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1 **Multi-scale analysis of Alkali-Silica Reaction (ASR): impact of**  
2 **alkali leaching on scale effects affecting expansion tests**

3  
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10 **Abstract**

11 Alkali-silica reaction expansions are disturbed by a variety of mechanisms (alkali  
12 leaching, ASR-gel permeation through cracks, chemical conditions in pore solution  
13 water and its dependence on temperature, etc.). An important consequence is the  
14 difficulty of using the expansion test on specimens to analyse the behaviour of ASR-  
15 damaged structures. The paper focuses on the influence of leaching: alkali transport  
16 and consumption are modelled using a multi-scale approach (aggregate and concrete  
17 scales). The evaluation of the alkali concentration below which expansion stops is  
18 needed to perform relevant analysis in various alkali conditions and this alkali  
19 threshold is quantified according to calcium concentration and temperature. The  
20 impact of the coupling between alkali transport in aggregate and silica reactivity is  
21 also studied. Lastly, the consequences of leaching on ASR-expansion are analysed in  
22 two case studies drawn from the literature.

23 **Keywords:** alkali-silica reaction (ASR) (C), alkali (D), expansion (C), leaching, modelling (E)

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## 26      **1. Introduction**

27    Expansion tests performed on mortar or concrete specimens are the most usual  
28    laboratory tool to evaluate the risk of Alkali-Silica Reaction in newly designed  
29    structures or to quantify the potential future expansion with a view to reassessing  
30    ASR-damaged structures. Several disturbing effects make the analysis of such tests  
31    difficult, by giving rise to scale effects. Alkali leaching [1]–[5], moisture gradient [6]  
32    and ASR-gel permeation through cracks [7]–[9] lead to larger expansions in larger  
33    specimens according to the storage conditions [5], [8]–[10]. These phenomena greatly  
34    impact the ASR-expansion measured on specimens, which raises the question of  
35    whether such measurements should be used to represent expansion in conditions  
36    existing in real structures. It is then necessary to analyse and quantify these effects so  
37    as to be able to use such usual tests as input data for structural assessment. It is  
38    difficult to estimate the contribution of each phenomenon to the differences of  
39    expansion with specimen size for the moment. In order to obtain a better prediction of  
40    expansion in structures, models have to be able to distinguish how much of the scale  
41    effect is due to alkali leaching and how much is induced by gel permeation through  
42    cracks for tests in leaching conditions. Expansion tests in the conditions the closest to  
43    structural reality are performed in a constant moist environment. For such  
44    experiments, one of the main scale effects is due to alkali leaching. This paper focuses  
45    on the alkali mass balance in ASR mechanisms and proposes modelling to reproduce  
46    the effect of alkali leaching on the expansion of prisms. The aim is to obtain a model  
47    that includes enough physical details to explain differences of expansion in conditions  
48    of alkali leaching but is simple enough to be usable for structural calculations.  
49    Two equations are proposed to quantify alkali actions in ASR kinetics and expansion:

- 50 - At aggregate scale, the mass balance equation of alkalis takes their diffusion  
51 and fixation in ASR-gels in aggregates into account,
- 52 - At concrete scale, the mass balance considers the alkali diffusion in a  
53 specimen in relation to the boundary conditions, while the alkali consumption  
54 in the specimen is evaluated from the previous scale.

55 The link between chemical modelling and expansion is obtained through a model  
56 based on poromechanical theory that takes account of creep and damage at the  
57 concrete scale. The description of this mechanical part has been kept as brief as  
58 possible and only the main improvements compared to the previous version of this  
59 model are presented. In particular, the scaling up from gel pressure inside the  
60 aggregate to aggregate pressure on the surrounding concrete is modified. Finally, two  
61 case studies are presented to analyse literature experiments involving scale effects due  
62 to alkali leaching and potential consequences on measured expansion are discussed.

## 63 **2. ASR mechanisms and alkali leaching**

### 64 ***2.1 Multi-scale chemical approach***

65 The chemical approach used in this paper is characterized by an alkali mass balance  
66 performed at two scales: the aggregate and the concrete scales (Figure 1).

67 At the aggregate scale, the alkali mass balance equation has to consider the diffusion  
68 and the fixation of alkali in ASR-gels. In order to be as representative as possible of  
69 the different types of aggregate attacks [11]–[13], analysis of ASR cannot consider  
70 the alkali diffusion in reactive aggregate as the only driving mechanism of ASR-  
71 kinetics. At least two main phenomena should be taken into consideration (Figure 1):  
72 ionic transport (to have alkali and silica in the same place) and the chemical reaction

73 (attack of silica to form gels). The impact of the coupling between alkali diffusion and  
 74 silica reactivity on the distribution of ASR-gels in aggregate and concrete is analysed  
 75 in the following part.

76 At concrete scale, the alkali diffusion equation takes the alkali flow  $\overrightarrow{\varphi_{Na}^c}$  due to  
 77 external boundary conditions into account (Figure 1). The alkali bound in ASR-gels  
 78 ( $S_{\Sigma Na_b}^c$  in Figure 1) can be evaluated as the sum of alkali flow at the boundary of the  
 79 aggregate ( $\overrightarrow{\varphi_{Na}^{agg}}(r = R_{agg})$  in Figure 1) determined at the lower scale.

80 The alkali concentration in the cement paste at the aggregate edge and at the concrete  
 81 scale ( $[Na^+]_x$  in Figure 1) has to be the same in order for the multi-scale chemical  
 82 approach to be consistent.

## 83 **2.2 Alkali mass balance at aggregate scale**

### 84 **2.2.1 Alkali transport**

85 The reactive silica is dissolved in presence of hydroxyl and alkali ions before ASR-  
 86 gels are formed. In most cases, alkali and hydroxyl come from the cement paste  
 87 solution and move to the silica in the aggregate to start the reaction. The mass balance  
 88 equation at aggregate scales represents the alkali diffusion in aggregates and the alkali  
 89 fixation in ASR-gels. It is applied for each size of aggregate, as proposed in previous  
 90 modelling [14]–[17]. It can be written, for a constant water saturation degree:

$$p_{agg} S_r \frac{\partial [Na^+]}{\partial t} = -div \left( \overrightarrow{\varphi_{Na}^{agg}} \right) + S_{Na} \quad (1)$$

91 with  $p_{agg}$  the aggregate porosity,  $S_r$  the degree of water saturation,  $[Na^+]$  the alkali  
 92 concentration in solution,  $\overrightarrow{\varphi_{Na}^{agg}}$  the alkali flow in the aggregate and  $S_{Na}$ , the rate of  
 93 alkali binding in ASR-gels per unit of time and of aggregate volume.

94 The alkali flow depends on the coefficient of diffusion of alkali in the aggregate  $D_{agg}$ :

$$\overline{\varphi_{Na}^{agg}} = -D_{agg} \overline{grad}[Na^+] \quad (2)$$

95 For this diffusion phenomenon, the Arrhenius energy was taken to be 20 kJ/mol [18]

96 to account for the increase of diffusion velocity with the temperature.

97 Despite the fact that alkali transport occurs in aggregate in diverse manners depending

98 on whether the reactive silica is in contact with cracks or contained in veins of the

99 aggregates [11], the coefficient of diffusion is assumed to be homogeneous in the

100 aggregate. This is an approximation that requires a calibration by inverse analysis of

101 expansion curves. The dependence of the expansion kinetics on the aggregate sizes

102 can be reproduced by the differences of alkali ingress into the aggregate.

103

## 104 **2.2.2 Alkali fixation in gels**

### 105 *Attack of silica and alkali fixation*

106 The rate of alkali binding in ASR-gels (the sink term  $S_{Na}$  of the mass balance equation

107 applied at the aggregate scale) is driven by the reactivity of the aggregate. In the

108 absence of precise quantification of the different mechanisms involved in the

109 aggregate attack, it is assumed that linear kinetics is sufficient to consider the silica

110 attack and the ASR-gel precipitation according to an alkali threshold [17]. This is a

111 simplified approach compatible with experimental results on pore solution extraction

112 [19].

113 The form chosen for the rate of alkali fixation is similar to the one used in [17]:

$$S_{Na} = -\frac{\partial Na_f}{\partial t} = -\frac{\langle [Na^+] - [Na^+]_{(Ca,T)}^{thr} \rangle^+}{\tau_{ASR}} \quad (3)$$

114 with  $\tau_{ASR}$  the characteristic time of silica attack, which can be considered to represent

115 silica reactivity (even though, in reality, it combines both the kinetics of the reactive

116 silica dissolution and the kinetics of the ASR-gel production) and  $[Na^+]_{(Ca,T)}^{thr}$  the  
117 alkali concentration “threshold” below which the reaction products cause negligible  
118 expansion. In the first version of this model [17], considering a constant threshold of  
119 alkali in equation (3) was necessary and sufficient to model the ASR-expansion of  
120 concrete with different alkali contents in moisture conditions [17]. But this same  
121 assumption leads to expansion rates that are too different for the expansion of  
122 specimens kept in NaOH solution and no threshold was taken into account for such  
123 calculations [9]. In fact, it is not really a threshold of silica attack, but an apparent  
124 threshold due to the difference of composition of the reaction products according to  
125 the calcium concentration [18]. The alkali concentration threshold, for which gel is no  
126 longer sufficiently expansive, is not constant as supposed in [17] but depends on the  
127 calcium concentration and the temperature, which can be approximated through the  
128 simplified approach proposed in the next part.

