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1 **Electrostatic properties of C-S-H and C-A-S-H for predicting calcium and**
2 **chloride adsorption**

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16

17 **Abstract**

18 The adsorption capacity of cement hydrates considerably affects the ionic ingress into cementitious
19 materials. In this study, the surface electrostatic properties of calcium silicate hydrate (C-S-H) and
20 calcium aluminosilicate hydrate (C-A-S-H) were determined to understand the effects of the
21 properties on calcium and chloride adsorption. The density of the surface functional groups was
22 determined by analysing the structure of C-S-H and C-A-S-H through ²⁷Al and ²⁹Si MAS NMR.
23 The surface sites of ≡SiOH and ≡AlOH are available in C-A-S-H whereas C-S-H has ≡SiOH groups
24 for ionic adsorption. We found that the incorporation of aluminium decreases the number of total
25 adsorption sites in C-A-S-H. Furthermore, the site density increased with Ca/(Si+Al). To
26 understand the C-A-S-H/solution interface, a triple-layer surface complexation model was

27 developed and the associated equilibrium constants for deprotonation, calcium, and chloride
28 adsorption were determined by fitting the experimental data of potentiometric titration and zeta
29 potential measurement results. The estimated surface complexation modelling parameters were
30 verified by predicting the experimental data of calcium and chloride adsorption on C-S-H and C-A-
31 S-H.

32
33 **Keywords:** Adsorption; Calcium-Silicate-Hydrate (C-S-H); Chloride; Zeta potential; Surface
34 Complexation model

35 36 **1. Introduction**

37 The characteristics of the cement paste matrix and concrete—such as porosity, tortuosity, the
38 composition of cement hydrates, and the properties of calcium silicate hydrate (C-S-H), which is the
39 main component of hydrated cement—significantly influence the uptake of chloride from the
40 external source and transport it to a greater depth via diffusion [1-4]. The penetrated chloride
41 partially reacts with monosulfoaluminate ($\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12}\cdot 6\text{H}_2\text{O}$) and forms Friedel's salt
42 ($\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}\cdot 4\text{H}_2\text{O}$). Another part of chloride may be adsorbed on the surface of C-S-H
43 through electrostatic interaction called physical adsorption, and the remaining chloride remains in
44 the pore solution as free chloride, contributing to the initiation of corrosion in reinforcement.
45 Therefore, the sorption ability of cement hydrates significantly influences the concentration of free
46 chloride in the pore solution [5-8]. It has been reported that a partial replacement of ordinary
47 Portland cement (OPC) by supplementary cementitious materials (SCMs), such as fly ash, ground
48 granulated blast-furnace slag, and calcinated clay, not only increases chloride binding, but also
49 shows high resistance to chloride ingress by densifying the microstructure [9-10]. Furthermore, the
50 physical adsorption of chloride is more dominant than the formation of Friedel's salt in SCM [3, 5,
51 11, 12].

52

53 Numerous experimental and modelling studies have reported the interaction of chloride with cement
54 hydrates [2-8, 10-16]. It is widely accepted that the formation of Friedel's salt occurs through the
55 thermodynamic equilibrium between chloride and monosulfoaluminate, called the chemical binding
56 of chloride. However, the physical adsorption of chloride is still subject to debate. Hirao et al.
57 proposed Langmuir chloride adsorption through adsorption experiments [6]. Beaudoin et al. showed
58 that the H_2O-SiO_2 and $CaO-SiO_2$ ratios of C-S-H significantly affect the chloride adsorption on its
59 surface [5]. De Weerd's group studied a lot of experimental and thermodynamic modelling of
60 chloride binding and analysed the effect of associated cations on the chloride adsorption on the C-S-
61 H surface [14]. They concluded that more adsorption was observed when associated cations of
62 calcium or magnesium were used compared with sodium, and the adsorbed chloride is in the diffuse
63 layer of C-S-H, which is available for diffusion [14]. A significant amount of temperature-
64 dependent chloride adsorption has been reported for fly ash-blended cement paste [12].
65 Elakneswaran et al. highlighted that the chloride adsorption on C-S-H occurs via calcium-adsorbed
66 surface sites and proposed a double layer surface complexation model to predict chloride adsorption
67 in hydrated OPC [8, 10]. In addition, the model is coupled with a reactive transport equation to
68 simulate chloride ingress [3]. On the other hand, it has been reported that there is no specific
69 adsorption of chloride on C-S-H, and it accumulates on the diffuse layer [15]. Therefore, the
70 proposed hypotheses and experimental results on chloride adsorption on C-S-H are inconsistent and
71 contradictory; more detailed experimental and modelling studies are necessary to understand
72 chloride interactions with C-S-H.

73

74 Alumina-rich SCMs increase the incorporation of aluminium in C-S-H and form calcium
75 aluminosilicate hydrate (C-A-S-H) phase [17-21]. The surface chemistry of C-A-S-H is
76 significantly different from that of conventional C-S-H and thus has an impact on the ionic
77 adsorption behaviour. Only a few studies have been conducted on the ionic adsorption on the C-A-
78 S-H surface [21-24]. To the best of our knowledge, there is no comprehensive study on chloride

79 interaction towards C-A-S-H. C-S-H possesses the surface functional group of the silanol site
80 ($\equiv\text{SiOH}$). At high pH, the $\equiv\text{SiOH}$ group deprotonates to $\equiv\text{SiO}^-$ and calcium can compensate for the
81 negative surface and change to a positive surface at high calcium concentrations. The partial
82 substitution of Si by Al in the silica tetrahedra could induce forming $\equiv\text{AlOH}$ surface functional
83 groups in C-A-S-H, in addition to $\equiv\text{SiOH}$, and this would influence C-A-S-H surface characteristics.
84 Therefore, more studies on the surface electrical properties of C-A-S-H phase (described by the
85 types of surface functional groups and their densities) are necessary to describe the ionic adsorption
86 behaviour in SCM.

87

88 The main purpose of this study is to analyse the interface between C-S-H/C-A-S-H phase and the
89 solution to understand its surface characteristics for calcium and chloride adsorption. The
90 synthesised C-S-H and C-A-S-H were characterised by solid-phase analysis to determine the
91 surface functional groups. Potentiometric titration, zeta potential, and adsorption experiments were
92 carried out to propose and validate a triple-layer surface complexation model for C-S-H/ and C-A-
93 S-H/solution interface.

94

95 **2. Materials and methods**

96 **2.1 Synthesis of C-S-H and C-A-S-H**

97 In this study, both C-S-H and C-A-S-H were synthesised at 50 °C. The $\text{Ca}(\text{OH})_2$ (special grade
98 reagent manufactured by Kanto Chemical Co.) and SiO_2 (AEROSIL200 with purity of 99.9% or
99 higher by Nippon Aerosil Co., Ltd.) in different proportions were mixed with pure water with a
100 water to powder ratio of 20 mL/g, and the mixture was cured for 10 days. The targets of the Ca/Si
101 ratios were 0.8, 1.0, and 1.5. In the preparation of C-A-S-H, $\text{Ca}(\text{OH})_2$, SiO_2 , and CaAl_2O_4 were
102 mixed for the target of $\text{Ca}/(\text{Si}+\text{Al})$ of 0.8, 1.0, and 1.5, and Al/Si of 0.19. The mix proportions are
103 reported in **Table 1**. The mixing water to powder ratio was 45 mL/g, and the mixture was sealed
104 after N_2 purging and cured for 5 weeks at 50 °C. After the curing time, the solid and liquid phases

105 were separated by suction filtration, and the solid phase was washed with deionised water three
106 times and then dried for 2 days by freeze-drying before use.

