4].

As the $\text{Ca}(\text{OH})_2$ content of concrete has been linked to an increased potential for ASR-related expansion, the reduced $\text{Ca}(\text{OH})_2$ content of concrete resulting from the pozzolanic reaction set off by SCMs is also regarded as another inhibition mechanism. Several authors [2,5-7] support that the calcium-rich ASR gel found in cement paste with available $\text{Ca}(\text{OH})_2$ is responsible for the creation of a reaction rim around reactive aggregate particles, with different models being proposed to explain the link between the observed reaction rim and the potential for higher ASR-related expansion. There is also evidence that the reduced Ca/Si ratio of the CSHs formed in the presence of SCMs results in an increased capacity to accommodate alkalis and further reduce the OH^- content of the pore solution, thus reducing ASR-related expansion [8].

Lithium salts have also been reported to have a reducing effect in ASR-related expansion mainly through modification of the microstructure [9] and chemical composition of the ASR gel [10].

Polymers have long been used for modification of cementitious materials, more notably for water absorption reduction and adhesion improvement of concrete repair mortars and cementitious coatings, but polymer modification of concrete has also been studied for its improved durability [11-13].

Polymers can improve properties in concrete with potential reducing effects on ASR-related expansion and damage, such as lower water absorption, reduced ionic permeability of the polymer-cement co-matrix [14] and higher tensile strength and ductility.

The complex process of mutual influence of cement hydration and polymer film formation in polymer-cement mortar (PCM) and concrete also modifies both the morphology and availability of certain cement hydration products. Due to the interaction between Ca^{2+} cations present in the pore solution of cement paste and both the carboxylate groups of polymers [14-16] and surfactants used in polymer additions [17], $\text{Ca}(\text{OH})_2$ content is reduced, particularly at the interfacial transition zone (ITZ), during early ages of cement hydration and for polymer to cement weight ratios above 10% [14,18,19]. The $\text{Ca}(\text{OH})_2$ crystals in PCMs are also both more compact, due to the polymer acting as an adhesion promoter between the $\text{Ca}(\text{OH})_2$ crystal layers [20], and more frequently found growing in pores [21-23] than those found in unmodified cement mortar (CM).

While there are reasons to believe that the properties of mortars and concrete that polymers have been shown to modify might have a reducing effect in ASR-related expansion, the few results reported in the literature [9,24] are inconclusive, using distinct test methods and covering only a limited range of the available polymer types.

This study presents the results of an assessment of the influence of styrene-butadiene,

acrylic-styrene and epoxy polymer additions on ASR in cement mortars along with an analysis of their potentially intervening mechanisms.

2 MATERIALS

2.1 Aggregates

Crushed pebblestone with original minimum (d) and maximum (D) dimensions of respectively 5.6 mm and 11.2 mm was used. The pebblestone aggregate was crushed again to obtain the grading specified in the ASTM C 1260 alkali reactivity test. 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 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. Figure 1 shows the granulometry curve of the aggregated used in this study.

Table 1 – Aggregate properties

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

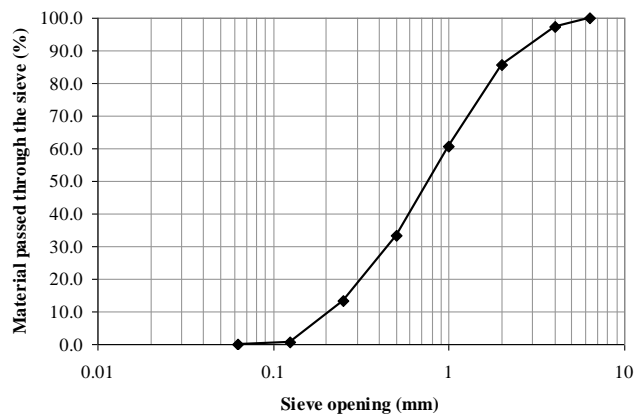


Figure 1 – Granulometric curve of the aggregate

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.

Table 2 – Chemical and mechanical properties of cement

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

Seven different polymer additions were initially considered, but low solid content polymer additions could not be used, as, for the intended relatively high polymer dosage, their high water content alone would lead to PCMs with excessively high water to cement ratios (W/C). Table 3 shows the solid content of all initially considered polymer additions according to the EN 480-8 method and the minimum W/C (due only to the water content of polymer additions, W_{pol}) of respective PCMs, considering the mix proportions used in this study (Table 5). A solid content of polymer addition to cement ratio (P/C) of 15% was considered. Commercially available of styrene-butadiene (SB 1 and SB 2) and acrylic-styrene (AS 1) dispersions and a two-component (diglycidil ether of bisphenol-A and an aliphatic amine hardener) aqueous epoxy (EP) were selected for cement mortar modification in this study. Other properties of the selected polymer additions were determined and are listed in Table 4. The glass transition temperature (T_g) represents the midpoint of the glass transition region observed in differential scanning calorimetry tests of polymer films (Figure 7). The specific mass was determined with a hydrometer and the pH was determined with a pH meter according to ISO 4316.

