Alkali-silica reaction (ASR) expansion: Pessimum effect versus scale effect
Xiao Xiao Gao, Stéphane Mulon, Martin Cyr, Alain Sellier

To cite this version:
Xiao Xiao Gao, Stéphane Mulon, Martin Cyr, Alain Sellier. Alkali-silica reaction (ASR) expansion: Pessimum effect versus scale effect. Cement and Concrete Research, Elsevier, 2013, 44, pp.25–33. 10.1016/j.cemconres.2012.10.015. hal-01724652

HAL Id: hal-01724652
https://hal.insa-toulouse.fr/hal-01724652
Submitted on 23 Mar 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Alkali-silica reaction (ASR) expansion: pessimum effect versus scale effect

Xiao Xiao Gao a, Stéphane Multon a*, Martin Cyr a, Alain Sellier a

(a) Université de Toulouse; UPS, INSA; LMDC (Laboratoire Matériaux et Durabilité des Constructions); 135, avenue de Rangueil; F-31 077 Toulouse Cedex 04, France

Abstract

The effect of aggregate size on ASR expansions has been largely studied and conflicting results exist concerning the aggregate size that leads to the highest ASR expansion. Most of the research works clearly show a pessimum effect of aggregate size on ASR expansion. However, all the results available in the literature were obtained using different experimental conditions and the combined effects of other important parameters, such as specimen size used in the expansion tests, have often been neglected. This paper aims to investigate the combined effect of specimen size and aggregate size on ASR expansion. Experimental results highlight a scale effect, a combination of the effects of aggregate size and specimen size on ASR expansion. This scale effect appears to be influenced by the reactive silica content of the aggregate. Modelling at microscopic level is used to propose a quantification of this effect.

Keywords: alkali-silica reaction (ASR), particle size, specimen size, expansion, scale effect

* Corresponding author. e-mail address: multon@insa-toulouse.fr (Stéphane Multon)
1. Introduction

Alkali-Silica Reaction (ASR) is a deleterious chemical reaction occurring in all types of structures that contain alkali-reactive aggregates: dams, bridges, roads, breakwaters, etc. The mechanism of expansion can be described in three main steps [1-4]: the diffusion of ionic species (Na\(^+\), K\(^+\), OH\(^-\), Ca\(^{2+}\)) into the aggregates, the disruption of the silanol and siloxane bonds contained in the reactive silicate, and the reaction of alkali silicate with ionic species (Na\(^+\), K\(^+\), Ca\(^{2+}\)) to form ASR gels. ASR gel induces pressure in the aggregate and in the cement paste, leading to stresses and thus cracking. ASR expansion depends on numerous parameters (amounts of alkali, reactive silica and water present, aggregate and specimen sizes, etc.).

It seems that the range of aggregate size causing the highest ASR expansion varies with the nature and composition of the aggregate. Numerous papers [5-23] discuss the effect on ASR expansion of particle sizes of reactive aggregates like opal [5-12], various kinds of silica glass, fused silica and waste silica glass, and so on [13-24]. Some research has shown that the expansion induced by ASR increases as the reactive particle size is reduced [9,14,17,19]. Some authors obtained insignificant expansion when the sizes of the reactive particles were under 50 to 150 µm [11,13,15,22]. Furthermore, the use of powder from reactive aggregates like pozzolans, with particle sizes up to about 100 µm, has been developed to counteract the effect of ASR [15,18,21]. Only a few exceptions with very small particles led to significant ASR expansions, all involving opal aggregates [5-7, 12]. Other research works have shown a pessimum effect for various types of aggregates, with pessimum values occurring in a wide interval of particle sizes [4,7,8,10-13,16,20,23,24]. It is observed that, in some cases, the most damaging size, leading to the highest ASR expansion, reaches more than 1 mm. The effect of “specimen size” has been much less studied [25-28]. Experiments performed with different
‘aggregate size to specimen size’ ratios show the effect of the size of the specimens on the ASR expansions measured. Lower expansions were measured on the smaller specimens [25,26].

First, a literature review showed that conflicting results exist concerning the most damaging reactive aggregate size, which leads to the highest ASR expansion. Secondly, experimentation performed by Zhang et al. [26] suggested that the two effects of aggregate and specimen sizes are combined. Therefore, the difficulty in generalizing results on the effect of the particle size of reactive aggregates could be explained by the differences in experimental conditions, and particularly the combined effects of aggregate size and specimen size on ASR expansion. This paper aims to investigate and quantify this scale effect and the influence the reactive silica content of aggregate has on the effect, in order to gain a better understanding of expansion tests.

The development of an ASR model at the microscopic level is a major concern of researchers trying to understand the mechanisms involved in the ASR and to predict future expansion. Previous modelling investigated the different aspects of the reaction: the mechanical consequences of ASR [29-32], the chemical mechanisms driving the attack of the aggregate by hydroxyl ions [33] and their coupling [34-38]. These works do not take into account the permeation of ASR gels in cracks which could be the main cause of the decrease of expansion by pessimum or scale effects. The concepts of fracture mechanics can explain the cracking phenomenon in the cases of aggregate in infinite matrix [39, 40] or of central penny-shaped crack in sphere [41]. However, it is difficult to apply such models in the cases of specimens containing aggregates with numerous interactions (interactions with other neighbour aggregates and with specimen boundaries). The experiments presented in this paper were used to point out the dependence of expansion with aggregate and specimen sizes. These results are explained by fracture mechanics concepts. The teachings pointed out by fracture mechanics
are then used to propose a simplified relationship to take into account the scale effect in an analytical modelling. Finally, the experimental results are used here to calibrate and discuss the validity and the capability of the model.

