1 **Alkali uptake in calcium alumina silicate hydrate (C-A-S-H)**

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9 **Abstract: (max. 150 words)**

10 Uptake of the alkalis K and Na by calcium silicate hydrate (C-S-H) gel and calcium alumina silicate
11 hydrate (C-A-S-H) of molar Ca/Si ratios = 0.6 to 1.6 and molar Al/Si ratio = 0 or 0.05 has been studied
12 at 20°C. Alkalis are thought to be bound in the interlayer space of C-A-S-H and show preferred uptake
13 by lower Ca/Si ratios and by higher alkali concentrations. A consequence of alkali uptake into C-A-S-H
14 is a rearrangement of the C-A-S-H structure. Less calcium is present in the interlayer and shorter silica
15 chains are observed.

16 No significant difference was observed between sodium and potassium uptake. Equilibration times of
17 91 days to 1 year or the solid phase being either C-S-H or C-A-S-H had seemingly no effect on alkali
18 uptake.

1. Introduction

The alkalis potassium and sodium are common to all Portland cement (PC) based materials, but no solid phase buffers their concentration in the pore solution. A direct result of high alkali contents is therefore a high pH pore solution, which affects the dissolution of all other minerals in the PC system and therefore the concentrations of other elements [1-4]. In addition, alkali and hydroxide concentrations in the pore solution determine whether and to what extent alkali silica reaction (ASR) can occur in concrete [5, 6]. The risk of ASR can be lowered by the addition of supplementary cementitious materials such as fly ash or silica fume, which act to decrease the Ca/Si ratio of C-S-H, leading to higher alkali uptake in its structure. Alkalis in PC based materials are mainly taken up by C-S-H, with only negligible amounts being taken up by other mineral hydrates such as portlandite, ettringite, hydrogarnet, or hydrotalcite [7, 8]. Rather than being phase pure however, C-S-H in PC based materials is a C-A-S-H gel, which becomes increasingly significant if a high aluminium content supplementary cementitious material is added [9, 10]. A detailed knowledge of the alkali uptake in C-A-S-H gel is therefore important.

Experiments with synthetic C-S-H [3, 11] and low pH cements [1, 12, 13] indicate that more alkalis are taken up into low-Ca/Si C-S-H than into high-Ca/Si C-S-H. A strong correlation between dissolved alkali concentrations and alkali uptake by C-S-H in the concentration range up to 300 mmol/L [1, 3, 14] was observed. At higher alkali concentrations of 500-1500 mmol/L, the alkali uptake by C-S-H increases less strongly with concentration, and maximum molar ratios of Na/Si and K/Si = 0.3-0.5 in C-S-H have been reported [11, 14].

Alkali sorption studies have identified either preferred or equivalent sodium or potassium sorption [1, 3, 11, 15-18]. Preferred sodium sorption was used to interpret pore solution analysis of PC by Taylor [19] and has also been measured for synthetic C-S-H gel [15]. Preferred potassium sorption, however, has also been measured on synthetic C-S-H [1]. Sodium as Na^+ has a larger solvated ionic radius than K^+ and so sodium uptake might be physically inhibited, which is consistent with observations of [1], but contradicts preferential sodium sorption [11, 15, 19].

Hong and Glasser [20] reported a strong increase of alkali sorption in the presence of C-A-S-H gel as opposed to C-S-H gel alone, and suggested that the replacement of SiO_2 by AlO_2^- would further increase alkali uptake to maintain charge balance. In contrast, Stade [11] observed less alkali uptake in

48 C-A-S-H than in C-S-H, while Chappex and Scrivener [8] and Bach et al. [1] observed no significant
49 difference in the alkali uptake whether aluminium was present or not. It also has been suggested that
50 alkalis may charge-balance the silanol group by the substitution of protons ($\text{SiOH} + \text{K}^+ + \text{OH}^- \rightarrow \text{SiO}^-$
51 $\dots\text{K}^+ + \text{H}_2\text{O}$) or of calcium ions ($\text{SiOH} + \text{Ca}^{2+} + \text{OH}^- \rightarrow \text{SiOCa}^+ + \text{H}_2\text{O} / \text{SiOCa}^+ + \text{K}^+ \rightarrow \text{SiO}^- \dots\text{K}^+ +$
52 Ca^{2+}) [3, 11, 21], or occupy empty sites in the interlayer [21].

53 The scatter of results reported in the literature indicates either that a large experimental error is
54 associated with the measurement of alkali uptake, that the synthesis protocol has an important
55 influence, and/or that a number of different mechanisms are responsible for the alkali uptake in C-S-H
56 and C-A-S-H, such that the results may vary depending on the alkali concentration, the C-S-H
57 composition, and the presence of other ions or solids. Moreover, ^{23}Na NMR data indicate the presence
58 of two different sites for sodium binding in C-S-H [22, 23].

59 In order to elucidate these seeming contradictions, the focus of the present paper was on the uptake
60 of the alkalis by synthetic C-A-S-H gel. Solid phases were characterized by thermal gravimetric
61 analysis (TGA), X-ray diffraction (XRD) and ^{29}Si nuclear magnetic resonance (NMR) and the liquid
62 phase by pH measurement and composition by ionic chromatography (IC).

2. Materials and methods

Both C-S-H and C-A-S-H gels were synthesized by a one-step protocol at 20°C as described in detail previously [4, 24] and summarized below.

2.1. Synthesis

Calcium oxide (CaO), silica fume (SiO₂) and monocalcium aluminate (CA: CaO·Al₂O₃) were used in different proportions to synthesize C-A-S-H. Ca/Si ratios = 0.6, 0.8, 1.0, 1.2, 1.4 and 1.6 and Al/Si = 0.05 were targeted as detailed in Appendix A. For comparison, the alkali uptake on some C-S-H samples without aluminium was also studied. In addition, samples with Ca/Si = 1.0 and Al/Si = 0.1 were synthesized and studied by ²⁹Si NMR as described previously [4]. Water to solid mass ratio equal to 45 was used to ensure the homogeneity of the samples. C-S-H and C-A-S-H was equilibrated in Milli-Q water or in potassium or sodium hydroxide solutions with a concentration between 0.01 and 0.5 mol/L. Synthesis and all sample handling were made in a N₂-filled glove box to minimize CO₂ contamination. For each equilibration time, a separate sample was prepared, which was stored in a 100 mL PE-HD container placed on a horizontal shaker moving at 100 rpm, and equilibrated at 20°C. After different equilibration times, the solid and liquid phase were separated by filtration using 0.45µm nylon filters and subsequently analysed.

2.2. Solid phase analysis

After filtration, the solid was washed with 30 mL of a 50%-50% water-ethanol solution, afterwards with 30 mL pure ethanol, dried for seven days by freeze drying, and then stored until analysis in N₂-filled desiccators in the presence of saturated CaCl₂ solutions (≈30% RH) and of NaOH pellets to act as a CO₂ trap. The solid phases were analysed by TGA, XRD/pattern decomposition and ²⁹Si NMR. TGA data were measured with a TGA/SDTA851^e Mettler Toledo device using approximately 30 mg of sample. The weight loss of the samples was recorded from 30°C up to 980°C with a heating rate of 20°C/min under N₂ atmosphere. The amount of portlandite was quantified from the weight loss around 450°C using the tangential method and the total water bound in the sample from the total water loss between 30 and 550°C. The water bound in C-S-H and C-A-S-H was the difference between the total water loss and the weight loss due to portlandite.