Table 3 – Solid content of the selected polymer additions and the minimum W/C ratio of respective PCMs with P/C ratios of 15%

Polymer addition	Solid content (%)	W_{pol}/C ratio of PCM for P/C=15%
AS 1	36.2	0.26
AS 2	19.1	0.64
SB 1	41.7	0.21
SB 2	38.6	0.24
SB 3	33.8	0.29
SB 4	19.6	0.62
EP	54.6	0.12

Table 4 – Properties of selected polymer additions

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
EP	1.075	-	-

2.4 Mix design and curing method

A P/C of 15% was chosen for the PCMs studied, as it is higher than the 10% P/C ratio usually associated with the beginning of formation of an effective polymer-cement co-matrix [14,25,26], while still being potentially cost-effective in field.

While the main purpose of the studied PCMs was the assessment of their alkali reactivity potential and the intended ASTM C 1260 alkali reactivity test specifies a fixed W/C ratio of 0.47, the plasticizing effect of polymer additions would lead to an extremely fluid PCM if the specified W/C had been used, especially considering the high 15% P/C dosage. Thus, a constant flow between the PCMs and an unmodified CM was sought. While the unmodified CM's mix followed the design specified in ASTM C 1260, the W/C of PCM mixes was adjusted so that their flow fell in the $\pm 7.5\%$ 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 5 lists the total water to cement ratio (W_{tot}/C) comprises both the added water and the liquid content of the polymer addition used, while the water to cement ratio (W_{added}/C) comprises only the added water of the mortars studied, as well as their flow and fresh air content according to the procedure described in ASTM C 1437 and C 231 (type B meter) respectively.

Table 5 – Mix proportions, flow and fresh air content of the studied mortars

Mortar mixes	P/C (%)	A:C	W/C	W_{tot}/C	Flow (%)	Fresh air content (%)
Ref CM	0	1:3	0.47	0.47	124	7.6
SB 1 PCM	15	1:3	0.11	0.32	125	10.1
SB 2 PCM	15	1:3	0.08	0.32	129	6.5
AS PCM	15	1:3	0.16	0.42	130	14.8
EP PCM	15	1:3	0.45	0.57	122	2.6

The results show that after the flow adjustment the resulting W_{tot}/C ratio of the AS and SB PCMs is lower than that of the unmodified mortar, which indicates the usual plasticizing effect of polymer additions. The EP polymer addition, however, didn't exhibit this effect, as the resulting PCM required a W_{tot}/C significantly higher than the unmodified mortar to attain the same flow. While both SB PCM mixes required the same W_{tot}/C , the fresh air content was distinct, which could be related, for instance, to different quantities of anti-foaming agent incorporated in the polymer additions by the respective manufacturers. While the AS addition greatly increased the air content of mortar, the EP addition significantly reduced it.

All mortars 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.

3 TEST METHODS

3.1 Alkali reactivity test

To assess the influence of polymer additions in ASR, an accelerated mortar bar test was chosen due to its fast results. Conditions similar to those specified in ASTM C 1260 were used, but a curing period was required before testing to assure proper polymer-cement co-matrix formation. After the 28-day curing period, mortar bars (25 x 25 x 285 mm) were immersed in water at 80 °C during 24 h after which they were immersed in a 1N NaOH solution at 80 °C for a period of 28 days.

3.2 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. Both polished sections and fractured surface samples were coated with gold and examined. Polished sections were obtained by impregnation of mortar samples with low-viscosity epoxy resin under vacuum before polish. SEM images were obtained in both composition mode of backscattered electron imaging (COMPO) and secondary electron imaging mode (SEI). The energy dispersive X-ray (EDX) microanalysis capability was used to identify the composition of the ASR products observed.

3.3 Differential scanning calorimetry

Since the ASTM C 1260 alkali reactivity test imposes severe thermal conditions to the polymer-cement co-matrix and because the thermal resistance of the polymer film resulting from the polymer additions is rarely provided by the manufacturers, the thermal stability of the polymer films was assessed through differential scanning calorimetry (DSC) tests according to ISO 11357, parts 1 and 2. DSC tests also allowed determination of phase transitions and respective temperatures, such as the glass transition temperature (T_g). Polymer film specimens were obtained through drying of an appropriate amount of polymer addition at room temperature for 24 h.

3.4 Water transport properties

The capillary water sorption coefficient was assessed through the EN 13057 test method. This method consisted of having circular specimens of 100 mm diameter and 20 mm thickness with the trowelled test face in contact with water and measuring their weight change (water uptake) in appropriate time intervals. The sorption coefficient is the gradient of the linear portion of the weight change curve expressed as a function of the square root of time.

