

Review and discussion of polymer action on alkali–silica reaction

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Abstract This paper compares the factors known to influence the deleterious alkali–silica reaction in concrete with the properties that polymers tend to modify in cementitious materials. A discussion on the potential ASR-influencing mechanisms of polymer additions is provided, along with a critical review of the existing literature on the subject. The influence of the potentially significant differences in mechanical properties and sorptivity between polymer-modified and unmodified cementitious materials on the expansion results of alkali reactivity tests is also discussed. According to the available results, the influence of polymers on ASR-related expansion seems to depend on both polymer type and dosage, suggesting the existence of concurrent, not yet well understood mechanisms by which polymers may influence ASR-related expansion. As polymer modification of cementitious materials can lead to significantly lower modulus of elasticity, higher tensile strength and resistance to microcracking, it is suggested that further research on the subject includes not only expansion tests but also an assessment of the resistance of polymer-modified cementitious materials to ASR-related damage, the main concern due to this deleterious phenomena.

Keywords Concrete · Mortar · Polymers · Alkali–silica reaction

1 Introduction

The alkali–silica reaction (ASR) was first identified as a cause of concrete degradation in the decade of 1940 in California, U.S.A. [55]. Since then, it has been identified in concrete in more than 40 countries all over the world [26].

The ASR is a chemical reaction between hydroxyl ion (OH^-) and alkali ions (sodium, Na^+ , and potassium, K^+), present in the strong alkaline pore solution of the cement paste, and deformed or poorly-crystallized forms of silica minerals present in certain aggregates of concrete. A hygroscopic reaction product, amorphous or crystalline, called alkali–silica gel is generated. Ionic species (Na^+ , K^+ and Ca^{2+}) and water present in the pore solution flow into the gel, which expands due to hydration, possibly inducing significant stresses inside the reactive aggregate particles and surrounding cement paste, causing cracking if their tensile strength is exceeded. Even in the presence of potentially reactive aggregate, significant expansion and concrete degradation occur only if the two other requirements are fulfilled namely sufficient alkalis and moisture, as discussed in Sect. 2.1.

The ASR is a particular form of alkali-aggregate reaction (AAR), which also includes the alkali–carbonate reaction (ACR) between alkali and

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hydroxyl ions and certain dolomitic limestones. The occurrence of ASR is very limited when compared with that of ASR and the first case was reported in the decade of 1950 in Ontario, Canada [18].

Polymers have been shown to modify cement mortar (CM) and concrete properties that may influence ASR development, particularly water absorption, mechanical properties and ionic mobility, and to delay and modify cement hydration products, as discussed in Sect. 4. Thus, their influence on ASR has been studied as part of an ongoing research program on the effects of polymer additions on mortar and concrete.

This paper presents a state-of-the-art report on ASR and polymer modification of mortar and concrete, a review of the existing literature on the polymer influence on ASR and further considerations on possible influencing mechanisms not previously covered in the existing literature.

2 Alkali–silica reaction in concrete

2.1 Factors influencing ASR-related expansion

Before discussing the possible intervening mechanisms of polymers in ASR, it is important to recall the main factors known to influence ASR.

The concentration of Na^+ and K^+ ions in the concrete pore solution reflects mainly the Na_2O and K_2O alkali oxides content of the anhydrous cement and the cement content of concrete. Other sources can supply alkalis to the pore solution of concrete, such as additions, mix water, admixtures and sometimes the aggregates themselves [18, 51]. The alkali content of the cement is usually given as an equivalent Na_2O content, calculated on the basis of the molecular weight of both oxides, $\text{Mr}(\text{Na}_2\text{O})/\text{Mr}(\text{K}_2\text{O}) = 0.658$, according to the following equation:

$$\text{Na}_2\text{O}_{\text{eq}} = \text{Na}_2\text{O} + 0.658 \text{K}_2\text{O}$$

Cements with low alkali content, corresponding to a $\text{Na}_2\text{O}_{\text{eq}}$ content lower than 0.6 % of the mass of cement (adopted as the maximum limit in ASTM specification C 150 for Portland cement whenever reactive aggregates are used), are unlikely to cause significant ASR-related expansion in concrete, as long as there are no alkalis released from other sources, and no such cases are known in the UK [26]. Another

common recommendation found in different sources [17, 26] is to limit the total alkali content, including alkali supplied by sources other than cement, to a maximum of 3 kg/m^3 . While this is known to effectively limit expansion in most cases, field structures exhibiting ASR-related damage exist with alkali content lower than 3 kg/m^3 . The actual level of prevention required depends on the aggregate type and can be determined through suitable laboratory tests [59].

Calcium hydroxide (CH) has an important role in ASR, as it supplies OH^- and Ca^{2+} ions, which are reagents in ASR, increasing the pH of the reaction environment. The following section addresses this issue in more detail.

The proportion of reactive aggregate in the total amount of aggregate can also affect the scale of the ASR-related expansion of concrete. For a given alkali content and for a specific environmental exposure, expansion in concrete increases with the proportion of reactive silica up to a critical value which leads to the maximum concrete expansion, the pessimum value, above which expansion decreases. Above the pessimum proportion, the existing hydroxide and alkali ions content in the pore solution might not be sufficient to extensively react with the high quantities of reactive silica of the aggregate particles and produce expansion of similar scale [25].