X-ray powder diffraction patterns were recorded on a PANalytical X'Pert Pro MDF diffractometer equipped with a X'Celerator detector. Diffraction patterns were collected in increments of 5° from 70° 2θ at a conventional step size of 0.017° 2θ and a step measurement time of 460s.

Phase composition was determined with X'Pert HighScore Plus. Pattern decompositions were carried out with calcium fluoride as external standard. This method avoids the normalization to 100 wt%; quantification of X-ray amorphous solids such as C-S-H can be determined by indirect measurement [4]. To determine the exact peak shifts position, anatase was added to some samples as internal standard.

The ²⁹Si NMR measurements were performed at room temperature using a Bruker Avance 400 MHz NMR spectrometer with a 7mm CP/MAS probe. The ²⁹Si MAS NMR single pulse experiments were recorded at 79.49 MHz using the following parameters: 4500 Hz spinning speed, 9216 scans, $\frac{\pi}{3}$ pulses of 2.5 μs, 20 s relaxation delays, the 90° Pulse at the decoupling power level of 8 dB is 7.5 μs. The RF field is calculated by $1/(4 \times 7.5 \mu s) = 33.3$ kHz. The chemical shifts of the ²⁹Si MAS NMR spectra were referenced to an external sample of tetramethylsilane (TMS). The observed ²⁹Si resonances were analysed using the Qⁿ(mAl) classification, where a Si tetrahedron is connected to n Si tetrahedral with n varying from 0 to 4 and m is the number of neighbouring AlO₄ tetrahedra.

Deconvolution of the Si-NMR data was carried out using the dmfit software [25]. Peak shapes were constrained as pseudo-voigt using a Lorentzian/Gaussian ratio = 0.5, full width at half height ≤ 3 ppm and constant chemical shifts between the different peaks as described in [4]. The dreierketten structure of the C-S-H was respected by defining the ratio $Q_p^2/(Q_b^2+Q_u^2)$ equal to 2, as for each bridging tetrahedra two pairing tetrahedra are present, as shown in Fig. 1. Q_b^2 denotes the number of bridging tetrahedra neighbouring Ca in the interlayer, $Q_{b\text{OH}}^2$ stand for bridging tetrahedra neighbouring H⁺ in the interlayer, Q_p^2 are the pairing tetrahedra. The mean dreierketten chain length (MCL) was calculated using equation 1, and the Al/Si ratio with equation 2.

$$MCL = \frac{2(Q^1 + Q_p^2 + Q_b^2 + Q_u^2 + \frac{3}{2}Q^2(1Al))}{Q^1} \quad (1)$$

$$\frac{Al}{Si} = \frac{\frac{1}{2}Q^2(1Al)}{Q^1 + Q_p^2 + Q_b^2 + Q_u^2 + Q^2(1Al)} \quad (2)$$

Figure 1: Schematic structure of C-A-S-H. Grey circle: calcium ion; empty circle: ion in the interlayer (water or alkali); light grey tetrahedra: protonated silicate; dark grey tetrahedra: aluminium; -: negative charge (compensated by proton, calcium or other cations). $Q_{(mAl)}^n$: n indicates the numbers of Si neighbours and m the number of aluminium neighbours, b: bridging position, p: pairing position. [4]

2.3. Solution analysis

The elemental concentrations of calcium, silicon, sodium, potassium and aluminium in the filtrates were determined with a Dionex DP ICS-3000 ion chromatograph. Each sample was diluted by a factor of 1, 5, 10, 100, and/or 1000 so that the standard solutions used of 0.1, 0.5, 1.0, 5.0, 10.0, 25.0 and 50.0 mg/L correctly bracketed all concentrations up to 50,000 mg/L. Samples were measured in duplicate. The relative error of the measurements was $\leq 10\%$ of the measured value. Silicon was analysed using sodium carbonate/bicarbonate eluent and sodium molybdate, and sodium lauryl sulfate in metasulfonic acid as a post-column reagent using an ion pack AS22 column.

To quantify the hydroxide concentration, pH measurements were performed at room temperature with a Knick pH meter (pH-Meter 766) equipped with a Knick SE100 electrode. The pH electrode was calibrated against KOH solutions of known concentrations in order to minimize the alkali error. The measurements were corrected to correspond to 20°C.

The amount of alkalis bound in the solid was determined by an indirect and a direct method. The indirect method used a mass balance calculation from the alkali concentration in solution. The relative error of the measured dissolved alkali concentrations is around 5-10%, which can lead to a large (up

to 100%) analytical error in the quantity of bound alkalis calculated from the mass balance approach, especially at high alkali concentrations. In the presence of 500 mmol/L potassium hydroxide, the relative error is 50 mmol/L, which represents in terms of a K/Si ratio an error of 0.3 (calculation based on the Ca/Si=1.0). Thus, in addition, a direct method was used where the amount of alkali bound in the solid was determined by dissolving 20 mg of the solid sample in 10 mL of 0.1 mol/L HCl; the amount of bound alkalis was then quantified by ionic chromatography. For both methods, the error was calculated with a 95% confidence interval. For the indirect method, three independent measurements at three different times were carried out as shown in section 3.3.4 and for the direct method, each dissolution was repeated three times.

2.4. Thermodynamic modelling

GEMS-Selektor v3.0 (<http://gems.web.psi.ch> [26, 27]) is a chemical thermodynamic modelling code capable of calculating equilibrium between solid, liquid and gas phases. Solid solutions can be included and saturation indices of solids [28] can be calculated. The built-in GEMS thermodynamic database [29, 30] was used, enhanced with thermodynamic data for cement minerals taken from the cemdata07 database [31, 32] updated with the recent solubility products of calcium aluminate hydrates and hydrogarnet [33, 34] and for C-S-H, using the CSHQ model by Kulik [35].

The activity of each species was calculated from the measured total concentrations at 20°C using GEM-Selektor. The activity coefficients of the aqueous species γ_i were computed with the built-in extended Debye-Hückel equation with common ion-size parameter a_i of 3.67Å for KOH and of 3.31Å for NaOH solutions [36]:

$$\log_{10} \gamma_i = \frac{-A_\gamma z_i^2 \sqrt{I}}{1 + B_\gamma a_i \sqrt{I}} + b_\gamma I \quad (3)$$

where z_i (-) denotes the charge of species i , I (mol.kg⁻¹) the effective molal ionic strength, b_γ (-) is a semi-empirical parameter (0.123 for KOH and 0.098 for NaOH at 25°C [36]), and A_γ and B_γ are P, T -dependent coefficients; at 20°C and 1 bar, $A_\gamma \approx 0.507 \text{ kg}^{0.5} \cdot \text{mol}^{-0.5}$ and $B_\gamma \approx 0.328 \text{ kg}^{0.5} \cdot \text{mol}^{-0.5} \cdot \text{\AA}^{-1}$. The activity of water was calculated from the osmotic coefficient, ϕ , and the sum of all species molalities, m_z , according to Helgeson et al [36] ($\ln a_{\text{water}} = -\phi m_z / 55.508$). This activity correction is thought to be applicable up to approx. 1 M ionic strength [37].