The LNEC E 394 specification is a regular test method used in LNEC for assessing the water absorption of immersed hardened concrete under atmospheric pressure and it was followed, with the exception of specimen size, to supplement the results of the EN 13057 capillary absorption test. Cubic specimens of 25 mm side were used to allow comparison with specimens cut from the mortar bars subjected to alkali reactivity tests. The specimens were

dried in a 105 °C oven until constant weight (less than 0.1% difference in at least 24 h) and then immersed in water up to 2 mm above the top surface and weighted again until constant weight was achieved. The resulting water absorption is the volume of absorbed water expressed as percentage of the specimen's volume.

3.5 Mechanical properties

Compressive strength was determined according to EN 12190, while flexural strength was determined according to EN 196-1 and the modulus of elasticity in compression was determined according to method 2 of EN 13412.

4 RESULTS AND DISCUSSION

The results of mechanical tests (Figure 2) show that generally the polymer additions significantly reduced the compressive strength but didn't significantly affect the flexural strength of mortar. However, the polymer addition used in the SB 2 PCM was able to significantly improve the flexural strength over the unmodified Ref CM without compressive strength loss.

The significant performance improvement of the SB 2 PCM over the SB 1 PCM, both modified with an SB polymer addition and with similar W/C ratio, may be justified by a possible higher amount of anti-foaming agent in the SB 2 addition. The significantly lower fresh air content of SB 2 PCM (Table 5) suggests that the SB 2 polymer addition has in fact a higher amount of anti-foaming agent when compared to the SB 1 polymer addition.

As expected, and according to Figure 2 b), polymer additions reduced the modulus of elasticity in compression of CM. However, EP and SB 2 PCMs had considerably higher modulus than the rest of the PCMs.

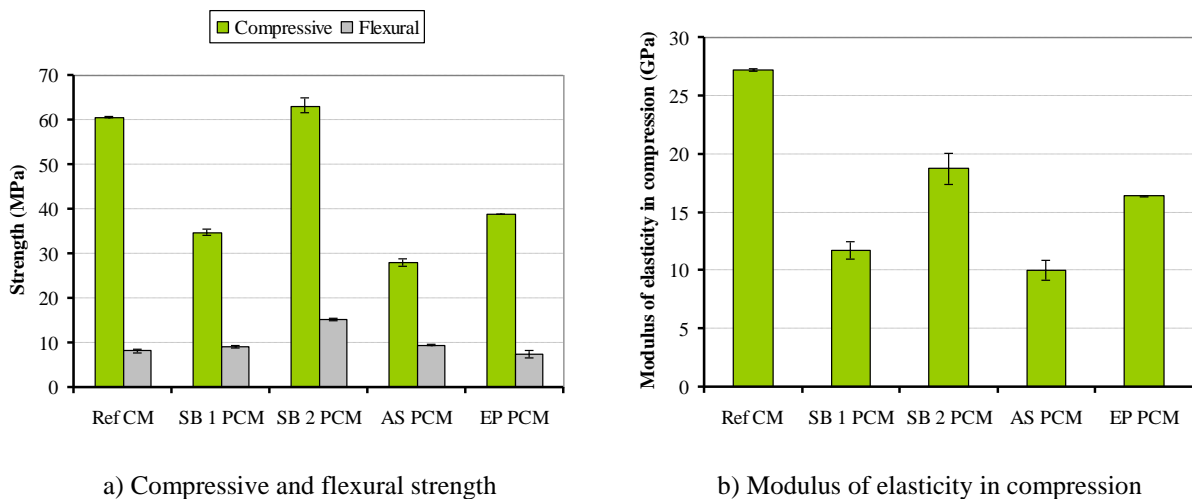


Figure 2 – Mechanical properties of the mortars studied

Given the fact that water plays an important role in ASR development and that the ASTM C 1260 alkali reactivity test requires the mortar bar specimens to be in permanent immersion in a NaOH solution, particular attention was given to water transport properties of PCMs.

Figure 3 shows the weight change of the mortars studied due to capillary water absorption. The stabilization of the weight change of the unmodified Ref CM shortly after the 1 h mark was due to the absorbed water front reaching the top of the specimen. The sorption coefficient of the water absorption curves shown in Figure 3 and the water absorption under atmospheric pressure of the mortars studied are reported in Table 6. As expected, considering the previous experience with PCMs and published data on this subject, the reduced water absorption of PCMs was confirmed, although the water absorption of the EP PCM was similar to that of the Ref CM.