129 For this mechanism of reaction, the Arrhenius energy is taken to be 80 kJ/mol [20] to  
130 represent the dependence on thermal conditions.

131 Equation 3 leads to an evaluation of the alkali bound in ASR-gels. Usually, the molar  
132 ratio between silica (SiO<sub>2</sub>) and alkali (Na<sub>2</sub>O) present in gels in laboratory conditions  
133 is about 5 [21] [22]). The number of ASR-gel moles produced by the reaction is  
134 assumed to be equal to the number of moles of silica attacked by alkalis and can thus  
135 be deduced from the following equation:

$$\frac{\partial n_{gel}^{mol}}{\partial t} = \frac{5}{2} \frac{\partial Na_f}{\partial t} \quad (4)$$

136

137 *Alkali threshold*

138 Based on thermodynamics modelling, Kim and Olek showed that the formation of  
139 ASR-gels stopped when the alkali concentration became lower than a threshold value  
140 [18]. The rate of alkali binding (Equation 3) can be read as a simplified representation  
141 using only the alkali concentration to represent the disequilibrium:

- 142 - For high alkali concentration (high  $[Na^+] / [Ca^{2+}]$  ratio), the silica attack is  
143 rapid and large quantities of alkali are bound by gels. ASR-gel contains  
144 mainly alkali and silica [18] and is very expansive [23] [24].
- 145 - For lower alkali concentration, portlandite is dissolved and calcium  
146 concentration increases (decrease of  $[Na^+] / [Ca^{2+}]$  ratio). The rate of alkali  
147 binding decreases and gel becomes rich in calcium [18]. Such gels with high  
148 calcium content have low bound water contents [25] and could cause less  
149 expansion [23], [24].

150 In consequence,  $[Na^+]_{(Ca,T)}^{thr}$ , the alkali limit under which expansion stops, is not  
151 constant and has to be quantified according to the calcium concentration and the  
152 temperature. Based on the thermodynamic equilibrium of portlandite [16], calcium  
153 concentration (in mol/l) in the pore solution can be approximated from alkali  
154 concentration (in mol/l) and absolute temperature by [26]:

$$[Ca^{2+}] = 0.357 \cdot \exp(386.8 \cdot [Na^+] - 0.01 \cdot T - 1.4 \cdot [Na^+] \cdot T) \quad (5)$$

155 The main interest of this simplified relation is that it enables calcium concentration to  
156 be evaluated from alkali and temperature. Thus, it is not necessary to model calcium  
157 diffusion, which limits the number of different variables in the numerical resolution.

158 Kim et al. [19] measured the evolution of alkali concentration in mortars subjected to  
159 ASR (Figure 2). From this experiment, it was possible to evaluate the alkali threshold  
160 at about 0.325 mol/l at 23°C. For such an alkali concentration and temperature,



161 Equation (5) gives a calcium concentration of about 0.11 mmol/l (Figure 3). At 23°C,  
162 if the alkali concentration becomes lower than 0.325 mol/l, Kim et al. show that  
163 expansion stops [19]. For this limit, the  $[Na^+] / [Ca^{2+}]$  ratio is around 3,000. Finally,  
164  $[Na^+]_{(Ca,T)}^{thr}$  can be defined as:

$$[Na^+]_{(Ca,T)}^{thr} = \rho_{sol}^{(T)} \cdot [Ca^{2+}] \quad (6)$$

165  $\rho_{sol}^{(T)}$ , the  $[Na^+] / [Ca^{2+}]$  limit ratio, depends on the different solubility constants of  
166 the species acting in these processes (silica gels with more or less alkali and calcium)  
167 and thus on temperature since the variations of the constants with temperature are  
168 different [18].

169 If the  $[Na^+] / [Ca^{2+}]$  ratio is higher than  $\rho_{sol}^{(T)}$ , alkali ions are predominant and gels  
170 are very expansive (Figure 3). If calcium becomes preponderant compared to alkali  
171 (ratio lower than  $\rho_{sol}^{(T)}$ ), expansive gel stops being produced [18]. Using Kim et al.'s  
172 experimental results ([19] – Figure 2), the ratio  $\rho_{sol}^{(T)}$  can be evaluated for three  
173 temperatures (23, 38 and 55°C – Figure 2). It is interesting to note the good agreement  
174 of the variation of  $\rho_{sol}^{(T)}$  determined from Kim et al.'s experiments with the Van't Hoff  
175 law for a standard enthalpy change of 205.9 kJ/mol (Figure 4), with  $\rho_{sol}^{(293)}$  equal to  
176  $1.54e^3$ . This law was used to perform the following case studies.

177 With such equations, it is important to note that the alkali threshold is not constant  
178 even during a single expansion test at a uniform temperature. In the case of an  
179 expansion test without external supply of alkali:

- 180 - Alkali ions are first predominant and  $[Na^+]_{(Ca,T)}^{thr}$  is equal to 0 at the beginning  
181 of the calculation,

182 - Then, alkalis are consumed in ASR-gels (and can be partly leached out) so  
183 alkali concentration in solution decreases,  $[Na^+]_{(Ca,T)}^{thr}$  (Equation 6) increases  
184 with the calcium concentration (Equation 5). Finally, expansion stops when  
185  $[Na^+]_{(Ca,T)}^{thr}$  becomes higher than the alkali concentration in solution  $[Na^+]$   
186 (Equation 3).

187 In the case of expansion in NaOH solution, alkali concentration stays high and  
188 calcium concentration too low to stop the production of expansive gels. In such  
189 conditions, there is no apparent threshold as shown in [9]. This is well reproduced by  
190 the proposed relations since  $[Na^+]_{(Ca,T)}^{thr}$  is then equal to 0 during the entire test  
191 ( $[Ca^{2+}]$  close to 0 for high alkali concentration – Equation 5). It can be noted that this  
192 approach could also be useful for the quantification of the alkali effect in the control  
193 of ASR risk [27].

194 Finally, the different reactive processes involved in ASR are condensed into a single  
195 characteristic time to be calibrated on an expansion test.

196

### 197 **2.2.3 Coupling transport / fixation in aggregates**

198 In the proposed modelling, two main processes are assumed to drive the kinetics of  
199 alkali-silica reaction: transport in aggregate and reaction mechanisms (silica attack  
200 and gel formation). Each mechanism is represented by one parameter: the diffusion  
201 coefficient in aggregate for the transport, and the characteristic time of ASR for the  
202 reactions. Transport kinetics is also dependent on aggregate size: the larger the  
203 aggregate, the slower the penetration of ions into it (whatever the diffusion  
204 coefficient). Thus, the difference of kinetics of ASR-gel formation with aggregate size  
205 is smaller for a coefficient of diffusion of  $1 \cdot 10^{-13}$  m<sup>2</sup>/s (as measured in [28]) than for a

206 coefficient of  $1 \cdot 10^{-14}$  m<sup>2</sup>/s (Figure 5). The difference becomes all the greater as the  
207 aggregate size grows (Figure 5).

208 However, it is not possible to obtain a realistic expansion of concrete containing  
209 mixes of reactive aggregate with different sizes from this transport equation alone, as  
210 shown in [16]. With the assumption that transport in aggregate totally drives the ASR  
211 kinetics, calculations lead to an overestimate of the impact of the smallest reactive  
212 particles in alkali binding. This leads to an underestimate of the expansion of concrete  
213 containing both small and large aggregate [16]. Reaction kinetics is not directly  
214 dependent on aggregate size but depends on the alkali concentration in the aggregate  
215 (thus indirectly on transport). In consequence, if the transport is fast compared to the  
216 chemical reaction (Figure 6-a), the ASR-gel development is proportional to bound  
217 alkali and appears to be homogeneous in the aggregate (Figure 7-a). Expansion is then  
218 little impacted by aggregate size. This is the case for aggregate with low reactivity  
219 [29]. Conversely, more slowly diffusing aggregate with very reactive silica leads to a  
220 diffusion front in the aggregate until the threshold is reached (at about 500 days in  
221 Figure 6-b), and therefore to a steep gradient of bound alkali in the aggregate (Figure  
222 7-b). Larger differences of expansion with aggregate size are observed [7] [30]. In  
223 reality, the front does not necessarily start from the external limit of the aggregate as  
224 in the simplified representation used in the model. It can also be a front starting from  
225 cracks existing in the aggregates before the ASR starts, as observed in [11]. Pore  
226 solution and alkali can move rapidly in such cracks, while the real diffusion impacting  
227 ASR-kinetics is a slower diffusion that takes place in the natural and less connected  
228 porosity of the aggregate.