3. Results and discussion

3.1. Effect of alkali on the solids

The presence of alkalis in C-A-S-H had little influence on the solids formed. In all cases, C-A-S-H is the main solid precipitated, as shown by the TGA and XRD data in Figure 2 to Figure 5 for C-A-S-H samples with 0.05 Al/Si ratio. A small quantity of portlandite is observed for higher concentrations of alkali hydroxide (Figure 2) and/or for high Ca/Si ratios (Figure 3). At high NaOH and KOH concentrations, the TGA data indicate an additional weight loss at 400°C, which is not associated with any crystalline phase in the XRD and was thus tentatively assigned to a calcium potassium sodium aluminate silicate hydrate (C-K-N-A-S-H) gel. The same weight loss at around 400°C is observed for samples prepared at 50 °C [38].

Figure 2: TGA of C-A-S-H with target Ca/Si=0.8 and Al/Si=0.05 after an equilibration time of 182 days at different alkali concentrations. * The weight loss between 450 to 500°C in 0.1 M NaOH is tentatively assigned to the decomposition of C-K-N-A-S-H. This weight loss has been observed for Ca/Si = 0.6 and Ca/Si = 0.8 with 0.1 M NaOH. Similar weight loss have also been observed at 50 °C [38].

187

188 Figure 3: TGA of C-A-S-H with target Ca/Si=1.6 and Al/Si=0.05 after an equilibration time of 182 days
 189 at different alkali concentration. In some samples, an additional weight loss at 400°C was observed
 190 (*), indicating the presence of very finely dispersed and somewhat coarser portlandite.

191

192 XRD indicates that the presence of alkali hydroxide decreases the mean basal spacing of the C-A-S-H
 193 as shown in Figure 4 for Ca/Si = 0.8, and in Figure 5 for Ca/Si = 1.2. An increase of the alkali
 194 concentration from 0 to 0.1 mol/L leads to a decrease of the mean basal spacing from 12.7 to ≈ 12.1 Å
 195 for Ca/Si=1.2 and to ≈ 13.3 Å at Ca/Si=0.8, as shown in Figure 6. No well-defined d_{002} diffraction peak
 196 is observed in our samples for Ca/Si ≤ 0.8 , but other studies report a d_{002} peak at ≈ 14 Å for Ca/Si = 0.8
 197 [39], consistent with the d_{002} of 14 Å tobermorite [40]. At Ca/Si ratios > 1.2 , where only a small amount
 198 of alkali uptake occurs, no significant influence of alkali hydroxide is found. Similarly to the
 199 observations reported here, a decrease of the mean basal spacing in the presence of sodium
 200 hydroxide has been observed by Lognot [41] and by Bach et al. [1].

201 Changes in the local bonding environment caused by a partial replacement of protons and calcium
 202 ions with potassium and sodium ions in the interlayer is a likely key factor contributing to the reduction
 203 in basal spacing, although at present the precise mechanism is unclear.

At equal concentrations, potassium and sodium have a similar effect of reducing the mean basal spacing. This is in contrast to the observations of Bach et al. [1], who observed a stronger decrease of the mean basal spacing in the presence of sodium hydroxide than of potassium hydroxide. The reasons for these contradictory observations are unclear, although they might be related to different washing procedures of the solids, the less harsh drying, and the shorter equilibration times used in the study of Bach et al. [1].

Figure 4: XRD diffractograms of C-A-S-H with Ca/Si=0.8 and Al/Si=0.05 in different alkali solutions after an equilibration time of 182 days. K: katoite.

Figure 5: XRD diffractograms of C-A-S-H with Ca/Si=1.2 and Al/Si=0.05 in different alkali solutions after an equilibration time of 182 days.

Figure 6: Mean basal spacing of C-A-S-H (Al/Si=0.05) as a function of initial alkali concentration after an equilibration time of 1 year (measured with anatase as an internal standard). Empty symbol: Ca/Si=1.2, grey symbol: Ca/Si=1.0, dark symbol: Ca/Si=0.8, diamond: C-A-S-H with a solution of potassium hydroxide, square: C-A-S-H with a solution of sodium hydroxide.

Four main different environments of silica in C-A-S-H can be observed by ^{29}Si -NMR as illustrated in Figure 7. The end of chain silica (Q^1) has a chemical shift in the range of -79.1 to -79.6 ppm, the bridging silica (Q^2_b) from -83.3 to -83.4 ppm, the pairing silica (Q^2_p) from -84.7 to -85.3 ppm [4, 42, 43], and the bridging tetrahedra connected by hydrogen bonding (Q^2_u) at $\sim$ -88.3 ppm [4, 44-46]. The presence of aluminium introduces an additional peak at $\sim$ -81.5 ppm, $Q^2_p(1\text{Al})$ [47-51].

As previously observed for C-A-S-H samples equilibrated at 20 °C [4, 52] and at 50 °C [38], the presence of alkali increases the relative Q^1 intensity, indicating a decrease of the dreierketten chain length, as shown in Table 1 and Figure 7. The potassium or sodium uptake results in a 1 - 3 ppm chemical shift to less negative values. In agreement with our data, a decrease of the silica chain length [22, 52, 53] and of the chemical shift [4, 21, 22] has been observed by different authors. Typically, the shielding of silica sites by protons or alkalis is weaker than by calcium, leading to less negative chemical shifts [54-56]. The less negative chemical shifts in the presence of alkali hydroxides indicate a decrease of the fraction of silica bound to calcium and a binding of silica to sodium or potassium ions. High alkali concentrations result in the replacement of a part of the divalent calcium ions at the surface by monovalent ions (potassium or sodium) as visible by the lower zeta potential of the C-S-H [4, 57, 58]. The replacement of calcium at the surface and in the interlayer by alkali ions leads to a structural reorganization of C-S-H and C-A-S-H as the total Ca/Si ratio in the experiment is constant. The calcium removed from the interlayer is integrated in the main CaO plane of C-A-S-H as also illustrated in Figure 7B. The increase of the fraction of CaO main layer leads to a rearrangement in the silica chains, i.e. to the presence of more silica dimers consistent with the shorter silica chain observed in presence of alkali with the increase of the relative Q^1 intensities, as shown in Table 1 and Figure 7A.

B) **C-S-H**

Figure 7: A) ²⁹Si MAS NMR spectra of C-A-S-H with target Ca/Si=1.0 and Al/Si=0.1 after 1 year. B) schematic redistribution of charge balancing calcium from the interlayer to the main calcium oxide layer, adapted from [4],

Table 1: Peak position (± 0.5), Relative fractions (± 2) of Q^n , Al/Si ratio (± 0.01) and mean chain length (MCL, $\pm 5\%$) obtained by deconvolution of ^{29}Si MAS NMR spectra, for C-S-H with a target Ca/Si=1.0.

Alkali	Q^1		Q^2_p		Q^2_b		Q^2_u		$Q^2(1\text{Al})$		Al/Si	MCL
concentration	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%		
<i>Al/Si=0.1</i>												
No alkali	-79.1	24	-84.9	43	-83.3	18	-88.3	4	-81.5	12	0.06	9
0.5 mol/L KOH	-78.4	46	-83.8	28	-82.2	10	-85.5	4	-80.9	12	0.06	5
0.5 mol/L NaOH	-78.2	48	-84.2	25	-82.7	9	-86.8	3	-81.3	15	0.08	5

3.2. Effect of alkali hydroxides on the aqueous phase composition

Figure 8 shows the effect of alkali hydroxide on the dissolved calcium, silicon and aluminium concentrations. At all Ca/Si ratios, a clear decrease of the calcium concentrations is observed in the presence of potassium hydroxide, while silicon and aluminium concentrations increase. The same tendencies have been observed for C-S-H systems in the presence of different quantities of sodium hydroxide [2, 14] and for C-A-S-H at Ca/Si = 1.0 in the presence of potassium hydroxide [4]. These changes are strongly related to the increase of the pH values due to the presence of alkali hydroxide.

