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## **The combined effect of potassium, sodium and calcium on the formation of alkali-silica reaction products**

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25 **Abstract:**

26 Both alkalis and calcium play essential roles in the formation of alkali-silica reaction (ASR)  
27 products. Investigation of their combined effect helps to better understand the conditions of  
28 ASR. In this study, samples with a constant Ca/Si ratio of 0.3 but different K(or Na)/Si and  
29 K/Na ratios have been synthesized at 80 °C. Experimental studies and thermodynamic  
30 modelling show that a sufficient amount of K or Na is essential to initiate ASR; at low alkali  
31 concentrations C-S-H is stabilized instead. However, too high alkaline concentrations ( $\geq 900$   
32 mM at K(or Na)/Si  $\geq 1$ ) also favor C-S-H formation and suppress ASR product formation.  
33 The results reveal a strong effect of the alkalis (K and/or Na) on calcium concentrations and  
34 on the formation of ASR products; a maximum ASR product formation is observed at Na or  
35 K concentrations between 200 to 500 mM and at initial Ca/Si ratio between 0.1 and 0.4.

36

37

38 **Keywords:** alkali-silica reaction; ASR-P1; Na-shlykovite; C-S-H; thermodynamic modelling

39

## 40 1. Introduction

41 Alkali-silica reaction (ASR) is one of the concrete durability issues causing expansion,  
42 cracking, and consequently shortening of the service life of concrete. Based on the chemical  
43 composition of the ASR products reported in a number of studies [1][2][3][4], it is clear that  
44 the presence of reactive silica, alkalis and some calcium are essential conditions for ASR. In  
45 addition to be incorporated into ASR products, both alkalis and calcium can also maintain a  
46 high pH of the solution which is necessary for dissolution and structural breakdown of  
47 reactive silica. However, under certain conditions, rather calcium-silicate-hydrate (C-S-H)  
48 containing some alkalis instead of ASR products forms [5][6]. This underlines the need to  
49 further explore more precisely the conditions of ASR or C-S-H formation. Moreover, most of  
50 the ASR mitigation approaches are based on the design of starting mixtures, such as by  
51 proper use of low alkali cements and/or supplementary cementitious materials (SCMs) during  
52 concrete manufacturing [7][2]. Thus a better understanding the formation conditions of ASR  
53 products is also significant for the development of new approaches to mitigate ASR in  
54 existing concrete structures.

55 Direct evaluation of the precise conditions for formation of ASR products in concrete is  
56 difficult due to the small amount and sizes of the ASR products formed in concrete  
57 aggregates. ASR products have been recently successfully synthesized in the laboratory [4],  
58 which makes it feasible to further investigate the formation conditions of ASR products in  
59 such model systems. In a parallel study, the effect of initial Ca/Si ratio on formation of ASR  
60 products has been investigated [8]. Both experimental studies and thermodynamic modelling  
61 have demonstrated that three different types of ASR products (K-shlykovite:  
62  $\text{KCaSi}_4\text{O}_8(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ , Na-shlykovite:  $\text{NaCaSi}_4\text{O}_8(\text{OH})_3 \cdot 2.3\text{H}_2\text{O}$ , and ASR-P1:  $\text{K}_{0.52}\text{Ca}_{1.16}\text{Si}_4$   
63  $\text{O}_8(\text{OH})_{2.84} \cdot 1.5\text{H}_2\text{O}$ ) could form depending on the initial Ca/Si ratios and type of alkalis. The  
64 results showed that all types of the ASR products tend to be converted to C-S-H at Ca/Si  
65 ratios over 0.5. More specifically, for the K-containing samples, conversion of the crystalline  
66 K-shlykovite to the nano-crystalline ASR-P1 and further to C-S-H was observed with  
67 increasing Ca/Si ratios.

68 In addition to calcium [4][9][10][7][8], also alkalis are essential to form ASR products,  
69 since ASR will not form in the absence of alkalis even if calcium hydroxide could also  
70 maintain the high level of pH. Small amounts of alkalis do not necessarily lead to the  
71 formation of ASR products as alkalis can be incorporated into C-S-H without damaging its  
72 intrinsic structure [5][6]. Only few studies determined the minimum OH<sup>-</sup> ion concentrations  
73 of the pore solution (0.2 – 0.25 M) required to initiate and sustain ASR in concrete [11][12].  
74 Because of the slow formation of ASR products, accelerated testing methods by boosting the  
75 alkali content of cements or exposing the samples to high alkaline solution were usually  
76 adopted [2]. However, severe alkali boosting might be problematic as it will mask the role of  
77 alkalis from the cements [2]. As a consequence, only very few studies have focused on the  
78 ASR in concrete with extensively high alkali content [2][13][14]. Interestingly, these studies  
79 have shown that extensively high alkali content tend to reduce the ASR expansion in concrete  
80 samples [2] and in the NaOH-activated slag mortars [13][14]. These observations could be  
81 related to the reduced calcium concentration at very high pH values, as calcium is essential  
82 for the formation of ASR products [10]. Other studies showed that very high alkali  
83 concentration and thus very high pH values (> 13) result in C-S-H with high Ca/Si ratios  
84 [15][16] without causing ASR.

85 In addition to the alkali concentration, the type of alkalis may also influence the ASR  
86 expansion of concrete, as higher expansion is observed for concrete with a relatively higher  
87 fraction of Na than K [17]. In fact, accelerated testing methods usually use NaOH instead of  
88 KOH and it was observed that the presence of K or Na resulted in formation of different ASR  
89 products, even though they have similar crystal structure [4]. Most of the cements contain a  
90 higher proportion of K<sub>2</sub>SO<sub>4</sub> than Na<sub>2</sub>SO<sub>4</sub> [7].

91 So far, it is not completely clear which calcium and alkalis concentrations lead to the  
92 formation of ASR products or C-S-H. In this study, samples with a constant initial Ca/Si ratio  
93 of 0.3 but different K(or Na)/Si and K/Na ratios are investigated. After synthesis of these  
94 samples at 80 °C, both solid and aqueous phases were analyzed with different techniques.  
95 Thermodynamic modeling using the developed thermodynamic data for three different ASR

96 products i.e., K-shlykovite, Na-shlykovite and ASR-P1 from [8], is also employed to  
97 calculate the aqueous compositions and solid phase assemblages. Although the samples were  
98 synthesized at high temperature, previous studies have shown strong similarity in term of  
99 chemical composition and structure between the synthesized ASR products and ASR products  
100 formed in concrete aggregates [4][18], in particular that the synthesized K-shlykovite was  
101 almost identical to ASR products formed in concrete aggregate after concrete prism test at  
102 60 °C according to Raman spectroscopy results [4], which support the use of the synthesized  
103 ASR products for further understanding ASR.

104

## 105 **2. Materials and methods**

### 106 **2.1 Sample preparations**

107 Samples with a constant Ca/Si molar ratio of 0.3 but different K(or Na)/Si and K/Na  
108 molar ratios were synthesized by mixing appropriate quantities of SiO<sub>2</sub> (hydrophilic silica,  
109 surface area 200 m<sup>2</sup>/g, from EVONIK industries) with CaO (obtained by burning calcium  
110 carbonate for 12 h at 1000 °C) and analytical KOH (≥ 85% KOH basis, 92 ± 3% based on IC  
111 measurements) and/or NaOH (≥ 99.9% NaOH basis) pellet as shown in Table 1 and Fig. 1. For  
112 the samples containing only K as alkali source, two series of experiments with high (60 – 100  
113 g per mixing) and low (30 – 50 g per mixing) water contents were prepared. For each series  
114 of experiments containing either K or Na as the only alkali source, the water content was  
115 somewhat increased for the samples with lower alkali/Si ratios in order to better disperse the  
116 solids during mixing. For the samples containing both K and Na, same amount of water was  
117 applied, as they have the same (K+Na)/Si molar ratio of 0.5.

118 All the samples were mixed in 100 mL hard polyethylene (PE-HD) bottles (from  
119 Semadeni AG) and equilibrated at 80 °C for 90 days. Afterwards, samples were filtrated using  
120 paper filters with mesh size of 20 µm. Roughly 5 mL solution was immediately filtered with  
121 0.45 µm syringe filter for pH measurements and analysis of the solution compositions. The  
122 solids were rinsed first with approximately 50 mL of 1:1 water-ethanol solution and then with  
123 50 mL 94% ethanol solution in the N<sub>2</sub> filled glove box. The obtained solids were then

124 vacuumed dried for 7 days, and stored in N<sub>2</sub> filled desiccators with CO<sub>2</sub> absorbent to minimize  
125 carbonation.

126

## 127 **2.2 Methods**

### 128 **2.2.1 Experimental methods**

129 The obtained solids were analyzed by a X-ray powder diffraction (XRD, PANalytical  
130 X'pert Pro) with CoK $\alpha$  radiation in a  $\theta$ – $\theta$  configuration. The samples were scanned with a step  
131 size of 0.017° 2 $\theta$  between 5 and 90° 2 $\theta$  with the X'Celerator detector during 150 min. The <sup>29</sup>Si  
132 MAS NMR spectra were recorded from two laboratories on a Bruker Avance III 400 MHz  
133 (9.39T) spectrometer at 79.5 MHz at Empa in Switzerland, and on a Varian Direct-Drive  
134 VNMR-600 (14.09 T) spectrometer at 119.1 MHz at Aarhus University in Denmark, using a  
135 home-built CP/MAS probes for 7 mm o.d. PSZ rotors. For the 400 MHz NMR spectrometer,  
136 the following parameters were applied: 4500 Hz sample rotation rate, minimum of 10240  
137 scans or more, 30° <sup>1</sup>H pulse of 2.5  $\mu$ s, 20 s relaxation delays, RF field strength of 33.3 kHz  
138 during SPINAL64 proton decoupling. For the 600 MHz NMR spectrometer, a spinning speed  
139 of 6.0 kHz, a 3.0  $\mu$ s excitation pulse for  $\gamma B_1 / 2\pi \approx 42$  kHz, a 60 s relaxation delay, and 2048  
140 scans were employed. The <sup>29</sup>Si isotropic chemical shifts are reported relative to neat  
141 tetramethyl silane.