229 In most cases, the role of the two mechanisms is important and has to be taken into  
230 account. The predominance of one equation over the other leads to behaviour that can

231 be more or less expansive for concrete containing a powder of small reactive particles,  
 232 according to the aggregate nature [31]. To distinguish between the contribution of the  
 233 diffusion and the contribution of the reaction kinetics, it is necessary to calibrate the  
 234 expansion on tests with aggregates of different sizes.

### 235 **2.3 Alkali mass balance at concrete scale**

236 Experiments [1]–[5] have shown the importance of alkali leaching on ASR-expansion  
 237 tests even in laboratory controlled conditions and at 95 % relative humidity.  
 238 Consequently, ASR-expansion is not a uniform phenomenon even at the scale of the  
 239 specimen (Figure 8). The analysis of such tests has to take the expansion gradient  
 240 induced by the alkali gradient into account (Figure 1). The diffusion of alkali in  
 241 concrete was determined by the usual mass balance:

$$p_c S_r \frac{\partial [Na^+]_c}{\partial t} = -div(\overrightarrow{\varphi_{Na}^c}) + S_{\Sigma Na_b}^c \quad (7)$$

242 with  $p_c$  the concrete porosity,  $S_r$  the degree of saturation (assumed constant),  $[Na^+]_c$   
 243 the alkali concentration in the concrete solution,  $\overrightarrow{\varphi_{Na}^c}$  the alkali flow at the specimen  
 244 scale, and  $S_{\Sigma Na_b}^c$  the sink term to account for alkali bound in ASR-gels at each time  
 245 step determined at the aggregate scale.

246 The alkali flow in concrete depends on its coefficient of diffusion in the concrete:

$$\overrightarrow{\varphi_{Na}^c} = -D_c \overrightarrow{grad}[Na^+]_c \quad (8)$$

247 The Arrhenius energy was taken to be 40 kJ/mol [32] [33] to represent the influence  
 248 of thermal conditions on diffusion with interaction with C-S-H in concrete.

249 The distribution of aggregate sizes is not homogeneous in specimens, and particularly,  
 250 close to the concrete skin. This concrete heterogeneity can be the cause of expansion  
 251 gradient between core and external surface. The impact of the aggregate sizes

252 distribution on ASR-expansion and cracking in specimens should be analysed through  
253 probabilistic approach in future work. By sake of simplicity, the assumption of  
254 homogeneous distribution is adopted in this work. The sink term of bound alkali can  
255 be calculated from the alkali flow in aggregate (Figure 1):

$$S_{\sum Na_b}^c = - \sum_{agg} N_{agg} \cdot 4\pi R_{agg}^2 \cdot \varphi_{Na}^{agg}(r = R_{agg}) \quad (9)$$

256 with  $N_{agg}$  the number of reactive aggregates of each size per concrete volume,  $R_{agg}$   
257 the aggregate size and  $\varphi_{Na}^{agg}(r = R_{agg})$  the alkali flow in the aggregate.

258

259 In the following calculations, the equations of transport in the aggregate and of ASR  
260 reaction (Equations (1) and (3), aggregate scale) and Equation (7) of global diffusion  
261 (concrete scale) are weakly coupled. The chemical approach proposed in the paper  
262 considers the diffusion in the specimen (top of Figure 8), takes the consumption of  
263 alkali ingress in aggregates into account (middle of Figure 8) and leads to the  
264 determination of the resulting gradient of volume of ASR-gels in the specimen  
265 (bottom of Figure 8). Due to the alkali gradient, the equations at the aggregate scale  
266 have to be solved at different points of the specimen. According to the kinetics of gel  
267 formation, the impact of alkali leaching can be more or less pronounced. The analysis  
268 is more difficult when the activation energies of the mechanisms involved are  
269 different. The acceleration of chemical reactions with temperature is larger than the  
270 acceleration of diffusive phenomena [18] [20]. In consequence, alkali leaching goes  
271 faster at high temperatures but the acceleration of chemical reactions is still greater  
272 and thus the consequences of alkali leaching cannot be directly compared without  
273 paying attention to the temperature conditions.

## 274 **2.4 ASR pressure and concrete damage**

275 The volume of ASR-gels was assessed by the multi-scale chemical approach. The  
276 consequences of the gel formation on concrete (expansion, damage) had to be  
277 analysed through mechanical considerations. From the volume of gels produced by  
278 the reaction, the mechanical effects on aggregate and concrete can be evaluated  
279 through various usual assumptions: imposed chemical strain [17] [34] [35] [36] or  
280 pressure [15], [37]–[43]. In this paper, the expansion is not obtained by the  
281 mechanical modelling proposed in [17] but through an existing poromechanical model  
282 previously developed and taking account of the damage and creep of concrete  
283 resulting from both external loading and internal pressure [44]. The consideration of  
284 creep during ASR-expansion is important to obtain a realistic evaluation of concrete  
285 damage [35] [44]. Concerning the mechanical aspect, the most important  
286 improvement compared to the previous modelling was the distinction between gel  
287 pressure in the aggregate and average aggregate pressure on the surrounding concrete  
288 (Figure 9). In most cases of ASR, cracking starts in the aggregate and aggregate  
289 cracks filled by the gel induce the cracking of the cement paste [11], [12] [45]. The  
290 consequences of ASR-gel formations were first assessed at the aggregate scale then  
291 deduced at the concrete scale (Figure 9).

### 292 **2.4.1 Pressure in ASR-gels**

293 At the aggregate scale (Figure 9), the gel pressure increases with the volumetric  
294 fraction of ASR-gels  $\varphi_{gel}$  (assumed to be proportional to the number of ASR-gel  
295 moles, determined by Equation (4) and to the molar volume of gels  $V_{gel}^{mol}$ ) and  
296 decreases with the volumetric deformation of the aggregate due to elastic strain  $\varphi_{el}^{agg}$

297 (elastic deformation of pore volume containing gels) and with the volumetric concrete  
298 cracking  $\varphi_{cr}^c$  (cracks are filled by ASR-gels).

299 It is also necessary to consider that a part of the volume of gel produced at the  
300 beginning of the reaction does not cause significant expansion. This can be  
301 established by two experimental observations:

302 - the absence of expansion for small reactive particles,  
303 - the delay of expansion at the beginning of the reaction for large reactive particles,  
304 followed by a slope break of the expansion rate, whereas alkali consumption does not  
305 show any slope break but has an exponential evolution [19] as would be expected for  
306 equations of diffusion and reaction.

307 Several assumptions can explain this behaviour. Previous modelling assumed that it  
308 could be explained by the migration of ASR-gels in connected porosity very close to  
309 the reactive aggregate [14]–[17], [39], [41], [46]. This assumption appeared to be  
310 valid since very small distances were necessary to obtain good quantification (less  
311 than 10  $\mu\text{m}$ ) [17]. This assumption may be suitable for very reactive aggregate. In this  
312 case, the gels are first produced close to the cement paste and can partly migrate in the  
313 surrounding porosity [11], [47]–[49]. However, many reactive aggregates do not show  
314 any gels in cement paste before the first cracking [11], [12], [45], [49]. Other  
315 explanations concerning the aggregates characteristics effects can also be derived  
316 from fracture mechanics: cracks development in aggregate and resulting concrete  
317 cracking are dependant of the internal reactive silica distribution in aggregate, of the  
318 shape, of the size of aggregates relatively to the specimen ones, and of the distance of  
319 the aggregates from the edges. Moreover, very large aggregates expand due to the  
320 effect of a network of cracks developing in them; this aggregate cracking could make  
321 the expansion slower. These factors, not yet considered in the model, can explain a

322 part of the difference in the start of expansions curves between small and large  
 323 aggregates. Chemical considerations could also explain the lack of expansion at the  
 324 beginning of the reaction by the differences of expansive behaviour of ASR-products  
 325 according to their time of formation. ASR-gels produced during the initial time of  
 326 reaction could be less efficient to cause expansion [50]–[53]. This phenomenon can  
 327 also be described as a non-expansive surface absorption of alkali by reactive silica at  
 328 the beginning of the processes [54].