2. Experimental conditions and results

2.1 Experimental conditions

Expansion was measured on mortar prisms with a water/cement ratio of 0.5 and a sand (1512 kg/m$^3$) / cement (504 kg/m$^3$) ratio of 3. Mixtures were adjusted by adding NaOH to the mixing water in order to have the same alkali concentration in the pore solution and in the storage solution. For the reference specimens, the sand was composed of the non-reactive marble only. For all the other specimens, the sand contained 30% of reactive aggregate and 70% of non-reactive marble. The prisms were stored in NaOH solution at 60°C. The expansion measurements were performed after the prisms had cooled to 20°C (~12 h) in the NaOH solution. Each variation of length value was calculated as the mean of three values from three replicate specimens measured using the scale micrometer method (specimens had shrinkage bolts in the two extremities) [42,43]. The experimentation presented in this paper aimed to study three particular points:

**Effect of alkali concentration**

As explained above, the specimens were kept immersed in NaOH solution. The aim of this part was to study three NaOH concentrations for immersion close to the standard conditions of 1 mol/l (0.77, 1 and 1.25 mol/l). Reactive siliceous limestone was used to study the effect of alkali concentration on ASR expansion. The specimen and aggregate sizes were respectively 20 x 20 x 160 mm and 315-1250 µm (15% of 315-630 and 15% of 630-1250 µm). Eighteen specimens (nine reactive and nine reference specimens) were used for this part of the experimentation.
Effect of reactive silica content

The second point concerned the effect of the reactive aggregate nature on ASR expansion. Four reactive aggregates with different reactive silica contents were chosen and tested. Opal (O) is known to be very reactive and to give large expansion if the amount of available alkali is sufficient. Quartzite (Q) and siliceous limestone (SL) are usually less reactive but can exhibit significant expansion in concrete. Quartz aggregate (QA), which contains mostly quartz, is considered as non-reactive. The silica contents of the aggregate [43] are given in Table 1. The aggregates were used to cast 20x20x160 mm specimens with 315-1250 µm reactive aggregate (15% of 315-630 and 15% of 630-1250 µm). The fifteen specimens were kept in 1 mol/l NaOH solution.

Combined effect of aggregate and specimen sizes

Four reactive aggregate size classes: C1 (0-315 µm), C2 (315-630 µm), C3 (630-1250 µm) and C4 (1250-2500 µm) and three specimen sizes: 20x20x160 mm, 40x40x160 mm and 70x70x280 mm were used to research the combined effect of aggregate and specimen sizes on ASR expansion. The forty-five specimens (thirty-six reactive and nine non-reactive specimens) were stored in 1 mol/l NaOH solution. Siliceous limestone was used as the reactive aggregate.

2.2 Experimental results

2.2.1 Effect of the alkali concentration

The final expansions for the three NaOH concentrations of 0.77, 1.0 and 1.25 mol/l were 0.67%, 0.64% and 0.60% respectively (Figure 1). The difference between two consecutive concentrations appeared to be small considering that the standard deviation for the specimens was in the range of 0–0.02%. Between 0.77 and 1.25 mol/l, the alkali concentrations could be considered to have little influence on ASR expansions in conditions of abundant alkali.
2.2.2 Effect of the reactive silica content

The ASR expansions obtained for the four aggregates are plotted in Figure 1. The specimens containing opal were the most reactive, with fast expansion and an asymptotic value of about 1.35%. The specimens with siliceous limestone exhibited rapid expansion, but the final expansions were lower (about 0.6%). The specimens with quartzite aggregate presented a slow expansion rate but reached a final expansion of about 0.55%. ASR expansion of the specimens containing quartz aggregate was about 0.14%. By the end of the experiment, the specimens containing opal were seriously damaged and cracked (crack width of about 425 µm) while the other specimens showed cracks with widths smaller than 10 µm (Figure 2). The reliability of measured expansions could have been affected by such cracking. However, the coefficient of variations obtained for three specimens was lower than 5%. It shows that the expansion scattering stayed quite small in spite of the large cracks.

2.2.3 Combined effects of aggregate and specimen sizes

The ASR expansions obtained for mortars containing the reactive siliceous limestone with various aggregate sizes and cast in specimens of different sizes are given in Figure 3. First, the specimens containing small reactive particles (0-315 µm) had the smallest expansion (lower than 0.15%), confirming results found in the literature. The ASR expansions were significant and higher than 0.5% for the other three aggregate sizes. Concerning final ASR expansion, the largest specimens showed the highest ASR expansion (Figure 4). This was particularly significant on the large aggregate class 1250-2500 µm (ASR expansions were twice as large for the 70x70x280-mm specimens as for the others). Moreover, ASR expansions presented a pessimum effect with the reactive aggregate size (with a final expansion larger for the aggregate size 315-630 µm than for 1200-2500 µm) for measurements performed on the smallest specimens (20x20x160 mm, 40x40x160 mm) but...
not for the largest ones (Figure 4). These observations show the significant combined effect of specimen size and aggregate size.