107

108

109

Table 1: Mixing proportions for C-S-H and C-A-S-H preparation

| Sample ID | Target | Target | Initial | Initial | Initial |
|-----------|------------|--------|-----------|------------------------|---|
| | Ca/(Si+Al) | Al/Si | CaO (mol) | SiO ₂ (mol) | CaOAl ₂ O ₃ (mol) |
| CSH-0.8 | 0.80 | - | 0.80 | 1.00 | - |
| CSH-1.0 | 1.00 | - | 1.00 | 1.00 | - |
| CSH-1.5 | 1.50 | - | 1.50 | 1.00 | - |
| CASH-0.8 | 0.80 | 0.19 | 0.72 | 0.84 | 0.08 |
| CASH-1.0 | 1.00 | 0.19 | 0.92 | 0.84 | 0.08 |
| CASH-1.5 | 1.50 | 0.19 | 1.42 | 0.84 | 0.08 |

110

111 2.2 Experimental procedure

112 C-S-H and C-A-S-H were characterised by a Rigaku X-ray generator with CuK α radiation, and the
113 measurement conditions were tube voltage 40 kV, scanning range of 5 to 70 ° (2 θ), sampling width
114 of 0.02 ° (2 θ), and scan speed of 6.5 ° / min. A fluorescent X-ray analyser element monitor
115 EA1200VX manufactured by Hitachi High-Tech Science was used to determine the solid
116 composition of C-S-H and C-A-S-H. The measurement conditions were target Rh, an excitation
117 voltage of 15 kV, and no primary filter. The measurements were conducted in a vacuum
118 atmosphere. Thermogravimetry/Differential Thermal Analysis (TG/DTA) was performed in
119 nitrogen using a HITACHI TG/DTA 7220 analyser at a heating rate of 293 K/min up to 980 °C. The
120 specific surface areas of C-S-H and C-A-S-H were measured using the Brunauer–Emmett–Teller
121 (BET) water adsorption method. Before the measurement, each sample was vacuum-degassed and
122 dried for one hour. Titration experiments for C-S-H and C-A-S-H suspensions were conducted
123 using an automated titration system. A 0.01 mol/L NaNO₃ solution (50 mL) was prepared, and the

124 pH of the solution with 5g/L of C-S-H/C-A-S-H and without C-S-H/C-A-S-H was measured by
125 titrating the solution with 0.25 mol/L NaOH. The suspension was equilibrated for one day and was
126 stirred for three minutes using an ultrasonic cleaner before titration. The ^{29}Si MAS NMR
127 experiment was conducted on MSL 400 9.4 T BRUKER at 79.48 MHz. The Q_8M_8 ($\text{Si}(\text{CH}_3)_8\text{Si}_8\text{O}_2$)
128 manufactured by Wako Pure Chemical Industries was used as a reference material for the
129 measurement. The measurement conditions for each sample were 90° pulse length of $5\ \mu\text{s}$ for ^{29}Si
130 recycling delay of 45 s and 2000 scans and 4 kHz of the number of rotations. The Win-nut program
131 was used for the analysis of ^{29}Si MAS NMR data. A JEOL ECA-700 was used to obtain ^{27}Al
132 spectra, where $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was used as a reference material. The measurement conditions for the
133 ^{27}Al spectra were 90° pulse length of $2.09\ \mu\text{s}$, delay time of 30 s, 2880 scans, and 18 kHz of
134 spinning rates with 3.2 mm MAS probe. The number of scans for CASH-1.5 was set to 5760 times,
135 as it was considered to have a small amount of Al uptake. All spectra were deconvoluted using the
136 Delta program.

137

138 A C-S-H/C-A-S-H suspension with a solid to liquid ratio of 0.1 g/L was prepared for zeta potential
139 measurement using a Zetasizer Nano series. The equilibrium time for the suspension in $\text{Ca}(\text{OH})_2$
140 solution was one day, whereas two days were adopted for the CaCl_2 solution. The ionic strength of
141 the solution was adjusted by NaNO_3 and kept constant at 20 mmol/L. The suspension was stirred
142 for 3 min using an ultrasonic cleaner before measurement at 25°C . The average of five
143 measurements was used as the zeta potential value. A batch experiment was performed with
144 $\text{Ca}(\text{OH})_2$ solution to determine calcium adsorption on C-S-H/C-A-S-H. The sample was immersed
145 in different concentrations of 10 mL $\text{Ca}(\text{OH})_2$ solution for one day, where 5 g/L of solid to liquid
146 ratio was adopted. After equilibrium, the solid and liquid phases were separated by handshaking,
147 and then the liquid phase was filtered with a $0.45\ \mu\text{m}$ syringe filter. The concentration of calcium in
148 the filtered solution was measured by ICP-OES. The calcium concentration difference between the
149 blank and C-S-H/C-A-S-H suspensions was the adsorbed calcium. In addition, the measured

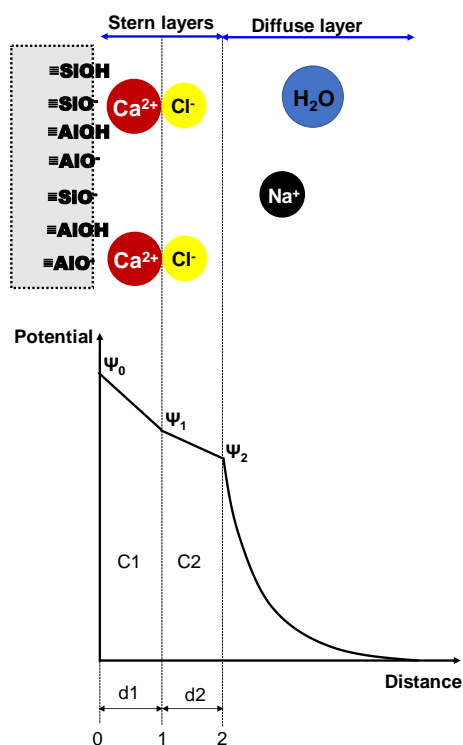
150 calcium concentration for the C-S-H/C-A-S-H suspension in water was considered as the dissolved
151 calcium from the sample, which was considered in by calculating the amount of adsorbed calcium.
152 The same experimental procedure was adopted for chloride adsorption. C-S-H/C-A-S-H was
153 equilibrated with different concentrations of 5 mL CaCl₂ for 5 days, and the solid to liquid ratio for
154 the chloride adsorption was 100 g/L. After equilibrium, the solid and liquid phases were separated
155 and the chloride concentration in the liquid phase was measured using ion chromatography to
156 determine its adsorption.

157

158 **2.3 Modelling approach**

159 The geochemical code PHREEQC was used for the speciation, thermodynamic equilibrium, and
160 surface complexation modelling calculations [25-26]. The charge-distribution-multi site
161 complexation model (CD-MUSIC) available in PHREEQC was adopted for the surface
162 complexation reaction between C-S-H/C-A-S-H and ionic species [27-28], as illustrated in **Fig. 1**.
163 The surface has three planes: the 0-, 1-, and 2-planes. The surface groups of C-S-H/C-A-S-H are
164 located at the 0-plane, and the diffuse layer begins at the 2-plane. The potential at the 0-plane is the
165 surface potential, and the zeta potential can be directly compared with the potential at the 2-plane.
166 The CD-MUSIC model requires the capacitance of the layers and change in charge at three layers
167 because of the dissociation of surface sites and adsorption of ions on the sites, in addition to surface
168 site density and equilibrium constants. The model can be implemented in PHREEQC using the
169 keyword data block of SURFACE and SURFACE_SPECIES with the charge distribution and the
170 capacitance of the inner and outer Stern layers [22].

171



172
173 **Fig. 1.** Schematic of the electrical triple-layer used in the CD-MUSIC model.
174

175 **3. Results and discussion**

176 **3.1 Characterisation and determination of surface site density of C-S-H and C-A-S-H**

177 To calculate the ionic adsorption using a surface complexation model, the types of surface
178 functional groups and their densities must be evaluated. The synthesised C-S-H/C-A-S-H samples
179 were characterised, and this information was used to evaluate the surface site densities. The XRD
180 patterns of the synthesised samples are aligned with the results reported by Myer et al. [29], which
181 was again confirmed by the TG/DTA (refer **Appendix A**). In addition, XRF measurements were
182 conducted on the synthesised samples to examine if the actual Ca/(Si+Al) ratio reaches the target
183 value (**Table 2**). In the samples with Ca/(Si+Al) of 0.8 and 1.0, the measured ratio was almost the
184 same as the target value. However, in the sample with a Ca/(Si+Al) of 1.5, the measured ratio was
185 lower than the target value. It is believed that a part of calcium in the samples was dissolved by
186 washing with de-ionic water in the preparation of the samples. Moreover, the higher water to solid
187 ratio (w/s = 45) adopted in the experiments provides high concentration of calcium in the solution,
188 which reduces the calcium in the samples. ²⁹Si and ²⁷Al NMR were used to characterise C-S-H and

189 C-A-S-H (refer **Appendix A**). The calculated mean chain length (MCL) of the samples, as a
 190 function of Ca/(Si+Al), is shown in **Fig. 2**. It is confirmed that MCL decreases with an increase in
 191 the Ca/(Si+Al) ratio due to a decrease in the Q²b proportion. Furthermore, the substitution of Si by
 192 Al increases the MCL.