142 The pH was measured for part of the filtrated solution at room temperature around 23 °C  
143 with a Knick pH meter (pH-Meter 766) equipped with a Knick SE100 electrode. The electrode  
144 was calibrated with KOH or NaOH solutions of known concentrations to minimize the alkali  
145 error caused by the presence of high K and Na concentrations [19]. Another part of filtrated  
146 solution was diluted in ratios of 1:10, 1:100 and 1:1000 with MilliQ water immediately after  
147 filtration and used for ionic chromatography (IC) analysis. The bulk chemical composition of  
148 the obtained solids is calculated by mass balance based on the chemical composition of the  
149 starting materials and the chemical composition of the solution at equilibrium by taking into  
150 account the bound water in the solids (wt.% of sample ignited at 980°C) measured by  
151 thermogravimetric analysis (TGA). For the reported chemical compositions, the impurities of

152 the KOH pellet used have been taken into account in the mass balance; and the reported  
153 errors are calculated by taking into account 10% of analytical error of the measured  
154 concentrations used for mass balance.

155

## 156 **2.2.2 Thermodynamic modelling**

157 In this study, the PSI/Nagra general thermodynamic database [20] and the Cemdata18  
158 database [21] are used to calculate the ion concentrations in the equilibrium solution and solid  
159 phases precipitated. The thermodynamic data for the C-N-S-H [22] and C-K-S-H [8] as  
160 summarized in Table 2 are used to predict the precipitation of C-S-H. Experimentally  
161 developed thermodynamic data for Na-shlykovite, K-shlykovite and ASR-P1 from another  
162 study [8] (see Table 2) are also incorporated in the GEMS codes to predict the formation of  
163 ASR products. It should be noted that the general thermodynamic database [20] used describes  
164 the aqueous silica complexes at high silica concentration only poorly, in particular at high  
165 temperatures as temperature parameters for polynuclear silica species are not available.

166

## 167 **3. Results**

### 168 **3.1 Samples containing either K or Na**

#### 169 **3.1.1 Phase assemblages**

170 The XRD patterns for the K- or Na-containing samples with high and low water contents  
171 after 90 days of reaction are shown in Fig. 2. For K-containing samples, the formation of only  
172 C-S-H is observed for the SCK<sub>0</sub> sample without any K as expected, together with some  
173 unreacted amorphous silica as reflected by the hump observed at 26° 2θ. In case addition of  
174 some K, an amorphous product is observed as the main reaction product for the samples with  
175 initial K/Si ratios ranging from 0.25 to 0.75. This phase was recently described by Shi et al.  
176 [4] as an nano-crystalline ASR product and named as ASR-P1:  $K_{0.52}Ca_{1.16}Si_4$   
177  $O_8(OH)_{2.84} \cdot 1.5H_2O$ . According to the previous studies [4][8], a crystalline ASR product (i.e.,  
178 K-shlykovite:  $KCaSi_4O_8(OH)_3 \cdot 2H_2O$ ) could also form in the CaO-SiO<sub>2</sub>-K<sub>2</sub>O system.  
179 However, K-shlykovite was only observed for the samples with initial Ca/Si ratios lower than

180 0.3 [8], which explains the absence of this phase in the present study due to the high Ca/Si  
181 ratio of 0.3 used for all the samples. Further increasing K/Si ratio up to 1, ASR-P1  
182 co-existing with C-S-H is observed in the SCK<sub>1</sub> samples with both high and low water  
183 contents. The results suggest that a possible destabilization of ASR products to C-S-H can  
184 occur at very high alkali content. The opposite, the conversion of C-S-H to ASR products  
185 could take place when K/Si ratio is increased from 0 to 0.25 as indicated by the XRD results  
186 in Fig. 2.

187 In contrast to the K-containing samples, where C-S-H is replaced by ASR-P1 at initial  
188 K/Si ratio of 0.25, C-S-H remains as the main reaction product when initial Na/Si ratio is up  
189 to 0.25 for Na-containing samples. With further increase of Na/Si ratio from 0.5 to 0.75, a  
190 crystalline ASR product, Na-shlykovite: NaCaSi<sub>4</sub>O<sub>8</sub>(OH)<sub>3</sub>·2.3H<sub>2</sub>O, is formed as the main  
191 reaction product. This phase has been recently identified by Shi et al. [4] to form at 80 °C in  
192 the presence of Na and has a similar structure as K-shlykovite. At highest Na/Si ratio of 1,  
193 C-S-H is again observed as the main reaction product, indicating a nearly full conversion of  
194 Na-shlykovite to C-S-H at high Na content, in contrast to the corresponding K-containing  
195 samples where ASR-P1 is only partially converted to C-S-H as shown in Fig. 2. No  
196 amorphous ASR product such as ASR-P1 is observed in any of the Na-containing samples.

197 The formation of ASR-P1 in K-containing samples and Na-shlykovite in Na-containing  
198 samples together with formation of C-S-H is also confirmed by <sup>29</sup>Si MAS NMR spectra on  
199 the selected samples as shown in Fig. 3. For the K-containing samples, the results show that  
200 mainly C-S-H with a chemical shift at -85 ppm and some unreacted amorphous silica with a  
201 chemical shift at -110 ppm are present in the SCK<sub>0</sub> sample. At higher K/Si ratio of 0.25, the  
202 intensity of the Q<sup>2</sup> sites associated with C-S-H is significantly reduced, followed by the  
203 increased intensity of Q<sup>3</sup> site with a chemical shift at -91 ppm associated with ASR-P1  
204 according to our previous study [4]. ASR-P1 co-existing with C-S-H is also observed from  
205 <sup>29</sup>Si NMR spectrum for the SCK<sub>0.75</sub> sample, although C-S-H is not yet visible from XRD due  
206 to the amorphous nature and smaller amount of the C-S-H formed in this sample.



207 For the Na-containing samples, the  $^{29}\text{Si}$  MAS NMR spectra show the presence of mainly  
208 low Ca/Si C-S-H and some traces of  $\text{Q}^3$  at around 95 ppm from surface Si-OH species of  
209 unreacted silica (-110 ppm) in the  $\text{SCN}_0$  sample. Minor fraction of  $\text{Q}^2$  species related to C-S-H  
210 and the dominating  $\text{Q}^3$  related to pure Na-shlykovite are observed in the  $\text{SCN}_{0.5}$  sample,  
211 suggesting that a nearly full conversion of C-S-H to Na-shlykovite has taken place by  
212 increasing Na/Si ratio up to 0.5. At highest Na/Si ratio of 1, mainly  $\text{Q}^2$  associated with C-S-H  
213 with traces of  $\text{Q}^3$  is observed, suggesting a phase conversion from ASR product to C-S-H. By  
214 comparing the  $^{29}\text{Si}$  NMR spectra between the samples  $\text{SCN}_0$  and  $\text{SCN}_1$ , around 2-3 ppm  
215 chemical shift to less negative values is observed for the  $\text{SCN}_1$  sample indicating an uptake of  
216 Na in the structure of C-S-H and thus less shielding of the  $^{29}\text{Si}$  NMR spectra as reported  
217 previously [6][23].

218

### 219 3.1.2 Solution chemistry

220 The measured concentrations of Ca, K (or Na) and Si in the supernatants together with the  
221 pH values measured at 23 °C for the K- or Na-containing samples with high and low water  
222 contents are shown in Table 3 and Fig. 4. The results show that the Si concentrations of the  
223 equilibrium solution are higher at higher initial K/Si or Na/Si ratios, which is due to the  
224 higher K or Na concentrations and thus higher pH values of the solution, as the solubility of  
225 amorphous silica is known to increase with the increase of pH [24]. For the two series of  
226 K-containing samples with high and with low water contents, the concentration of K and Si  
227 are higher for the samples with lower water content. However, no significant differences in  
228 the pH values are observed between these two series of experiments as both K and Si  
229 concentrations are increased. This effect has been also observed in another study [8]. In  
230 contrast to these observations, the calcium concentrations of the equilibrium solutions are one  
231 order of magnitude lower for the samples with lower water contents where high Si and K  
232 concentrations were present. Moreover, the calcium concentrations decrease with increasing  
233 K/Si or Na/Si as a result of the common ion effect between K (or Na), Si and Ca, similar to  
234 the tendencies observed for C-(A)-S-H samples in the presence of different quantities of

235 alkali hydroxide solutions [6][25][26]. This common ion effect indicates the formation of  
236 solids, which contain calcium, silicon and potassium.

237

### 238 **3.1.3 Thermodynamic modelling**

239 The changes in measured concentrations of the equilibrium solutions and pH values,  
240 together with the phase assemblages with increasing K/Si or Na/Si ratio are predicted by  
241 thermodynamic modelling as shown in Fig. 5 based on the thermodynamic data for the  
242 synthesized ASR products: K-shlykovite, Na-shlykovite and ASR-P1 summarized in Table 2.  
243 For comparison, the experimental data from Table 3 are also plotted in the same figure.  
244 Generally, thermodynamic modelling shows similar trends for the changes in equilibrium  
245 concentrations and pH values with increasing K/Si or Na/Si ratio as the experimental  
246 observations. At low K/Si or Na/Si ratios, where ASR-P1 or Na-shlykovite are present, both K  
247 (or Na) and Si concentrations increase in parallel, while at higher K/Si or Na/Si ratio (> 0.8)  
248 where only C-S-H is predicted, the K or Na concentrations and thus also pH increases while the  
249 Si concentrations remains rather constant. For the K-containing samples, the modelled pH  
250 values change similarly for the two series samples at high and at low water contents. Some  
251 differences in the absolute values between the calculated and measured data were observed,  
252 which might be related to poorly described aqueous polynuclear silica complexes at high Si  
253 concentrations and at high temperature as already observed in other studies [4][8].

254 In addition to the equilibrium concentrations, the stable solid phases are also calculated as  
255 shown in Fig. 5. The results show that only ASR-P1 is predicted in the K-containing samples  
256 for both high and low water contents, which agrees very well with the XRD (Fig. 2) and <sup>29</sup>Si  
257 NMR (Fig. 3) observations. Na-shlykovite is predicted in the SCN<sub>0.5</sub> sample, which is also  
258 observed from XRD (Fig. 2) and <sup>29</sup>Si NMR (Fig. 3) results. The amount of C-S-H is predicted  
259 to decrease and then increase with increasing K/Si or Na/Si ratio. The predicted minimum  
260 amount of C-S-H is found to be related to the formation of maximum amount of ASR-P1 or  
261 Na-shlykovite.