The reactive aggregate dimensions also influence the scale of ASR-related expansion in concrete. Since the attack of hydroxide ion initiates at the reactive aggregate surface, for the same reactive aggregate a higher specific surface is expected to lead to higher expansion in concrete [22].

Water also has an important role in the magnitude of the ASR in concrete, both as a reagent and a means of transport of ions and also enabling the development of the gel expansion [39].

The influence of the reduction of the water to cement ratio (W/C) on ASR is a factor still not completely understood. While with the reduction of W/C the concrete's mechanical strength increases and permeability and ion mobility decrease due to the resulting reduction in porosity, the alkali content in the pore solution is raised, thus increasing the potential for ASR [40].

An internal relative humidity (RH) of concrete of about 80–85 % is the typical range above which significant ASR-related expansion occurs [18, 26].



This means that in thin concrete elements exposed to dry environments, expansion is not likely to take place. In massive or sealed concrete elements, the residual mix water can sustain a relatively high internal RH capable of inducing expansion even in dry environments. On the other hand, immersed thin concrete elements are also not expected to be affected by ASR-related expansion. In these conditions, the leaching of the alkalis out of the concrete can be significant and inhibit expansion [18].

According to Nixon et al. [32], moisture movement in concrete can also cause the migration of alkalis and locally increase their level above that needed to induce significant expansion.

As in most chemical reactions, high temperature accelerates ASR but reduces the ultimate expansion and consequently induces less damage in concrete than those obtained from a slower expansion rate [10].

Finally, according to Ramachandran [40], porosity may also have a role on the delaying of ASR-related expansion and damaging. The voids created by air entraining agents can accommodate the expanding ASR products, thus delaying damage in concrete.

2.2 The role of calcium hydroxide in ASR

Being a complex chemical reaction, both ASR and its potential to induce damage in concrete are governed by several factors which are important to summarize and clarify.

According to the extensive research conducted in the last decades, several models have been proposed to explain ASR with different assumptions of the role of CH, but according to the authors referenced in this section, it appears to be consensual that a high Ca^{2+} content in the concrete pore solution surrounding the reactive aggregate is essential for the occurrence of expansion due to ASR.

The CH content of concrete cement paste was early considered as one of the factors influencing the damaging potential of ASR in concrete. Chatterji [9] studied cores taken from road structures in Denmark containing known reactive aggregates and exposed to significant amounts of alkalis from NaCl salt used as de-icing agent. Although some cores exhibited ASR-related damage, there were cases in which no damage was detected. Further studies revealed that the absence of free CH in the undamaged cores inhibited the ASR-related deleterious expansion. At the time, there was

just empirical evidence of the role of CH in ASR and no mechanism was known or suggested.

Chatterji [10] proposed a model of ASR mechanism focused on silica dissolution, in which the grains of reactive siliceous mineral are ionized by OH^- ions. Firstly the outer surface of the grain is ionized and then, with the increase of ionic strength of the pore solution, OH^- ions can penetrate into the grains with accompanying ingress of Na^+ , K^+ , Ca^{2+} ions and water, generating an expansive pressure. In the OH^- ionization process, the breakdown of internal bonds of quartz releases some silica (Si^{4+}), which can migrate out of the grains, relieving the pressure. Silica migration out of the grains opposes the pressure generated by the amount of materials entering the grains (OH^- , Na^+ , K^+ , Ca^{2+} and water), with the net expansion pressure being the sum of this two processes. According to Chatterji, the CH content of the pore solution, mainly from the Portland cement hydration, controls the silica migration out of the grains, as CH is both the source of OH^- ions, fundamental to the attack of the reactive silica grain, and of Ca^{2+} ions, which concentrate around the reactive grain and hinders the migration of silica out of the reactive grain besides recycling the Na^+ and K^+ ions of the ASR gel through ionic exchanges.

Bleszynski and Thomas [7] studied the influence of CH on the ASR and based the reaction mechanism on surface chemistry theory. These authors observed a “banding” effect at the aggregate-cement paste interface of reactive flint aggregate. This “banding” effect was created by a reaction rim consisting of a double layer band of calcium-rich silica gel with higher Ca/Si ratio on the outer side, followed by two other silica gel bands, one with high sodium content and other with high potassium content. Cracks were also found crossing the reacted flint aggregate and extending into the surrounding cement paste. Neither the distinct “banding” nor significant cracking was found in concrete specimens with 40 % fly ash cement replacement, which the authors suggested to be related with the reduction of CH at the aggregate-cement paste interface. In this case, “rivers” of amorphous high sodium gel were observed in the surrounding cement paste, while the high potassium silica gel was still found at the aggregate-cement paste interface.