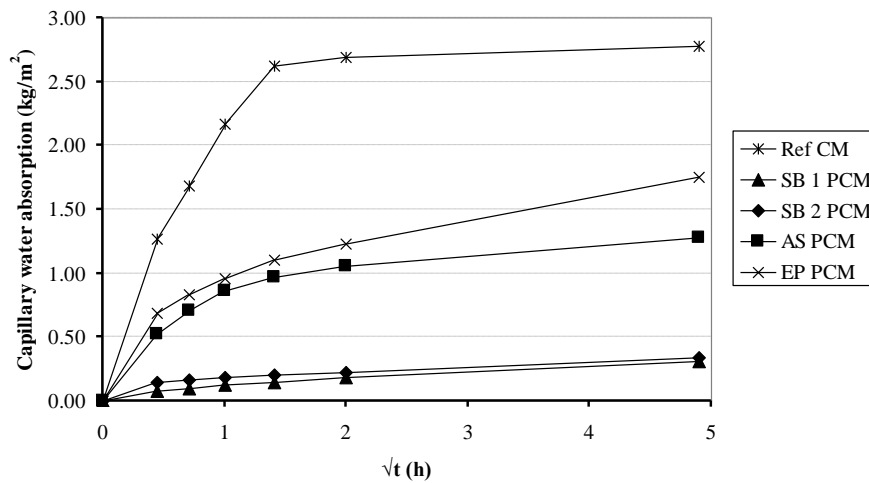


Figure 3 – Capillary water absorption

Table 6 – Water absorption of the mortars studied

Mortars	Capillary sorption Coefficient (kg/(m ² .h ^{0.5}))	Water absorption under atmospheric pressure (%)
Ref CM	1.65	11.5
SB 1 PCM	0.04	5.8
SB 2 PCM	0.04	4.3
AS PCM	0.07	8.9
EP PCM	0.18	11.3

Even though polymers usually increase the total pore volume of mortar due to their air-entraining effect, the increase is reflected mainly in the larger pore dimensions and thus contribute to reduce the capillary absorption by interrupting the network of capillary pores. Polymer particles can also fill the smaller capillary pores of the cement paste, explaining the usually reported reduced pore volume of PCMs in the capillary range of pore radius and a

shift to the lower pore dimensions in this range [19,27-29], although this effect may depend on the polymer type.

Despite the lower water absorption of PCMs possibly reducing both the exposure of their aggregate particles to the attack of the OH⁻ ions present in the NaOH solution and increasing water absorption and expansion of ASR gel, their expansion in the alkali reactivity test was higher than that of the unmodified Ref CM, as shown in Figure 4.

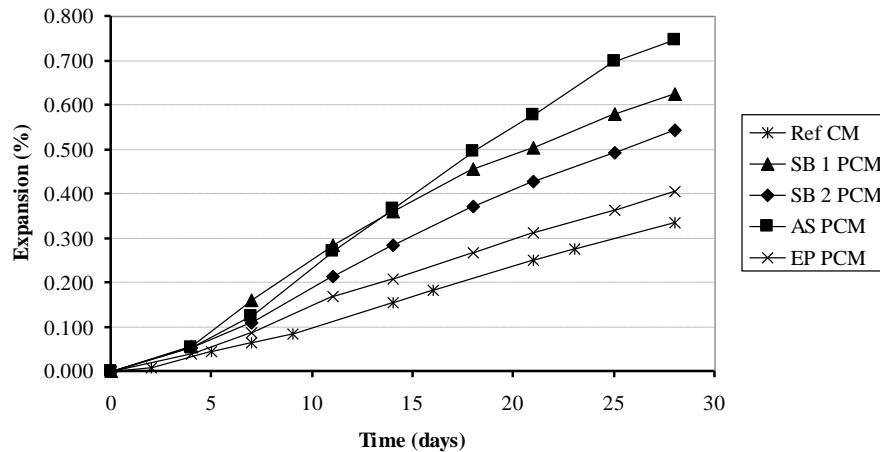


Figure 4 – Expansion due to ASR in the alkali reactivity test

The weight change of specimens was also monitored after the specimens were immersed in the NaOH solution and, although their capillary and water absorption were lower than those of the Ref CM (Table 6), the weight change of PCMs in the NaOH solution was higher, as shown in Figure 5. This suggests that, unexpectedly, the water uptake of PCMs in the alkali reactivity test conditions was higher. Higher water uptake of PCMs was probably due to changes of the water absorption kinetics, as in the 80 °C environment of the alkali reactivity test the water viscosity drops significantly compared to the 20 °C room temperature under which water absorption tests are conducted. The high temperature environment thus favoured both the absorption of NaOH solution in the PCMs over the Ref CM and the exposure of their aggregate particles to the OH⁻ ions attack.

With higher water absorption during the alkali reactivity test, the SB and AS PCMs were expected to have been more extensively affected by ASR and thus a higher amount of ASR gel was also expected in these PCMs. The comparison of water absorption under atmospheric pressure before and after the alkali reactivity tests expressed in Figure 6 seems to confirm that a higher amount of ASR gel was produced in PCMs compared to the Ref CM. As the specimens were dried at 105 °C prior to the determination of water absorption, the ASR gel was expected to be volatilized in this process, exposing the voids resulting from the silica dissolution in the aggregate particles affected by ASR and increasing the water absorption.