193

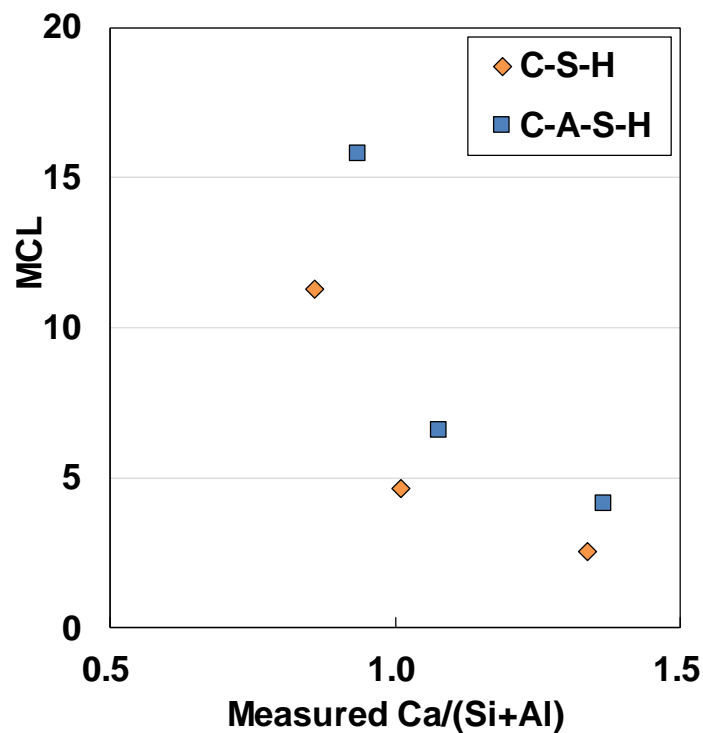
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Table 2: XRF results on C-S-H and C-A-S-H

| Sample ID | Target Ca/(Si+Al) | Measured Ca/(Si+Al) | Target Al/Si | Measured Al/Si |
|-----------|----------------------|------------------------|-----------------|-------------------|
| CSH-0.8 | 0.80 | 0.86 | - | - |
| CSH-1.0 | 1.00 | 1.01 | - | - |
| CSH-1.5 | 1.50 | 1.34 | - | - |
| CASH-0.8 | 0.80 | 0.94 | 0.19 | 0.11 |
| CASH-1.0 | 1.00 | 1.08 | 0.19 | 0.13 |
| CASH-1.5 | 1.50 | 1.37 | 0.19 | 0.13 |

195

196



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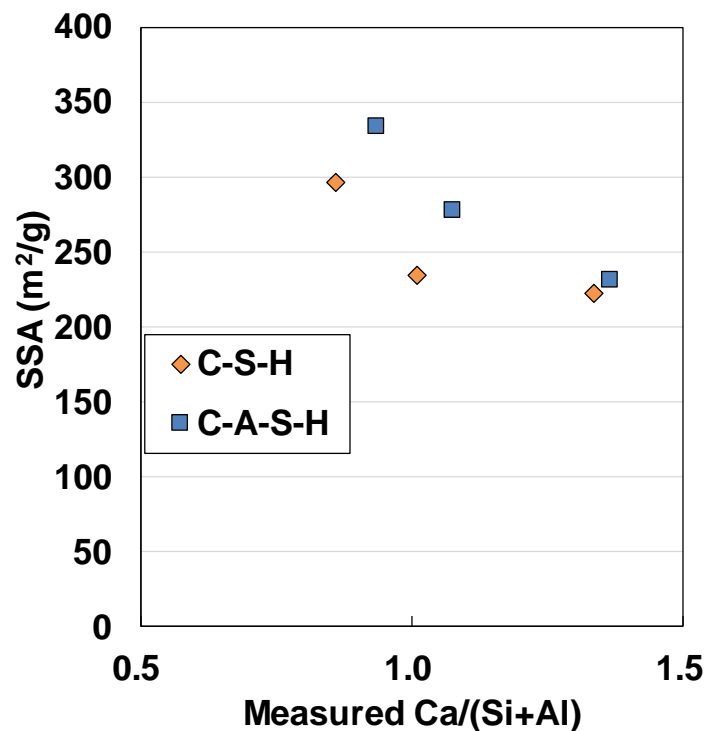
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Fig. 2. Mean chain length of synthesised C-S-H and C-A-S-H.

199

200 The calculated specific surface from the water vapor adsorption data using BET method is shown in
201 **Fig. 3.** as a function of Ca/(Si+Al) ratio. The Ca/(Si+Al) and aluminium incorporation affect the
202 specific surface area, which increases with decreasing Ca/(Si+Al) and aluminium substitution. Haas
203 et al. (2015) reported that there is a correlation between Ca/(Si+Al) and the number of layers in α ,
204 β , and γ -C-S-H [30]. Therefore, in this study, it was assumed that the synthesised C-S-H
205 corresponded to β -C-S-H, and the layers were calculated from the results of the specific surface
206 area. The results are shown in **Fig. 4,** as a function of the Ca/(Si+Al) ratio, and it increases with an
207 increase in Ca/(Si+Al).

208



209

210

Fig. 3. Specific surface area of synthesised C-S-H and C-A-S-H.

211

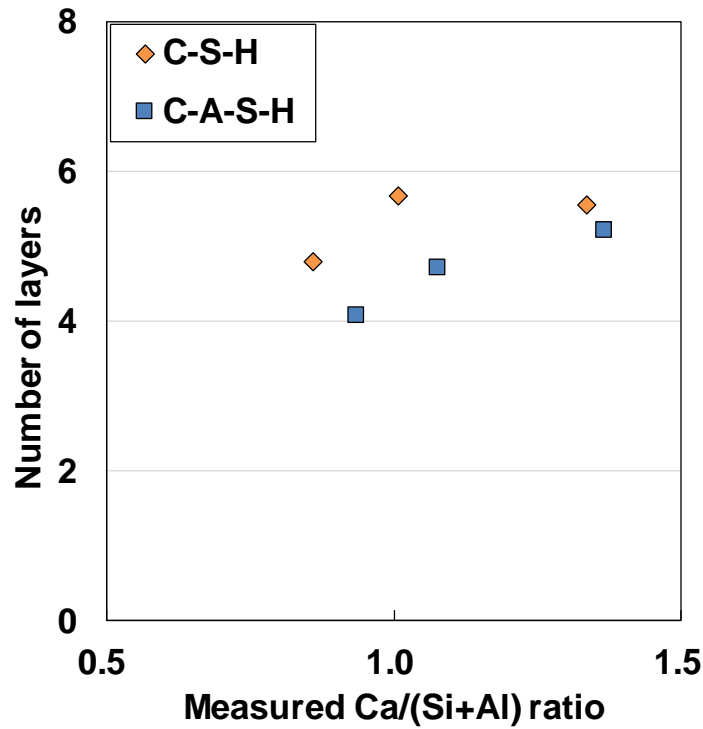


Fig. 4. The number of staking layers in synthesised C-S-H and C-A-S-H.

212

213

214

215 Information about the number of layers was used to estimate the surface site density of C-S-H and
 216 C-A-S-H. It was assumed that the structure of C-S-H and C-A-S-H is close to tobermorite-type
 217 crystal structure [19], and the C-S-H has surface functional group of $\equiv\text{SiOH}$, whereas C-A-S-H
 218 possesses both $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ groups. The basic unit is a tetrahedron of the two silicates that
 219 make up the dimer, and the surface reactive groups are present in the bridges and end chains of
 220 silica and aluminium. The area occupied by the dimer is 41.123\AA^2 and is constant regardless of the
 221 $\text{Ca}/(\text{Si}+\text{Al})$ ratio [30-31]. Nonat proposed that the layered structure of C-S-H was a $60 \times 30 \times 5$ nm
 222 elliptical cylinder [32]. Based on the above information and the results shown in **Fig. 4**, the density
 223 of surface sites presents in Q^1 and Q^{2b} can be calculated using the equations given below:

224

$$N_{s-Q^1} = \frac{S_{\text{ellipse}}}{S_{\text{unit}}} \times \frac{MCL}{2} \times \frac{1}{2} \times \frac{Q^1}{MCL} \times \frac{1}{S_{\text{ellipse}}} \times 2N_{\text{lamella}}$$

226 (1)

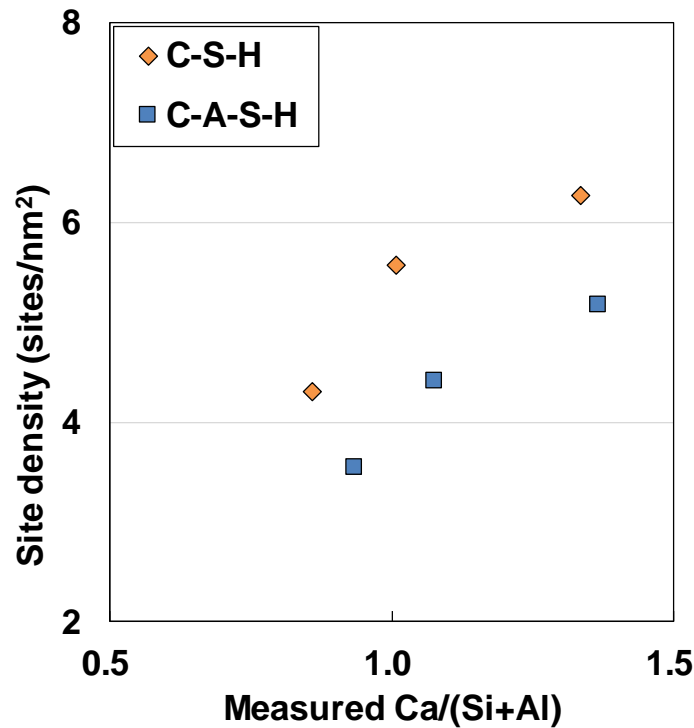
$$N_{s-Q^2} = \frac{S_{ellipse}}{S_{unit}} \times \frac{MCL}{2} \times \frac{1}{2} \times \frac{2 \times Q_b^2}{MCL} \times \frac{1}{S_{ellipse}} \times 2N_{lamella}$$