Bleszynski and Thomas also reported, like several other authors, that CH acts as a “buffer”, maintaining a high OH^- ion concentration in the pore solution, and

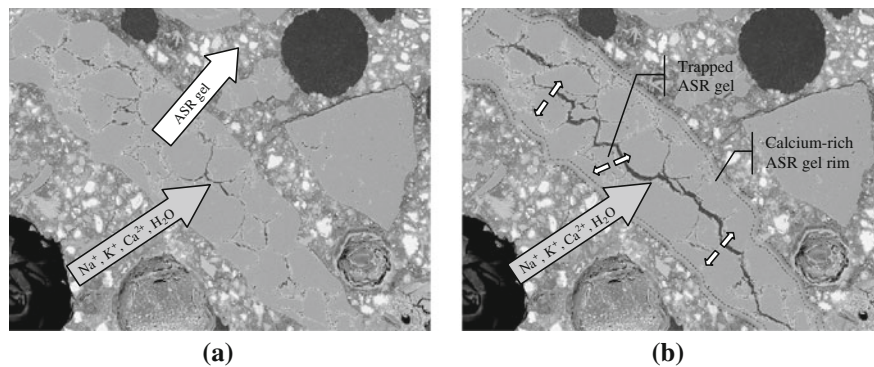


Fig. 1 Present authors' interpretation of the mechanism of expansive pressure due to ASR in the presence of CH, as proposed by Ichikawa and Miura [24]. **a** ASR mechanism in the absence of significant amount of CH, with dispersion of the ASR

supplying Ca^{2+} ions that exchange with alkalis in ASR gel, recycling and making them available for further ASR reaction.

Supporting Bleszynski and Thomas's suggestion, Struble and Diamond [56] synthesized calcium sodium silica gel and found that, contrary to the other sodium silica gels also synthesized and studied, it remained solid after water absorption in both free swell and swell under constant applied load tests. This behaviour was attributed to the lack of structural rearrangement within the affected gel, unlike the other synthesized sodium silica gels. According to the same authors, liquefied gel can easily disperse through the pore structure of the cement matrix, delaying the ASR-related damage. The test results were not clear with respect to the ability of gels with calcium to expand either more or less than the other synthesized gels.

Even though the role of CH in ASR-related expansion and the existence of a calcium-rich reaction rim around the aggregate are acknowledged, there is still no agreement on the mechanism by which they lead to the cracking of the aggregate.

Ichikawa and Miura [24] tried to explain how the existence of a semi-permeable rigid reaction rim induces cracking on the aggregates. These authors confirmed that concrete degradation due to ASR is only possible if the soft and fluid hydrated alkali silicate gel resulting from ASR develops after the formation of a rigid reaction rim around the reactive aggregate particle. Ichikawa and Miura proposed a modified model of the ASR mechanism, in which a rigid insoluble tight reaction rim is generated from the reaction of Ca^{2+} ions, present in the pore solution due

gel into the surrounding cement paste. **b** ASR mechanism in the presence of significant amount of CH, with expansive pressure generation by the trapped ASR gel and resulting cracking of the reactive aggregate particle

to the consumption of OH^- ion for the attack of reactive silica, with the alkali silicate that covers the ASR-affected aggregate. The aggregate is "packed" by this reaction rim that allows the penetration of alkalis (Na^+ , K^+), Ca^{2+} and OH^- ions and water but prevents the leakage of alkaline silicate gel.

Figure 1 is an illustration by the present authors of the role of the calcium-rich rigid reaction rim proposed by Ichikawa and Miura [24]. The reaction rim allows the continuous development of alkali silicate gel, which accumulates inside the aggregate, and due to the existence of preferential ASR developing sites in the aggregate, resulting from discontinuities such as cracks and higher reactivity or porosity sites, enough expansive pressure is eventually generated to crack the aggregate, as shown in Fig. 1b, as well as the surrounding cement paste.

This model claims that if the formation of ASR gel is completed before the formation of the rigid reaction rim, it does not cause the deterioration of concrete, as happens with the small silica-rich particles of pozzolanic materials (Fig. 1a). The relevance of discontinuities of aggregate particles in the cracking mechanism induced by ASR has been observed by Marinoni et al. [30] and, based on their existence, Dunant and Scrivener [13] developed a finite element model capable of reproducing the cracking pattern found in experimental observations.

Hou et al. [23] suggested a mechanism focused on the reaction products formed and gel repolymerization. The authors reported the existence of a similar coating around reactive aggregate grains, named "transport barrier" and probably consisting of silica-rich polymerized calcium silicate hydrates (CSH),

neither continuous nor completely impermeable, which prevents silica from migrating so rapidly out of the site of dissolution and increases the reactive silica concentration. According to Hou et al. high reactive silica concentration is needed to form ASR gel. The same study supported the idea of an ASR gel forming sequence starting with calcium-rich depolymerized CSH and CH produced from the initial cement hydration stage. As the pH of the pore solution increases during cement hydration, OH^- ion attacks the reactive aggregate grains, causing the reactive silica dissolution. Initially, silica reacts with CH to produce more depolymerized C-S-H, similarly to a pozzolanic reaction, and then, after Ca^{2+} is depleted, silica starts reacting with existing CSH to form a silica-rich polymerized CSH. Finally, the silica content in the site of dissolution further increases until gelation of ASR gel.