329 Consequently, a part of the gels produced by ASR,  $\varphi_{0\_exp}$ , has to be removed from  
 330 the total gel volume to represent this effect. Finally the pressure in ASR-gel can be  
 331 written as:

$$p_{gel} = M_{gel} \cdot (\varphi_{gel} - \varphi_{0\_exp} - \varphi_{el}^{agg} - \varphi_{cr}^c) \quad (10)$$

332 with  $M_{gel}$  the Biot Modulus of gel in aggregate. As not all the porosity of aggregate is  
 333 filled by ASR-gels, the Biot Modulus is assessed according to the volume of ASR-  
 334 gels  $\varphi_{gel}$  contained by the aggregate as proposed by usual poromechanics [55]–[57].

335 The mechanisms resulting in only little expansion at the beginning of the reaction  
 336 should be progressive. Therefore, the volume of ASR-gels leading to slight expansion  
 337 at the beginning of the reaction was taken to be proportional to ASR-gel pressure as  
 338 proposed in [58].

$$\varphi_{0\_exp} = \frac{4}{3} \pi \left( R_{agg}^3 - (R_{agg} - t_{0\_exp})^3 \right) \cdot \frac{p_{gel}}{R_t} \quad (11)$$

339 with  $t_{0\_exp}$  an average thickness to quantify the volume of the gels inefficient for  
 340 expansion. This parameter was calibrated to obtain the volume of ASR-gels that had  
 341 to be removed to obtain non-expansion of the smallest reactive particles and the delay  
 342 in expansion for the largest.



343 With equation (11), gel pressure acts on the concrete as soon as gel is formed but the  
344 majority of the gel does not cause expansion until the gel pressure causes stress equal  
345 to the tensile strength of the material. Once the stress induced by this gel pressure  
346 exceeds the tensile strength, the volume of gels inefficient for expansion is assumed to  
347 be reached and all the supplementary gels cause pressure.

348 In poromechanics, the elastic volumetric deformation of pore volume containing gels

349  $\varphi_{el}^{agg}$  can be assessed by:

$$\varphi_{el}^{agg} = b_{gel} \cdot \varepsilon_{el}^{agg} \quad (12)$$

350  $b_{gel}$  is the Biot coefficient due to gel formation in the aggregate. As for the Biot  
351 modulus, it is assessed according to the gel volume in the aggregate [55]–[57].

352 The volume of concrete cracks  $\varphi_{cr}^c$  can be assessed by plastic or damage modelling.

353 The calibration of the parameters acting on the expansion level ( $V_{gel}^{mol}$  and  $t_{0\_exp}$ ) will  
354 be modified according to the capacity of the concrete to restrain the expansion due to  
355 gel formation [59]. Therefore, the parameters  $V_{gel}^{mol}$  and  $t_{0\_exp}$  will depend on the  
356 assumptions of the mechanical modelling used and particularly on the assessment of  
357 the loss of rigidity due to cracking (with or without crack reclosure, consideration of  
358 creep, etc.). In the present work, the previous anisotropic damage modelling coupled  
359 with creep presented in [44] was used. However, the cracking criterion is on the gel  
360 pressure (equation 10) here, which causes aggregate cracking first and then leads to  
361 concrete cracking.

#### 362 **2.4.2 Resulting pressure in concrete**

363 At the concrete scale (Figure 9), the volumetric deformation of aggregate under ASR-  
364 gel pressure,  $\varphi_{def}^{agg}$ , leads to the deformation of the concrete, which can be evaluated  
365 through the action of an equivalent pressure of aggregate on the concrete:

$$p_{agg} = M_{agg} \cdot (\varphi_{def}^{agg} - \varphi_{el}^c) \quad (13)$$

366 with  $M_{agg}$  the Biot Modulus of aggregate in concrete determined by usual  
 367 poromechanics [55]–[57] and  $\varphi_{el}^c$  the elastic deformation of the concrete,  
 368 and:

$$\varphi_{el}^c = b_{agg} \cdot \varepsilon_{el}^c \quad (14)$$

369 with  $b_{agg}$  the Biot coefficient of aggregate pressure on concrete (due to gel pressure  
 370 in the aggregate). It is assessed according to the aggregate content in the concrete  
 371 through usual poromechanics relationships [55]–[57]. It is thus possible to evaluate  
 372 the gel pressure according to the conditions of compressibility of ASR-gels, aggregate  
 373 and concrete.

374 Finally, the aggregate pressure on the concrete is linked to the gel pressure through:

$$p_{agg} = b_{gel} \cdot p_{gel} \quad (15)$$

375 As proposed in [43], [56], the poromechanical constitutive law then becomes:

$$\sigma = K_d^c \cdot (\varepsilon - \varepsilon_{an}) - \sum_{agg} b_{agg} \cdot p_{agg} \quad (16)$$

376 with  $K_d^c$  the concrete compressibility taking account of damage in the mechanical  
 377 modelling used here, and  $\varepsilon_{an}$  the anelastic strains due to creep and cracking.

378 Finally, in the poromechanics approach proposed in this paper, the ASR-expansion of  
 379 concrete results from two causes: the pressure due to the aggregate deformation under  
 380 ASR-gel formation and the cracking induced by ASR-gels in the aggregate.

### 381 **3. Case studies**

382 The previous equations are now used to analyse two experiments in leaching  
 383 conditions drawn from the literature. The first one is the well-documented experiment

384 on the impact of leaching on ASR-expansion performed by Lindgård [5], [60]. In this  
385 study, the alkali leaching and expansion were both evaluated on the same specimens.  
386 This provided data that was very interesting for the analysis of the effect according to  
387 specimen size and environmental storage. The second experiment is one used to  
388 evaluate the impact of the competition between diffusion into reactive aggregates and  
389 leaching out of the specimen. To simplify the analysis and the comparison, the values  
390 of the parameters depending on temperature are given for the reference temperature of  
391 20°C. In the calculations, the values at storage temperature during the test are  
392 calculated through the Arrhenius law with the activation energies given in the first  
393 part of this paper.

### 394 ***3.1 Impact of leaching on expansion***

395 The impact of leaching on ASR-expansion was analysed from experimental results  
396 obtained at 38°C on specimens with cross sections of 70x70 mm and 100x100 mm  
397 kept at 95% RH and in water [5], [60], [61]. The experiments gave alkali leaching  
398 (Figure 10) and measured expansion (Figure 11) over two years for the two sizes of  
399 specimens and for two moisture conditions (95% with limited leaching and in water  
400 with high leaching) [5]. The total alkali leaching (alkali content at the bottom of the  
401 storage containers and alkali content in the lining) was given at two time steps (1 and  
402 2 years). For the other time steps, the alkali content at the bottom of the storage  
403 containers was given (but not the alkali content in the lining). To obtain data of the  
404 total leaching for intermediate time steps between the beginning and the first year and  
405 between the first and the second years, it was supposed that the ratio between alkali in  
406 the containers and total leached alkali was the same throughout the experiments  
407 (Figure 10).

408 The first difficulty encountered in analysing the results was to represent the external  
409 conditions of leaching. The storage at 95% RH does not give a boundary condition  
410 that is easy to model for alkali external diffusion since such storage should not lead to  
411 leaching. In reality, the leaching was due to the condensation of water vapour on the  
412 surfaces of specimens following small temperature variations during the tests. The  
413 boundary condition was obtained by inverse analysis of the total leached alkali given  
414 by experiments (Figure 10). As alkali bound by ASR-gels influences this total amount  
415 of leached alkali, the inverse analysis of boundary conditions and the calibration of  
416 expansion parameters were performed simultaneously for the most limited leaching  
417 (specimens with cross section of 100x100 mm kept at 95% RH). Once expansion  
418 parameters had been determined for these conditions (Table 1), only the boundary  
419 conditions were modified to obtain the other leaching curves (Figure 10 – storage in  
420 water and specimens with cross sections of 70x70 mm) with no modification of the  
421 expansion parameters. With good reproduction of leaching results (Figure 10), ASR-  
422 expansions calculated by the previous equations were in good agreement with  
423 expansions measured during experiments (Figure 11). The differences of expansion  
424 for the two sizes of specimens studied in [5] could be quantified by the differences of  
425 ASR-advancement in specimens (Figure 12) due to alkali leaching. In the specimens  
426 with severe conditions of leaching, expansion stopped when the alkali concentration  
427 dropped below the alkali threshold obtained through Equations (5) and (6) (for 38°C,  
428 the alkali threshold is estimated at about 260 mmol/l). This analysis validated the  
429 simplified representation of the alkali threshold for the assessment of ASR-expansion  
430 in various alkali conditions. Moreover, the decrease of expansion with the specimen  
431 size could then be explained by the alkali leaching alone. In this case, it was not  
432 useful to assess the volume of gels lost by permeation through cracks as for

433 experiments on specimens kept in alkali solution [9]. This effect of gel permeation  
434 appeared to be negligible compared with the alkali leaching effect for the sizes of  
435 specimens and the conditions of this experiment. Lastly, modelling can assess a  
436 theoretical value of expansion which could appear in concrete if no leaching occurred  
437 (Figure 11) within the outlines of the assumptions proposed here. This is an important  
438 value for structural analysis since, in the core of large damaged structures, leaching  
439 should be negligible. However, it cannot be stated that it will represent the real  
440 expansion in damaged structures, because of environmental conditions (moisture  
441 conditions, temperature effects on viscosity and/or molar volume of ASR-gels,  
442 mechanical conditions) or other disturbing effects (gel permeation through cracks).  
443 The modelling confirms the large impact of alkali leaching on ASR-expansion  
444 measured on specimens. Commonly used expansion tests should not be extrapolated  
445 to large structures without using multi-scale analysis.