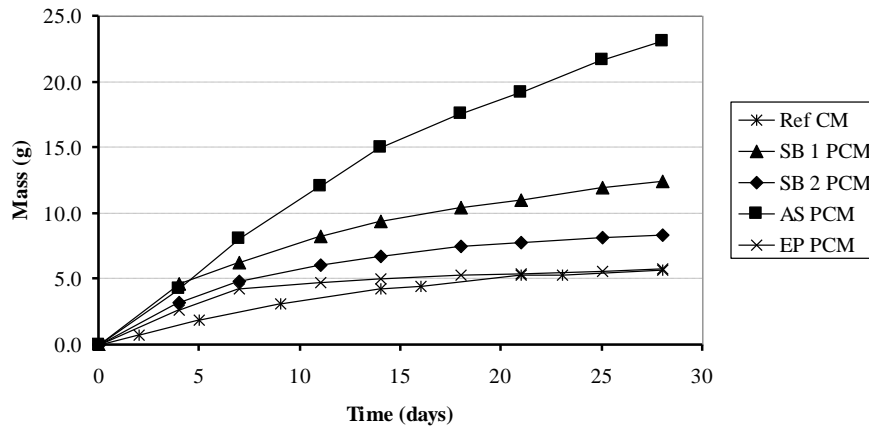


Figure 5 – Weight change during the alkali reactivity test

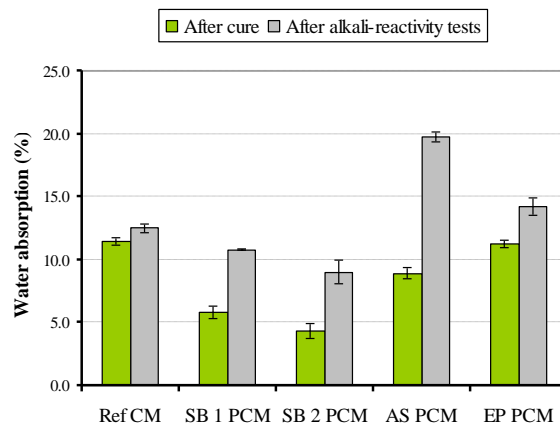


Figure 6 – Comparison of water absorption before and after the alkali reactivity test

While the weight change results shown in Figure 5 agree qualitatively with the expansion results (Figure 4), other factors might have influenced expansion. Mortars with higher porosity can accommodate a higher volume of ASR gel, thus relieving the expansive pressure caused by its water absorption. On the other hand the internal stresses developed due to ASR are expected to result in higher expansion in mortars with lower modulus of elasticity. PCMs might also have higher coefficient of linear thermal expansion [28,29], but its effect on the expansion results was eliminated by the 24 h period of 80 °C water immersion prior to the actual test period in an 80 °C NaOH bath, as specified in ASTM C 1260. The OH⁻ ions present in the concrete and mortar pore solution have been reported to improve the hardening process of epoxy, leading to the research of the possibility of using hardener-free epoxy in mortar and concrete [32-34] and self-healing epoxy-modified cement mortar [35]. Saccani and Motori [24] reported that curing of an epoxy film similar to that used in the present study in an 80 °C highly alkaline saturated Ca(OH)₂ solution improved its tensile strength and

decreased its elongation at break, resulting in increased modulus of elasticity. A similar mechanism might have influenced the expansion of the EP PCM in the 80 °C NaOH solution bath of the alkali reactivity test.

Even though PCMs expanded more than the Ref CM, expansion shouldn't be the only measure of performance of mortar or concrete affected by ASR whenever materials with distinct mechanical properties are compared. Ultimately, resistance of concrete or mortar to cracking and degradation under ASR action should be used to assess their performance.

Due to their higher tensile strength and ductility, the resistance to microcracking of PCMs can be higher than that of unmodified CMs [36,37,38]. The refinement of the ITZ [39], the improved adhesion between aggregates and cement paste and the bridging capabilities of polymer film on the onset of microcracking explain the higher tensile strength and ductility of PCMs. Schorn et al. [40] was able to directly observe the polymer bridging of microcracks on small specimens attached to a special loading device inside of an environmental SEM's chamber. As DSC tests of the polymer films (Figure 7) showed no relevant state changes at temperatures higher than T_g (Table 4) and up to 200 °C, it is possible that the integrity of the polymer-cement co-matrix and the potential for higher resistance to microcracking of PCMs remained even in the aggressive 80 °C NaOH solution bath of the ASTM C 1260 test. However, it is important to notice that the T_g of SB 2 and AS polymer additions being around room temperature (Table 4), the mechanical behaviour of the respective PCMs expressed in Figure 2 are expected to vary both in the alkali reactivity tests and across the range of ambient temperatures found in field conditions.