In the models discussed above, there are no findings or general agreement that calcium-rich ASR gel generates either more or less ASR-related expansion in concrete. However, it seems consensual that CH has a significant role in the formation of a calcium-rich ASR gel rim around aggregate particles. Along with the existence of discontinuities in the aggregate particles that form preferential reaction sites, the calcium-rich gel rim appears to be responsible for the build-up of expansive pressure, resulting in cracking of both aggregate and surrounding cement paste.

3 ASR mitigating measures

In the diagnosis and assessment of damage in concrete structures affected by ASR, one of the visual clues is the superficial “map-cracking” pattern typical of ASR-affected unreinforced concrete. This pattern can be altered by restrains in concrete, such as applied stress, adjacent concrete with different ASR-related expansion rate and reinforcement [26], but it always increases the permeability of the concrete, further accelerating ASR and any potential deleterious phenomena with external origin, thus reducing the concrete durability and the service life of the structure. As ASR continues, ASR gel exudation and efflorescence may also appear.

ASR mitigating or precautionary measures (M1–4, Table 1) consist of controlling the alkali content

of the binder (M1), using a non-reactive aggregate combination (M2), whose availability is often limited due to geographical location, environmental concerns or transport costs, preventing moisture access (M3) and ensuring a non-expansive gel by modifying its characteristics (M4), e.g. through the use of chemical admixtures (such as lithium salts) or reduction of available CH.

According to Ian Sims at a recent course on concrete dams subjected to AAR, the soon to be published RILEM International Specification AAR-7.1 establishes four levels of precaution against ASR (P1–4, Table 1) based on the combination of three environmental categories (E1–3, Table 1) and three structural risk categories (S1–3, Table 1). For each level of precaution (P1–4, Table 1), at least one of four precautionary measures (M1–4) is recommended, except for the P1 level which requires no special precautions.

Alkali reduction (M1, Table 1) is usually achieved with the replacement of part of the cement with supplementary cementitious materials (SCMs) such as silica fume, fly ash, metakaolin and other pozzolans.

The main inhibition mechanism of SCMs in ASR-induced expansion is the reduction of Na^+ , K^+ and OH^- ions concentration in the pore solution [18]. This mechanism can be partially justified by the alkali dilution as the result of the replacement of part of the cement with SCMs of lower $\text{Na}_2\text{O}_{\text{eq}}$ content, but other explanations exist, as even SCMs with higher $\text{Na}_2\text{O}_{\text{eq}}$ content than the cement replaced can lead to ASR-related expansion reduction [12]. The CaO/SiO_2 ratio of the CSH formed in the pozzolanic reaction also influences the alkali content of the pore solution. There is evidence that the CSHs formed in the presence of SCMs (having a reduced CaO/SiO_2 ratio) have an increased capacity to accommodate alkalis and further reduce the OH-content of the pore solution [40].

Although it is consensual that SCMs are effective in this role, the variability of the nature and properties of these materials and of the reactive aggregates worldwide has not allowed the establishment of an international standard for the dosage of SCMs required to control ASR.

Ohama et al. [33] studied the effectiveness of lithium admixtures such as sodium silicofluoride (Na_2SiF_6), alkyl alkoxy silane and lithium carbonate (Li_2CO_3), lithium fluoride (LiF) and lithium hydroxide (LiOH) in mitigating ASR-related expansion in CM. It was concluded that the ASR gel formed in the presence of

Table 1 Precautionary measures and levels of precaution based on the structural risk and environment according to RILEM International Specification AAR-7.1

Environment/structural risk	E1 protected from external moisture	E2 exposed to external moisture	E3 exposed to external moisture and additionally to aggravating factors	Precautionary measures
S1—low risk e.g. temporary or short life structures	P1—no special precautions	P1	P1	M1—controlling alkali content
S2—normal risk e.g. most buildings and civil engineering structures	P1	P2—normal level of precaution: one of four precautionary measures	P3—special level of precaution: same as P2 plus design to resist aggravating factors	M2—Non-reactive aggregate combination M3—preventing moisture access
S3—high risk e.g. nuclear installations, dams, tunnels, exceptionally important bridges and viaducts	P2	P4—extraordinary level of precaution: combined application of two or more precautionary measures	P4	M4—ensuring non-expansive gel

the chemical admixtures added to mortar appeared to present a distinct and less cracked microstructure due to its conversion to an insoluble compound.

According to a recent critical review by Feng et al. [15] of the studies on the mechanism by which lithium inhibits the ASR-related expansion in new concrete, lithium salts react with silica to form a lithium CSH gel which seems not produce expansion in mortar or concrete laboratory specimens. However, the effectiveness of lithium compounds strongly depends on the kind of lithium compounds used, the lithium to alkali molar ratio ($[Li]/[Na + K]$), the nature of the reactive aggregate and also on the Na_2O_{eq} content of the mortar or concrete mixture. These research findings demonstrated that among the several lithium salts studied, LiOH and $LiNO_3$ seemed to be the most effective in suppressing ASR-related expansion. A minimum $[Li]/[Na + K]$ in the range of 0.6–1.2 showed to be effective in suppressing the ASR-related expansion for most of the lithium salts studied.

Despite the existence of an agreement about the effectiveness of lithium salts, the mechanisms involved in the ASR-related expansion reduction effect remain insufficiently explained, as it is frequently referred to as a result either from the formation of a non-expansive or non-swelling gel or from the insolubility of the gel.