### 446 ***3.2 Competition between alkali diffusion in aggregate and*** 447 ***external leaching***

448 The previous equations were finally used to analyse the pessimum effect of expansion  
449 with aggregate size [62]–[64]. The pessimum effect obtained in [59] can be  
450 reproduced by the previous equations (Figure 13 and Figure 14) with a single set of  
451 parameters (Table 1) and thus could be explained by alkali leaching in conditions of  
452 moisture similar to Lindgård's ones (95% RH). Obtaining smaller expansion for  
453 larger reactive aggregate can then be explained by the competition between alkali  
454 diffusion in the aggregate and external leaching. The time necessary for alkali to reach  
455 the core of the aggregate is longest for the largest aggregates. At the same time, part  
456 of the alkali is leached out of the specimens. The result of the competition between

457 the two transport systems is that a larger amount of alkali is leached for concrete  
458 containing larger reactive aggregate and thus smaller resulting expansion even after a  
459 long time of stabilization of the phenomena (Figure 13).

460 Differences can be noted between the parameters of the first case study and this one  
461 (Table 1). For the diffusion in the aggregate, characteristic time of silica attack and  
462 thickness of non-expansive gels, they could be explained by differences in the nature  
463 and size of the reactive aggregates. The difference of molar volume of ASR-gels can  
464 be due to the effect of storage temperature on the composition of gels (differences of  
465 expansion with temperature were observed on the concrete studied in Lindgård's  
466 experiments [5]). This second study confirms, by calculations, that the pessimum  
467 effect with aggregate size in leaching conditions could be due to the competition  
468 between diffusion into the aggregate and alkali diffusion out of the specimens.  
469 However this remains theoretical since no leaching data was available and a  
470 pessimum effect can exist even when leaching is impossible (storage in alkali  
471 solutions [9]). Experiments with different sizes of reactive aggregate and control of  
472 alkali leaching would be necessary to estimate the proportions of expansion decrease  
473 that are due to alkali leaching and to gel permeation (which is the explanation  
474 proposed in the case of storage in alkali solution) and finally to validate such  
475 modelling.

476

#### 477 **4. Conclusion**

478 Alkali-silica reaction expansion tests can be disturbed by several phenomena in  
479 laboratory conditions. One of the main consequences is the difficulty of using  
480 expansion tests on specimens to analyse the behaviour of ASR-damaged structures.

481 Modelling has to take these effects into account to help in the analysis of laboratory  
482 tests and to make the link between experimentation on specimens and structural  
483 diagnosis. Scale-up methods have been used and combined to quantify the  
484 phenomenon (alkali diffusion and chemical reactions at the aggregate scale, alkali  
485 transport at the specimen scale taking into account the alkali consumption from the  
486 lower scale). At the aggregate scale, a mass balance equation with a sink term is  
487 necessary to obtain simplified but realistic kinetics of ASR-expansion. The alkali  
488 transport in aggregate is necessary to reproduce the dependence of the ASR kinetics  
489 on size for aggregates with high and intermediate reactivity. The sink term depending  
490 on alkali concentration is necessary to represent alkali fixation and to reproduce ASR  
491 kinetics of aggregates with low reactivity and mixes of reactive aggregate of different  
492 sizes (particularly the impact of the finest reactive particles for aggregates with  
493 intermediate reactivity).

494 The main interest of the present work lies in:

- 495 - The possibility to assess the apparent alkali threshold according to temperature  
496 and calcium concentration with simplified equations. Thus the alkali threshold  
497 defined in the first modelling [17] can be explained by the conditions of  
498 equilibrium between alkali and calcium ions [18]. Alkali concentration below  
499 which there is no expansion is not a threshold in silica attack but a  
500 concentration under which gels contain mainly calcium and are not  
501 significantly expansive. Differences of expansions on specimens in leaching  
502 conditions drawn from literature have been reproduced using the proposed  
503 equations to assess the alkali threshold.
- 504 - The analysis of the impact of the coupling between alkali transport in  
505 aggregate (characterized by a coefficient of diffusion) and silica reactivity

506 (determined through a characteristic time of silica attack) on ASR-gel  
507 production to reproduce kinetics according to aggregate size and distribution.  
508 The volume of gels thus calculated can be used in mechanical modelling.  
509 - The combination of the mass balance at aggregate scale with the alkali  
510 transport at the concrete scale taking the alkali diffusion in aggregate, the  
511 binding of alkali in ASR-gels and the alkali diffusion out of specimens into  
512 account simultaneously. Due to the high mobility of alkali ions, alkali leaching  
513 should not be neglected in ASR-modelling, particularly when analysing  
514 expansions in specimens, since it induces a significant expansion gradient  
515 between the core and the external surface.

516 After the development of modelling at the aggregate scale [15]–[17], this work is a  
517 second step to obtain the capacity to analyse ASR-expansion in specimens kept in  
518 usual conditions in the laboratory. Based on this multi-scale modelling, it is possible  
519 to analyse the causes of the ASR scale effect due to alkali leaching, which can induce  
520 differences of expansion with specimen sizes. The next step will be to consider the  
521 permeation of ASR-gels through cracks.

522

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526

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701 **Table**

702 Table 1: Parameters for the calculations presented in the two case studies for the

703 reference temperature of 20°C

704

		Lindgård et al.	Multon et al.
$T$	storage temperature (°C)	38°C	60°C
$D_c$	alkali diffusion in concrete (m <sup>2</sup> /s)	1.e-12	1.e-12
$D_{agg}$	transport in aggregate (m <sup>2</sup> /s)	1.35e-15	0.4e-15
$\tau_{ASR}$	characteristic time of silica attack (day)	400.	1200.
$t_{0\_exp}$	thickness of non-expansive gels (µm)	12.	5.
$V_{gel}^{mol}$	molar volume of ASR-gels (cm <sup>3</sup> /mol)	105.	71.

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**Aggregate scale**

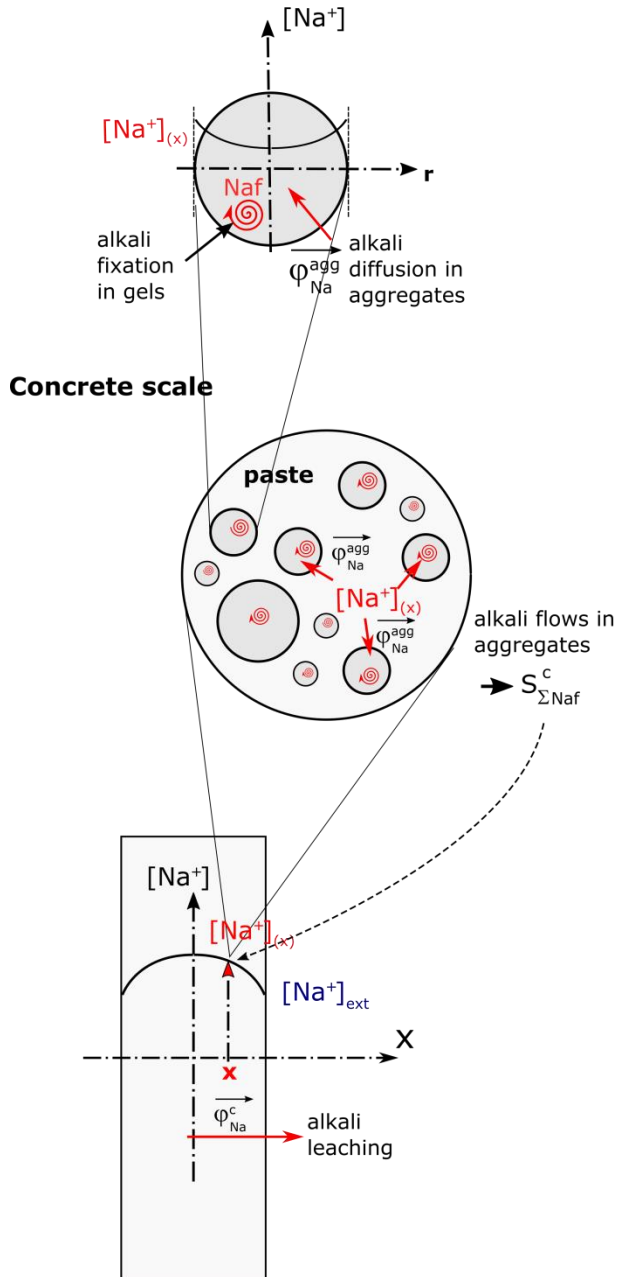


Figure 1: Alkali mass balance at aggregate scale (with diffusion and fixation in ASR-gels), at concrete scale and at specimen scale (diffusion in the specimen)