### 2.2.4 Scale effect

**Mechanisms**

In order to understand the scale effect (combination of the aggregate- and specimen-size effects on expansion), the ASR development can be described in four phases:

1. Ions (hydroxyls and alkalis) from the pore solution diffuse into the aggregates whatever the reactive silica distribution in the aggregate (uniform or in veins – Figure 5-a).

2. Ions react with reactive silica and ASR gel is created in and/or around the aggregate (according to the distribution of the reactive silica in the aggregate, a part of the reactive silica can even be in direct contact with cement paste – Figure 5-b). A part of the gel can fill the connected porous volume surrounding the aggregate without leading to damage [33-35,39] (Figure 5-b) and also a part of the porosity of the aggregate close to the reactive site which can lead to the cracking of veined aggregates [41]. This can explain why the smallest aggregates lead to small expansion. For the same reactive silica content, more of the gel can migrate in the connected porosity for the smallest aggregates than for larger aggregates. Thus, a small amount of ASR gel is able to cause expansion [23,34,39]. It is easier for the cement paste to accommodate ASR gel when the gel is created by a large number of small sites rather than by a small number of scattered, larger sites.

3. ASR gel exerts pressures on the surrounding aggregate and cement paste when a part of the connected porosity is filled (Figure 5-c) and the gel can no longer move in the porosity. In order to assess the gel pressure $p_g^a$ for the aggregate of size $a$, an analogy with previous modelling [23, 34] can be made. In these works, the ASR mechanical effect was assumed to be an imposed strain of the aggregate on the surrounding cement paste equal to:
\[
\varepsilon_{imp}^a = \frac{\langle V_{\text{gel}}^a - V_{\text{poro}}^a \rangle^+}{V_a}
\]

\(\langle X \rangle^+\) is the positive part of \(X\): if \(X < 0\), \(\langle X \rangle^+ = 0\) otherwise \(\langle X \rangle^+ = X\)

\(V_{\text{gel}}^a\) is the volume of ASR gel formed in reactive aggregates and \(V_a\), the volume of the reactive aggregate, \(V_a = \frac{4}{3} \pi \cdot R_a^3\) (if spherical shape is assumed for aggregate).

\(V_{\text{poro}}^a\) is the volume of the porosity in which the ASR gel can migrate without causing expansion. It was assumed that the proportion of gels filling the porosity connected to the reactive sites (cement paste and aggregate) without creating pressure was the total volume of porosity filled by the gel with an equivalent thickness \(t_c\), which was assumed to be independent of the aggregate size:

\[
V_{\text{poro}}^a = \varphi \frac{4}{3} \pi \cdot (R_a + t_c)^3 - R_a^3
\]

where \(\varphi\) is the porosity of the mortar. In reality, it includes a part of aggregate porosity but, by sake of simplicity, the model considers the thickness \(t_c\) as the average distance of gel penetration which should depend on the gel pressure: penetration is more or less difficult due to the ASR gel viscosity, its surface tension and the size of the pores of the aggregate and of the cement paste surrounding the reactive sites [39]. Once the gel reaches \(t_c\), it cannot penetrate in the paste anymore due to the combination of these three main parameters. They were assumed to be the same for all the aggregates and that’s why the equivalent thickness \(t_c\) was assumed to be independent with the aggregate size.

In order to assess the effect of ASR-gel on the cement paste in term of pressure, similar relationship can be used. \(p_g^a\), the gel pressure can be assumed to be proportional to \(M_g\) the gel bulk modulus and to the increase of volume due to ASR-gel production:

\[
p_g^a(t) = M_g \left\langle V_{\text{gel}}^a - \varphi \frac{4}{3} \pi \left((R_a + t_c)^3 - R_a^3\right)\right\rangle
\]
$V_{a}^{gel}$, the volume of ASR gel formed in reactive aggregates, is proportional to the number of moles of ASR gel formed after the attack of the reactive silica:

$$V_{a}^{gel} = n_{a}^{gel} \cdot V_{gel}^{mol}$$ (4)

with $n_{a}^{gel}$ (mol): the number of moles of ASR gel produced by the aggregate $a$ and $V_{gel}^{mol}$ (m$^3$/mol): the molar volume of the gel.

The number of moles of ASR gels produced by the reaction is defined by the number of moles of silica attacked by alkalis and can be taken proportional to $s$ the reactive silica content (in mol/m$^3$):

$$n_{a}^{gel} = \frac{4}{3} \pi R_{a}^{3} \cdot s \cdot \zeta(t)$$ (5)

$\zeta(t)$ is the chemical advancement of the alkali-silica reaction (which depends on temperature, moisture and alkali conditions and is assessed by the diffusion of ionic species in the aggregate and by the time necessary for the attack of the reactive silica by hydroxyl ions and for the formation of ASR-gels [34]).