4 Polymer action on ASR

Polymers have been used for modification of cementitious materials for many decades, but the available

studies on polymer-cement mortars (PCMs) far exceed those on polymer-cement concrete [14, 29, 50]. Due to this and to the fact that short-term alkali-reactivity tests are carried on mortar bar specimens, the discussion on the potential polymer action on ASR is based on data from studies of PCMs.

A significant study of PCM properties has already been carried out by several authors, such as Wang and Wanget al. [61, 62] from China, Ohama [33, 34] from Japan, Afridi et al. [1–3] from Pakistan, Knapen and Van Gemert [27] from Belgium, Plank and Gretz [38] from Germany, Rossignolo [46] from Brazil, Aguiar [4] and Ribeiro et al. [44] from Portugal and Fowler [19] from U.S.A., just to name a few.

Polymer-cement mortars (PCMs) are traditional mortars with polymer as a new component and that is usually added to the mixing water with a dosage between 10 and 40 % by mass of cement. Polymers that are being used with cement are usually polymer dispersions (latexes), redispersible polymer powders, water-soluble polymers, liquid resins and polymers [34].

Generally, polymer modification affects the properties of fresh mortar by improving the workability, extending the setting times and causing heavy air entrainment in the absence of anti-foaming agents. Also, the addition of polymers may lead to the improvement of the properties of hardened mortar, such as lower water absorption, higher tensile and flexural strengths, adhesion and chemical resistance but with no increase in compressive strength or modulus of elasticity.

The improved properties of hardened mortar by polymer modification are the result of a polymeric film

being formed amidst aggregates and cement hydration products. The continuity of the film increases for increasing polymer to cement ratios (P/C) and for a P/C ratio of $\sim 10\%$ an effective co-matrix of polymer and cement paste can be observed [3, 6, 63].

Other parallel effects of polymer addition in the microstructure of CM have been presented by several studies, which can be of importance to the study of polymer action on ASR in CMs and are discussed in the next section.

4.1 Calcium hydroxide content and crystal morphology

It is well known that polymers may delay the cement hydration process and influence the morphology of the hydration products [34, 38, 52, 61, 62]. With particular relevance to ASR, several researches have shown that PCMs have lower CH content than comparable unmodified CM, which might reduce ASR-related expansion if the formation of a calcium-rich reaction rim around the grain of reactive siliceous aggregate is inhibited, as described in Sect. 2.2.

Polymers with carboxylate groups have been shown to chemically react with Ca^{2+} ions from the cement hydrates [20, 28, 34, 63], and thus the CH quantity produced is expected to be lower. The reduction of CH quantity in PCMs when compared to unmodified CM was detected by Ray et al. [42] in X-ray diffraction (XRD) and differential scanning calorimetry (DSC) tests of mortars modified with a variety of polymers and Yang et al. [63] observed a similar behaviour in Fourier transform infrared (FT-IR) analysis of styrene-butadiene (SB) PCMs.

Afridi et al. [1, 2] confirmed this behaviour of CH reduction in PCMs and also reported the layered deposition of CH crystals arranged in stacks in a much more compact and undistorted manner in the presence of polymer additions. Like Afridi et al. Knapen and Van Gemert [27] reported that it is assumed the polymers acted as an adhesion promoter between the different layers of the CH crystals, through polymer “bridges” for high P/C ratios, resulting in more complex and compact crystal structures.

Afridi et al. and Knapen and Van Gemert [27] also found well developed CH crystals growing in the pores of PCMs, a feature not so clearly observed in unmodified CM, which was attributed to the possible

existence of the polymer film in the co-matrix hindering the mobility of CH. For the same reason, ionic mobility in pore solution of PCMs might also be reduced, as reported by Yang et al. [63], thus reducing the rate of ASR and the resulting related expansion.

Ribeiro [43] also found lath-like and euhedral shaped CH crystals growing in a more compact manner in PCMs (Fig. 2a), instead of randomly, as observed in an unmodified CM with similar properties (Fig. 2b).

Besides results showing the chemical interaction between Ca^{2+} ions and polymer in PCMs, Larbi and Bijen [28] also observed that styrene-acrylate polymer increased the OH^- content of the pore solution, which, if significant, can have a detrimental effect in ASR, increasing the potential for dissolution of the aggregate grains. However, Larbi pointed out that this behaviour should depend on the type of polymer, as the use of a polyvinylidene chloride (PVDC) polymer actually reduced the OH^- ion content in the pore solution of the cement paste.

According to Rossignolo [46], the reduction of CH content in the interfacial transition zone (ITZ) between cement paste and aggregate can be attributed to the concentration of polymer film in the region due to the higher water quantity, as a result of the wall effect. It was also observed a reduction of the ITZ's thickness in PCMs with increasing SB polymer dosage, which locally decreases porosity, not allowing extensive CH crystal growth.