262

### 263 **3.1.4 Bulk chemical compositions of the solids**

264 Using the initial compositions of the mixtures and the measured concentrations at  
265 equilibrium, the bulk compositions of the solids for the K- or Na-containing samples with both  
266 high and low water contents are also calculated by mass balance as summarized in [Table 3](#) and  
267 shown in [Fig. 6](#). For comparison, the chemical compositions of the K-shlykovite, ASR-P1 and  
268 Na-shlykovite from another study [\[8\]](#) are also plotted in the same figure. The results show that  
269 the bulk Ca/Si ratio of the obtained solids increases with the increase of initial K/Si or Na/Si  
270 ratio. The observation of higher Ca/Si ratio than those of K-shlykovite, ASR-P1 and  
271 Na-shlykovite support the co-precipitation of C-S-H with ASR products observed from  
272 experiments and predicted by thermodynamic modelling ([Fig. 5](#)). The bulk K/Si ratios for the  
273 obtained solids also increase with increasing initial K/Si ratio for the K-containing samples  
274 with low water contents, while the bulk K/Si ratio of the obtained solids for the samples with  
275 high water contents increases and then decreases with increasing the initial K/Si ratios. The  
276 Na/Si ratio of the solids increases first and then tends to be stabilized at  $\text{Na/Si} = 0.25$  at very  
277 high initial Na/Si ratios. This is also in agreement with the amount of solid phases predicted by  
278 thermodynamic modelling in [Fig. 5](#), which is decreasing for ASR products and increasing for  
279 C-S-H (similar to K-containing samples). The maximum alkali binding capacity (K or Na) of  
280 low C-S-H is about 0.25 [\[6\]](#), comparable to K/Si or Na/Si ratio of 0.25 for Na(K)-shlykovite.

281 In summary, the Na-containing samples show a similar behavior as the K-containing  
282 samples: in both cases ASR products (Na-shlykovite or ASR-P1) are stabilized at  
283 intermediate alkali hydroxide concentrations in the range of 200 to 500 mM (see [Table 3](#)),  
284 while at lower and higher concentrations C-S-H is stabilized instead. The results also show  
285 that Na-shlykovite is somewhat less stable than ASR-P1.

286

## 287 **3.2 Samples containing both K and Na**

### 288 **3.2.1 Phase assemblages**

289 In addition to the pure K- or Na-containing samples, ASR products with varying  
290 combinations of K and Na in different proportions are also synthesized; all with a total

291 alkali/Si ratio of 0.5; i.e., at conditions where mainly Na-shlykovite or ASR-P1 had formed as  
292 discussed above. Their XRD patterns obtained after 90 days of reaction are shown in Fig. 7  
293 together with two endmembers (SCK<sub>0.5</sub> and SCN<sub>0.5</sub>) presented in previous sections. No major  
294 differences are observed for all of these samples as ASR-P1 is the only ASR product formed  
295 except for the Na-endmember (SCN<sub>0.5</sub>), where Na-shlykovite is present instead. Based on the  
296 results in Fig. 2, pure ASR-P1 (e.g. in sample SCK<sub>0</sub>) and C-S-H (e.g. in sample SCK<sub>0.25</sub>) can  
297 be distinguished by their XRD patterns based on the slight different peak positions. In  
298 addition, their XRD patterns between 30 and 35° 2θ also show different line shapes. Pure  
299 C-S-H phase synthesized in this study has a narrow and strong asymmetric line shape, while  
300 pure ASR-P1 show a broad and nearly symmetric line shape. Thus, the characteristic of both  
301 broad and asymmetric line shape for the reaction products formed in the samples containing  
302 both K and Na in Fig. 7 indicate the presence of C-S-H in addition to ASR-P1, which is also  
303 confirmed by <sup>29</sup>Si MAS NMR spectra on the selected samples as shown in Fig. 8. No  
304 K-shlykovite is observed in any of the samples, as the relatively high Ca/Si ratio of 0.3 favors  
305 the formation of ASR-P1 [4][8]. Na-shlykovite, which is able to form at Ca/Si ratio of 0.3, is  
306 not observed in any of the samples containing K, which suggests that the presence of K  
307 stabilizes ASR-P1. Overall, the results suggest that ASR-P1 is a quite stable phase, which is  
308 able to form at a wide range of K/Na ratios at the investigated temperature of 80 °C.

309

### 310 **3.2.2 Solution chemistry and thermodynamic modelling**

311 The measured concentrations of Ca, K, Na and Si in the supernatants together with the pH  
312 values for the samples containing both K and Na with different K/Na ratios and constant  
313 (K+Na)/Si ratio of 0.5 are shown in Table 4 and Fig. 9. As the total alkali concentration  
314 (K+Na) is nearly constant, some variation of pH is always accompanied by change of the Si  
315 concentration, since the negatively charged silicate ions affect the concentration of OH<sup>-</sup> in  
316 solution to charge balance Na<sup>+</sup> and/or K<sup>+</sup> ions. Overall, in contrast to the samples containing  
317 only K or Na presented in previous sections where the equilibrium concentrations and the  
318 measured pH are significantly affected by the initial alkali/Si ratios, the differences in the

319 measured concentrations and pH values are less significant for all the samples with different  
320 K/Na ratios. The similar chemistry environment of the equilibrium solutions supports the  
321 XRD observations that mainly one type of ASR products (i.e., ASR-P1) is formed in these  
322 samples containing both Na and K.

323 Thermodynamic modelling for these samples (Fig. 10) also shows that the equilibrium  
324 concentrations and pH values are expected to remain more or less constant, which is in line  
325 with the experimental results. The main differences between the different samples are the  
326 relative concentration of K and Na, which is increasing for K and decreasing for Na with  
327 increasing initial K/Na ratios. Both the measured and predicted constant concentration of Si  
328 suggests that the dissolved amount of silicon is mainly controlled by the formation of  
329 ASR-P1 and thus by the total alkali content and pH. Also some C-S-H is expected to be  
330 present in all of the samples. The calculated changes in the K and Na concentrations in the  
331 equilibrium solutions agree well with experimentally observed changes. Also the presence of  
332 a comparable amount ASR-P1 is predicted for all of these samples as the only type of ASR  
333 product, except for the sample with no (or very low) K content.

334

### 335 **3.2.3 Bulk chemical compositions of the solids**

336 Based on the initial composition and the measured concentration of the equilibrium  
337 solutions, the bulk compositions of the solids for the samples containing both K and Na are  
338 calculated by mass balance as summarized in Table 4 and shown in Fig. 11. Generally, the bulk  
339 Ca/Si ratios are above 0.3 as shown in Table 4, which are higher than Ca/Si ratio of shlykovite  
340 and ASR-P1 without Na, and support the presence of some C-S-H in the samples. The results  
341 in Table 4 also show an increase in bulk K/Si ratio and a decrease in Na/Si ratio with increasing  
342 initial K/Na ratio. However, the Ca/(K+Na) ratios remain more or less constant except for the  
343 SCK<sub>0.38</sub>N<sub>0.12</sub> sample.

344

#### 345 4. Discussion

346 The effect of alkali/Si ratio on the formation of ASR products is similar for both K- and  
347 Na-containing samples. ASR products form at intermediate alkali contents, while at low and  
348 high alkali contents rather C-S-H is stable. At higher initial alkali/Si ratio of 1, ASR products  
349 are destabilized to C-S-H, and co-precipitation of ASR product with C-S-H for K-containing  
350 sample or formation of only C-S-H in Na-containing is observed. In fact, few studies have  
351 demonstrated that ASR expansion could be lowered after extensively boosting the alkalis  
352 [2][13][14], in particular for the alkali-activated slag mortars which contain less calcium than  
353 Portland cement [13][14]. The present study indicates that the reduced ASR expansion at  
354 very high alkali content [2][13][14] is likely due to formation of C-S-H instead of ASR  
355 products. The destabilization of ASR products to C-S-H has also been observed in some other  
356 studies [3][4][8][27][28] and has been attributed to excess amount of calcium due to the  
357 increased initial Ca/Si ratio of the model system [4][8][27], or to the ingress of calcium from  
358 its environment in the case of ASR products found near the cement paste of concrete  
359 [3][28][18].

360 The opposite, the conversion of C-S-H to ASR products could take place when alkali/Si  
361 ratio is increased from 0 up to over 0.25 as indicated by the XRD results in Fig. 2. Several  
362 studies in model systems stated that C-S-H was firstly formed and then converted to ASR  
363 products after portlandite was depleted [29][30][27][31]. However, this phenomenon has  
364 been so far only identified in model system, where the solutions are initially saturated with  
365 portlandite, which may be different from the actual sequence of ASR in concrete. The present  
366 study indicates that the formation sequence of ASR products and C-S-H in model system is  
367 dependent on the relative amounts of alkalis (K or Na) and of Ca, which can be controlled  
368 when mixing the materials in laboratory studies. However, in real concrete  $K^+$  and/or  $Na^+$   
369 ions may enter easier and faster into aggregate due to its smaller radius of hydrated ions  
370 compared to the hydrated  $Ca^{2+}$  ions [32]. In addition,  $K^+$  and  $Na^+$  concentrations in the pore  
371 solution are much higher than Ca concentrations [33][34], which also eases the transport of  
372 alkalis into the aggregates. Thus, it is likely that ASR products are firstly formed within the

373 aggregates in concrete, followed by gradual uptake of calcium and further conversion to  
374 C-S-H as evidenced in many studies by the increased Ca/Si of the reaction products away  
375 from the center of aggregates [3][28][18]. In addition, it can be expected that the presence of  
376 other ions in concrete such as aluminum, lithium as well as the limited availability of water  
377 and temperature history would play a further role, indicating the needs of more dedicated and  
378 systematic work to reveal the mechanism of ASR.

379

## 380 **5. Conclusions**

381 The presence of K and/or Na together with a limited amount of Ca is essential to form  
382 ASR products. Different ASR products are formed at 80 °C with different types of alkalis.  
383 For the K-containing samples, a nano-crystalline ASR product, ASR-P1 ( $K_{0.52}Ca_{1.16}$   
384  $Si_4O_8(OH)_{2.84} \cdot 1.5H_2O$ ), is observed. In none of the samples is K-shlykovite ( $KCaSi_4O_8$   
385  $(OH)_3 \cdot 2H_2O$ ) observed, as the relatively high initial Ca/Si ratio of 0.3 stabilizes rather  
386 ASR-P1 than K-shlykovite. In contrast, in the Na-containing samples a crystalline ASR  
387 product, Na-shlykovite ( $NaCaSi_4O_8(OH)_3 \cdot 2.3H_2O$ ), is formed as Na-shlykovite is slightly  
388 more stable than K-shlykovite.