Finally, $p_{g}$, the gel pressure at the time-step $t$, can be assessed from:

$$p_{g}^{a}(t) = M_s \left( \frac{4}{3} \pi R_{a}^{3} \cdot V_{gel}^{mol} \cdot s \cdot \zeta(t) - \frac{4}{3} \pi \left( R_{a} + t_c \right)^{3} - R_{a}^{3} \right)$$ (6)

4. The pressure causes cracking of the aggregate and cement paste. Whatever the reactive silica distribution in the aggregate, the propagation of cracks in small specimens containing large aggregate can be rapid and can occur for low pressures, while the propagation is more difficult for larger specimens containing smaller aggregates and needs higher pressure (Figure 5-d). In the framework of fracture mechanics [44-45], the maximal normal stress in the vicinity of an inclusion (e.g. the aggregate) that induces pressure on a matrix (e.g. the cement paste) is given by:

$$\sigma(r) = \frac{K_I}{\sqrt{2\pi r}}$$ (7)
With $\sigma$, the maximal normal stress at the point $M$ located at distance $r$ from the edge of the inclusion (Figure 5-d) and $K_I$, the stress intensity factor obtained for a specimen in stress-free conditions from the relation:

$$K_I = p^a_s \cdot f\left(\frac{R_a}{L}\right)$$  \hspace{1cm} (8)

where $f$ is a function increasing with the ratio $R_a/L$ (which can be obtained in [41]), with $R_a$ the aggregate radius and $L$ the dimension of the specimen ($a$: superscript relative to the size of the reactive aggregate).

**Smaller expansion in smaller specimen**

The larger the aggregate size compared to the specimen size, the larger the normal stress at a given distance from the aggregate (Equations 7 and 8). Thus, the tensile strength at the boundary of the specimen can be reached for a smaller pressure (Figure 5-d) and cracks can be initiated earlier. Once concrete cracks, ASR-gels can be accommodated by cracking without creating supplementary pressure [46,47] and can even leach off through the porosity induced by cracking. Thus, the pressure in the gels falls, which stops the expansion.

If the pressure necessary to cause cracks is lower for small specimens containing large-sized aggregate, the pressure of the gel will fall sooner in the case of the 20x20x160-mm specimens containing the 1250-2500-µm aggregate than for the 70x70x280-mm specimens containing the same aggregate, and thus cause smaller expansion.

**Pessimum effect or scale effect**

The scale effect can also explain the pessimum effect of ASR expansion with aggregate size. For the largest aggregates, a part of the difference of expansion can be explained by a delay in the attack of the reactive silica by the hydroxyl ions due to the diffusion of the ions into the aggregate [23]. Measurements confirmed that the expansion rate was slower in the largest particles whatever the size of the specimens (Figure 3). However, even when the final value was reached, ASR expansion remained lower for the largest aggregates in the smallest
specimens. As explained above, the 20x20x160-mm specimens containing the 1250-2500-µm aggregate were more affected by the scale effect than the specimens containing the 315-630-µm aggregate: a larger aggregate induced a greater stress intensity factor (Equation 8). Therefore, the part of reactive silica consumed when cracking appeared is lower when cracking appears in the specimens containing the largest aggregate. Once cracking occurs, the gel is accommodated by the cracks and the gel produced after cracking leads to little supplementary pressure. Expansion ceases before the chemical reaction stops, giving a final expansion lower than that for the largest aggregate. This is consistent with the experimental determination of the degree of reaction performed with chemical attack [47] and SEM image analysis [48]: expansion stopped while the degree of reaction was still increasing. The pessimum effect versus specimen size is not an intrinsic phenomenon; it is due to the scale effect, which depends on the ‘specimen size to aggregate size’ ratio. In this experimentation, only mortars were tested and the pessimum effect disappeared for aggregate of 1.25-2.5 mm when tests were performed in specimens of 70 mm. For concrete, the pessimum still exists for aggregate of 4-8 mm in specimens of 70 mm [24]. If the scale effect (combination of the aggregate size effect and the specimen size effect) is identical for concrete, specimens of more than 250 mm could be necessary to remove the pessimum effect for such aggregates. Supplementary investigations are necessary to analyse this effect on concrete.

Effect of the reactive silica content on the scale effect

At last, it can also be used to analyse the effect of the reactive silica content on ASR expansion (Figure 1). As shown in Figure 6, the final expansions measured on specimens containing the different aggregates were not proportional to the reactive silica content. Moreover, the specimens containing opal were much more damaged and cracked than those with the other aggregates. This could have been due to the large concentration of reactive silica contained in opal. A larger reactive silica content would induce a higher gel pressure
(Equation 6) and thus a greater stress intensity factor (Equation 8) for opal than for the siliceous limestone. Therefore, the ratio between the total reactive silica and the reactive silica consumed when cracking appeared was not the same. The part of reactive silica consumed would be lower when cracking appeared in the specimens containing opal than in the specimens containing the siliceous limestone. Once cracking had occurred, cracks accommodated the gel, and expansion stopped before the chemical reaction finished, without proportionality with the total reactive silica. This effect was probably very important in the case of specimens containing opal in which cracks were very large at the end of the experiment (Figure 2).

The concept of stress intensity factor appears to be important for an understanding of the development of ASR expansion in concrete. The larger the stress intensity factor $K_I$ is, the faster cracks appear and the cracking could lead to reduction of the expansion through gel accommodation and exudation. The ratios between specimen and aggregate sizes were very high in these experiments. This shows that it could be difficult to use specimens large enough to avoid the scale effect. One possibility would be to try to control the aggregate and the specimen sizes so as to perform the test with similar stress intensity factors and thus to have similar cracking conditions as proposed in [42,43] but this would be difficult to do, particularly as far as controlling the aggregate size is concerned. Another possibility is to understand the scale effect through a model that can be used to analyse expansion tests. This is the aim of the modelling presented in the next part.