Polymer modification is also known to reduce the thickness of the ITZ in PCMs [46, 58]. Although the mechanical and transport properties of the ITZ differ from those of the bulk cement paste due to its higher porosity and greater deposition of CH crystals, according to recent studies [11, 41] the differences are not as significant as once thought and their influence on the mechanical and transport properties of mortar and concrete appears to be marginal. It is also not clear that any local differences in mechanical or transport properties at the ITZ would affect the development of ASR. However, besides its reduced extension, Rossignolo [46] observed that the ITZ in PCMs is characterized by a lower CH content than in unmodified mortars and both features may lead to a reduction in calcium content of ASR gel, thus influencing its structure and reducing mortar expansion according to the mechanisms discussed in Sect. 2.2.

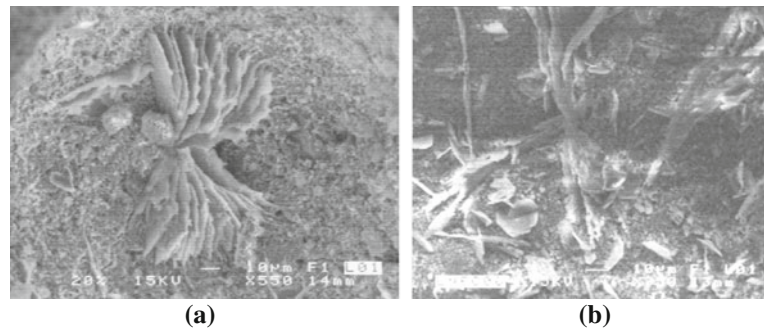


Fig. 2 CH crystal development in the pores of PCMs and unmodified mortars. **a** MEV image of CH crystals growing inside a pore of an SB PCM with a P/C ratio of 20 % [43]. **b** MEV image of CH crystals growing inside a pore of an unmodified mortar [43]

4.2 Water mobility

The lower water absorption of PCMs can be a desirable property for the inhibition of ASR-related expansion, reducing the amount of available water for the ASR gel to absorb and thus the potential for expansion and damage. However, as a polymer film begins to form as soon as dry curing conditions are verified, it creates a barrier not only to the ingress of water, but also to the exit of the free internal water of the mortar. The physical barrier created by the polymer film provides the PCM with an internal cure that can reduce its drying shrinkage and consequently its initial cracking which has been identified as a potentially ASR-reducing property by Song et al. [53]. However, on the other hand, it should provide retention of moisture for longer periods, increasing the availability of water for ASR gel expansion particularly in larger concrete elements.

As migration of moisture to the outside is governed by water vapour permeability and increasing polymer content reduces the characteristic value of this property and water absorption [34], an optimum polymer content should be sought.

4.3 Porosity

As the pores of the CM can accommodate the expanding ASR gel and thus delay the deleterious damage of expansion, the influence of polymer addition on the porosity of PCMs should also be taken into account in its potential action on ASR.

Due to the surfactants present as emulsifiers or stabilizers on the surface of polymer particles of mortar and concrete-modifying polymer additions, a higher amount of air is usually entrained in PCMs

compared to unmodified CM. Even though anti-foaming agents seem to be incorporated in most commercially available polymer additions, the resulting air content is still higher than the air content of unmodified CM, depending on the type of polymer, P/C ratio, fine aggregate dimension and its nature, mixing time and manufacturer [44].

The higher amount of entrained air in PCMs is mainly reflected in the larger pore dimensions associated with this phenomenon. Mercury intrusion tests usually indicate that PCMs have a total porosity similar to that of unmodified CM in the range of open pores smaller than 10 μm , albeit more homogenous and with a shifting of the porosity peak to smaller pore dimensions [36, 42, 45, 47]. The reduced pore volume in the capillary range and consequently the reduced capillary water absorption should result from polymer particles filling the pores in this range, as Ollitrault-Fichet et al. [36] found that after polymer pyrolysis the volume of pores with dimensions similar to those of polymer particles ($\sim 0.2 \mu\text{m}$) increased and pore volume distribution resembled that of unmodified mortar.

4.4 Mechanical properties

Generally, PCMs exhibit higher tensile strength and resistance to cracking than unmodified CM [37, 44, 54]. It is considered that these improved properties are a result of both the higher adhesion between cement paste and aggregate [5] and the crack bridging capability of the existing network of polymer film [49] in PCMs.

The improved adhesion between cement paste and aggregate in PCMs may be explained by the accumulation of polymer particles with colloidal dimensions at this interface due to the wall effect around the

aggregate particles. Higher adhesion allows a better stress transfer between cement paste and aggregate, increasing the stress transferred to the aggregate particles. However, the improvement seems to depend on the dosage and type of polymer, the curing conditions and the nature of the aggregate [57]. The crack bridging capability of the network of polymer film in PCMs has been observed by Schorn and Schiekell [49] and delays the widening of cracks from their onset.

As the improvement of both resistance to cracking [53] and tensile strength [16] have been previously identified as potentially having an inhibiting or delaying effect on ASR, polymer modification of concrete may lead to reduced or delayed ASR-related damage.

Other mechanical properties such as the modulus of elasticity and the creep behaviour may influence the expansion of mortar or concrete under the effect of ASR. Indeed, recently developed ASR numerical models [8, 13, 21, 31] acknowledge and take into account the influence of these mechanical properties on the predicted ASR-related expansion.