389 The formation of Na-shlykovite is observed only at  $Na/Si > 0.25$ , while in the  
390 K-containing systems ASR-P1 is formed at lower K/Si ratios. In the presence of K, ASR-P1  
391 is stabilized instead of Na-shlykovite, such that in all samples containing both K and Na,  
392 ASR-P1 is dominant solid formed, indicating that ASR-P1 is more stable than shlykovite at  
393 Ca/Si ratios above 0.25 in agreement with our previous observation [8]. Na-shlykovite is  
394 observed experimentally only in the absence of K.

395 Both IC analysis and thermodynamic calculations show that the increase of the initial  
396 K(or Na)/Si ratios leads to an increase in pH values and K(or Na) concentrations, but to a  
397 reduction in Ca concentrations. As a result, the bulk Ca/Si ratios of the obtained solids  
398 increase with increasing initial K(or Na)/Si ratio. In comparison, the increase of the bulk K(or  
399 Na)/Si ratio in the obtained solids with increasing the initial K(or Na)/Si ratio is limited and  
400 even reduced, for instance for the K-containing samples with high water contents as in

401 addition to ASR products C-S-H is formed. No obvious changes in solution chemistry and  
402 solid compositions are observed for the samples containing both K and Na, as also predicted  
403 by thermodynamic modelling.

404 At a fixed initial Ca/Si ratio of 0.3, ASR products form at intermediate alkali contents,  
405 while at low and high alkali contents rather C-S-H and/or amorphous silica are stable. At a  
406 fixed alkali/Si ratio of 0.5, ASR products are formed at intermediate Ca/Si ratios from 0.1 to  
407 0.4; at lower Ca/Si ratio SiO<sub>2</sub> is expected to dominate while at higher Ca/Si ratio more C-S-H  
408 is present. Together as indicated in [Fig. 12](#), Ca/Si, K/Si and Na/Si ratios at which maximum  
409 ASR product formation can be expected.

410

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502  
503

504 Table 1

505 Starting materials and mixing proportions for the samples.

Samples	SiO <sub>2</sub>	CaO	NaOH	KOH	H <sub>2</sub> O <sup>a</sup>	water/solid	Ca/Si	(K+Na)/Si	K/Na
	g	g	g	g	g	g/g	mol/mol		
CaO-SiO <sub>2</sub> -K <sub>2</sub> O with high(low) water contents									
SCK <sub>0</sub>	4	1.12	-	0	100	19.5	0.3	0	-
SCK <sub>0.25</sub>	4	1.12	-	0.94	100(50)	16.5(8.25)	0.3	0.25	-
SCK <sub>0.5</sub>	4	1.12	-	1.87	60(30)	8.6(4.3)	0.3	0.5	-
SCK <sub>0.75</sub>	4	1.12	-	2.8	60(30)	7.6(3.8)	0.3	0.75	-
SCK <sub>1</sub>	4	1.12	-	3.74	60(30)	6.8(3.4)	0.3	1	-
CaO-SiO <sub>2</sub> -Na <sub>2</sub> O with only high water contents									
SCN <sub>0</sub>	4	1.12	0	-	100	19.5	0.3	0	-
SCN <sub>0.25</sub>	4	1.12	0.67	-	100	17.3	0.3	0.25	-
SCN <sub>0.5</sub>	4	1.12	1.33	-	60	9.3	0.3	0.5	-
SCN <sub>0.75</sub>	4	1.12	1.99	-	60	8.4	0.3	0.75	-
SCN <sub>1</sub>	4	1.12	2.66	-	60	7.7	0.3	1	-
CaO-SiO <sub>2</sub> -K <sub>2</sub> O-Na <sub>2</sub> O									
SCK <sub>0.455</sub> N <sub>0.045</sub>	4	1.12	0.12	1.69	60	8.6	0.3	0.5	10
SCK <sub>0.43</sub> N <sub>0.07</sub>	4	1.12	0.19	1.6	60	8.7	0.3	0.5	6
SCK <sub>0.38</sub> N <sub>0.12</sub>	4	1.12	0.33	1.4	60	8.7	0.3	0.5	3
SCK <sub>0.30</sub> N <sub>0.20</sub>	4	1.12	0.53	1.12	60	8.8	0.3	0.5	1.5
SCK <sub>0.25</sub> N <sub>0.25</sub>	4	1.12	0.67	0.93	60	8.9	0.3	0.5	1
SCK <sub>0.17</sub> N <sub>0.33</sub>	4	1.12	0.88	0.62	60	9.1	0.3	0.5	0.5

506 <sup>a</sup> Two series of samples were prepared for the K-containing samples with low (30 – 50) and high (60 –  
507 100) water contents.

508

509

510

511 Table 2.

512 Solubility products for the C-(N-)K-S-H solid solution and three ASR products at 1 atm.

Phases <sup>a</sup>	Log <sub>10</sub> K <sub>S0</sub> <sup>b</sup>	Ref
<i>Solubility products for the C-(N-)K-S-H solid solution at 25 °C</i>		
T2C <sup>*</sup> : C <sub>3/2</sub> S <sub>1</sub> H <sub>5/2</sub>	-11.6	[22]
T5C <sup>*</sup> : C <sub>5/4</sub> S <sub>5/4</sub> H <sub>5/2</sub>	-10.5	[22]
TobH <sup>*</sup> : C <sub>1</sub> S <sub>3/2</sub> H <sub>5/2</sub>	-7.9	[22]
INFCN: C <sub>1</sub> N <sub>5/16</sub> S <sub>3/2</sub> H <sub>19/16</sub>	-10.7	[22]
INFCK: C <sub>1</sub> K <sub>5/16</sub> S <sub>3/2</sub> H <sub>19/16</sub>	-11.2	[8]
<i>Solubility products for the ASR products at 80 °C</i>		
K-shlykovite: KCaSi <sub>4</sub> O <sub>8</sub> (OH) <sub>3</sub> ·2H <sub>2</sub> O	-25.8 ± 2.0 <sup>c</sup>	[8]
ASR-P1: K <sub>0.52</sub> Ca <sub>1.16</sub> Si <sub>4</sub> O <sub>8</sub> (OH) <sub>2.84</sub> ·1.5H <sub>2</sub> O	-27.1 ± 1.1 <sup>c</sup>	[8]
Na-shlykovite: NaCaSi <sub>4</sub> O <sub>8</sub> (OH) <sub>3</sub> ·2.3H <sub>2</sub> O	-26.5 ± 2.0 <sup>c</sup>	[8]

513 <sup>a</sup> For the nomenclature of C-(N-)K-S-H, the cement chemistry term is used, i.e., C = CaO, N = Na<sub>2</sub>O,  
 514 K = K<sub>2</sub>O, S = SiO<sub>2</sub> and H = H<sub>2</sub>O. Extrapolation from 25 to 80°C is done using the tabulated entropy  
 515 and heat capacity values as detailed in [22] and [8].

516 <sup>b</sup> The solubility products refer to the solubility with respect to the species SiO<sub>2</sub><sup>0</sup>, OH<sup>-</sup>, H<sub>2</sub>O, Ca<sup>2+</sup>, K<sup>+</sup> and  
 517 Na<sup>+</sup>.

518 <sup>c</sup> The solubility product of ASR products refer to: K<sub>S0,K-shlykovite</sub> = {K<sup>+</sup>} · {Ca<sup>2+</sup>} · {SiO<sub>2</sub><sup>0</sup>}<sup>4</sup> ·  
 519 {OH<sup>-</sup>}<sup>3</sup> · {H<sub>2</sub>O}<sup>2</sup>; K<sub>S0,Na-shlykovite</sub> = {Na<sup>+</sup>} · {Ca<sup>2+</sup>} · {SiO<sub>2</sub><sup>0</sup>}<sup>4</sup> · {OH<sup>-</sup>}<sup>3</sup> · {H<sub>2</sub>O}<sup>2.3</sup>; K<sub>S0,ASR-P1</sub> =  
 520 {K<sup>+</sup>}<sup>0.52</sup> · {Ca<sup>2+</sup>}<sup>1.16</sup> · {SiO<sub>2</sub><sup>0</sup>}<sup>4</sup> · {OH<sup>-</sup>}<sup>2.84</sup> · {H<sub>2</sub>O}<sup>1.5</sup>.

521

522 **Table 3**

523 The measured dissolved concentrations in the equilibrium solutions and compositions of the  
 524 solids for the K- or Na-containing samples with high and low water contents, together with  
 525 the phases identified in these samples by XRD and <sup>29</sup>Si NMR.

Samples	Si	K	Ca	pH <sup>a</sup>		Ca/Si	K(or Na)/Si	Bound water	Identified phases	Log <sub>10</sub> K <sub>SO</sub> <sup>b</sup>
	mM	mM	mM	23 °C	80 °C	Solids (mol/mol)		wt%		ASR-P1
K containing samples with high water contents										
SCK <sub>0</sub>	0.9	≤ 0.002	0.98	9.5	8	0.30 ± 0.01	-	14.1	C-S-H	-
SCK <sub>0.25</sub>	6.9	28.1	0.03	10.7	9.2	0.30 ± 0.01	0.19 ± 0.01	10.3	ASR-P1	-25.5
SCK <sub>0.5</sub>	135	228	0.33	12.2	10.7	0.34 ± 0.01	0.31 ± 0.03	13.3	ASR-P1	-26.5
SCK <sub>0.75</sub>	308	553	0.34	13.1	11.7	0.41 ± 0.02	0.32 ± 0.08	15.9	ASR-P1+C-S-H	-28.4
SCK <sub>1</sub>	448	983	0.09	13.5	12	0.49 ± 0.04	0.16 ± 0.16	18.9	ASR-P1+C-S-H	-29.9
K-containing samples with low water contents										
SCK <sub>0.25</sub>	38.8	42.3	0.05	10.8	9.3	0.31 ± 0.01	0.21 ± 0.01	12.3	ASR-P1	-24.9
SCK <sub>0.5</sub>	399	421	0.1	12.4	10.9	0.36 ± 0.01	0.36 ± 0.02	15.9	ASR-P1	-27.3
SCK <sub>0.75</sub>	603	922	0.02	13.4	11.9	0.41 ± 0.01	0.44 ± 0.07	17.2	ASR-P1	-30.1
SCK <sub>1</sub>	858	1446	0.03	13.6	12.2	0.47 ± 0.03	0.54 ± 0.13	18.4	ASR-P1+C-S-H	-30.4
Na-containing samples with low water contents										
SCN <sub>0</sub>	3.7	≤ 0.01	1	9.2	7.7	0.30 ± 0.01	0	16.6	C-S-H	-
SCN <sub>0.25</sub>	99	82	0.32	11.1	9.7	0.35 ± 0.01	0.15 ± 0.02	20	C-S-H	-
SCN <sub>0.5</sub>	442	382	0.07	11.7	10.2	0.49 ± 0.04	0.27 ± 0.07	21.3	Na-shlykovite+C-S-H	-26.8
SCN <sub>0.75</sub>	427	632	0.01	12.9	11.4	0.48 ± 0.03	0.31 ± 0.12	22.7	Na-shlykovite	-29.1
SCN <sub>1</sub>	659	987	0.02	13.1	11.6	0.71 ± 0.11	0.32 ± 0.29	26	C-S-H	-

526 <sup>a</sup> The pH values have been measured at 23°C and corrected for the effect of temperature on measured  
 527 pH values by deducing 1.47 pH units to account for the strong decrease of measured pH values at  
 528 higher temperature of 80 °C even at constant OH<sup>-</sup> concentrations.