228 (2)

229

230 where N_{s-Q^1} and N_{s-Q^2} are the surface site density (sites/nm²), $S_{ellipse}$ is the area of the ellipse (5654
 231 nm²), S_{unit} is the area of the unit cell (0.41123 nm²), MCL is the mean chain length of the silica
 232 chain, and $N_{lamella}$ is the number of stacking layers. The estimated total surface site densities of C-S-
 233 H and C-A-S-H as a function of the Ca/(Si+Al) ratio is shown in **Fig. 5**. The site density increased
 234 with increasing Ca/(Si+Al) ratio due to the increase in the number of stacking layers. The quantified
 235 total surface site densities of C-S-H and C-A-S-H were 4.3–6.3 and 3.5–5.2 sites/nm², respectively.
 236 These values are not significantly different from those reported in the literature [13, 30-31, 33-35];
 237 a value of 4.8 sites/nm² has been reported for C-S-H in many studies [30-31, 33].

238



239

240 **Fig. 5.** Estimated total surface site density of C-S-H and C-A-S-H

241

242 **3.2 Electrostatic interaction between C-A-S-H and hydroxyl, calcium, and chloride ions**

243 The total sites determined in section 3.1 were divided further into strong and weak sites, where the
 244 weak sites were easy to dissociate, while the strong sites were difficult to dissociate. Charukov et al.
 245 performed a simulation based on the different degrees of dissociation in Q^1 and Q^{2b} , each of which
 246 exists at a ratio of 1:1 [33]. A similar approach was adopted in this study to estimate the density of
 247 weak and strong sites. In the silicate chain, Q^{2b} exists only on the flat surface and is distributed to
 248 sites with different dissociation ratios of 1:1. However, Q^1 exists on both flat surface and edge, and
 249 the surface area ratio between the end surface and the layer surface can be calculated based on the
 250 layered structure proposed by Haas et al. [30]. The Q^1 sites on the flat surface can form a hydrogen
 251 bond and are considered to be strong sites, whereas the sites at the edge surface are less affected by
 252 hydrogen bonds and considered as weak sites. The strong and weak surface site densities of C-S-H
 253 and C-A-S-H are presented in **Table 3**.

254

255 The strong and weak of $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ surface sites are dissociated in the alkaline solution as
 256 follows:

257



259 (3)

260 *X: Si or Al*

261

262 where K_{OH} is the intrinsic equilibrium constant for dissociation, $(\equiv XOH)$, $(\equiv XO^-)$ are concentrations
 263 of the surface species of surface sites (mol/m^2), a_{H^+} is the activity of H^+ (mol/L), ψ_i is the potential
 264 at the 0-, 1-, or 2-plane (V), Δz_i is the charge distribution, R is the universal gas constant equal to
 265 $8.31451 \text{ J}/(\text{mol}\cdot\text{K})$, and T is the absolute temperature (K).

266

267 In the titration experiment, the pH of the solution containing C-S-H/C-A-S-H was lower than the
268 initial blank pH because of the H⁺ dissociation. The amount of dissociated H⁺ can be calculated as
269 follows [36]:

270

$$271 \quad Excess/deficit[H^+] = \frac{([H^+]_{initial} - [H^+]_{fin}) * (V_{initial} + V_{NaOH.add})}{(V_{initial} + V_{NaOH.add}) * A * SSA}$$

272 (4)

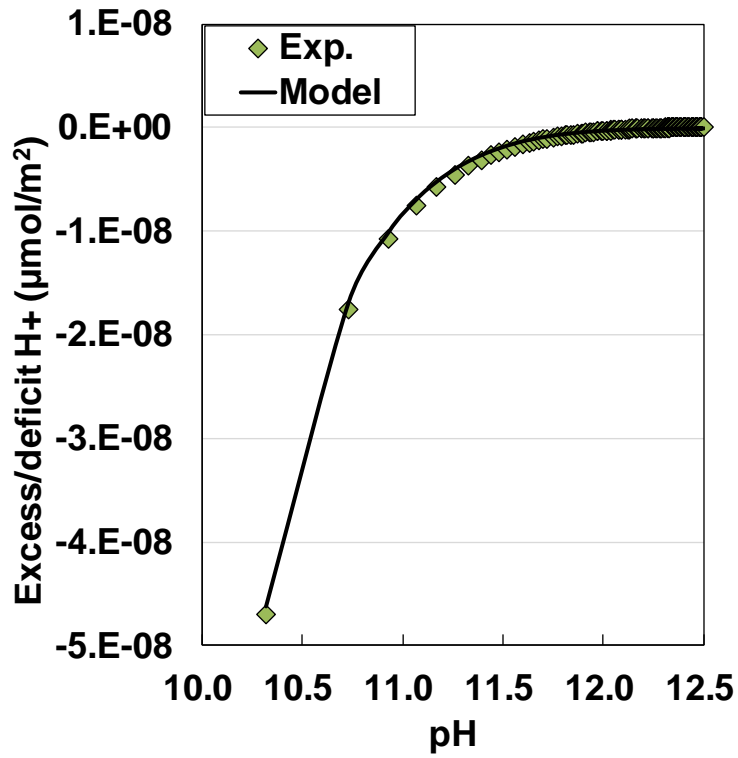
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274 where $[H^+]_{initial}$ is the H⁺ concentration in the blank solution (mol/L), $[H^+]_{fin}$ is the H⁺ concentration
275 in the solution containing sample (mol/L), $V_{initial}$ is the initial volume (mL), $V_{NaOH.add}$ is the amount
276 of added NaOH (mL), SSA is the specific surface area (m²/g), and A is the solid to liquid ratio (g/L).

277

278 The titration experimental results from Eq. (4) were fitted to the surface complexation modelling
279 results to estimate the K_{OH} of both strong and weak sites. It was assumed that a water molecule was
280 attached to the inner and outer Stern layers of the triple-layer surface complexation model for the
281 interaction of C-S-H/C-A-S-H in NaOH solution (**Fig. 1.**). An example of fitting results for C-S-H
282 with a Ca/Si ratio of 1.5 is shown in **Fig. 6.** A similar fitting was performed for other C-S-H and C-
283 A-S-H samples in NaOH solution. The estimated equilibrium constant for the dissociation of
284 surface sites as a function of Ca/Si is shown in **Fig. 7** and presented in **Table 3.** The determined
285 pK_{OH} for weak and strong sites were 6.6 and 13.0, respectively, irrespective of Ca/Si or aluminium
286 incorporation into the C-S-H. The results indicated that the surface of C-S-H/C-A-S-H was affected
287 by the presence and ionisation of weak sites in NaOH solution, and not by the strong sites. The
288 estimated equilibrium constants are comparable to the results reported in the literature; Pointeau et
289 al. reported 7.6 for both strong and weak $\equiv SiOH$ sites [34], Hass and Nonat reported 7.7 for $\equiv SiOH$
290 [30], Elakneswaran et al reported 12.7 for $\equiv SiOH$ [8], Viallis-Terrisse et al. reported 12.3 [31] and
291 Pointeau et al. reported 12.0 for $\equiv SiOH$ sites [13].