3. Modelling ASR expansion

The model used in this paper is an improvement on the microscopic model [34]. It was based on previous models [33, 35-37,39] and attempted to predict the damage and the expansion of a Representative Elementary Volume (REV) of concrete containing a mix of reactive
aggregates of different sizes. The reaction between the reactive silica and the alkali was
determined through the mass balance equation, which describes the diffusion mechanism in
the aggregate and the fixation of the alkali in the ASR gels. The mechanical part of the model
is based on damage theory in order to assess the decrease of stiffness of the mortar due to
cracking caused by ASR and to calculate the expansion of the REV [34]. Some modifications
were made in this model: the threshold of alkaalis was re-evaluated in accordance with the
results present above and the combined effects of specimen and aggregate sizes and reactive
silica content on expansions were taken into account.

3.1 Presentation of the model

3.1.1 Diffusion of alkali

The diffusion of ions in the aggregate partly controls the kinetics of the chemical attacks and
of the expansion. At the beginning of ASR, hydroxyl ions attack the reactive silica of the
aggregate. Hydroxyl ions come from the pore solution and thus the external boundary of the
reactive aggregates is attacked first. If the reactive silica is uniformly distributed in the
aggregate, the reactive silica closest to the pore solution is attacked first (Figure 5-a top). If
the reactive silica occurs in veins, the penetration of hydroxyl ions is not uniform but veins in
contact with the pore solution are attacked first (Figure 5-a bottom). Therefore, in both cases,
the transport of ionic species in the aggregate can be modelled by an equivalent diffusion of
ions from the pore solution to the aggregate core. The diffusion is not the only phenomenon
which impacts the kinetics of ASR-expansion: the time necessary for the attack of the reactive
silica by hydroxyl ions and for the formation of ASR-gels is taken into account through a
depletion term in the mass balance equation [34]. This term models the alkali consumed by
the ASR-gel formation. This alkali consumption is assumed to be linear with the alkali
concentration in the aggregate. The temperature of storage for the experiment was 60°C. It
accelerates ASR considerably compared to the environmental conditions of real damaged
structures and can affect the nature of the gel. It impacts the values of the kinetic parameters but should not affect the principle of the modelling.

As in the previous model [34], only the diffusion of ions in the aggregate was considered since the kinetics of diffusion in aggregates was much slower than in cement paste [35]. Therefore, the alkali concentration at the surface of aggregates was assumed to be equal to the concentration of the NaOH solution. The kinetics of the expansion was thus partly controlled by the diffusion in the aggregate, which is one of the kinetic parameters of the model. This assumption is relevant for small specimens or when there is no chemical exchange with the environment but it can be discussed for larger specimens immersed in NaOH solution. In the experiments presented here, the largest specimens showed the slowest rate of ASR-expansion (Figure 3). This can be explained by the diffusion of the alkali into the specimens. The initial alkali concentration in the pore solution was sufficient to initiate the reaction. Alkalis were quickly consumed by the ASR gel and supplementary alkalis were necessary to maintain gel production. The alkali came from the solution and diffused into the mortar. Thus, more time was necessary for alkali to reach the centres of the largest specimens than the centres of smaller ones. Thus an alkali gradient appeared in the specimens. In consequence, at a given time, a gradient of expansion existed between aggregates located close to the external boundary and aggregates located in the core of the specimen. Only complete discretization of the whole specimen [24,31,32] would allow this difference of expansion to be considered.

The aim of the modelling used in this paper was to evaluate the material behaviour that could be represented by measurements performed on small specimens. Therefore, the phenomenon of diffusion in the specimen was not taken into account. This modelling can give a good representation of the expansion kinetics of concrete damaged by ASR measured on small specimens (with width smaller than 40 mm, for which the effect of the alkali gradient is negligible).
3.1.2 Threshold of alkali concentration

In the previous model, a threshold of alkali concentration of 0.625 mol/l of Na\(^+\) was considered, under which ASR did not occur [34]. It was based on experimental data showing that, with an alkali content lower than 3 kg per m\(^3\) of concrete, no ASR-expansion was observed [49-52]. In tests performed in non-saturated conditions (in air with RH above 95%), the concentration of alkali played an important role in the attack of the silica. In the present work, all the specimens were kept immersed in alkali solution and, thus, the alkali was supplied in abundant quantities. The experiments performed on specimens immersed in three alkali concentrations (0.77, 1 and 1.25 mol/l) showed negligible differences. Considering a threshold of 0.625 mol/l, the expansion of the mortars kept in 0.77 mol/l solution should be significantly slower than the expansion of the mortars kept in 1.25 mol/l solution. With this threshold, the alkali concentration in the aggregate has to be higher than 0.625 mol/l before the reactive silica is attacked. The gel production kinetics is then proportional to the difference between the alkali concentration in the paste and the threshold. The alkali concentration gradient between the paste and the aggregate remains too small to induce the same reaction speed as for the other concentrations. This is not in accordance with the expansion kinetics measured on specimens (Figure 1). Therefore, the gradient must be close for the three concentrations and consequently the alkali consumption by the silica must begin as soon as alkalis are present in the aggregate, without a threshold. The result of this assumption is shown in Figure 7: if no threshold is taken into account, the expansions determined by the modelling at 50 days are of the same order as the expansions obtained for the measurements. The apparent threshold effect observed in experimentations [49-52] can be explained by the alkali fixation in C-S-H. This fixation consumed a part of alkali which are no more available in the pore solution and reduced the attack kinetics and consequently the ASR-
expansion kinetics. All these phenomena can be explained without considering a threshold of alkali concentration for the attack of the silica.