529 <sup>b</sup> At high total Si concentration, polynuclear Si-species dominate the solution; their speciation and  
 530 stability at higher temperature is not well known, which associates the obtained solubility products with  
 531 an increased error. The solubility products of ASR-P1 and Na-shlykovite calculated are added for  
 532 comparison only.

533

534 **Table 4**

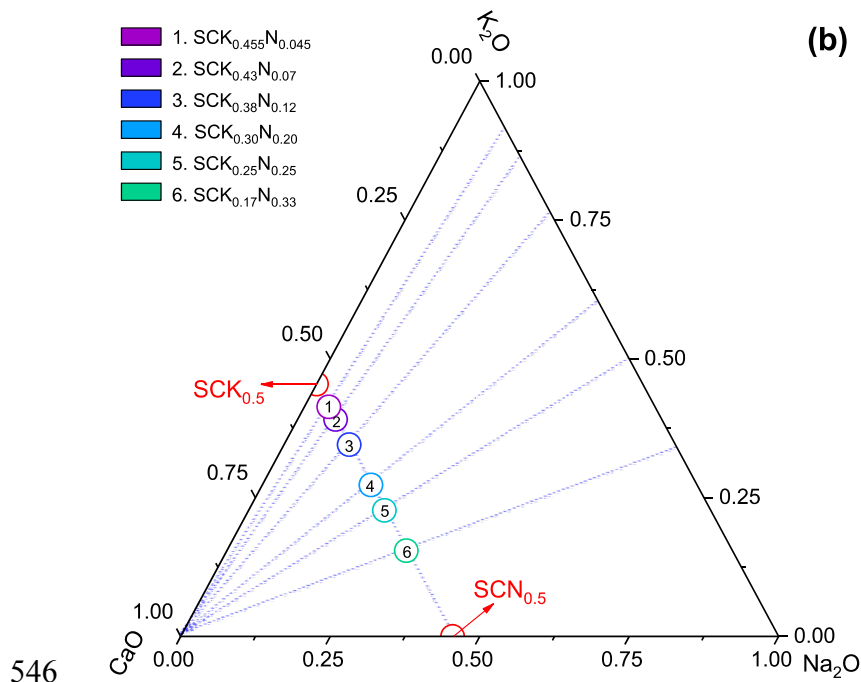
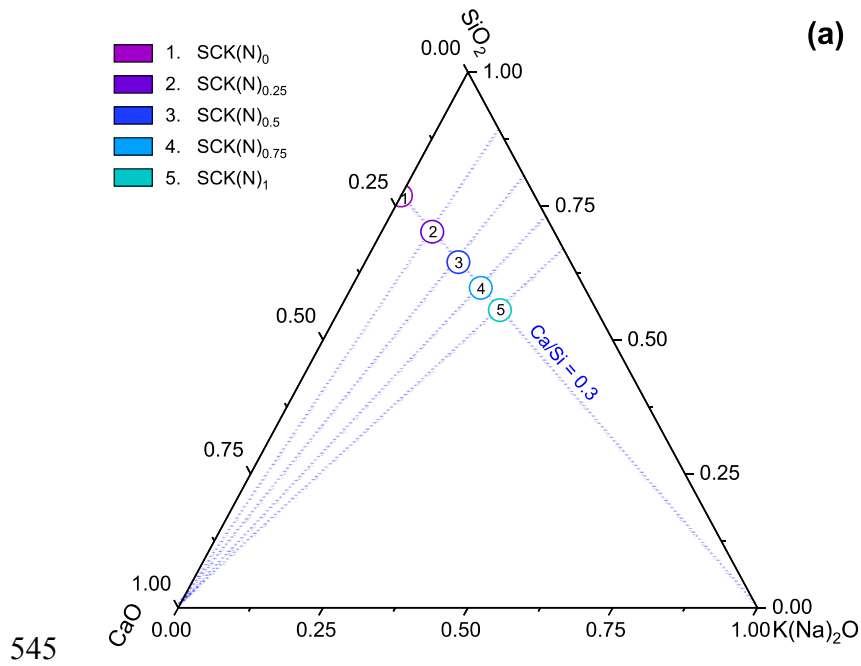
535 The measured dissolved concentrations in the equilibrium solutions and compositions of the  
 536 solids for the samples containing both K and Na together with the phases identified in these  
 537 samples by XRD.

Samples	Si	Na	K	Ca	pH <sub>cal</sub>		Ca/Si	K/Si	Na/Si	Bound water wt%	Identified phases	Log <sub>10</sub> K <sub>S0</sub> <sup>b</sup>
	mM	mM	mM	mM	23 °C	80 °C <sup>a</sup>	Solids (mol/mol)					ASR-P1
SCK <sub>0.455</sub> N <sub>0.045</sub>	241	17.9	224	0.03	11.9	10.4	0.38 ± 0.01	0.28 ± 0.03	0.04 ± 0.01	16.5	ASR-P1	-27.2
SCK <sub>0.43</sub> N <sub>0.07</sub>	227	32.2	198	0.11	11.9	10.4	0.38 ± 0.01	0.27 ± 0.03	0.05 ± 0.01	17.1	ASR-P1	-26.6
SCK <sub>0.38</sub> N <sub>0.12</sub>	400	92	228	0.02	11.6	10.1	0.46 ± 0.03	0.22 ± 0.05	0.07 ± 0.01	16.0	ASR-P1	-27.4
SCK <sub>0.30</sub> N <sub>0.20</sub>	215	119	110	0.04	12.0	10.6	0.37 ± 0.01	0.22 ± 0.02	0.12 ± 0.01	17.3	ASR-P1	-27.5
SCK <sub>0.25</sub> N <sub>0.25</sub>	196	149	71.2	0.02	12.1	10.7	0.36 ± 0.01	0.20 ± 0.01	0.14 ± 0.01	16.4	ASR-P1	-28.0
SCK <sub>0.17</sub> N <sub>0.33</sub>	177	193	19.9	0.04	12.1	10.7	0.36 ± 0.01	0.16 ± 0.01	0.19 ± 0.01	17.6	ASR-P1	-28.0

538 <sup>a</sup> The pH values have been measured at 23 °C and corrected for the effect of temperature on measured  
 539 pH values by deducing 1.47 pH units to account for the strong decrease of measured pH values at  
 540 higher temperature of 80 °C even at constant OH<sup>-</sup> concentrations.

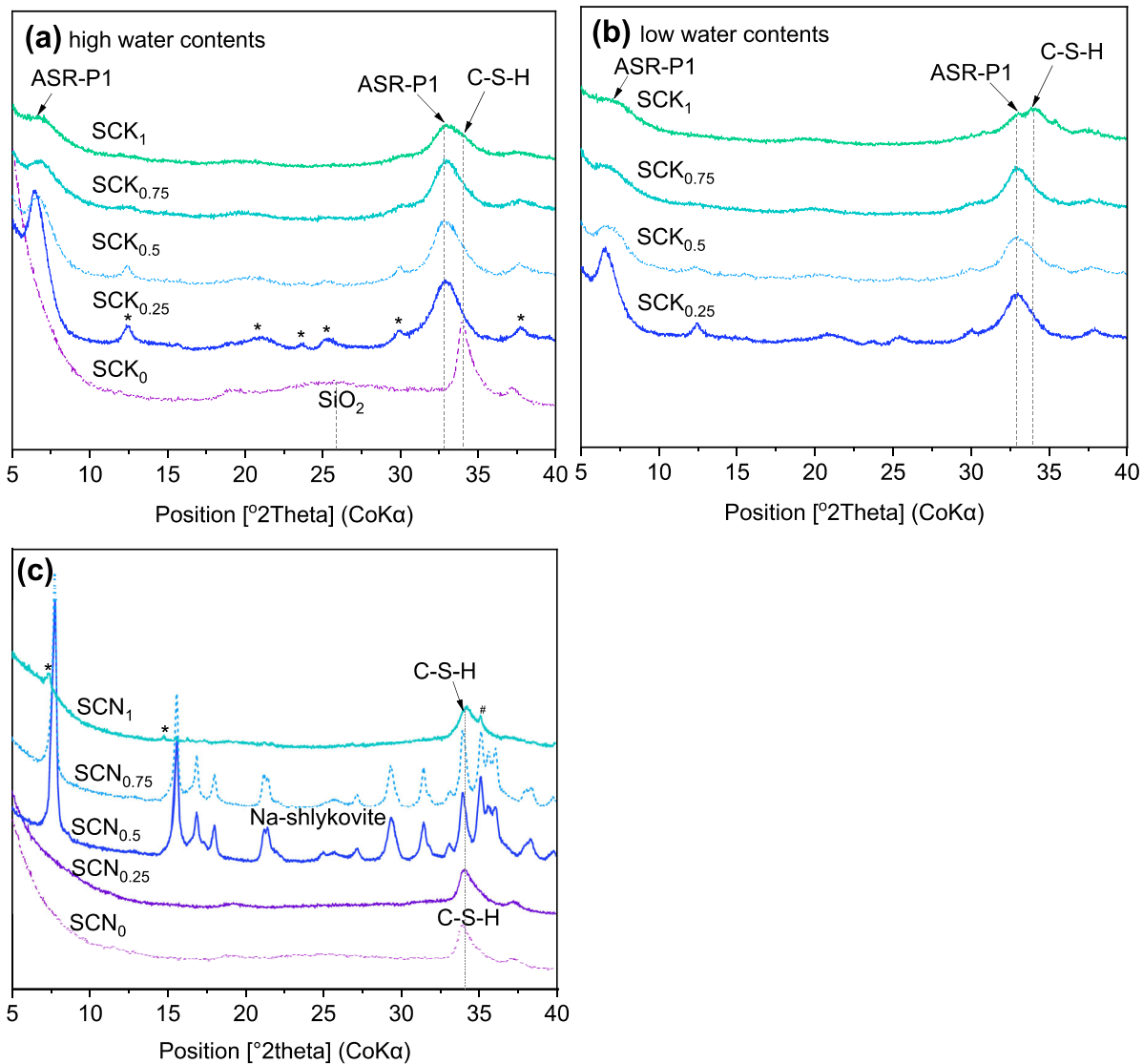
541 <sup>b</sup> At high total Si concentration, polynuclear Si-species dominate the solution; their speciation and  
 542 stability at higher temperature is not well known, which associates the obtained solubility products with  
 543 an increased error. The solubility products of ASR-P1 calculated are thus added for comparison only.