Figure 8: A. Calcium, B. silicon, C. aluminium concentrations in solution as a function of Ca/Si ratios in equilibrium with C-A-S-H (Al/Si = 0.05) after 1 year.

Figure 9A shows the dissolved concentration of calcium, silicon and aluminium as a function of the measured pH values. At low Ca/Si ratio (target Ca/Si = 0.6), the measured pH values increase from 9.8 in the absence alkali hydroxides to 13.5 in 0.5 mol/L potassium hydroxide. The higher pH values in the presence of alkali hydroxides increase the silicon and aluminium concentrations, while the calcium concentrations decrease.

The measured dissolved concentrations are compared to thermodynamic predictions using the GEM-Selektor code and the simplified CSHQ solid solution model for C-S-H [35], as recent publications [24, 38, 59] have shown that the presence of a small amount of aluminium has little effect on the observed calcium and silica concentrations. The recently published C-N-A-S-H model of Myers et al. [60] was not used as potassium uptake is not included. The development of a new sublattice solid solution C-K-N-A-S-H thermodynamic model to describe aluminium and alkali uptake in the different structural sites of a tobermorite-like C-S-H structure is beyond the size and scope of the present contribution and will be described elsewhere [61].

Figure 9A shows for C-A-S-H with Ca/Si = 0.6 in the absence of alkali hydroxides that the measured concentrations agree well with the modelled concentrations and pH values, which indicates that the system is near saturation with respect to amorphous silica and C-S-H. The addition of alkali

hydroxides increases the pH values and leads to undersaturation with respect to amorphous silica, as indicated in Figure 9A. In the presence of more than 0.05 mol/L alkali hydroxide, i.e at $\text{pH} \geq 11.5$, lower calcium concentrations are measured than calculated by the CSHQ solid solution model that does not take into account the uptake of alkali by C-S-H.

Figure 9B shows that for C-A-S-H at high Ca/Si ratio (target Ca/Si = 1.6), the measured pH increases from 12.5 in the alkali-free systems to 13.6 in the presence of 0.5 mol/L potassium hydroxide. The addition of alkali hydroxide leads to a decrease of the dissolved calcium concentrations when portlandite is present, while the silicon and aluminium concentrations increase. As for low Ca/Si C-S-H, the measured concentrations are compared with calculated concentrations in equilibrium with the CSHQ solid solution model of C-S-H [35]. Figure 9B shows that the system is near saturation with respect to portlandite and C-S-H, which is in agreement with the phases observed in the sample (Figure 9B). However, the CSHQ model overestimates the silicon concentrations at higher pH values, indicating that this model, developed based on the data for alkali-free C-S-H [62], has to be extended for the uptake of alkalis and adapted for high pH values [61].

A) Ca/Si = 0.6

B) Ca/Si = 1.6

Figure 9: Effect of pH on total dissolved calcium (diamonds), silicon (triangles) and aluminium (squares) concentration in the presence of C-A-S-H (Al/Si = 0.05) at A) Ca/Si = 0.6 and B) 1.6. For comparison, the calculated calcium (grey curve) and silicon (black curve) concentrations in the presence of amorphous silica, C-S-H and portlandite are indicated (CSHQ model). The boxes used to indicate the stable domain.

3.3. Alkali uptake in C-A-S-H

3.3.1. Effect of the method of measurement

Figure 10 shows the alkali uptake in C-A-S-H obtained using two different methods: the indirect method based on the decrease of the potassium or sodium concentrations in solutions and mass balance calculations (filtered solution) [11, 20], and the direct method based on a complete dissolution of the filtered solid in HCl. Both methods have advantages and disadvantages. At high alkali concentrations, the indirect determination can be associated with a large error, as the ionic chromatography measurements have about 10% relative error. The amount of bound alkalis determined by the direct method could be too low due to the washing of the solid with water-ethanol and ethanol that may remove some of the alkali ions present in the diffuse layer, as has been reported for cesium ions by Viallis et al. [63].

Figure 10 compares the measurements of alkali uptake by the indirect (filtered solution) with the direct method (washed sample). The direct method results in a 20 to 50% lower K/Si ratio, which indicates that at least a part of the loosely bound alkalis is removed by the washing procedure. As the alkali concentrations in pore solutions affect the pH values and the transport properties in concrete, it is more relevant to determine the K/Si ratio by the indirect method that includes the ions present in the diffuse layer. Although the preference was given to the indirect method in this paper, it should be noted that the measurements at high alkali concentrations can be associated with a large relative error as explained above, which can even lead to apparently negative alkali uptake.

Figure 10: The effect of the measuring method on the alkali/Si ratio in C-A-S-H (Al/Si ratio=0.05). Grey symbols: direct method = analysis of the solid after washing, dark symbols: indirect method = analysis of the filtered solution. Error: 95% confidence interval. The curves are eye-guides only.

3.3.2. Effect of aluminium on the alkali uptake

Figure 11 compares the uptake of potassium in C-S-H and C-A-S-H at different Ca/Si ratios. The K/Si ratio is not significantly affected by the presence of aluminium, as previously observed for synthetic C-S-H and C-A-S-H [1] and in cement pastes [8]. This is in contrast to observations by Hong and Glasser [20] of an increase in alkali uptake in the presence of aluminium, or Stade [11] who reported a decrease. The scatter of results in the literature could be related either to the significant experimental error associated with the determination of alkali uptake in C-S-H based on the decrease of the dissolved alkali concentrations as in Stade [11] and Hong and Glasser [20] (indirect method), or to the presence of other solids such as amorphous silica, stratlingite or katoite, which can change the silica fraction present in C-S-H. In addition, stratlingite might also bind alkalis, as has been suggested based on the pore solution analysis in calcium sulfoaluminate cement [64]. Unfortunately, neither paper of Stade [11] nor Hong and Glasser [20] reported any analysis of the solid phases formed, so the reasons for their diverging observations cannot be further clarified.

It has been suggested that the replacement of silica (SiO_2) by aluminium (AlO_2^-) introduces additional negative charge, and thus increase the alkali uptake [20]. However, not only the difference in charge between Al^{3+} and Si^{4+} but also the acidity of the hydroxyl groups (=tendency to deprotonate) and the calcium concentrations must also be considered. Recent Monte Carlo simulations of the intrinsic acidity of silanol sites in C-S-H showed that the bridging silica deprotonate below pH 10 ($\text{pK}_a = 6.2$ and 8.6 [65]), resulting in near complete deprotonation to $=\text{SiO}_2^{2-}$ at the pH values >10 , which results in a negatively charged C-S-H surface as observed by zeta potential measurements [66]. The deprotonation/protonation of aluminium in the bridging sites is presently not well investigated. However, a slightly more negative zeta potential has been measured at low Ca/Si ratio in the presence of aluminium [66] and little difference in the presence of more calcium. This small increase in negative charge at low Ca/Si does not seem to significantly enhance potassium uptake in C-S-H and C-A-S-H, as shown in Figure 11.

359

360

361 Figure 11: Alkali uptake in C-S-H and C-A-S-H (Al/Si=0.05) in equilibrium with a solution containing
 362 0.5 mol/L [KOH] equilibrated for 182 days. Error: 95% confidence interval.