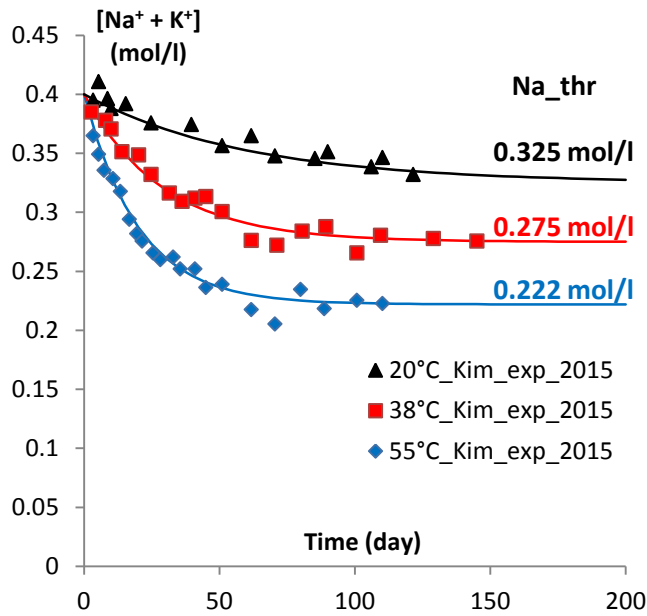


Figure 2: Evolution of alkali concentration in mortars subjected to ASR for three temperatures (experimental results from Kim et al., 2015 [19])

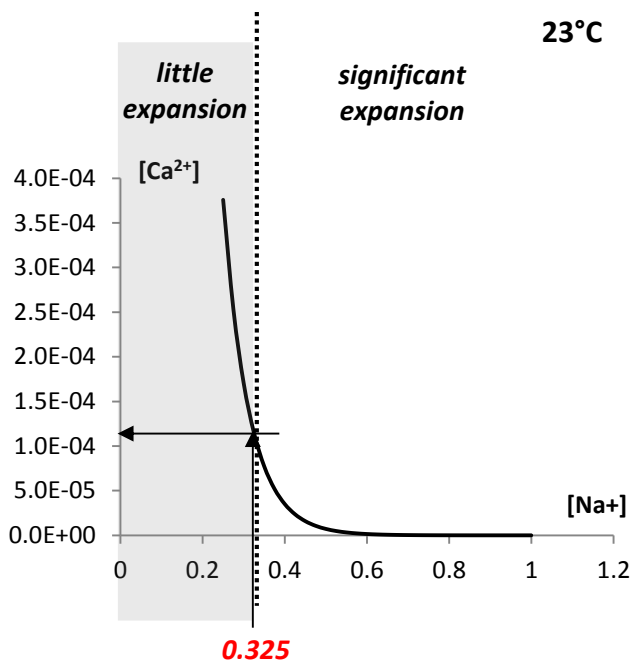


Figure 3: Calcium concentration (mol/l) according to alkali concentration (mol/l) in solution at 23°C due to portlandite equilibrium and limit of expansion of ASR-gels

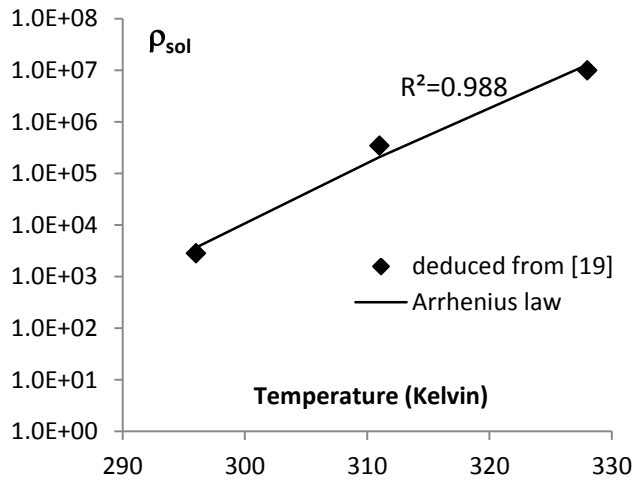


Figure 4: Evolution of  $\rho_{sol}^{(T)}$  for the determination of alkali threshold with temperature

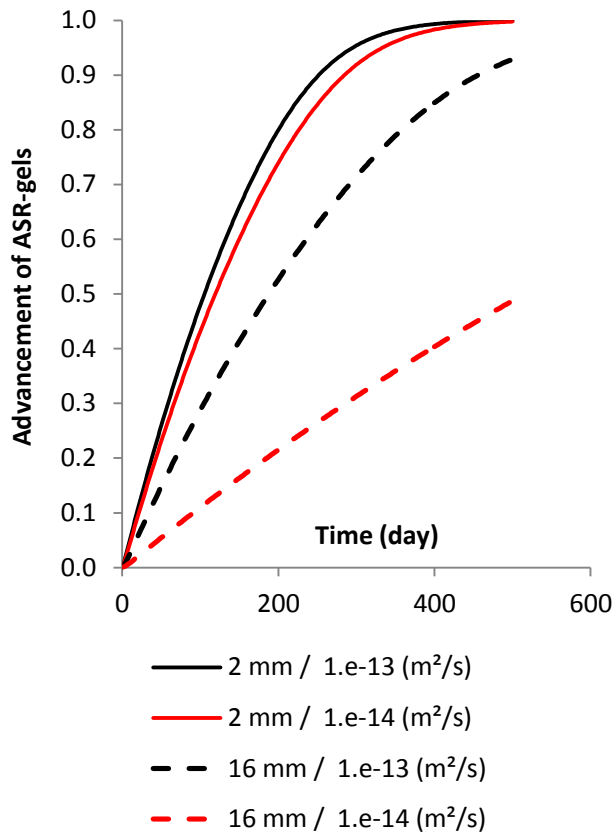
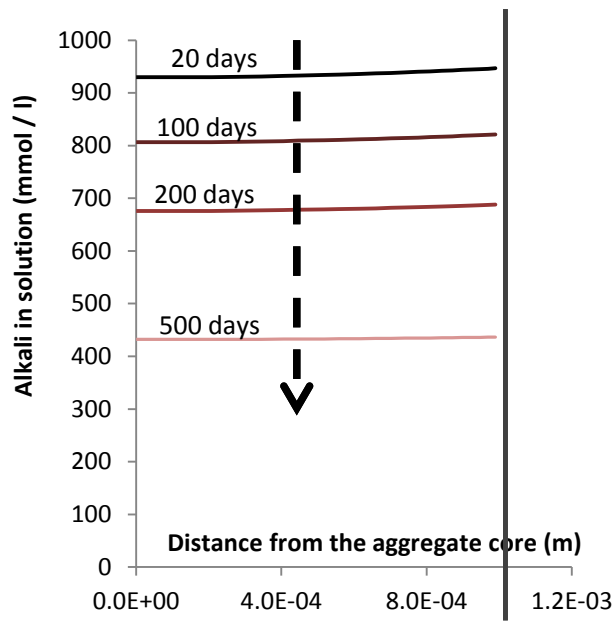


Figure 5: Kinetics of gel formation for coefficients of diffusion of  $1.e^{-13} \text{ m}^2/\text{s}$  and  $1.e^{-14} \text{ m}^2/\text{s}$  and the same characteristic time of reaction of 500 days for two sizes of aggregate (mean diameters 2 and 16 mm)