544



547 **Fig. 1.** Bulk chemical compositions (units in molar fraction) of the starting materials  
 548 projected in ternary diagram for (a) the K- or Na-containing samples, and (b) the samples  
 549 with different K/Na ratios including the two end-members from (a).  
 550



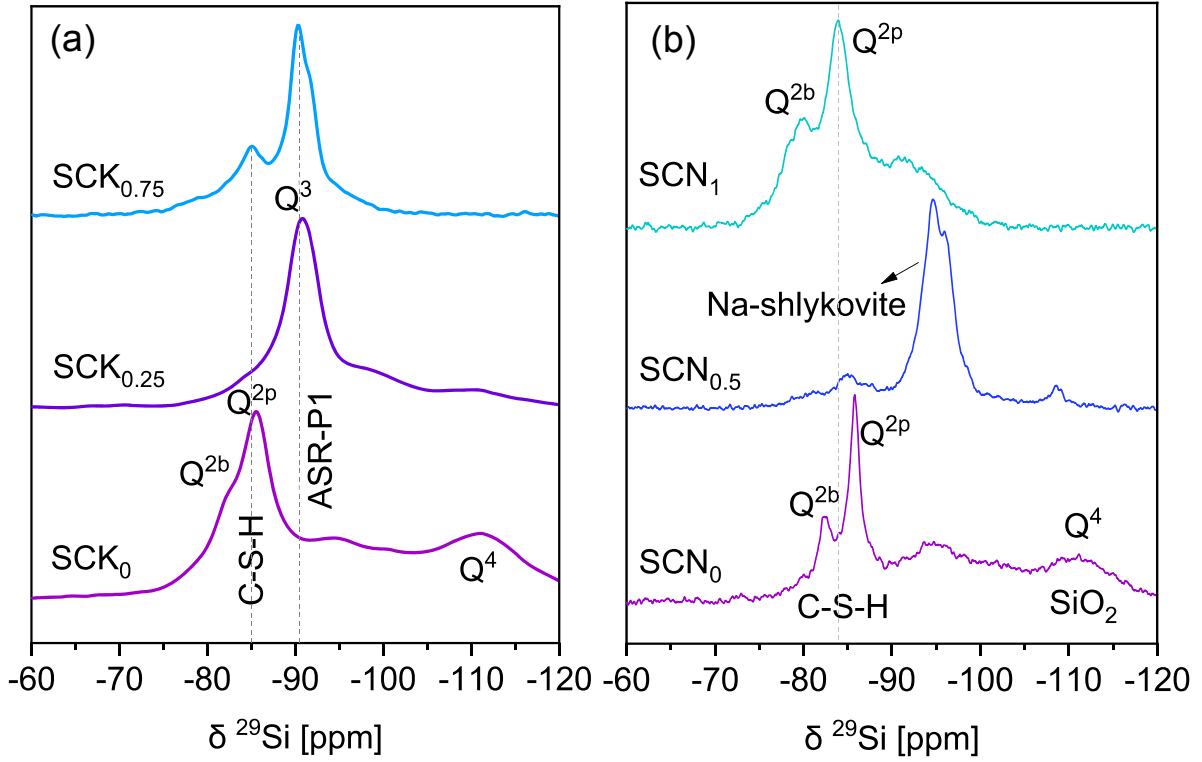


551

552

553 **Fig. 2.** XRD patterns for the solids obtained after 90 days of reaction for the K-containing  
 554 samples with (a) high and (b) low water contents, and (c) for the Na-containing samples with  
 555 high water contents. Note: the asterisk (\*) designates the unidentified peaks; the pound sign  
 556 (#) indicates the presence of natrite ( $\text{Na}_2\text{CO}_3$ , PDF# 98-006-8104) due to a slight carbonation  
 557 of the alkaline solutions. C-S-H: calcium-silicate-hydrate; ASR-P1: a nano-crystalline ASR  
 558 product described in [4]. Na-shlykovite is the only crystalline product formed in  
 559 Na-containing samples with Na/Si ratio of 0.5 and 0.75.

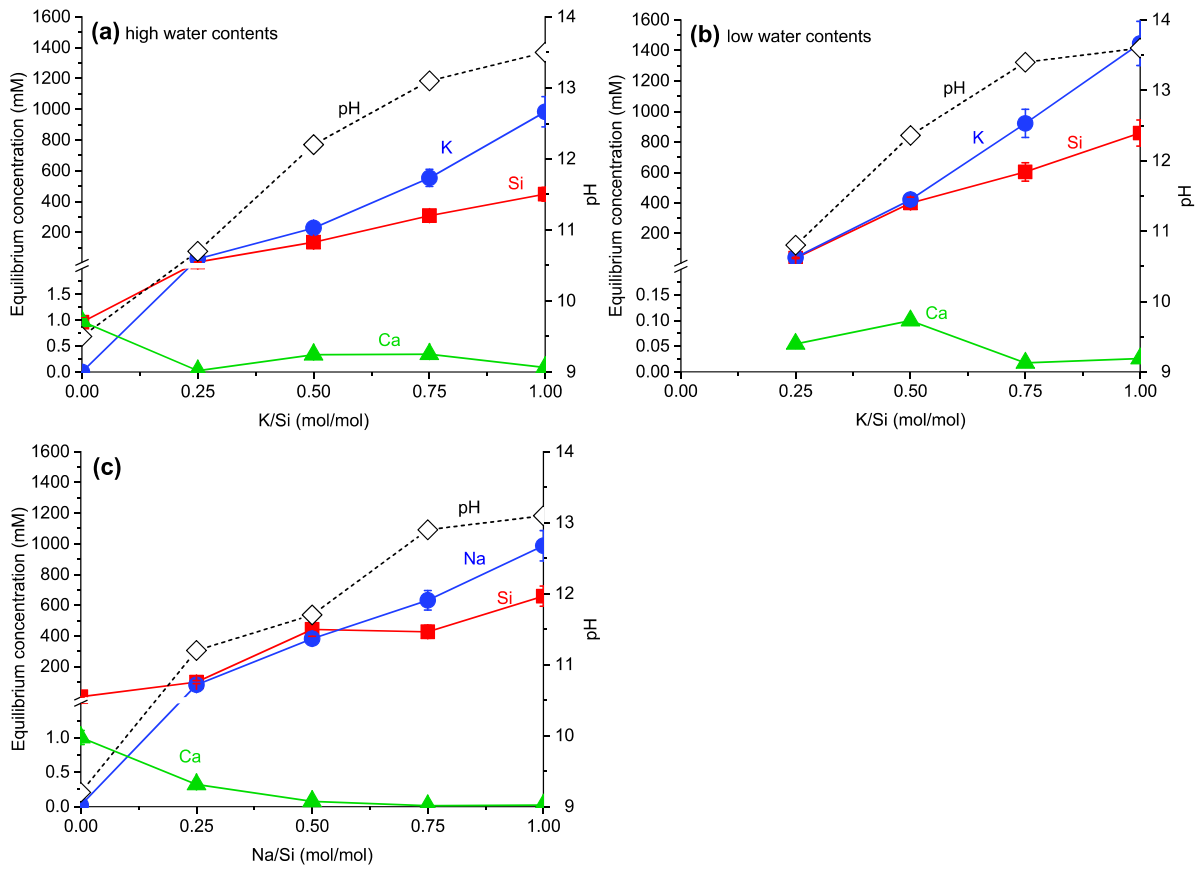
560



561

562 **Fig. 3.**  $^{29}\text{Si}$  MAS NMR spectra acquired (a) at 79.5 MHz for the selected K-containing  
 563 samples with high water contents, and (b) at 119.1 MHz for the selected Na-containing  
 564 samples.