### 3.1.3 Effective ASR-gel

The ASR expansion calculated by the model is imposed by the effective volume of ASR-gel. The effective volume of gel is deduced from the total volume of gel, which is proportional to the number of moles of ASR gel formed after the attack of the reactive silica (Equation 7). Once cracking appears in the specimens, a part of the rest of the gel \( V_{gel} - V_{pore} \) is assumed to be accommodated by cracks created in the aggregate and in the cement paste by the ASR-gel pressure. This gel accommodation by cracks stops the increase of the ASR-gel pressure. This part depends on the scale effect: the larger the aggregate in comparison to the specimen, the greater the volume of ASR gel accommodated. This phenomenon is also affected by the reactive silica content of the aggregate. As explained in the analysis of the experiments, the greater the reactive silica content is, the stronger is the non-linearity due to cracking. Fracture mechanics concepts show that the aggregates closest to the external boundary are the first to produce cracks. In order to quantify this effect, it can be assumed that these aggregates lead to less pressure than the aggregates located in the core of the specimens. As for the diffusion in cement paste, this will lead to a gradient of deformation between the external boundary and the core and thus to internal stresses. The scale effect appears to be a highly non-linear phenomenon. Therefore, an exponential function is proposed to model the consequences on ASR expansions. An empirical relationship to quantify the reduction of the gel amount effectively used to assess the pressure is thus assumed and applies equally to all the aggregates of a given size \( i \) without consideration for their location compared to the specimen boundary:

\[
V_{a}^{eff} = \left( V_{a}^{gel} - V_{a}^{pore} \right)^{+} \times \max \left[ \exp \left( -c \frac{2R_a}{L} s^{+} \right) \right]
\]  

(9)
With $V_{a eff}$: the effective volume of gel, $c$: the scale effect fitting coefficient and $\chi$: the silica content exponent.

The pressure imposed on the aggregate and thus on the cement paste depends on the effective volume of gel. Moreover, if the distribution of the reactive silica is uniform in the aggregate, the pressure will be isotropic (Figure 5-c). If the reactive silica is contained in veins in the aggregate, the large number of aggregate particles in the specimens means that the orientation of the veins in the specimens is randomly distributed and the mean resulting pressure can be considered as isotropic too (Figure 5-c). The effective volume of gel is then used in the mechanical model presented in [34] to deduce the resulting expansion.

### 3.2 Comparison with experiments

#### 3.2.1 Parameters

Table 2 sums up the parameters used in the modelling, stating the symbols, the methods used for the identification, the values and the units. Three parameters (unique, independent of the other variables, and usable for all experiments and all aggregate types studied in this work) of the physicochemical modelling (thickness of the connected porous interface zone $t_{c}$, molar volume of ASR gel $V_{gel mol}$, and scale effect fitting coefficient $c$ – equations 4, 6 and 9) were obtained by curve fitting on the final expansions measured on the specimen of size 70 x 70 x 280 mm with the four different size classes (0-315, 315-630, 630-1250 and 1250-2500 µm) of siliceous limestone (SL – Figure 8). The parameters were first determined without considering the effect of the silica content exponent ($\chi = 0$) since the specimens involving the curve fitting contained the same aggregate. Once these three parameters had been assessed, the value of $\chi$ was determined by fitting the final expansion of mortars containing opal as aggregate (O – Figure 8). As explained above, the coefficient of alkali diffusion in aggregate, $D_{a}$, was used as a kinetic parameter. This coefficient can depend on the nature of the aggregate. It was obtained by curve fitting the results obtained on specimens of size 20 x 20 x
160 mm (Figure 9). The coefficients of diffusion in aggregate ($D_a$) thus obtained by curve fitting were respectively equal to $2.0 \times 10^{-15}$, $5.0 \times 10^{-14}$, $4.0 \times 10^{-16}$ and $2.0 \times 10^{-16}$ m$^2$/s for the siliceous limestone, opal, quartzite and quartz aggregate. It can be noted that the values were considerably lower than the usual value of diffusion coefficient determined for cement paste (about $10^{-12}$ m$^2$/s); the assumption of fast alkali supply at the surface of aggregate is thus verified. However, these values appear to be very small compared to coefficient of diffusion measured for quartzite [53]. It can be explained by the assumption used to determine the kinetics of the formation of ASR-gels. In this modelling, the kinetics was driven by two main phenomena: the diffusion of ions in the aggregates and the kinetics of the attack of reactive silica by alkali and hydroxyl [34]. The attack was assumed to be linear with the alkali concentration in the aggregate and only one parameter was used for all the aggregates. This parameter was fitted for siliceous limestone [34]. In the reality, the mechanisms leading to the gel formation are more complex and this simplified assumption can be responsible of the overestimation of the speed of the silica attack. It can lead to underestimation of the speed of diffusion. Improvements of the assumed kinetics of silica attack could lead to more realistic coefficients of diffusion for aggregates. However, this kinetics of silica attack could depend on the nature of the reactive silica and on the pH of the pore solution and several parameters could be necessary to obtain relevant results which could be very difficult to measure.