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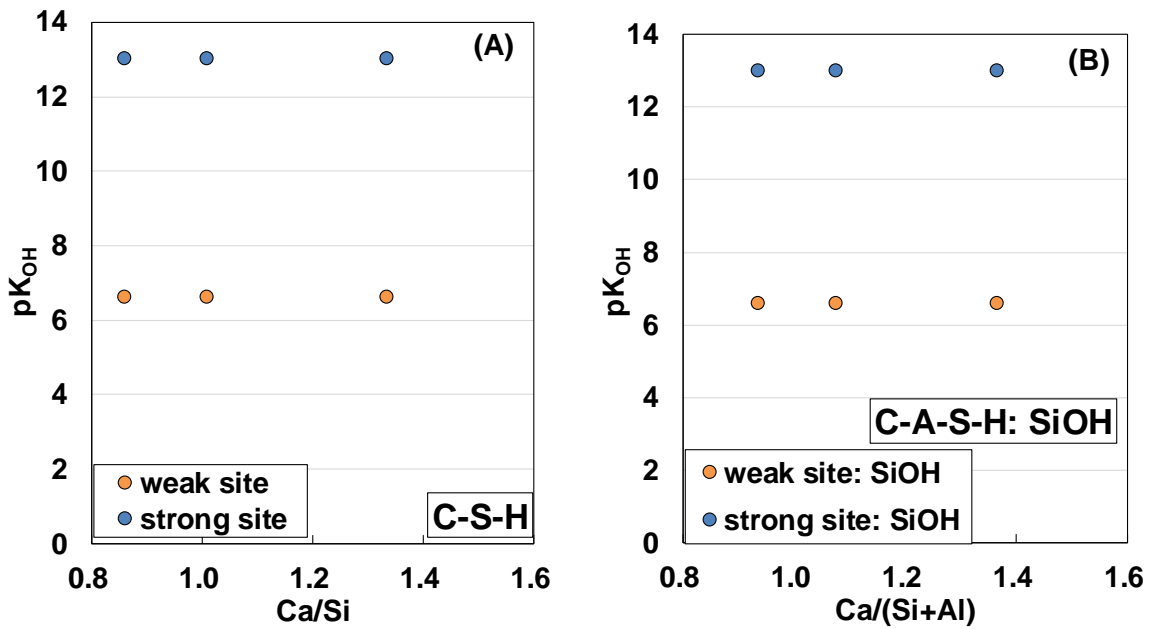


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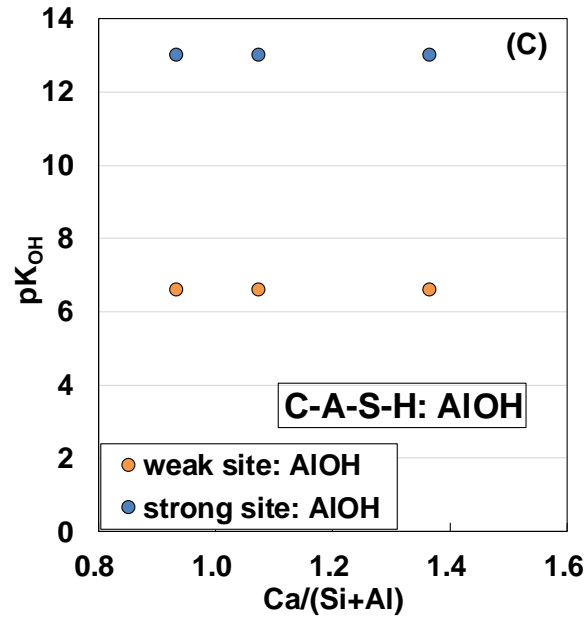
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Fig. 6. Fitting of titration experimental data with modelling results for CSH:1.5

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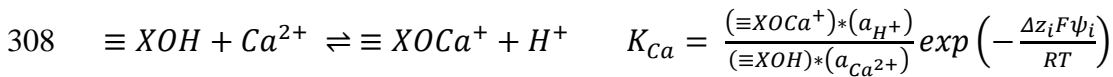
297

298 **Fig. 7.** Determined dissociation equilibrium constant for strong and weak sites: (A) $\equiv\text{SiOH}$ sites in
 299 C-S-H; (B) $\equiv\text{SiOH}$ sites in C-A-S-H; (C) $\equiv\text{AlOH}$ sites in C-A-S-H.

300

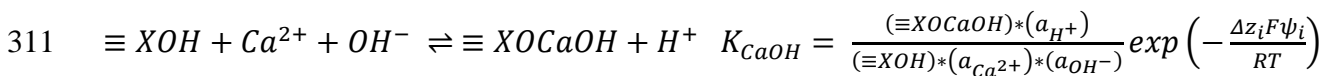
301 To understand the interaction of Ca^{2+} on the surface of C-S-H/C-A-S-H, zeta potential experiments
 302 were conducted, and the results were fitted to surface complexation modelling results to develop a
 303 model for Ca^{2+} adsorption. The model considers the presence of CaOH^+ ions in the pH solution and
 304 its adsorption on C-S-H/C-A-S-H. The adsorption of Ca^{2+} and CaOH^+ on strong and weak $\equiv\text{SiOH}$
 305 and $\equiv\text{AlOH}$ surface sites was considered as the following inner-sphere surface complexation
 306 reaction:

307



309 (5)

310



312 (6)

313 X: Si or Al

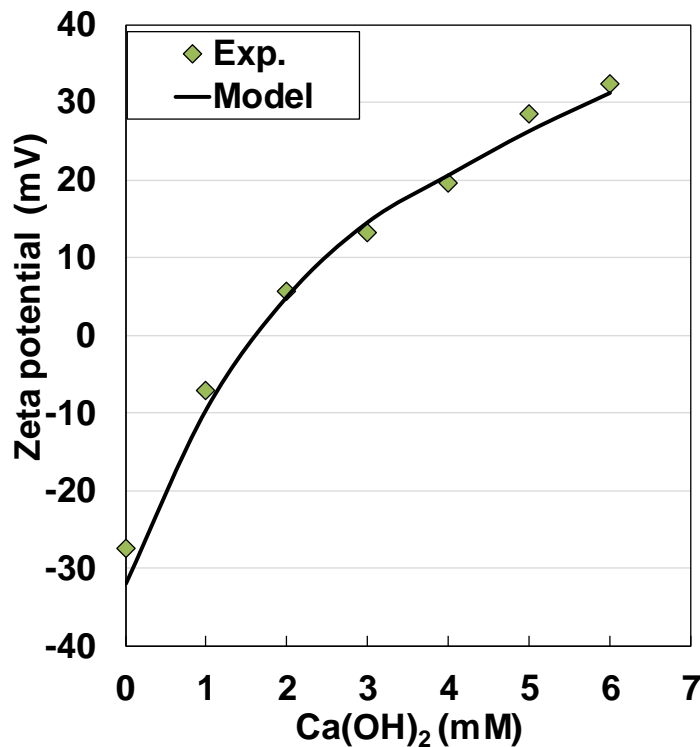
314

315 where K_{Ca} , and K_{CaOH} are the intrinsic equilibrium constants for calcium adsorption, ($\equiv XOCa^+$) and
316 ($\equiv XCaOH$) are the concentrations of the surface species of surface sites (mol/m^2), and $a_{Ca^{2+}}$ is the
317 activity of Ca^{2+} (mol/L).

318

319 The experimental data for the C-S-H/C-A-S-H in $Ca(OH)_2$ solution were fitted to the modelling
320 results to estimate K_{Ca} , and K_{CaOH} . An example of such fitting is shown in **Fig. 8**. Furthermore, the
321 change in the determined equilibrium constant with Ca/Si is shown in **Fig. 9** and presented in **Table**
322 **3**. As observed for the dissociation of sites in the NaOH solution (**Fig. 7**), the weak sites
323 significantly influence the adsorption of calcium ions. Moreover, the equilibrium constant of
324 $\equiv AlOH$ is nearly equal to that of $\equiv SiOH$.