565

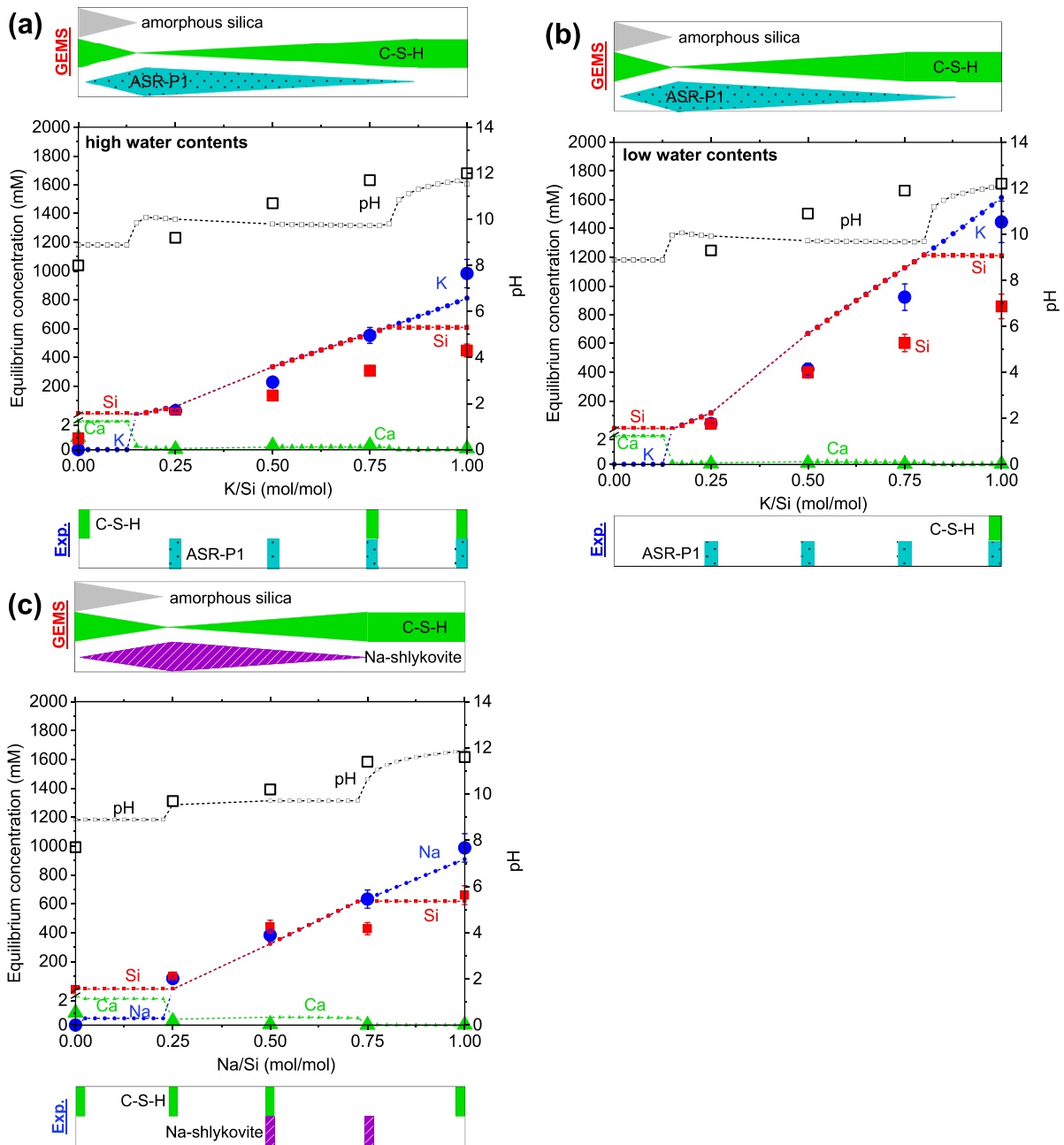


566

567

568 **Fig. 4.** Effect of initial alkali/Si ratio on the measured concentrations and pH (measured at  
 569 23 °C) of the equilibrium solutions for the K-containing samples with (a) high and (b) low  
 570 water contents, and (c) for the Na-containing samples.

571

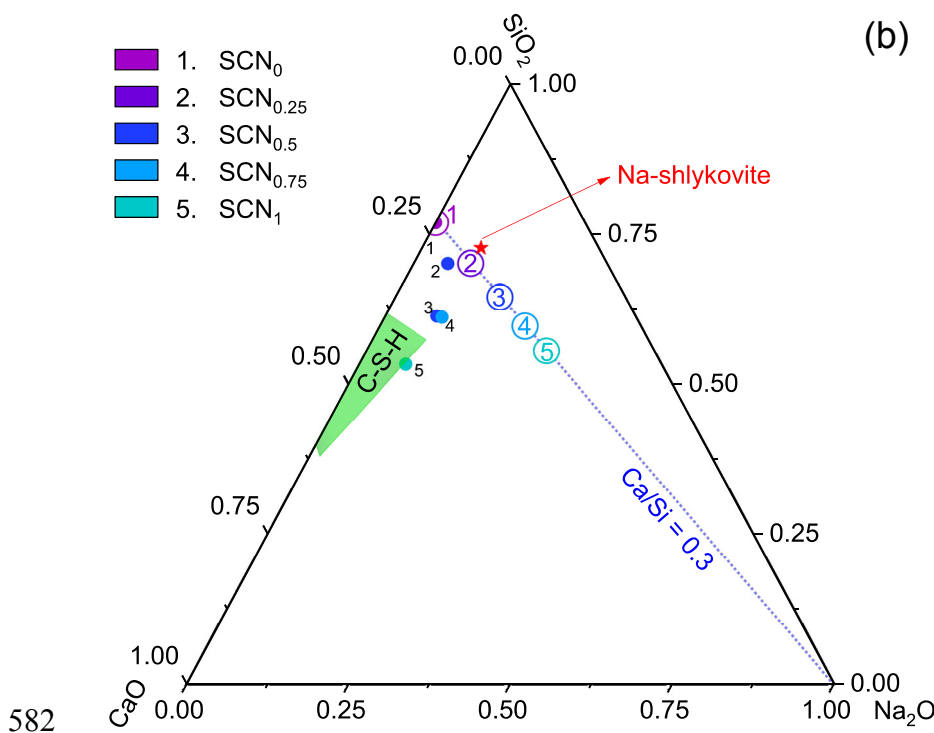
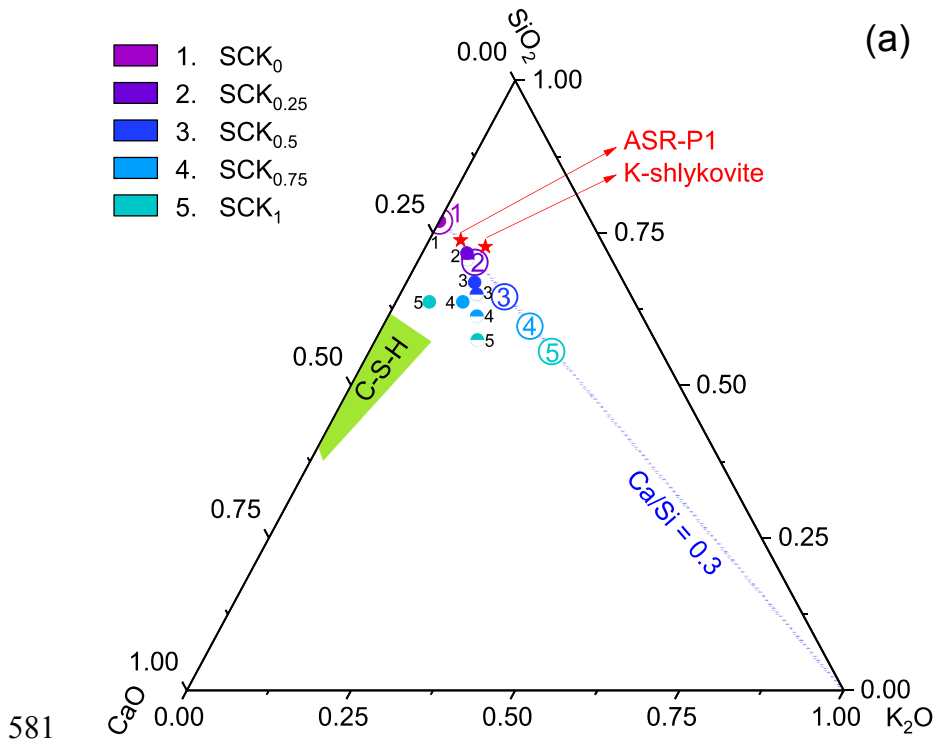


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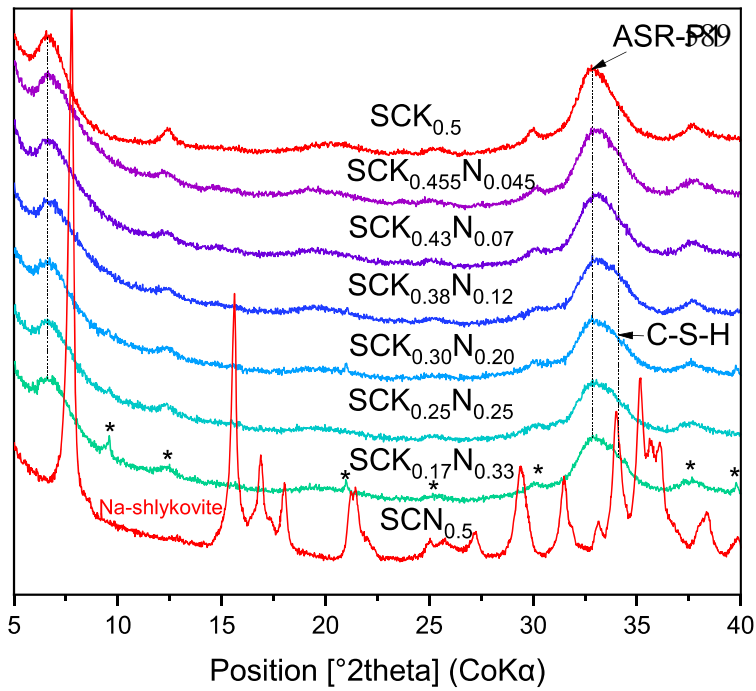
573

574 **Fig. 5.** Effect of initial K/Si or Na/Si ratio on the solution chemistry and phase assemblages  
 575 for the K-containing samples with (a) high and (b) low water contents, and (c) Na-containing  
 576 samples with high water contents at 80 °C. The symbols with smaller size on the dashed lines  
 577 refer to the data calculated from thermodynamic modelling. No calculations are executed at  
 578 initial K/Si or Na/Si ratio between 0.25 and 0.5 due to the change of water content. The larger  
 579 symbols correspond to the experimental data.

580



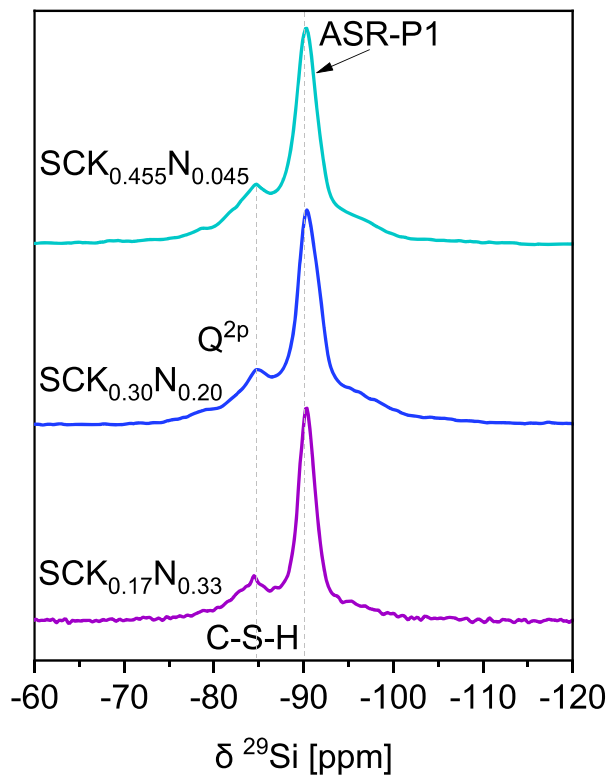
583 **Fig. 6.** Bulk chemical compositions (molar fraction) of the starting materials (empty circle)  
 584 and the solids obtained for the (a) K-containing samples and (b) Na-containing samples after  
 585 90 days of reaction at 80 °C (filled circle for the samples with high water contents, and  
 586 half-filled circle for the samples with low water contents). The chemical compositions for the  
 587 K-shlykovite, ASR-P1, Na-shlykovite from [8] and the range of C-S-H composition from [6]  
 588 are also indicated in the diagram.