### 3.2.2 Calculations

Expansions obtained by modelling are compared with the measurements in Figures 9 and 10. Figure 9 shows the expansions obtained with 20 x 20 x 160-mm specimens containing two aggregate sizes (15% of 315-630 and 15% of 630-1250 µm) for the four natures of aggregate. Only the coefficient of diffusion and the silica content exponent were fitted on these results. The fitting concerning the final expansion of the siliceous limestone was only performed on the largest specimens (70x70x280 mm) and for specimens containing only aggregate of the
same size. Except for the kinetics of expansion obtained for specimens containing opal, both
kinetics and final expansions obtained by the calculations were in accordance with the
measurements for the four types of aggregate. The description of the expansion kinetics by
the model is globally possible: presence of a latent time before initiation of the expansion,
followed by a high rate of expansion and ending by a low rate to reach the final expansion.
Concerning the effect of the alkali concentration of the immersion solution, the difference
between the final expansion predicted by the model (0.70%) and the mean measured
expansion (0.65%) is lower than 10%. The calculation does not show any difference in final
expansions between the three alkali concentrations: the model assumes that all the reactive
silica is consumed in the three conditions and, thus, the volume of ASR gel created is the
same, leading to the same ASR-expansion. The expansion rates obtained by the model at the
beginning of expansion are in good agreement with experiments. This confirms that, in the
case of specimens immersed in alkali solutions, no alkali threshold has to be considered
(unlike for specimens exposed to a saturated environment [34]).

The curve obtained by the model for opal did not fit the experimental results well. At the
beginning of the experiment, the slopes of the two curves were the same but, after about 50
days, the measurements showed a speeding-up of the expansions which was not obtained by
the calculation. This can probably be attributed to crack opening for opal specimens as the
specimens containing opal aggregate presented much larger cracks than specimens of the
same size cast with the other aggregates. First, cracks opening increased the apparent
expansion. These cracks could also cause a great increase in diffusion in the specimens, which
could accelerate the reaction.

The comparison of the calculated final expansions obtained for the three specimen sizes (20 x
20 x 160 mm, 40 x 40 x 160 mm, 70 x 70 x 280 mm) and the four aggregate sizes of the
siliceous limestone with the measurements is shown in Figures 10 and 11. Concerning these
values, only the measurements performed on the largest specimens were used for parameter identification. The calculated results for all the combinations are in good accordance with the measurements (Figure 10). The scale effect of ASR expansion pointed out in experimentations is rather well-predicted (Figure 11). The differences between calculated and measured expansions are lower than 15% except for the expansions obtained on the smallest specimens (20x20x160 mm) containing the largest aggregate (1250-2500 µm), where the difference is about 30% (Figure 10).

3.2.3 Discussion

The molar volume of ASR gel obtained by curve fitting in this work was about 170 cm$^3$/mol. It was higher than the molar volume obtained in the previous modelling performed for specimens kept in air at 95% relative humidity [34] and higher than the molar volume of C-S-H (about 100 cm$^3$/mol [54]). The differences can be explained by the conditions of conservation (in saturated air in [34] and immersed in NaOH solution in this work) which could have had a marked effect on the gel morphology and thus on the gels’ capability to absorb water. The ASR gels were produced in pore solution with different water contents and alkali concentrations. The compositions of the gel were therefore different and thus the molar volume was different. Concerning the water, ASR gels formed in specimens kept in solution can absorb much more water than those in humid air (R.H. >95%).

The thickness of the connected porous interface zone ($t_c$ equal to 14.0 µm) was also higher than that found in [34], which was about 1 µm. This value was determined to obtain the final expansions of four aggregate sizes while only two aggregate sizes were studied in the previous work. The molar volume of the gel was higher and therefore more connected porous volume was necessary to accommodate the gel. The ASR gels could permeate over a long distance because the molar volume was high and because the viscosity was small due to high water and alkali contents. This value is in accordance with the results found in the literature.
481 [55-56] showing that the interfacial transition zone between aggregate and cement paste can
482 reach 20 µm.

483 4. Conclusion

484 This paper has aimed to investigate and quantify the combined effects of aggregate and
485 specimen sizes on ASR expansion and the influence of the reactive silica content of aggregate
486 on this effect. In order to quantify these effects on ASR expansion, a microscopic model was
487 improved. The main conclusions can be summarized as follows:

488 1. A scale effect, combining the effects of aggregate size, reactive silica content and
489 specimen size on ASR expansion, has been highlighted by experimentation. A
temporary pessimum size effect had previously been shown to exist due to the speed
of the attack of the reactive silica on the aggregate: the larger the aggregate, the slower
the penetration of ions into the aggregate and thus the slower the expansion [23]. In
this paper, only stabilized expansions were compared, which pointed out another
pessimum effect. The pessimum size effect of stabilized expansion appears not to be
an intrinsic phenomenon of ASR expansion but to depend on the size of the specimen
used to perform the expansion test. For the largest specimens, no pessimum effect was
detected for the aggregate size used in this study. The scale effect has been explained
by fracture mechanics concepts: the larger the ratio between the aggregate and
specimen sizes, the larger the stress intensity factor around the aggregate and the faster
the cracking around the aggregate. After cracking, a part of the ASR gels can be
accommodated by cracks.