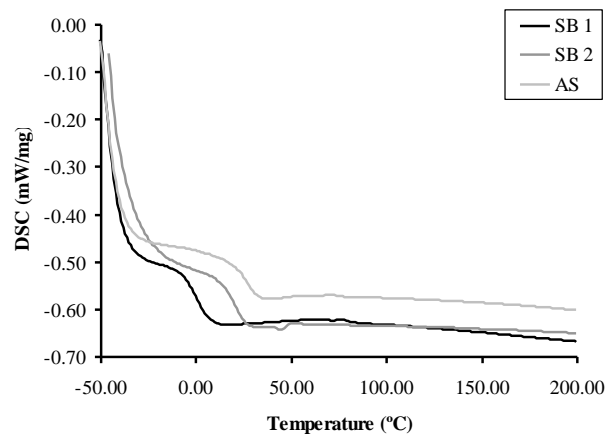


Figure 7 – DSC tests of SB 1, SB 2 and AS polymer films

SEM/EDX observations followed the alkali reactivity tests to confirm the presence of ASR products and look for physical evidences of degradation or alternative causes for the observed higher expansion in PCMs compared to the unmodified Ref CM.

SEM images in Figure 8 confirmed the higher porosity of SB 1 PCM (Figure 8 a) compared to the SB 2 PCM (Figure 8 b) due to the higher air entraining effect of the SB 1 polymer addition. The darker areas of Figure 8 correspond to pores impregnated with epoxy resin during preparation of the polished samples.

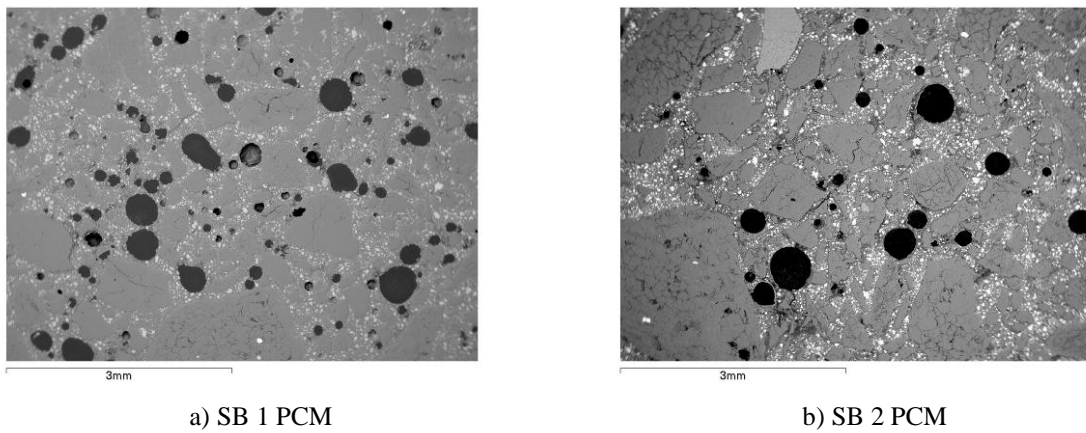


Figure 8 – Overall porosity of PCMs shown in SEM images in COMPO mode

ASR gel was detected in all specimens subjected to the alkali reactivity test and pores were usually found filled or lined with ASR gel, as shown in Figure 9 a). In this figure, the darker area inside the circular pore corresponds to epoxy resin impregnated during preparation of the polished samples while the rest of the pore area is filled with ASR gel with distinct textures, for which EDX analysis are given in Figure 9 b). The EDX analysis showed that the Ca/Si ratio of the gel near the pore rim was higher than that of the inner textured gel. The textured gel observed inside the pores of polished samples corresponded to crystalline gel, as shown in the fractured sample image of Figure 10, while the gel found near the pore rim was the more common amorphous ASR gel.

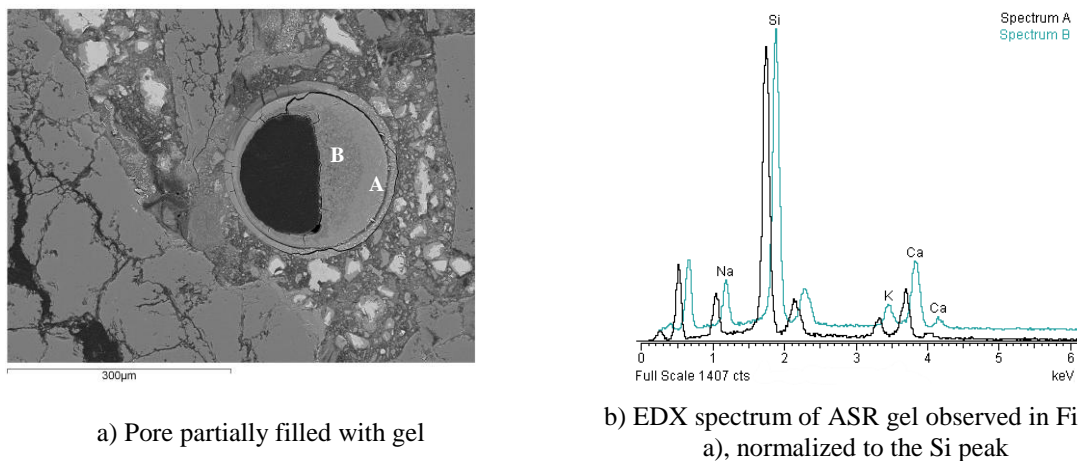
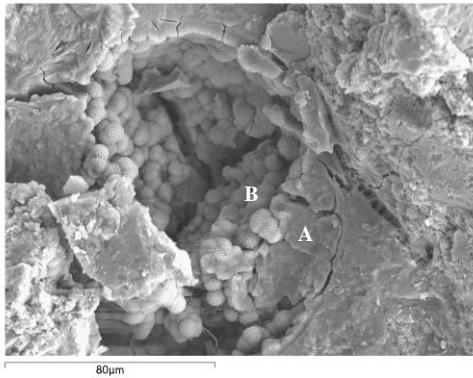