363

364 3.3.3. Comparison of potassium uptake with sodium uptake

365

366 The alkali uptake is not influenced by the type of cation. For potassium and sodium similar (K or Na)/Si
 367 ratio are observed as shown in Figure 12. In the literature, contradicting findings have been reported
 368 with sodium higher than potassium [15, 19], comparable [3, 11], and sodium lower than potassium
 369 uptake [1, 67]. In many cases, the difference may be attributed to the error associated with mass
 370 balance calculations based on high aqueous concentrations or to the experimental protocol, although
 371 no clear trends between the results and the methods could be identified. The scatter of results reported
 372 in the literature could also indicate that a number of different mechanisms are responsible for the alkali
 373 uptake in C-S-H; the results may vary depending on the alkali concentration, the C-S-H composition
 374 and the presence of other solids.

375 The maximum K/Si and Na/Si ratio observed are in the range 0.2-0.3 for Ca/Si = 0.6 (Figure 11, Figure
 376 12 and Appendix C). These values agree with the maximum Na/Si and K/Si ratios reported by [11, 14]

for low-calcium C-S-H. The observed alkali uptake at lower alkali concentration is similar to the uptake observed by Bach et al. [1] as shown further below, while Hong et al. [3] report a lower uptake.

Figure 12: Alkali uptake in C-A-S-H (Al/Si=0.05) after an equilibration time of 182 days. Error: 95% confidence interval

3.3.4. Factors influencing alkali uptake in C-A-S-H

The amount of alkali available is one of the main factors which determine the alkali uptake in C-A-S-H. Figure 12 and Figure 13A shows that the alkali uptake in C-A-S-H increases as a function of the aqueous alkali concentrations. At low alkali concentrations, a linear relation between the initial potassium concentrations and the K/Si in C-A-S-H is observed, while at higher alkali concentrations, 250 and 500 mmol/L, the alkali uptake increases much less strongly than the dissolved concentrations in solution. This trend is characteristic for an adsorption isotherm and this behaviour can be described e.g. by a Langmuir isotherm: $\theta_i = \alpha \cdot C_i / (1 + \alpha \cdot C_i)$ where θ_i is the surface fractional coverage of i-th component, C_i is its dissolved aqueous concentration, and α is the Langmuir adsorption constant. At low alkali concentrations, the amount of potassium or sodium bound in C-S-H is small in comparison to the total number of available sites, i.e. the deprotonated silanol groups, such that the uptake

increases strongly with the alkali concentrations. At higher concentrations, the amount of potassium or sodium ions is comparable to the total amount of deprotonated silica.

Figure 13: A) Potassium (KOH) uptake on C-A-S-H with $Ca/Si=0.8$ and $Al/Si=0.05$ compared with potassium uptake in C-S-H with similar Ca/Si ratio in KOH or KNO_3 [1]. Error: 95% confidence interval. The curve represents the Langmuir equation with $\alpha = 0.0065$. B) Effect of alkali on the calcium concentrations in the presence of alkali hydroxide (data from this paper and from Bach et al. [1]). Solutions in equilibrium with synthetic C-S-H and C-A-S-H ($Ca/(Si+Al) = 0.8-0.85$)

Figure 14 shows the measured potassium uptake as a function of the Ca/Si ratio after 91, 182 and 365 days. The Ca/Si ratio strongly influences the alkali uptake in C-S-H as visible in Figure 14 and as

previously reported by different authors [3, 11, 14]. Both alkali and calcium ions can compensate the negative charge of C-S-H surfaces: $\text{SiO}^- + \text{K}^+ \rightarrow \text{Si-OK}$, $\text{SiO}^- + \text{Ca}^{2+} \rightarrow \text{Si-OCa}^+$, as shown by Labbez et al. [57] experimentally and by Monte Carlo simulations. Divalent cations such as Ca^{2+} are preferentially adsorbed compared to monovalent cations such as Na^+ or K^+ due to the stronger electrostatic interactions [58]. Thus, high dissolved calcium concentrations can inhibit the alkali uptake. As a consequence, the alkali uptake by high Ca/Si C-S-H, which is in equilibrium with high calcium concentrations, is low [3, 11, 14, 57] as shown in Figure 14. Even if the alkali concentration is much higher than the calcium concentration, two orders of magnitude in the case of the data presented in Figure 14b, calcium concentrations still have a very strong influence on the alkali uptake. In contrast, the alkali uptake is strongly enhanced in presence of low Ca/Si C-S-H and thus low dissolved calcium concentrations; maximum Na/Si and K/Si ratios reported are in the range 0.3-0.5 [11, 14].

Figure 14: Potassium uptake in C-A-S-H ($\text{Al/Si}=0.05$) plotted versus A) the Ca/Si ratio in the C-A-S-H and B) measured calcium concentrations. Empty symbol: 91 days, grey symbol: 182 days, dark symbol: 365 days equilibration time. Error: 95% confidence interval. The curves are eye-guides only.

The addition of alkali hydroxide leads to a strong increase of pH and lowers the calcium concentrations as seen in Figure 9 and Figure 13B. If not alkali hydroxide, but alkali nitrate or alkali chloride solutions are added, the pH does not change significantly, and an increase of the calcium concentrations is observed at higher alkali concentrations (Figure 13B) as some of the calcium ions in the interlayer of the C-S-H are replaced by alkali ions.

The addition of alkali hydroxide lowers not only dissolved calcium concentrations but leads also to more de-protonation of silanol sites and, thus, to more negatively charged C-S-H surface [4, 57, 68]. Both factors contribute to an increased binding of sodium and potassium in solutions containing hydroxides compared to solutions with nitrates or chlorides, as shown by the higher alkali/Si ratio for C-A-S-H in Figure 14. The presence of charge-balancing potassium or sodium instead of calcium results in shorter silica chain lengths and a decrease of the “dreierketten” chain length observed by ^{29}Si NMR as shown in Figure 7, and to a decrease of the basal spacing (Figure 6, [1]) .

Studies using ^{23}Na -NMR [23, 69, 70] indicate two different environments for alkali uptake in C-S-H. At all Ca/Si ratios, a sharp sodium signal is observed, which was assigned to highly symmetrically bound Na or to mobile Na or NaCl. At low Ca/Si ratio, an additional broad sodium signal at ≈ 10 ppm is observed, indicating a low-mobility, “bound” sodium [23]. The fraction of “bound” sodium is observed to decrease strongly with increasing Ca/Si ratio in the presence of relatively low Na concentration (total $\text{Na/Si} = 0.1$ [23]).

4. Conclusions

The alkali uptake in C-S-H and C-A-S-H depends strongly on the Ca/Si ratio. At high Ca/Si ratios, very little alkalis are taken up, while a decrease of the Ca/Si ratio results in an increase of the alkali uptake. The alkali uptake is also influenced by the dissolved alkali concentrations. For a C-A-S-H (Al/Si=0.05) with nominal Ca/Si = 0.6, the molar K/Si ratio in C-A-S-H raises from 0.03 in 10 mmol/L KOH to 0.27 in 500 mmol/L KOH. The presence of aluminium and the hydration time have no significant effect on the alkali uptake, and no significant difference between potassium and sodium uptake in C-S-H was observed.