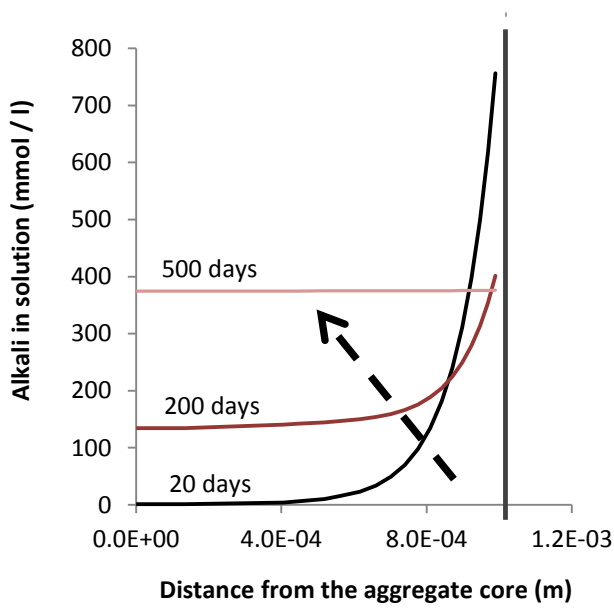
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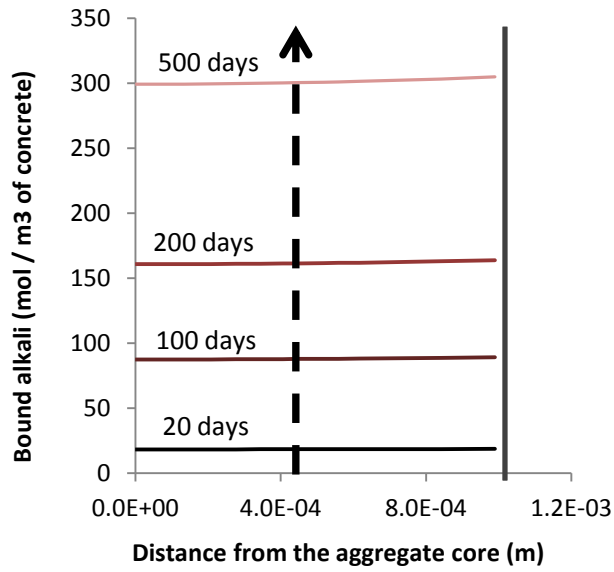


(a)

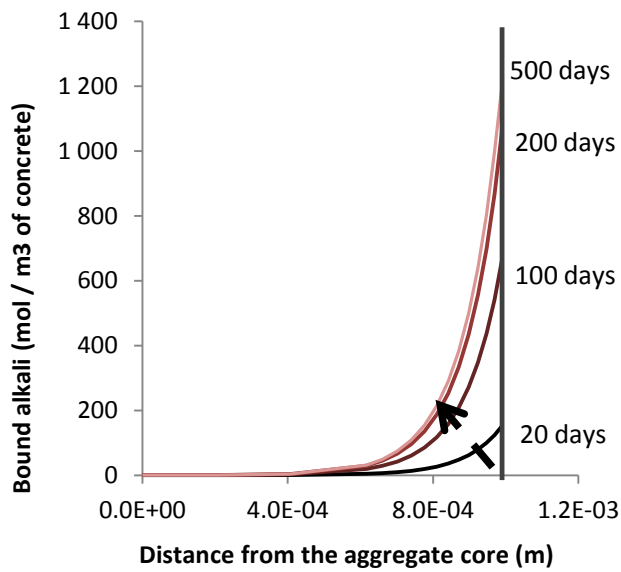


(b)

Figure 6: Profiles of free alkali in an aggregate of mean diameter of 2 mm: (a) coefficient of diffusion of  $1 \cdot 10^{-13} \text{ m}^2/\text{s}$  and characteristic time of reaction of 1000 days, (b) coefficient of diffusion of  $1 \cdot 10^{-15} \text{ m}^2/\text{s}$  and characteristic time of reaction of 100 days



(a)



(b)

Figure 7: Profiles of alkali bound in ASR-gels for an aggregate of mean diameter of 2 mm: (a) coefficient of diffusion of  $1 \cdot 10^{-13} \text{ m}^2/\text{s}$  and characteristic time of reaction of 1000 days, (b) coefficient of diffusion of  $1 \cdot 10^{-15} \text{ m}^2/\text{s}$  and characteristic time of reaction of 100 days

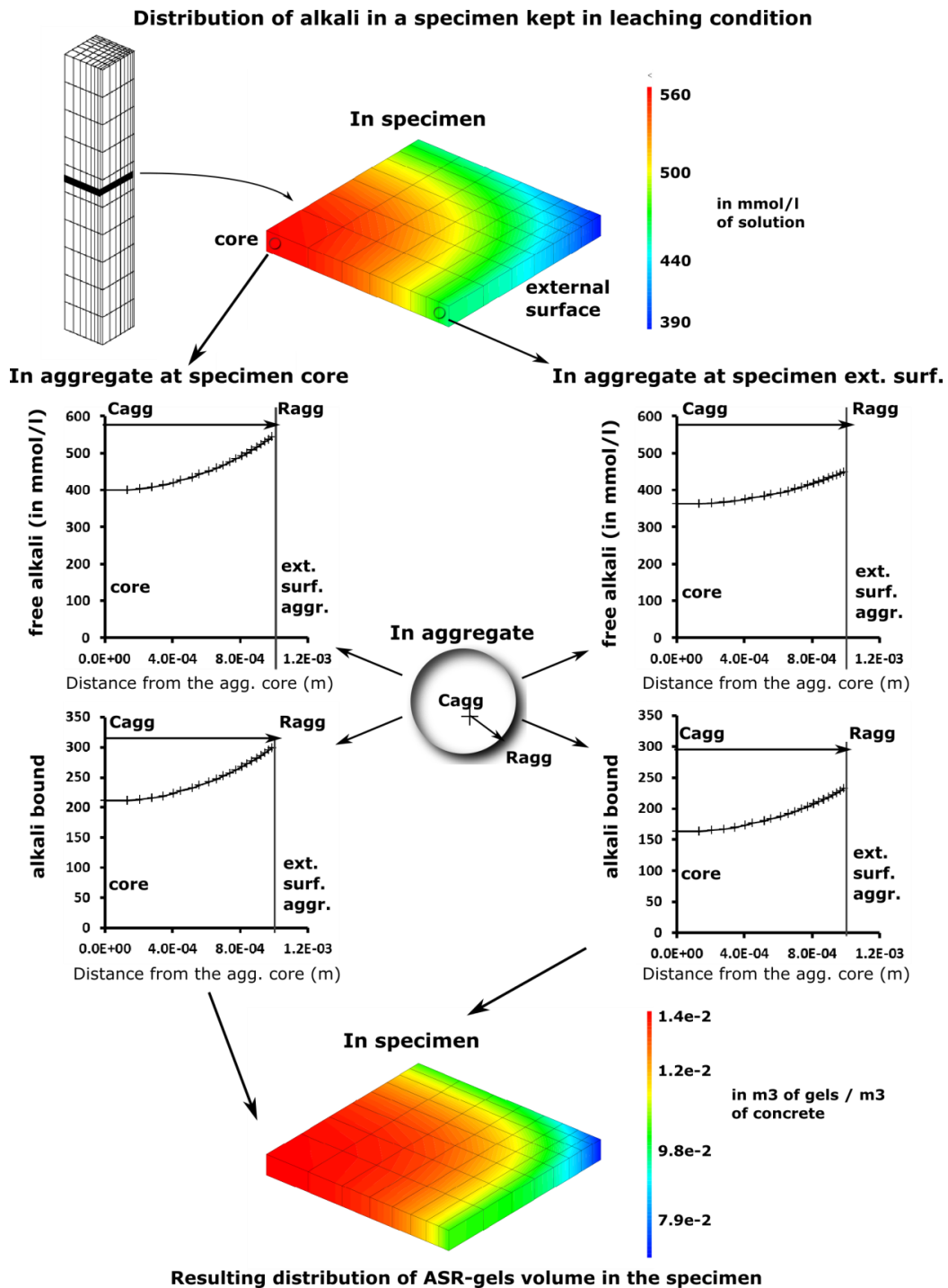


Figure 8: Slices of specimens (100x100 mm cross section) subjected to ASR in moderate leaching condition (aggregate coefficient of diffusion of  $1 \cdot 10^{-14}$  m<sup>2</sup>/s and characteristic time of reaction of 500 days). Top: distribution of alkali in specimen, middle: gradient of free and bound alkali in aggregates in the core and at the external surface of the specimen, bottom: resulting distribution of ASR-gels in specimen