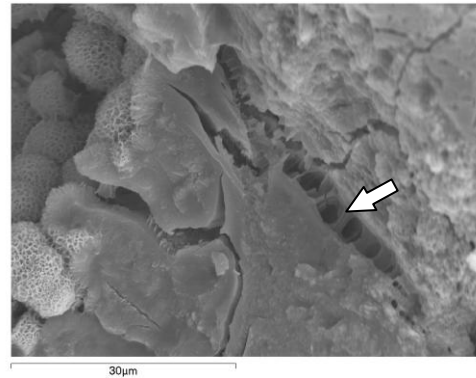
Figure 9 – ASR gel in a pore of a SB 2 PCM sample (SEM image of polished sample in COMPO mode)

Evidence of polymer film formation in the cement paste of PCMs is not usually easy to observe without previous acid dissolution of the cement hydration products, especially in ASR-affected specimens where most existing voids are filled with ASR gel. However,

evidence of polymer film bridging aggregate and cement paste was observed on a fractured sample of AS PCM, as shown in Figure 10 b).



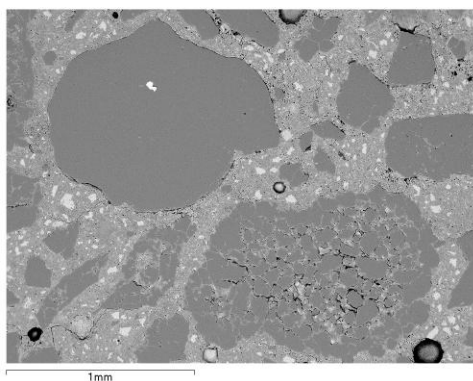
a) Pore containing amorphous (A) and crystalline (B) ASR gel



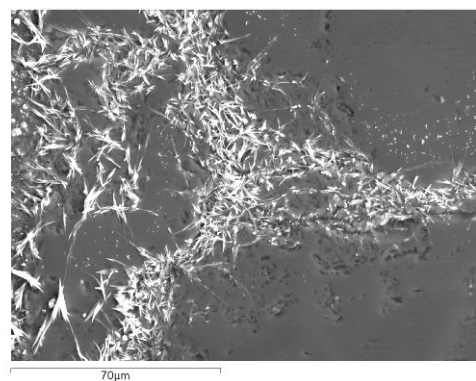
b) Detail of Figure 10 a) showing evidence of polymer film bridging aggregate and cement paste

Figure 10 – Crystalline ASR gel in pore and evidence of polymer “bridges” (SEM image of fractured AS PCM sample in SEI mode)

Additional evidence of ASR was found in the interior of aggregate particles. Porous aggregate particles were often observed and found to be preferential ASR developing sites. Figure 11 a) shows the coexistence of porous and homogeneous aggregate particles. Figure 11 b) shows in more detail the porous sites observed in aggregate particles similar to that found in Figure 11 a). The bright spots in Figure 11 b) are NaOH crystals attached to the surfaces exposed in the porous sites of aggregate particles.



a) Porous aggregate particle (bottom) and homogeneous particle (top) (SEM image of Ref CM sample in COMPO mode)



b) Porous site of aggregate particle; bright spots represent attached NaOH crystals (SEM image of SB 2 PCM sample in SEI mode)

Figure 11 – Example of porous aggregate particles, where ASR develops preferentially

SEM observations were able to detect widespread microcracking in the cement paste of the unmodified Ref CM (Figure 12), a feature not present in PCMs, where significant damage was only present in the interior of the aggregate particles. Figure 13 shows that despite extensive evidence of ASR gel and degradation of the aggregate particles and significantly higher expansion (Figure 4), microcracking in the cement paste was much less frequent in the SB 1 PCM compared to the Ref CM. Similar conclusions were drawn from the observations of the remaining PCMs studied.