The addition of alkali hydroxides increases the pH values and lowers the calcium concentrations, while in alkali nitrate or chloride solutions little pH change but higher calcium concentrations were observed. The comparison of alkali uptake shows that, at a constant target Ca/Si ratio, more alkalis are bound in alkali hydroxide solutions due to the lower calcium concentration than in alkali nitrate or chloride solutions. Both calcium and alkali ions are assumed to be taken up in the interlayer and at the surface of C-S-H to compensate the negative charge of the C-S-H caused by the deprotonation of the silanol groups. In this process, the divalent calcium ion is strongly preferred in comparison to monovalent alkali ions, such that the alkali sorption is suppressed in the presence of higher aqueous calcium concentrations as present at high Ca/Si ratios. Thus, a higher alkali uptake is observed in the presence of low calcium concentrations, such as those in equilibrium with low-Ca/Si C-S-H or in the presence of high alkali hydroxides concentration.

The presence of sodium and potassium in the interlayer does not significantly change the structure of C-S-H, but can at high concentrations decrease the interlayer distance in C-A-S-H and shorten the silica chain length as observed by ^{29}Si NMR, thus indicating the uptake of alkali in the interlayer space of C-S-H.

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5. Appendixes

Appendix A Samples studied: mixing proportions used to prepare C-S-H and C-A-S-H (in g per 90mL of solution).

Ca/Si	CaO (g)	Initial composition	
		SiO ₂ (g)	CaO.Al ₂ O ₃ (g)
Al/Si=0			
0.6	0.718	1.282	
1.0	0.966	1.034	
1.6	1.198	0.802	
Al/Si=0.05			
0.6	0.670	1.248	0.082
0.8	0.809	1.118	0.074
1.0	0.921	1.012	0.067
1.2	1.014	0.925	0.061
1.4	1.093	0.851	0.056
1.6	1.159	0.789	0.052
Al/Si=0.1			
1.0	0.879	0.991	0.130

Appendix B Aqueous dissolved concentrations

* Normalized potassium or sodium ((Measured dissolved potassium or sodium concentration target initial concentration)/ Measured initial alkali concentration (from the blank solution)), -: not observed.

C-A-S-H (Al/Si=0.05)

Initial alkali concentration	Time (days)	Si	Ca	Al (mmol/L)	K*	Na*	OH	pH
Ca/Si=0.6								
Alkali free	91	9.4	1.0	≤ 0.0037	-	-	0.100	10.0
	182	7.7	1.2	≤ 0.0037	-	-	0.050	9.8
	364	3.4	1.3	≤ 0.0037	-	-	0.048	9.8
[KOH]=0.01M	91	4.6	0.346	≤ 0.0037	2.6	-	0.13	10.3
	182	4.1	0.385	≤ 0.0037	2.6	0.1	0.00	10.3
	364	4.1	0.440	≤ 0.0037	2.5	0.07	0.23	10.5
[KOH]=0.05M	91	15	≤ 0.0025	≤ 0.0037	15	0.15	1.4	11.3
	182	13	0.015	0.0041	16	0.16	2.4	11.5
	364	13	0.011	0.0070	14	0.15	2.4	11.6
[KOH]=0.1M	91	32	0.020	0.020	44	0.39	21	12.5
	182	25	0.020	0.024	43	0.37	26	12.6
	364	30	0.0072	0.0086	43	0.38	14	12.2
[KOH]=0.25M	91	38	≤ 0.0025	0.29	185	1.1	147	13.2
	364	30	0.0033	0.28	185	1.5	139	13.2
[KOH]=0.5M	91	39	0.015	1.4	445	2.7	319	13.5

	182	6.7	0.0062	1.4	439	3.1	307	13.6
	364	0.77	0.045	0.32	-	3.5	406	13.6
	91	24	0.022	0.017	-	24	0.84	11.1
[NaOH]=0.05M	182	18	0.041	0.013	-	21	2.21	11.5
	364	17	0.046	0.014	-	22	1.6	11.3
	91	30	0.014	0.036	-	60	13	12.2
[NaOH]=0.1M	182	33	0.020	0.028	-	47	9.1	12.1
	364	33	0.033	0.031	-	46	16	12.3
Ca/Si=0.8								
	91	3.8	0.91	≤ 0.0037	-	-	0.28	10.5
Alkali free	182	3.7	0.94	≤ 0.0037	-	-	0.23	10.5
	364	1.8	1.1	≤ 0.0037	-	-	0.05	9.8
	91	1.7	0.11	0.010	3.4	0.037	4.4	11.7
[KOH]=0.01M	182	1.6	0.078	0.013	3.6	0.083	1.4	11.3
	364	1.6	0.13	0.010	3.5	0.054	2.5	11.5
	91	1.0	≤ 0.0025	0.10	19	0.17	19	12.4
[KOH]=0.05M	182	1.6	0.0061	0.10	21	0.18	17	12.4
	364	1.6	0.0026	0.083	22	0.19	19	12.4
	91	5.4	≤ 0.0025	0.11	49	0.40	45	12.8
[KOH]=0.1M	182	4.3	≤ 0.0025	0.16	48	0.39	42	12.7
	364	4.1	≤ 0.0025	0.15	49	0.44	40	12.7
	91	3.2	0.0053	0.10	-	23	9	12.1
[NaOH]=0.05M	182	4.6	0.0085	0.081	-	20	12	12.2
	364	4.5	0.0027	0.088	-	22	11	12.2
	91	6.4	≤ 0.0025	0.25	-	66	35	12.6
[NaOH]=0.1M	182	5.0	0.0085	0.25	-	52	35	12.6
	364	4.9	0.0036	0.25	-	71	46	12.7
Ca/Si=1.0								
	91	0.17	2.2	0.021	-	-	3	11.7
Alkali free	182	0.15	2.1	0.020	-	-	5	11.8
	91	0.12	1.2	0.029	7.6	0.064	9	12.1
[KOH]=0.01M	182	0.10	1.3	0.028	7.6	0.090	8	12.0
	364	0.12	1.3	0.023	7.4	0.071	11	12.2
	182	0.22	0.21	0.056	34	0.26	32	12.6
[KOH]=0.05M	364	0.21	0.21	0.046	37	0.28	38	12.7
	91	0.59	0.046	0.15	70	0.51	80	13.0
[KOH]=0.1M	182	0.43	0.047	0.15	67	0.50	65	12.9
	364	0.21	0.21	0.05	69	0.28	66	12.9
	91	0.62	0.040	0.22	213	1.3	195	13.3
[KOH]=0.25M	182	1.2	0.076	0.22	217	1.5	189	13.4
	364	0.49	0.026	0.68	203	1.5	195	13.3
	91	0.76	0.032	0.37	404	2.8	405	13.6
[KOH]=0.5M	182	1.8	0.055	0.35	465	3.1	396	13.7
	91	0.51	0.082	0.13	-	33	33	12.6
[NaOH]=0.05M	182	0.39	0.091	0.10	-	32	30	12.6
	364	0.42	0.054	0.080	-	34	27	12.5