Both the tensile and compressive modulus of elasticity of PCMs are increasingly reduced with increasing polymer dosage [34, 44]. It is thus expected for the internal stress developed due to ASR to result in higher expansion in PCMs with significantly lower elasticity modulus.

PCMs can also exhibit a significantly lower creep strain than unmodified CM, but this behaviour should depend on the nature of the polymer used [34]. As ASR expansion occurs over long periods of time, a lower creep strain may reduce the long-term expansion of PCMs compared to an unmodified CM if an equal expansive pressure is considered. However, due to their potential significantly lower modulus of elasticity, the ASR-related expansion of PCMs is expected to be higher than that of unmodified CM right from the onset of ASR.

4.5 Previous studies on ASR in PCMs

Amongst other chemical admixtures, Ohama et al. [33] studied the effect of different dosages of an SB polymer on the expansion of CM prisms subjected to an ASR rapid test by adding the necessary NaOH quantity to raise the $\text{Na}_2\text{O}_{\text{eq}}$ content of the mortar mixes to 2.0 % of the mass of cement and autoclaving

the specimens at 128 °C and 2.5 kgf/cm² during 4 h, after an initial 24 h moist curing period. As shown in Fig. 3, these authors concluded that up to a 15 % P/C ratio, the SB polymer increased expansion, while a P/C ratio of 20 % resulted in a reduction of ~30 % compared to an unmodified CM.

Ohama et al. explained this reduction as being the result of the restraint effect of the network of polymer film on the widening of cracks developed in the polymer-cement co-matrix, suggested by the detection of polymer “bridges” in mortar cracks. Similar polymer “bridging” can be found between aggregate and cement paste as shown in the SEM image of Fig. 4.

However, according to Ribeiro et al. [44], the restraint effect of the polymeric “bridges” that are created in the ITZ between cement paste and aggregate might not be significant, since the polymeric film formed exhibits a much lower Young modulus than that of the cement paste.

As discussed in the previous section, even though Ohama et al. observed increasing mortar expansion for P/C ratios up to 15 %, the expansion of PCMs in standard alkali-reactivity tests is expected to be higher than that of comparable unmodified mortars due to their lower elasticity modulus. However, under these circumstances the expansion results are not directly linked to the degree of ASR-related damage, as PCMs may also have higher tensile strength and resistance to microcracking.

Given the fact that the damage due to ASR is the main concern (and not expansion itself), any performance comparison between PCMs and unmodified mortars should not rely on expansion results alone, but instead on

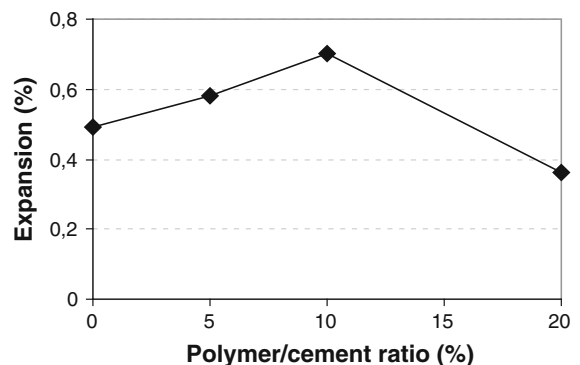


Fig. 3 Expansion of 2.0 % $\text{Na}_2\text{O}_{\text{eq}}$ SB-modified mortar prisms after autoclaving procedure (adapted from [33])

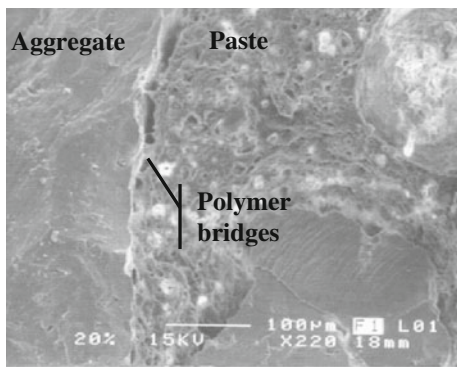


Fig. 4 MEV image of polymer “bridges” at the ITZ, between an aggregate and the cement paste of an SB PCM with a P/C ratio of 20 % ($\times 220$) [44]

a more thorough assessment including the degree of degradation of the material. To this effect, scanning electron microscope (SEM) observations or more advanced techniques such as computed tomography scanning (CT) should be helpful. Marinoni et al. [30] and Voltolini et al. [60] developed a method of quantitative characterization of damage resulting from ASR, including aggregate dissolution and microcracking, based on 3D images obtained from CT scanning which more precisely detects the extent of microcracking.

The fact that for a P/C ratio of 20 % Ohama et al. [33] found a significant expansion reduction compared to the unmodified mortar shows that the presence of polymer is responsible for conflicting mechanisms affecting ASR. It is possible that, compared to a 15 % P/C ratio, the effectiveness of some of the previously discussed potential inhibiting mechanisms, such as reduced ionic mobility and water absorption, was suddenly increased for a P/C ratio of 20 %.

It is also not clear if the procedure followed by Ohama et al. allowed proper curing of the polymer, as a dry curing period is usually required to allow coalescence of polymer particles.