492 2. Considering that the scale effect is unavoidable for experimental specimens (the ratio
493 between specimen and aggregate sizes should be larger than 100 to significantly
decrease the effect), the results of expansion tests should be analysed with respect to
this effect. The modelling proposed took the scale effect into account through an empirical relationship considering underlying linear fracture mechanics concepts. Calculations are in good accordance with experiments for expansion tests performed with ratios higher than 10 between specimen and aggregate sizes for the four aggregates studied.

Finally, this paper points out the complexity of ASR expansion and states the numerous parameters that have to be taken into account to obtain relevant calculations. Another important conclusion is that stress-free expansions obtained on specimens cannot be directly used as input parameters in structural models because they are strongly dependent on the specimen size and on the conservation conditions during the expansion test. To be used, stress-free expansion test results should be interpreted by considering the phenomena pointed out in this work. Such an approach is possible: free expansion tests can be carried out to assess the AAR advancement in aggregates, while the expansion in the conditions of the damaged structures is assessed through a finite element inverse analysis able to combine the fitting of the expansion measured on structures with the chemical advancement kinetics deduced from laboratory tests [57].

Acknowledgements
The authors are grateful to Pr Eric Garcia-Diaz, Pr Benoît Fournier, Pr William Prince, Mr Eric Bourdarot and Mr Etienne Grimal for their advice and suggestions, which have helped to improve the analysis and the modelling.

References


[21] M. Moisson, M. Cyr, E. Ringot, A. Carles-Gibergues, Efficiency of reactive aggregate powder in controlling the expansion of concrete affected by alkali-silica reaction (ASR), 12th


## Table 1: Reactive silica contents of different aggregates [43]

<table>
<thead>
<tr>
<th>Reactive silica (SiO$_2$)</th>
<th>SL</th>
<th>O</th>
<th>Q</th>
<th>QA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Percentage by mass (%)</strong></td>
<td>6.9</td>
<td>50.4</td>
<td>7.6</td>
<td>2.7</td>
</tr>
<tr>
<td><strong>Content (mol/m$^3$ of aggregate)</strong></td>
<td>3000</td>
<td>21900</td>
<td>3300</td>
<td>1170</td>
</tr>
</tbody>
</table>

## Table 2: Parameters of model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Identification</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aggregate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactive silica content</td>
<td>$s$</td>
<td>measurement</td>
<td>D.N.A.*</td>
<td>mol/m$^3$</td>
</tr>
<tr>
<td>Coefficient of diffusion</td>
<td>$D_a$</td>
<td>curve fitting</td>
<td>D.N.A.*</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>Porosity</td>
<td>$p$</td>
<td>usual value</td>
<td>0.01</td>
<td>%</td>
</tr>
<tr>
<td><strong>Paste</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity of mortar</td>
<td>$p_{mort}$</td>
<td>measurement</td>
<td>18.0</td>
<td>%</td>
</tr>
<tr>
<td>Thickness of the connected porous interface zone</td>
<td>$t_c$</td>
<td>curve fitting</td>
<td>14.0 x $10^{-6}$</td>
<td>m</td>
</tr>
<tr>
<td><strong>Gel</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar volume of ASR gel</td>
<td>$V_{gel}^{mol}$</td>
<td>curve fitting</td>
<td>$1.7 \times 10^{-4}$</td>
<td>m$^3$/mol</td>
</tr>
<tr>
<td>Scale effect coefficient</td>
<td>$c$</td>
<td>curve fitting</td>
<td>0.037</td>
<td>(mol/m$^3$)$^\chi$</td>
</tr>
<tr>
<td>Silica content exponent</td>
<td>$\chi$</td>
<td>curve fitting</td>
<td>0.75</td>
<td>-</td>
</tr>
</tbody>
</table>

* depends on the nature of the aggregate
**FIGURES**

**Figure 1:** ASR expansions according to the alkali concentration of the immersion solution for SL (0.77, 1.0 and 1.25 mol/l) and to the nature of the aggregate (O: opal, SL: siliceous limestone, Q: quartzite and QA: quartz aggregate) stored in the 1 mol/l NaOH immersion solution.

**Figure 2:** Cracking patterns of specimens cast with the siliceous limestone (a) and with opal (b).
Figure 3: ASR expansions on prismatic specimens 20x20x160 mm (a), 40x40x160 mm (b) and 70x70x280 mm (c)
Figure 4: Final ASR expansions according to specimens size and aggregates size.

Figure 5: Four phases of ASR development: ion diffusion (a), reaction with the reactive silica (b), gel pressure (c), and stress development (d). Top line: diffuse reactive silica distribution, bottom line: veins.
**Figure 6:** Final expansions according to reactive silica content

**Figure 7:** Measured and calculated expansions at 50 days according to the alkali concentration of the solution (calculations performed with or without the threshold of 0.625 mol/l)
**Figure 8:** Identification of the modelling parameters

**Figure 9:** Comparison of calculated and measured expansions according to the alkali concentration of the immersion solution (0.77, 1.0 and 1.25 mol/l) and to the nature of the aggregate (O: opal, SL: siliceous limestone, Q: quartzite and QA: quartz aggregate)
Figure 10: Comparison of calculated and measured final expansions for all the combinations between the sizes of aggregates and specimens with siliceous limestone.

Figure 11: Scale effect of ASR expansion: experimental and modelling results.