[NaOH]=0.1M	182	0.46	0.061	0.18	-	70	100	13.1
	364	0.59	0.027	0.15	-	74	74	12.9
Ca/Si=1.2								
Alkali free	91	0.10	4.4	0.011	-	-	0.22	11.9
	182	0.17	4.2	0.0066	-	-	9.4	12.1
	364	0.042	5.0	0.0070	-	-	9.4	12.1
[KOH]=0.01M	91	0.031	4.0	≤ 0.0037	9.3	0.1	16	12.3
	182	0.029	4.0	≤ 0.0037	9.3	0.1	14	12.3
	364	0.031	3.9	≤ 0.0037	9.1	0.1	18	12.4
[KOH]=0.05M	182	0.057	1.1	0.016	45	0.30	44	12.8
	364	0.072	1.0	0.020	47	0.33	48	12.8
[KOH]=0.1M	91	0.26	0.21	0.035	83	0.58	102	13.1
	182	0.18	0.23	0.032	82	0.56	77	13.0
	364	0.19	0.27	0.027	83	0.64	78	12.9
[KOH]=0.25M	91	0.029	0.52	0.015	236	1.1	217	13.3
	182	≤ 0.0036	2.1	0.065	257	1.8	212	13.3
	364	0.10	0.37	0.039	206	1.7	215	13.4
[NaOH]=0.05M	91	0.14	0.54	0.027	-	41	40	12.7
	182	0.11	0.62	0.023	-	43	41	12.7
	364	0.11	0.55	0.018	-	44	36	12.7
[NaOH]=0.1M	182	0.19	0.24	0.041	-	81	69	12.9
	364	0.20	0.25	0.036	-	86	89	13.0
Ca/Si=1.4								
Alkali free	91	0.0079	13	0.0059	-	-	16	12.3
	182	0.16	12	0.0039	-	-	29	12.6
	364	0.0069	13	≤ 0.0037	-	-	18	12.4
[KOH]=0.01M	91	0.0061	12	≤ 0.0037	9.8	0.076	29	12.5
	182	0.0051	11	≤ 0.0037	9.8	0.079	25	12.5
	364	0.0059	12	≤ 0.0037	9.7	0.084	31	12.6
[KOH]=0.05M	91	0.0065	6.7	0.0060	51	0.28	76	13.0
	182	0.0092	6.8	0.0041	51	0.33	58	12.9
	364	0.010	6.8	≤ 0.0037	51	0.35	60	12.9
[KOH]=0.1M	182	0.029	1.4	0.015	95	0.73	90	13.1
	364	0.029	1.6	0.019	95	0.76	89	13.0
[NaOH]=0.05M	91	0.025	3.4	0.0084	-	50	50	12.8
	182	0.023	3.5	0.013	-	48	55	12.8
	364	0.024	3.1	0.012	-	52	45	12.7
[NaOH]=0.1M	91	0.031	1.5	0.017	-	130	89	13.0
	182	0.026	1.5	0.017	-	94	100	13.1
	364	0.042	1.6	0.022	-	99	107	13.1
Ca/Si=1.6								
Alkali free	91	≤ 0.0036	22	0.002	-	-	29	12.5
	182	0.019	18	≤ 0.0037	-	-	26	12.6
	364	0.012	21	≤ 0.0037	-	-	30	12.6
[KOH]=0.01M	91	0.0039	17	≤ 0.0037	10	0.084	39	12.6

	182	≤ 0.0036	14	≤ 0.0037	10	0.084	34	12.6
	364	≤ 0.0036	17	≤ 0.0037	9.7	0.077	34	12.6
	91	0.0059	9.1	≤ 0.0037	53	0.26	80	13.0
[KOH]=0.05M	182	0.0087	8.8	≤ 0.0037	50	0.33	63	12.9
	364	0.010	9.3	0.0039	51	0.33	65	12.9
	91	0.058	4.0	0.0056	98	0.67	137	13.2
[KOH]=0.1M	182	0.015	4.4	0.0047	97	0.66	97	13.1
	364	0.014	4.5	0.0046	99	0.69	97	13.0
	91	≤ 0.0036	2.0	0.0061	271	1.3	236	13.4
[KOH]=0.25M	182	0.050	0.63	0.020	241	1.7	212	13.3
	364	0.032	1.4	0.011	191	1.8	224	13.4
	91	≤ 0.0036	0.89	0.012	506	2.5	473	13.6
[KOH]=0.5M	182	0.030	0.94	≤ 0.0037	552	3.6	441	13.6
	364	0.072	0.77	0.0045	562	3.4	421	13.7
	91	0.0088	8.8	0.0063	-	52	61	12.9
[NaOH]=0.05M	182	0.012	6.6	0.0056	-	49	67	12.9
	364	0.022	7.9	0.0054	-	53	54	12.8
	91	0.016	4.4	0.0081	-	134	107	13.1
[NaOH]=0.1M	182	0.013	4.5	0.0089	-	97	109	13.1
	364	0.025	4.2	0.0077	-	103	113	13.1

484

485 C-A-S-H (Al/Si=0.1)

Initial alkali concentration	Time (days)	Si	Ca	Al (mmol/L)	K*	Na*	OH	pH
								-
Ca/Si=1.0								
Alkali free	364	0.17	1.9	0.0039	-	-	3.0	11.6
[KOH]=0.5M	364	0.60	0.039	0.59	208	-	336	13.5
[NaOH]=0.5M	364	0.68	0.059	0.63	458	-	360	13.5

486

487 C-S-H

Initial alkali concentration	Time (days)	Si	Ca	Al (mmol/L)	K*	Na*	OH	pH
								-
Ca/Si=0.6								
[KOH]=0.5M	182	38	≤ 0.0025	-	453	-	376	13.5
Ca/Si=1.0								
[KOH]=0.5M	182	0.59	0.08	-	457	-	419	13.5
Ca/Si=1.6								
[KOH]=0.5M	182	0.04	0.80	-	493	-	420	13.5

488

489

490 Appendix C Samples compositions (-: not observed., nm: not measured)

491 C-A-S-H (Al/Si=0.05)

Initial alkali concentration	Time (days)	C-S-H composition					CH
		Ca/Si	Ca/(Si+Al)	Al/Si	H ₂ O/Si ±0.3	(KorNa)/Si	(wt%)
Ca/Si=0.6							
Alkali free	91	0.62	0.59	0.05	1.4	-	-
	182	0.62	0.59	0.05	1.4	-	-
	364	0.60	0.57	0.05	1.1	-	-
[KOH]=0.01M	91	0.61	0.58	0.05	1.2	0.031	-
	182	0.61	0.58	0.05	1.4	0.032	-
	364	nm	nm	nm	nm	0.032	nm
[KOH]=0.05M	91	0.64	0.61	0.05	1.3	0.13	-
	182	0.63	0.60	0.05	1.8	0.15	-
	364	0.63	0.60	0.05	1.2	0.16	-
[KOH]=0.1M	91	0.69	0.66	0.06	2.2	0.27	-
	182	0.67	0.64	0.06	1.1	0.25	-
	364	0.69	0.65	0.06	1.2	0.28	-
[KOH]=0.25M	91	0.72	0.68	0.06	1.3	0.26	-
	364	nm	nm	nm	nm	0.33	nm
	[KOH]=0.5M	91	0.72	0.69	0.05	1.2	0.24
182		0.62	0.59	0.05	1.1	0.27	-
364		nm	nm	nm	nm	-1.21	nm
[NaOH]=0.05M	91	0.67	0.63	0.06	1.4	0.11	-
	182	0.65	0.62	0.05	1.4	0.14	-
	364	0.65	0.61	0.05	1.4	0.10	-
[NaOH]=0.1M	91	0.69	0.65	0.06	1.4	0.14	-
	182	0.70	0.64	0.06	1.3	0.26	-
	364	0.70	0.66	0.06	1.4	0.26	-
Ca/Si=0.8							
Alkali free	91	0.81	0.77	0.05	1.4	-	-
	182	0.81	0.77	0.05	1.5	-	-
	364	0.80	0.76	0.05	1.5	-	-
[KOH]=0.01M	91	0.81	0.77	0.05	1.3	0.031	-
	182	0.81	0.77	0.05	1.5	0.030	-
	364	nm	nm	nm	nm	0.031	nm
[KOH]=0.05M	91	0.80	0.77	0.05	1.3	0.12	-
	182	0.81	0.77	0.05	1.1	0.13	-
	364	0.81	0.77	0.05	2.7	0.13	-
[KOH]=0.1M	91	0.82	0.78	0.05	1.1	0.24	-
	182	0.82	0.78	0.05	1.0	0.23	-
	364	0.82	0.78	0.05	1.2	0.25	-
[NaOH]=0.05M	91	0.81	0.77	0.05	1.3	0.12	-
	182	0.82	0.78	0.05	1.3	0.15	-
	364	0.82	0.78	0.05	1.4	0.11	-
[NaOH]=0.1M	91	0.83	0.78	0.05	1.3	0.12	-
	182	0.82	0.78	0.05	1.1	0.23	-
	364	0.82	0.78	0.05	1.5	0.14	-
Ca/Si=1.0							