Saccani and Motori [48] studied the effect of an epoxy polymer addition on ASR-related expansion of CM prisms using Pyrex glass reactive aggregate and found a 20 % P/C content to significantly reduce ASR-related expansion (Fig. 5), almost to the same level as a comparable unmodified CM using sound aggregate. The ASR-related expansion was induced by increasing the $\text{Na}_2\text{O}_{\text{eq}}$ content of the mortar mixes to 2.4 % of the cement mass by adding NaOH to the mixing water and subjecting the resulting specimens to a 30 day cure at 80 °C and 100 % RH, after a mixed initial moist and

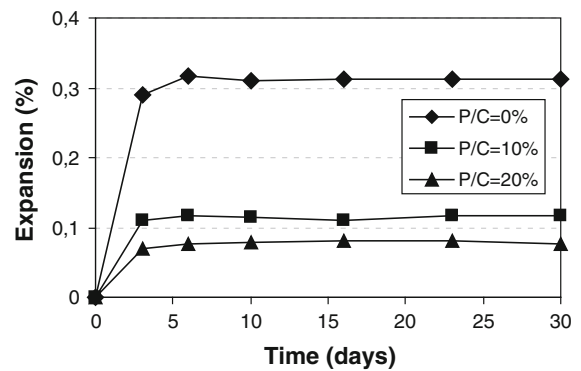


Fig. 5 Expansion of 2.4 % $\text{Na}_2\text{O}_{\text{eq}}$ epoxy-modified mortar prisms in 80 °C and 100 % RH environment (adapted from [48])

semi-dry curing period to allow both the cement hydration and the coalescence of polymer particles.

Thermogravimetric tests showed that the CH content of the PCMs was significantly lower than that of an unmodified CM, which was pointed out as the main potential inhibiting mechanism of polymer addition on ASR-related expansion.

The authors also reported an increased pore volume for the epoxy-modified mortar in the overall range of pore dimensions analyzed (0.003–50 μm). The higher pore volume compared to the unmodified mortar could also have increased either the volume of voids available to accommodate ASR expanding products or the leaching of alkalis away from the PCM specimens in the humid conditions, thus contributing to the observed reduced expansion. Epoxy-modified mortars have also been reported to have self-healing properties [35], which may contribute to an increased resistance to crack opening and thus to reduce expansion.

The leveling of expansion observed after day 3 is not usually expected in short-term alkali reactivity tests on specimens with moderately reactive aggregates and was probably due to the highly reactive Pyrex glass used by Saccani and Motori, which is known to have a pessimum proportion. The significantly lower expansion in the epoxy-modified specimens was thus a result of their lower expansion rates during a very short test period and further data would be needed to assess the evolution of expansion rates and confirm the apparent inhibiting of ASR.

Even though both Ohama et al. and Saccani and Motori directly added NaOH to the mixing water in their respective tests, in short-term alkali-reactivity

tests ASR is usually accelerated by immersion of test specimens in NaOH solution at high temperatures which acts as an external source of alkalis and hydroxyl ions. Under these conditions, any potential differences in water sorptivity between PCMs and unmodified mortars would result in ASR being more aggressively promoted in specimens with higher sorptivity. It should be assured that the analysis of the expansion results take these differences into account and that the influence of high temperature on the water absorption of both materials is known.

5 Conclusions

Polymer modification leads to the improvement of several mortar and concrete properties that have been linked to a potential for inhibiting or delaying effects on ASR and related damage.

CH has been acknowledged by several authors to increase the potential for ASR and thus the reduced CH content achieved with polymer modification, particularly at the ITZ, may have an inhibiting effect on ASR. There is however a concern over the possibility of some polymers increasing the OH⁻ content of the pore solution, thus increasing the silica dissolution.

Polymer additions are also known for their air-entraining effect which increases the voids available to accommodate the expanding ASR gel, a mechanism previously identified as having a relief effect on ASR-induced pressure and expansion.

Despite its air entraining effect, polymer modification reduces the water absorption of mortar and concrete, thus potentially limiting the water available to take part in ASR gel expansion. However water vapour permeability is also reduced, promoting retention of existing moisture in large concrete elements. Field implementation of polymer to reduce concrete susceptibility to ASR would then need careful consideration to balance vapour permeability and water absorption.

Polymer-modification also leads to improved mechanical properties, such as higher tensile strength and resistance to microcracking and lower creep strains, which have previously been identified as potentially having a delaying effect on the damage resulting from ASR-related expansion.

However, as laboratory alkali-reactivity tests usually rely solely on expansion results, the performance of polymer-modified mortar and concrete may be misinterpreted due to their lower elasticity modulus, which implies higher strains for similar expansive pressure compared to unmodified mortar or concrete.

Due to all the differences in mechanical properties compared to unmodified mortar and concrete, the correct assessment of the performance of polymer-modified concrete and mortar under ASR requires quantitative damage analysis, e.g. based on SEM or CT scanning methods.

The differences in water absorption between unmodified and polymer-modified concrete and mortar also need to be considered, particularly in short-term laboratory tests using high temperature NaOH solution baths, where ASR is more aggressively promoted in specimens with higher absorption. It's also not clear if the water absorption of both materials is influenced in the same manner by high temperature.

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