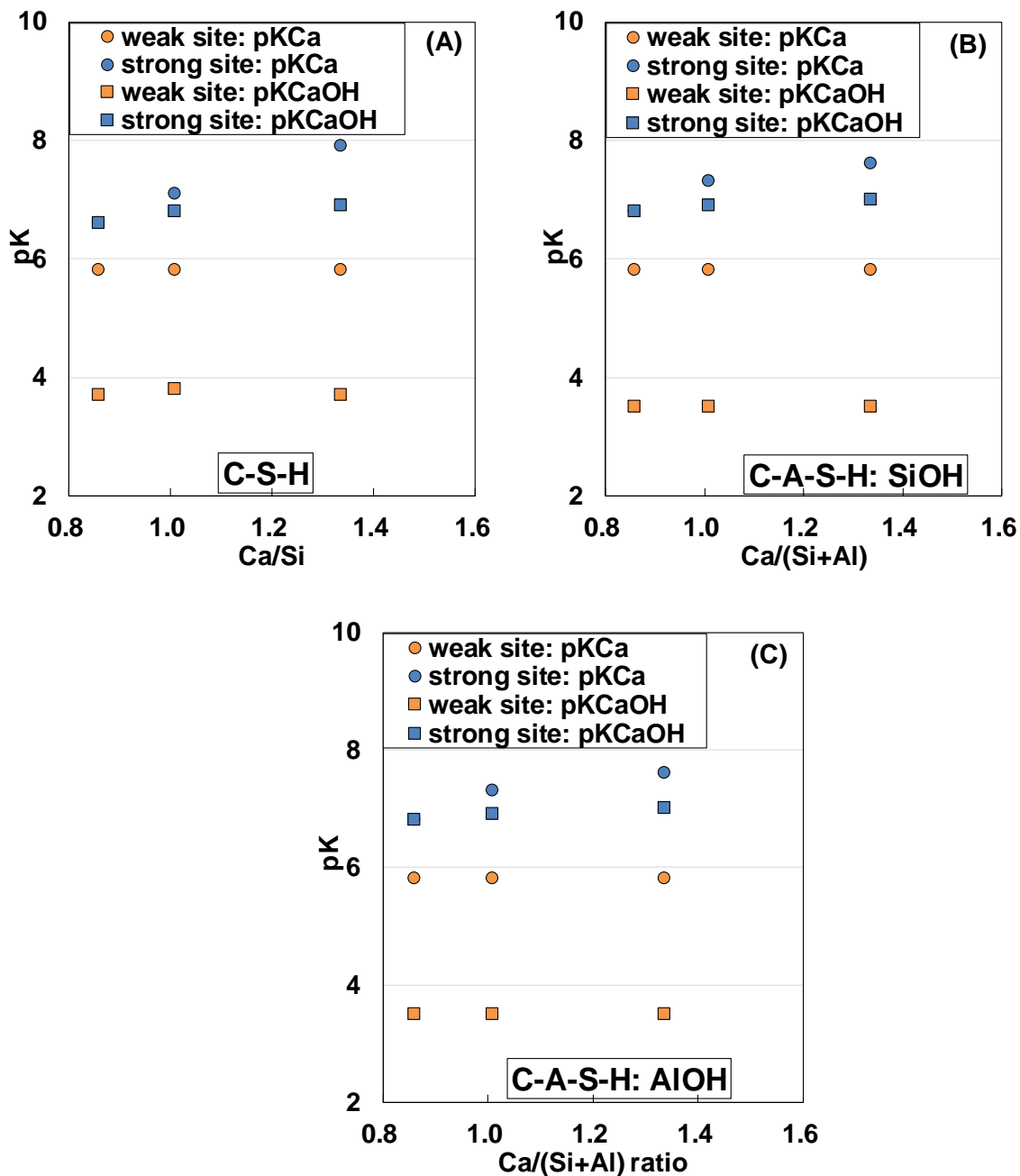
325



326

327 **Fig. 8.** Fitting of zeta potential experimental data with modelling results for CSH:1.5

328



329

330

331 **Fig. 9.** Determined equilibrium constant of calcium absorption for strong and weak, (A) $\equiv\text{SiOH}$
 332 sites in C-S-H; (B) $\equiv\text{SiOH}$ sites in C-A-S-H; (C) $\equiv\text{AlOH}$ sites in C-A-S-H. Note: pKCa and
 333 pKCaOH for strong site of CSH-0.8 and CASH-0.8 are identical values and overlap in the figure.

334

335 It has been reported that the associated divalent cation shows higher chloride binding compared
 336 with monovalent ions [14]. The positive surface of C-S-H/C-A-S-H strong and weak sites in the
 337 presence of calcium can adsorb chloride ions via the following surface complexation reaction:

338

339 $\equiv XOH + Ca^{2+} + Cl^{-} \rightleftharpoons \equiv XOCaCl + H^{+}$ $K_{CaCl} = \frac{(\equiv XOCaCl) \cdot (a_{H^{+}})}{(\equiv XOH) \cdot (a_{Ca^{2+}}) \cdot (a_{Cl^{-}})} \exp\left(-\frac{\Delta z_i F \psi_i}{RT}\right)$
 340 (7)

341 *X: Si or Al*

342

343 where K_{CaCl} is the intrinsic equilibrium constant for chloride adsorption, $(\equiv XOCaCl)$ is the
 344 concentration of the surface species of surface sites (mol/m²), and $a_{Cl^{-}}$ is the activity of Cl⁻ (mol/L).

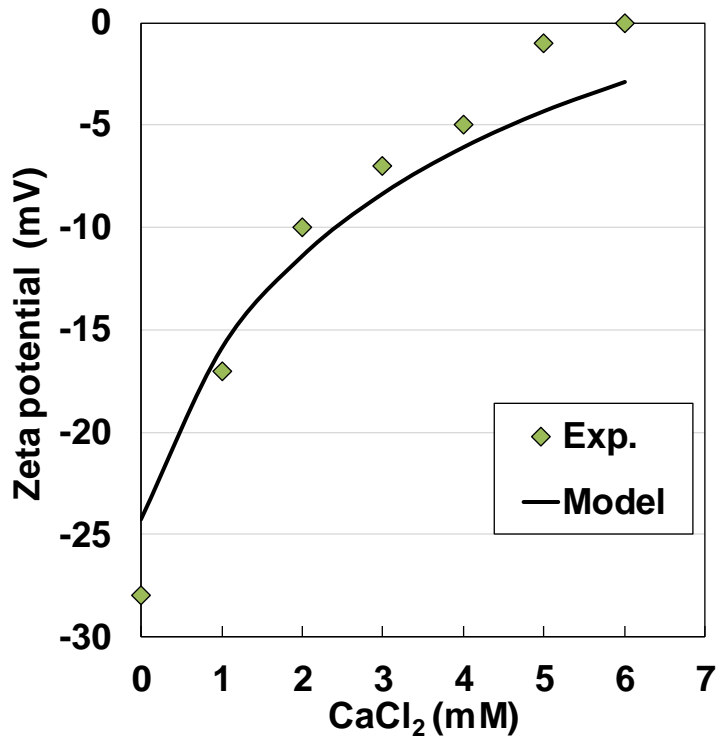
345

346 A similar approach was adopted for calcium used in here to estimate the equilibrium constant for
 347 chloride adsorption in the presence of calcium. The zeta potential results of C-S-H/C-A-S-H in
 348 CaCl₂ solution were fitted to the modelling results (an example is shown in **Fig. 10**). The estimated
 349 equilibrium constants for both C-S-H and C-A-S-H, as a function of Ca/Si, are shown in **Fig. 11**
 350 and presented in **Table 3**. Again, the weak sites control the chloride adsorption on C-S-H/C-A-S-H.
 351 Moreover, the equilibrium constant of the $\equiv AlOH$ group is smaller than that of $\equiv SiOH$, indicating a
 352 higher chloride interaction towards $\equiv AlOH$ than that in $\equiv SiOH$ sites.

353

354 A summary of the determined surface site densities of C-S-H and C-A-S-H and their equilibrium
 355 constants is presented in **Table 3**. The fitted equilibrium constants for calcium and chloride
 356 adsorption on weak sites are constant regardless of the site density or Ca/Si. However, the
 357 equilibrium constant for strong sites increases with the site density or Ca/Si, which would affect the
 358 quantity of adsorbed ions.

359

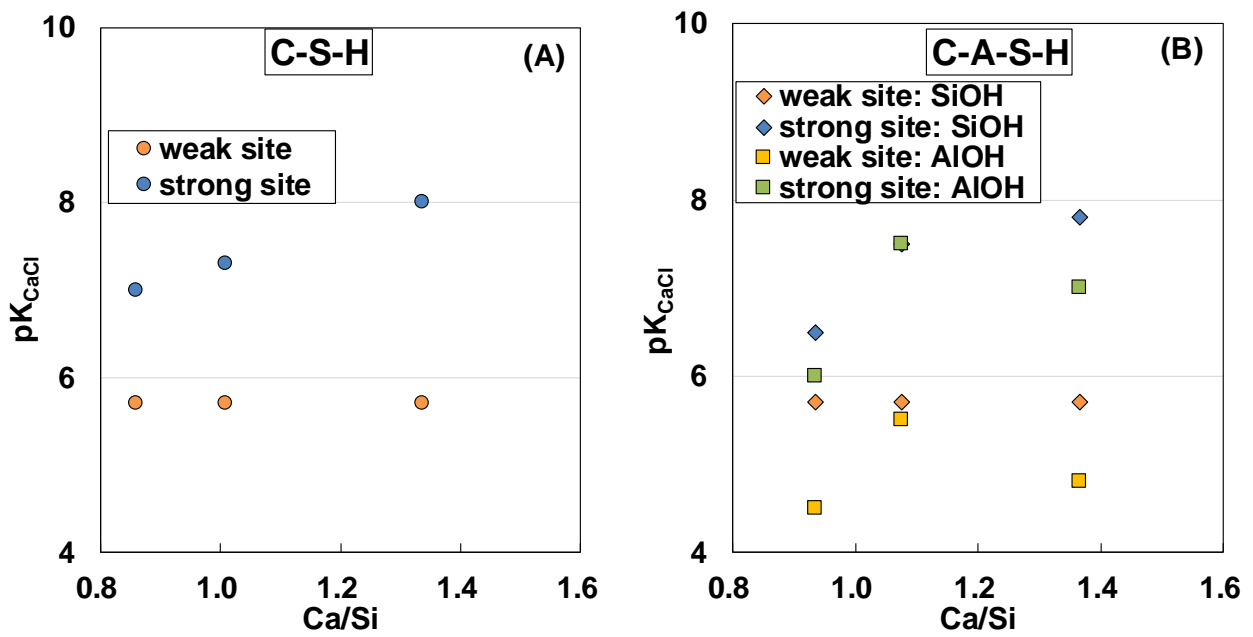


360

361

Fig. 10. Fitting of zeta potential experimental data with modelling results for CSH:1.5

362



363

364

Fig. 11. Determined equilibrium constant of chloride adsorption for strong and weak, (A) $\equiv\text{SiOH}$

365

sites in C-S-H; (B) $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ sites in C-A-S-H.