Alkali free	91	0.99	0.94	0.05	1.3	-	-
	182	0.99	0.94	0.05	1.4	-	-
	364	nm	nm	nm	nm	-	nm
[KOH]=0.01M	91	0.99	0.95	0.05	1.5	0.013	-
	182	0.99	0.95	0.05	1.7	0.013	-
	364	nm	nm	nm	nm	0.014	nm
[KOH]=0.05M	182	1.00	0.95	0.05	1.4	0.079	-
	364	1.00	0.95	0.05	1.4	0.064	-
	91	1.00	0.96	0.05	1.3	0.15	-
[KOH]=0.1M	182	1.00	0.95	0.05	1.3	0.16	-
	364	1.00	0.95	0.05	1.6	0.17	-
	91	1.00	0.96	0.05	1.3	0.15	-
[KOH]=0.25M	182	1.01	0.96	0.05	1.1	0.18	-
	364	nm	nm	nm	nm	0.26	nm
	91	1.00	0.96	0.05	1.2	0.43	-
[KOH]=0.5M	182	1.01	0.96	0.05	1.3	0.19	-
	91	1.00	0.95	0.05	1.4	0.077	-
	182	1.00	0.95	0.05	1.5	0.10	-
[NaOH]=0.05M	364	1.00	0.95	0.05	1.5	0.067	-
	182	1.00	0.95	0.05	1.5	0.16	-
	364	1.00	0.96	0.05	1.5	0.14	-
Ca/Si=1.2							
Alkali free	91	1.18	1.12	0.05	1.8	-	-
	182	1.18	1.12	0.05	1.9	-	-
	364	nm	nm	nm	nm	-	nm
[KOH]=0.01M	91	1.18	1.12	0.05	1.6	0.0037	-
	182	1.18	1.12	0.05	1.8	0.0043	-
	364	nm	nm	nm	nm	0.0052	nm
[KOH]=0.05M	182	1.19	1.14	0.05	1.5	0.030	-
	364	1.19	1.14	0.05	1.3	0.018	-
	91	1.20	1.14	0.05	1.2	0.092	-
[KOH]=0.1M	182	1.20	1.14	0.05	1.3	0.095	-
	364	1.20	1.14	0.05	1.7	0.10	-
	91	1.20	1.14	0.05	1.3	0.068	-
[KOH]=0.25M	182	1.19	1.13	0.05	1.4	-0.04	-
	364	nm	nm	nm	nm	0.32	nm
	91	1.20	1.14	0.05	1.6	0.043	-
[NaOH]=0.05M	182	1.20	1.14	0.05	1.6	0.041	-
	364	1.20	1.14	0.05	1.6	0.029	-
	182	1.20	1.14	0.05	1.5	0.11	-
[NaOH]=0.1M	364	1.20	1.14	0.05	1.7	0.079	-
Ca/Si=1.4							
Alkali free	91	1.32	1.25	0.05	1.6	-	-
	182	1.32	1.26	0.05	1.9	-	-
	364	nm	nm	nm	nm	-	nm
[KOH]=0.01M	91	nm	nm	nm	nm	0.0010	nm
	182	nm	nm	nm	nm	0.0014	nm
	364	nm	nm	nm	nm	0.0021	nm

	91	1.36	1.29	0.05	1.9	-0.0060	-
[KOH]=0.05M	182	1.36	1.29	0.05	1.7	-0.0076	-
	364	1.36	1.29	0.05	1.6	-0.0079	-
[KOH]=0.1M	182	1.39	1.33	0.05	1.5	0.031	-
	364	nm	nm	nm	nm	0.034	nm
[NaOH]=0.05M	91	1.38	1.31	0.05	2.0	0.00063	-
	182	1.38	1.31	0.05	1.6	0.011	-
	364	1.38	1.31	0.05	1.7	-0.0088	-
[NaOH]=0.1M	91	1.39	1.32	0.05	1.9	-0.14	-
	182	1.30	1.23	0.05	1.6	0.038	4.08
	364	1.39	1.32	0.05	1.8	0.0048	-
Ca/Si=1.6							
	91	1.43	1.37	0.05	1.8	-	0.71
Alkali free	182	1.44	1.37	0.05	1.9	-	1.68
	364	1.39	1.33	0.05	1.9	-	2.32
	91	1.409	1.342	0.05	1.5	-0.0010	3.21
[KOH]=0.01M	182	1.437	1.368	0.05	1.8	0.000093	2.69
	364	nm	nm	nm	nm	0.0022	nm
	91	1.46	1.39	0.05	1.9	-0.014	3.17
[KOH]=0.05M	182	1.45	1.38	0.05	1.7	0.0031	3.79
	364	1.40	1.34	0.05	1.7	-0.008	5.3
	91	1.54	1.47	0.05	1.9	0.012	1.2
[KOH]=0.1M	182	1.52	1.44	0.05	1.7	0.016	2.2
	364	nm	nm	nm	nm	0.0081	nm
	91	1.43	1.36	0.05	1.4	-0.11	6.42
[KOH]=0.25M	182	nm	nm	nm	nm	0.063	nm
	364	1.46	1.39	0.05	2.1	nm	5.11
	91	1.44	1.37	0.05	1.5	-0.038	6.42
[KOH]=0.5M	182	1.25	1.19	0.05	1.3	-0.34	14
	364	1.20	1.14	0.05	1.4	-0.37	16
	91	1.51	1.44	0.05	2.0	-0.014	1.19
[NaOH]=0.05M	182	1.51	1.44	0.05	1.7	0.0055	1.87
	364	nm	nm	nm	nm	-0.015	nm
	364	nm	nm	nm	nm	-0.018	nm
	91	1.54	1.47	0.05	1.9	-0.17	1.22
[NaOH]=0.1M	182	1.51	1.44	0.05	1.9	0.019	2.46
	364	nm	nm	nm	nm	-0.018	nm

492

493 C-S-H

Initial alkali concentration	Time (days)	C-S-H composition					CH (wt%)
		Ca/Si ¹	Ca/(Si+Al) ¹	Al/Si ¹	H ₂ O/Si ±0.3	(KorNa)/Si	
Ca/Si=0.6							
[KOH]=0.5M	182	0.72	0.72	-	1.3	0.23	-
Ca/Si=1.0							
[KOH]=0.5M	182	1.0	1.0	-	1.3	0.21	-
Ca/Si=1.6							

494	[KOH]=0.5M	182	1.52	1.52	-	1.5	0.048	2.90
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