590

591 **Fig. 7.** XRD patterns of the solids obtained after 90 days of reaction at 80 °C for the samples  
 592 containing both K and Na with different K/Na ratios indicating the presence of mainly  
 593 ASR-P1 plus some C-S-H. Two endmembers containing only K (SCK<sub>0.5</sub>) or Na (SCN<sub>0.5</sub>)  
 594 from previous sections are also plotted in this figure for comparison. Note: the asterisk (\*)  
 595 designates the unidentified peaks.

596

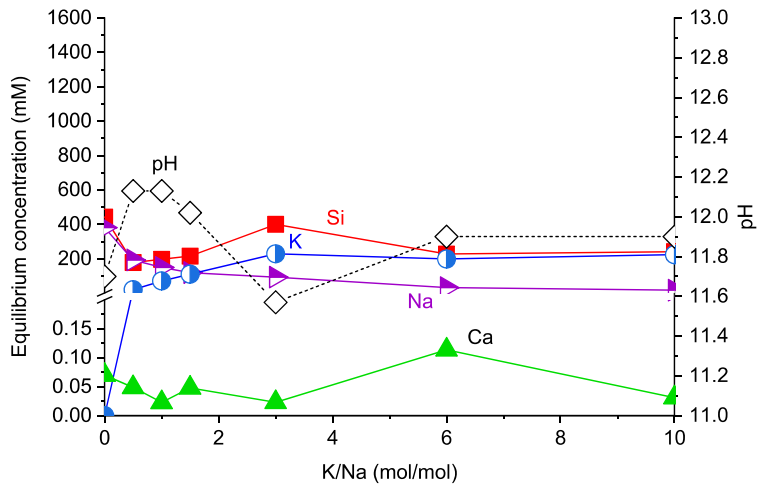


597

598 **Fig. 8.**  $^{29}\text{Si}$  MAS NMR spectra acquired at 79.5 MHz for the selected samples containing

599 both K and Na after 90 days of reaction at 80 °C.

600

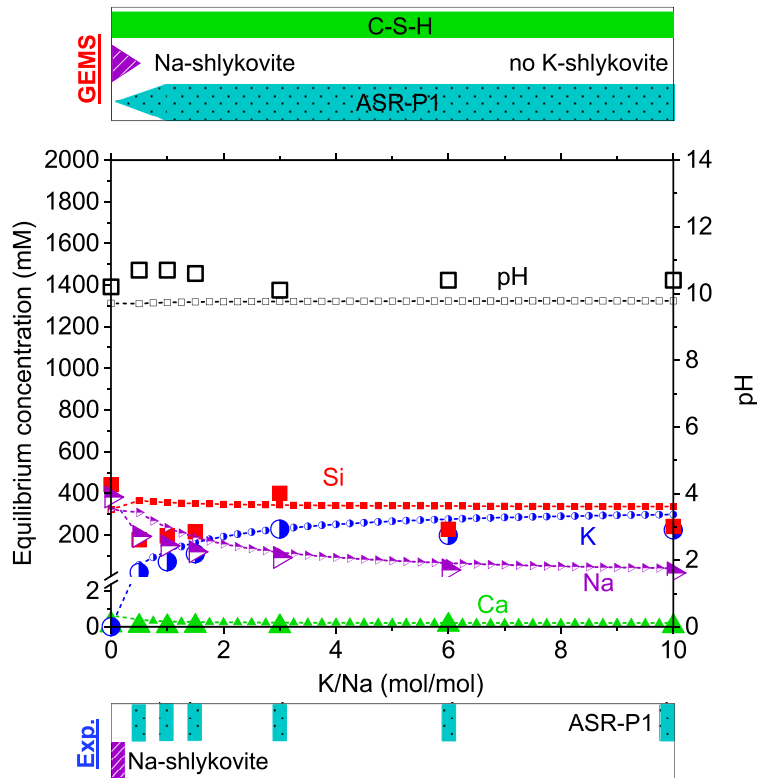


601

602 **Fig. 9.** Changes of the measured concentrations of the equilibrium solutions together with the  
 603 measured pH values at 23 °C for the samples containing both K and Na with a constant  
 604 (K+Na)/Si ratio 0.5 but different K/Na ratios. The Na-endmember (SCN<sub>0.5</sub>) with K/Na ratio  
 605 of 0 from previous section is also plotted in this figure for comparison.

606

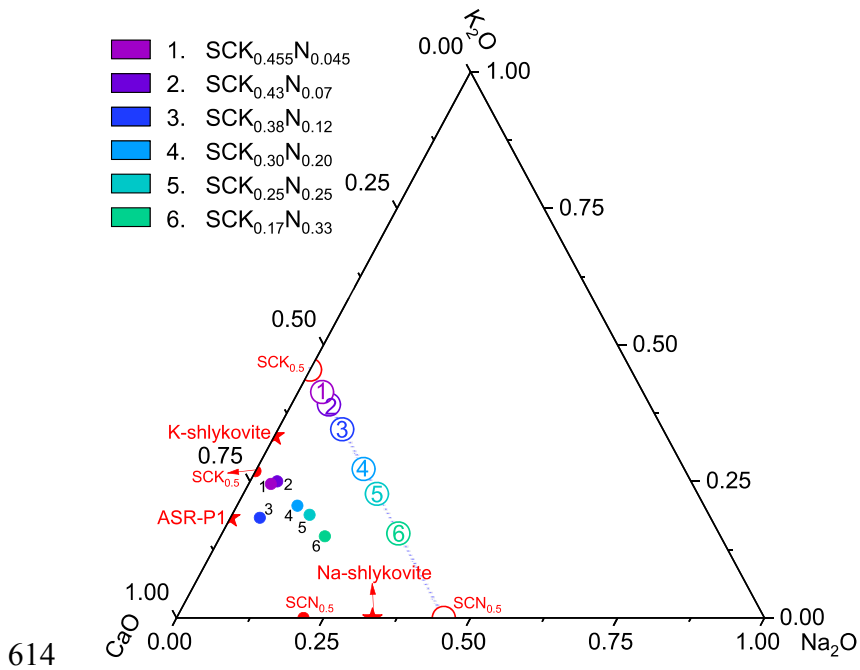




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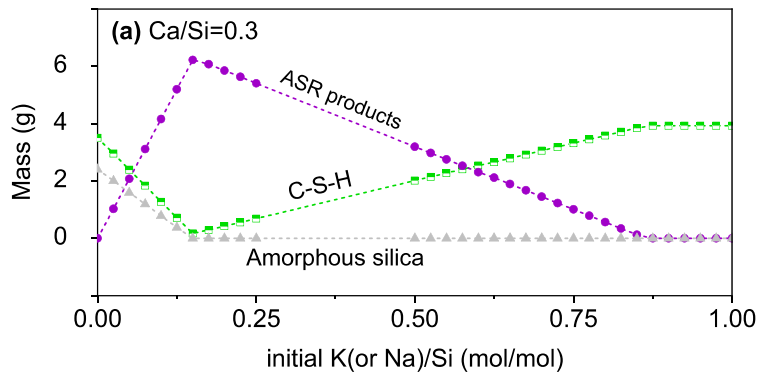
608 **Fig. 10.** Effect of K/Na ratio on the solution chemistry and phase assemblages in the samples  
 609 containing both K and Na as alkali source. The symbols with smaller size on the dashed lines  
 610 are data calculated from thermodynamic modelling. The larger symbols correspond to the  
 611 experimental data. The Na-endmember (SCN<sub>0.5</sub>) with K/Na ratio of 0 from previous section is  
 612 also plotted in this figure for comparison.

613

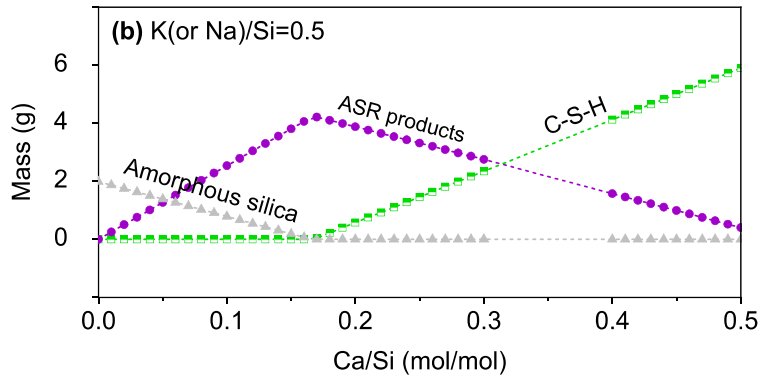


614

615 **Fig. 11.** Bulk chemical compositions (molar fraction) of the starting materials (empty circles)  
 616 and the solids (filled circles) obtained after 90 days of reaction at 80 °C for the samples  
 617 containing both K and Na. The chemical compositions for the K-shlykovite, Na-shlykovite  
 618 and ASR-P1 from [8] are plotted in red star in the diagram. Two endmembers containing only  
 619 K ( $SCK_{0.5}$ ) or Na ( $SCN_{0.5}$ ) from previous sections are also plotted in this figure for  
 620 comparison.



621



622

623 **Fig. 12.** a) Effect of initial K/Si or Na/Si ratio on the formation of ASR products (ASR-P1 or  
 624 Na-shlykovite) in the K- or Na-containing samples at a constant initial Ca/Si ratio of 0.3. b)  
 625 Effect of Ca/Si ratio on formation of ASR products (K-shlykovite, ASR-P1 or Na-shlykovite)  
 626 in the K- or Na-containing samples at a constant initial K(or Na)/Si ratio of 0.5; reproduced  
 627 from [8]. The symbols on the dashed lines are data calculated from thermodynamic modelling.  
 628 No calculations were executed at alkali/Si ratio between 0.25 and 0.5 due to the change of  
 629 water content.