366

367

Table 3: Estimated surface complexation modelling parameters for C-S-H/C-A-S-H

| | | | Site density (sites/nm ²) | pK _{OH} | pK _{Ca} | pK _{CaOH} | pK _{CaCl} |
|-----------------|-------------|-------------|--|------------------|------------------|--------------------|--------------------|
| CSH-0.8 | SiOH | weak site | 1.54 | 6.6 | 5.8 | 3.7 | 5.7 |
| | | strong site | 2.76 | 13.0 | 6.6 | 6.6 | 7.0 |
| CSH-1.0 | SiOH | weak site | 1.44 | 6.6 | 5.8 | 3.8 | 5.7 |
| | | strong site | 4.12 | 13.0 | 7.1 | 6.8 | 7.3 |
| CSH-1.5 | SiOH | weak site | 1.13 | 6.6 | 5.8 | 3.7 | 5.7 |
| | | strong site | 5.14 | 13.0 | 7.9 | 6.9 | 8.0 |
| CASH-0.8 | SiOH | weak site | 1.22 | 6.6 | 5.8 | 3.5 | 5.7 |
| | | strong site | 2.02 | 13.0 | 6.8 | 6.8 | 6.5 |
| | AIOH | weak site | 0.15 | 6.6 | 5.8 | 3.5 | 4.5 |
| | | strong site | 0.15 | 13.0 | 6.8 | 6.8 | 6.0 |
| CASH-1.0 | SiOH | weak site | 1.07 | 6.6 | 5.8 | 3.5 | 5.7 |
| | | strong site | 2.89 | 13.0 | 7.3 | 6.9 | 7.5 |
| | AIOH | weak site | 0.22 | 6.6 | 5.8 | 3.5 | 5.5 |
| | | strong site | 0.22 | 13.0 | 7.3 | 6.9 | 7.5 |
| CASH-1.5 | SiOH | weak site | 1.06 | 6.6 | 5.8 | 3.5 | 5.7 |
| | | strong site | 3.73 | 13.0 | 7.6 | 7.0 | 7.8 |
| | AIOH | weak site | 0.16 | 6.6 | 5.8 | 3.5 | 4.8 |
| | | strong site | 0.22 | 13.0 | 7.6 | 7.0 | 7.0 |

369

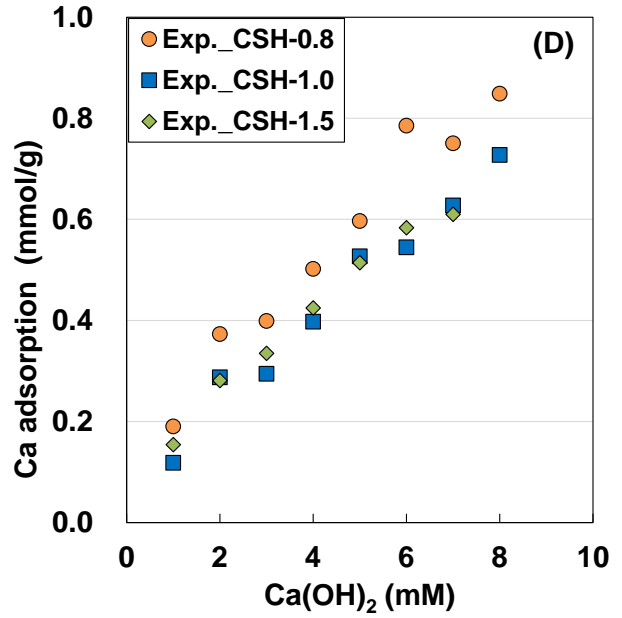
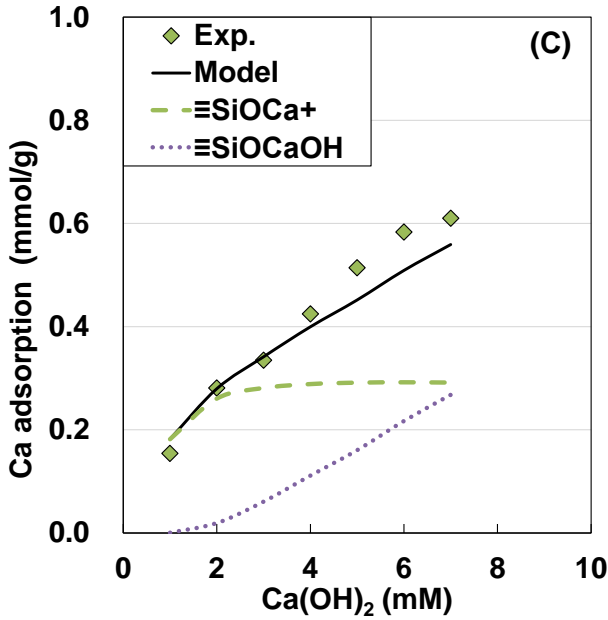
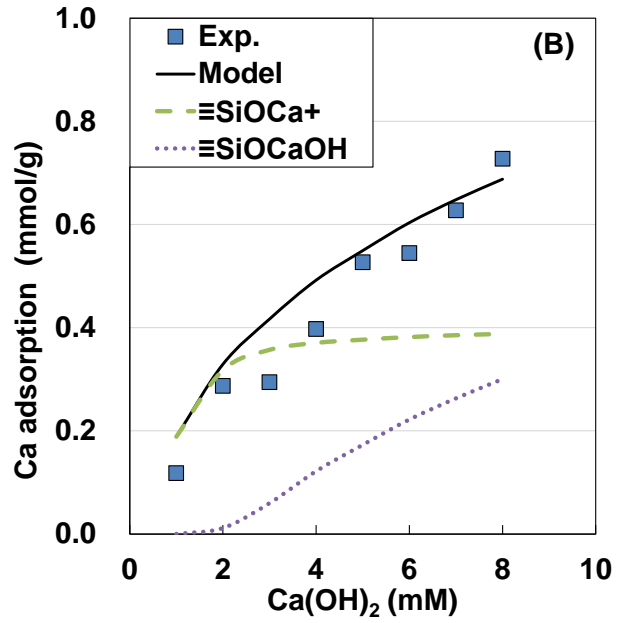
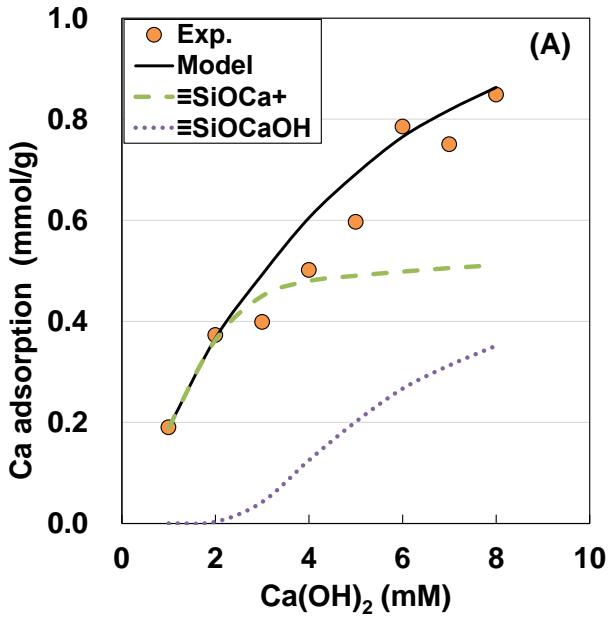
370 3.3 Prediction of calcium and chloride adsorption on C-A-S-H

371 The estimated surface complexation modelling parameters (**Table 3**) were used to predict the
372 adsorption of calcium and chloride. The predicted calcium adsorption on C-S-H and C-A-S-H was
373 compared with experimental data for different Ca/Si ratios in **Figs. 12** and **13**, respectively. The

374 model successfully predicted calcium adsorption as a function of calcium concentration. As can be
375 seen from the model prediction, both Ca^{2+} and CaOH^+ adsorb on the surface sites, but the
376 adsorption of CaOH^+ contributes at a high concentration of calcium. Therefore, both surface
377 complexation reactions (Eqs. (5) and (6)) are necessary to understand calcium adsorption on C-S-H
378 and C-A-S-H. The Ca/Si or Ca/(Si+Al) ratios significantly affect calcium adsorption; the adsorption
379 decreases with an increase in the ratio (**Fig. 12 (D)** and **Fig. 13 (D)**). This is due to the equilibrium
380 pH and calcium concentration, which rise as the Ca/Si or Ca/(Si+Al) ratio increases [37]. Both
381 experimental and modelling results indicate that aluminium incorporation in C-A-S-H does not
382 influence the total calcium adsorption. The substitution of silica by aluminium decreases the total
383 surface sites in C-A-S-H (**Fig. 5**), but a fraction of available silica sites changes to $\equiv\text{AlOH}$ sites.
384 Therefore, both $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ sites contribute to calcium adsorption in C-A-S-H and show an
385 equal amount of adsorption as in C-S-H.