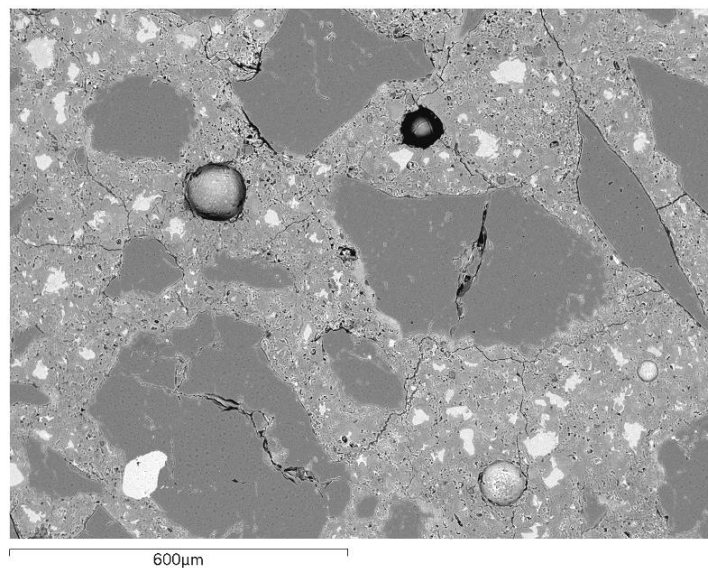


Figure 12 – Widespread microcracking in the cement paste of Ref CM (SEM image in COMPO mode)

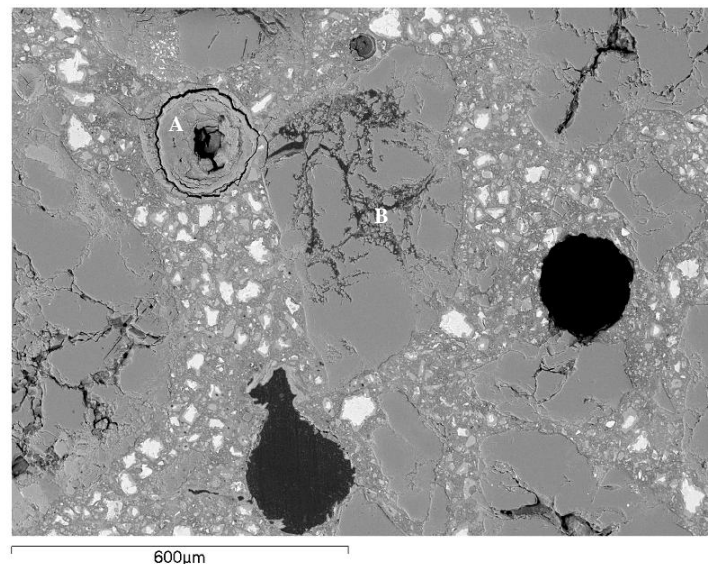


Figure 13 – Absence of microcracking in the cement paste of the SB 1 PCM despite extensive evidence of ASR gel in the pores (A) and aggregate particle degradation (B) (SEM image in COMPO mode)

SEM observations thus confirmed the potential for polymers to delay the onset of cracking and degradation of mortar or concrete caused by ASR. It was also shown that expansion results alone are not suitable to assess the performance of polymer modified cement mortar or concrete by comparison with unmodified materials.

Long term alkali reactivity tests at temperatures closer to those found in field conditions may even reveal a higher potential for PCMs to delay the onset of ASR-related damage. The aggressive ASTM C 1260 test conditions were particularly penalizing for PCMs, whose mass increase was higher than that of the unmodified Ref CM, contrary to what was verified in water absorption tests under standard laboratory climate.

5 CONCLUSION

All the PCMs studied exhibited lower capillary sorption coefficient and water absorption under atmospheric pressure than the unmodified Ref CM, thus showing potential for a reducing effect in ASR due to lower exposure of ASR gel to water necessary for its expansion. Additionally, other known properties of PCMs relevant to ASR, such as lower ionic mobility, improved ITZ and lower availability and different morphology of $\text{Ca}(\text{OH})_2$ crystals, were believed to potentially reduce ASR-related expansion.

Despite this, the expansion results of PCMs in an accelerated alkali reactivity test were higher than those of the Ref CM, particularly for the SB and AS PCMs.

Higher expansion coincided with higher mass increase in the aggressive conditions of the alkali reactivity test (80 °C 1N NaOH solution bath), which suggested that under these particular conditions the water absorption of PCMs was higher than that of the unmodified Ref CM, contrary to what was verified in water absorption tests under standard laboratory climate. This resulted in higher exposure of the aggregate particles of PCMs to the NaOH solution during the alkali reactivity tests, which was confirmed by more extensive evidence of ASR and ASR gel formation in SEM observations. Lower modulus of elasticity and higher porosity were also identified as possible factors influencing expansion of PCMs compared to the Ref CM.

Although PCMs expanded more due to the unsuitability of the alkali reactivity test used, subsequent SEM observations revealed significantly reduced microcracking in their cement paste compared to that of the unmodified CM, even in AS PCM samples which expanded more than twice as much. This behaviour was in agreement with the often reported higher tensile strength, ductility and resistance to microcracking of PCMs, which, according to DSC tests of polymer films, likely remained in the aggressive 80 °C environment of the alkali reactivity tests. It was thus shown the potential for polymers to reduce ASR-related damage in mortar and concrete.

The potential for polymers to reduce ASR-related damage may be further evidenced in long term alkali reactivity tests at lower temperature, under which PCMs have lower water absorption than unmodified CMs.

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