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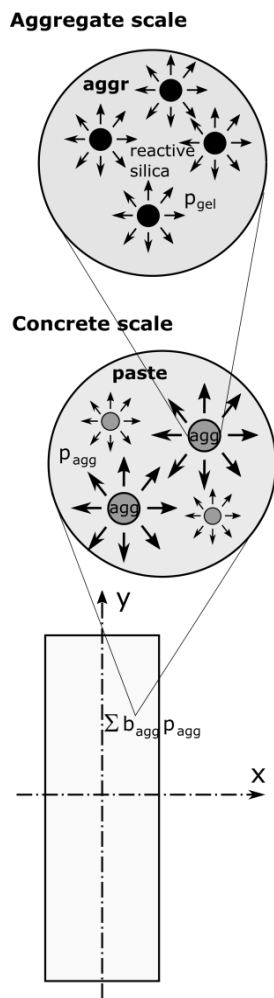
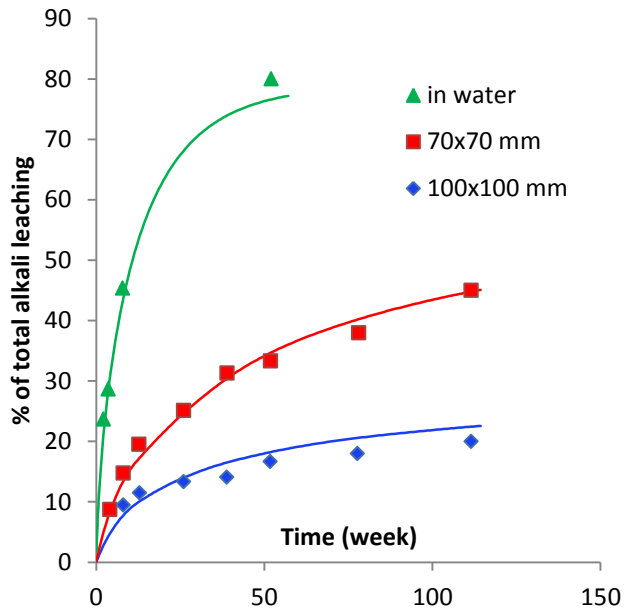
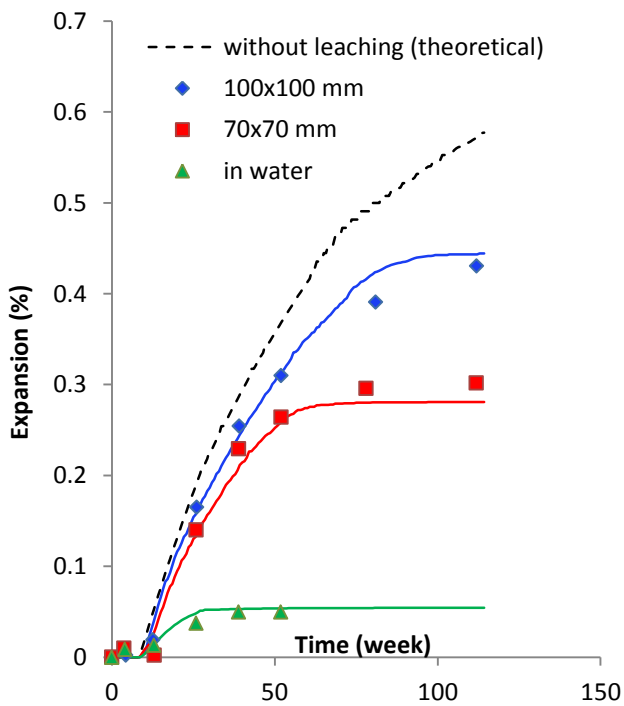


Figure 9: Pressure induced by ASR-gels in aggregate and resulting pressure in concrete



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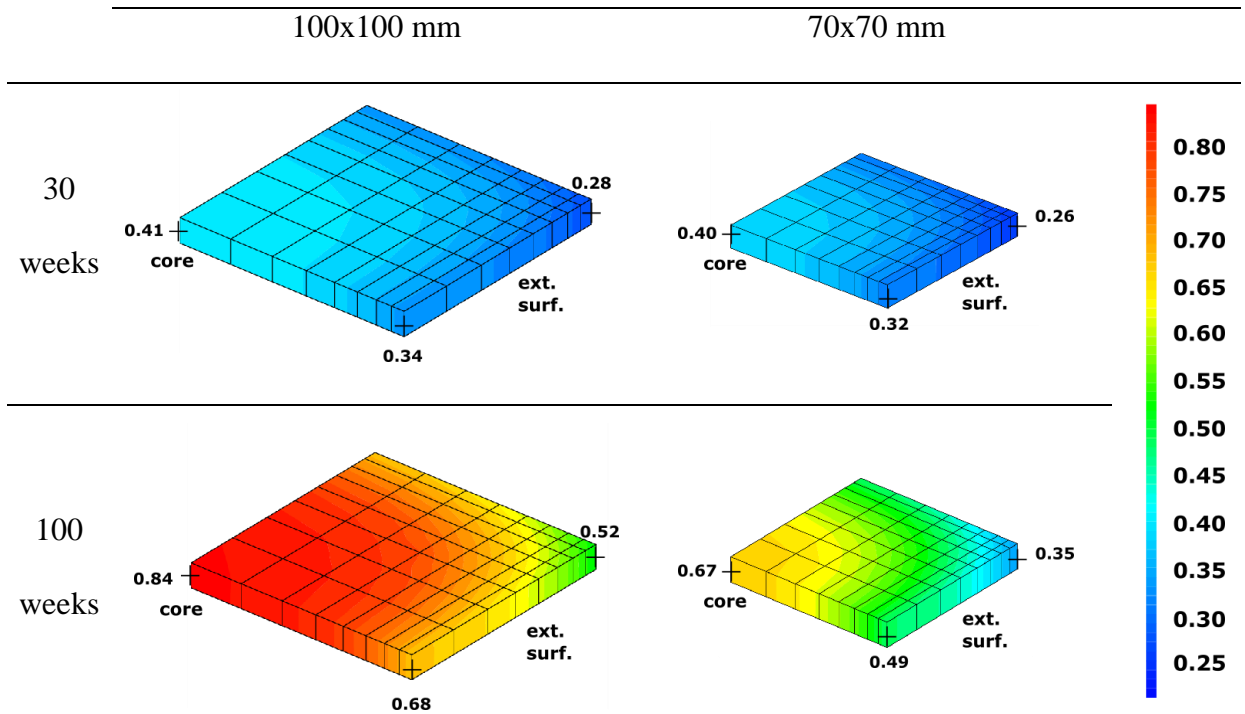
719 Figure 10: Total alkali leaching according to specimen size and storage in Lindgard's  
 720 experiments [5] (points) and numerical modelling (curves)  
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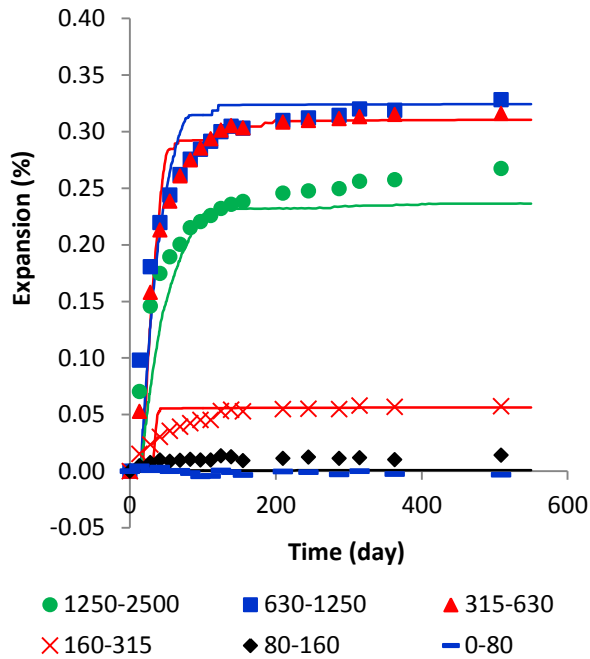
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723 Figure 11: Expansion according to specimen size and storage in Lindgard's  
 724 experiments [5] (points) and numerical modelling (curves)

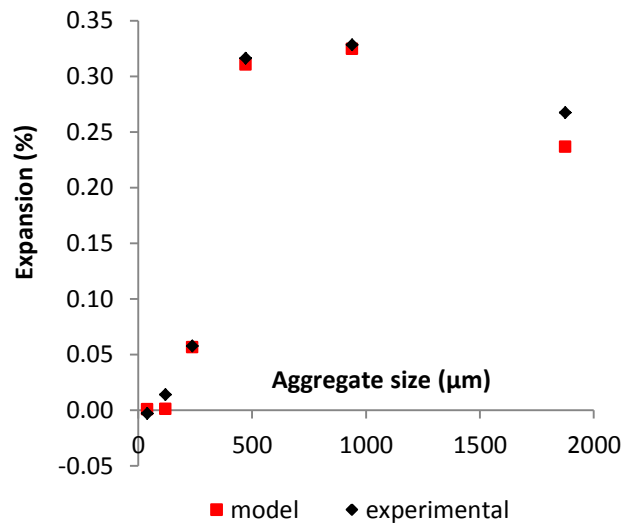
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730 Figure 12: Advancement of ASR in one size of aggregate in the specimens of  
 731 Lindgard's experiments [5] after 30 and 100 weeks  
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 734 Figure 13: Expansion according to aggregate size [59] (points) and numerical  
 735 modelling (curves)  
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738 Figure 14: Pessimism effect in expansion due to aggregate size, experimentation and  
 739 modelling

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