386

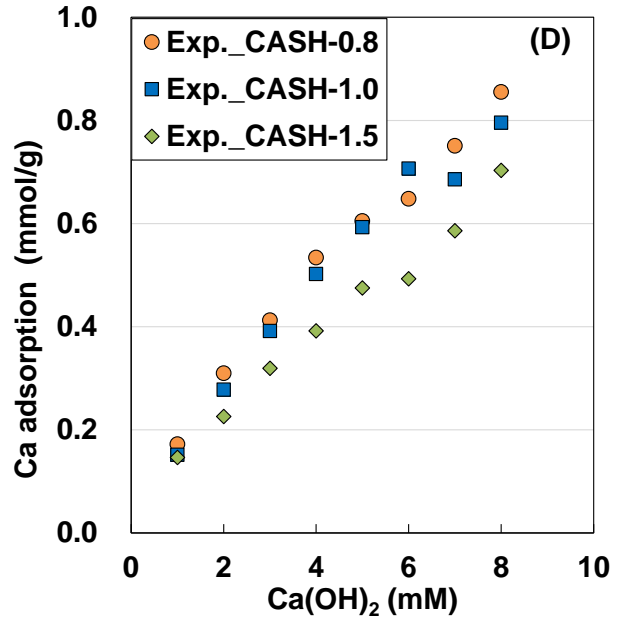
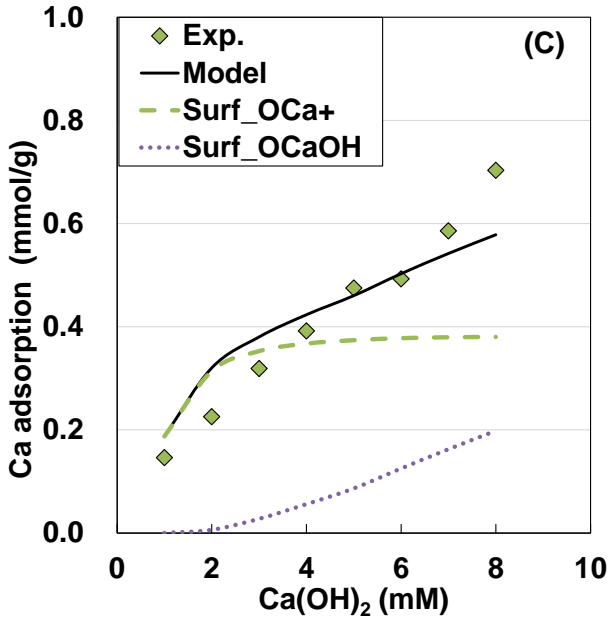
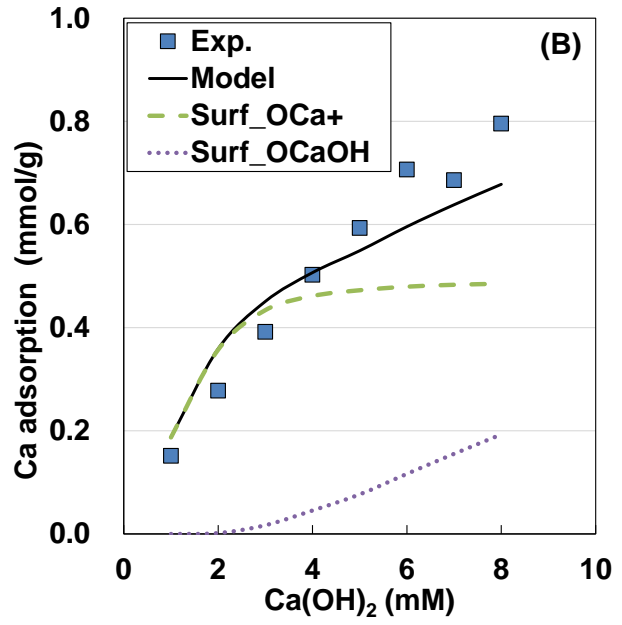
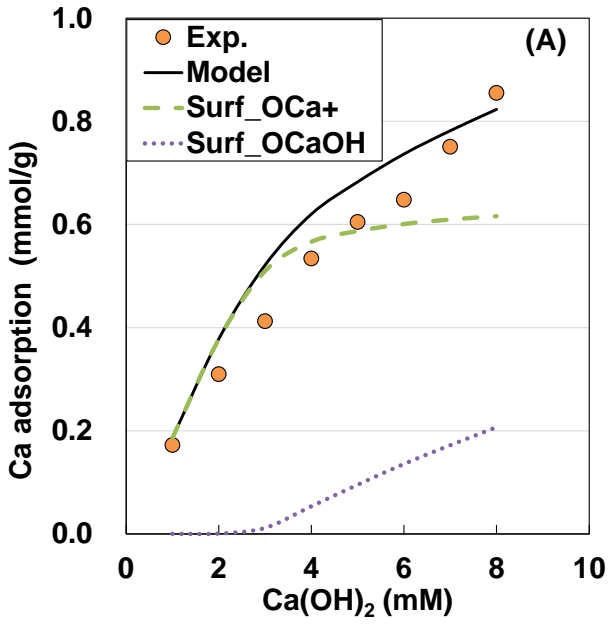
387 The surface complexation reactions given in Eqs. (3), (5), (6) and (7) were used to predict chloride
388 adsorption on C-S-H and C-A-S-H in CaCl_2 solution. A high concentration of CaCl_2 solution was
389 selected to enhance chloride adsorption on C-S-H and C-A-S-H, as reported in ref. [12] where 20–
390 70% of chloride adsorption was observed when cement paste was exposed to CaCl_2 solutions. Both
391 the strong and weak of the $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ sites compete for chloride adsorption via the surface
392 complexation reaction given in Eq. (7). However, the surface site density and equilibrium constants
393 presented in **Table 3** control the amount of adsorption. A comparison between the predicted and
394 measured chloride adsorption on C-S-H and C-A-S-H is shown in **Figs. 14** and **15**, respectively. A
395 very good agreement between the predicted results and experimental data indicates the validity of
396 the model and estimated parameters. Both experimental data and modelling results show that
397 aluminium incorporation in C-S-H reduces chloride adsorption irrespective of the Ca/Si ratio.



398

399

400 **Fig. 12.** Comparison of the predicted and measured calcium adsorption on C-S-H with (A) Ca/Si of
 401 0.8; (B) Ca/Si of 1.0; (C) Ca/Si of 1.5. (D) Comparison of the measured calcium adsorption on C-S-
 402 H with different Ca/Si ratios.



403

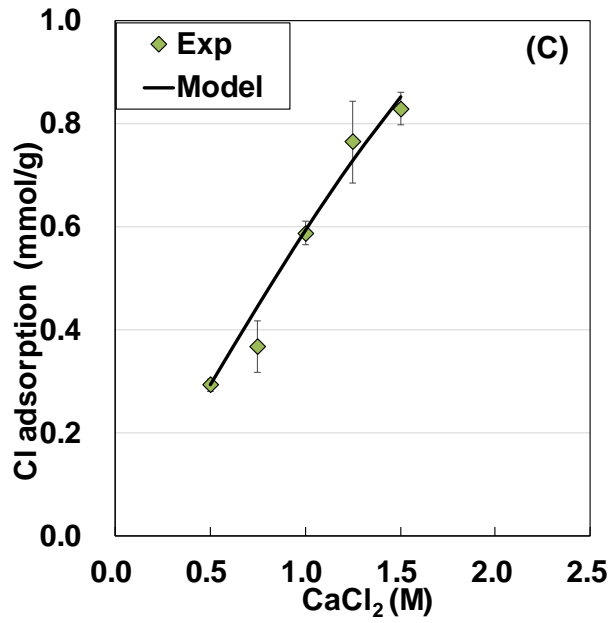
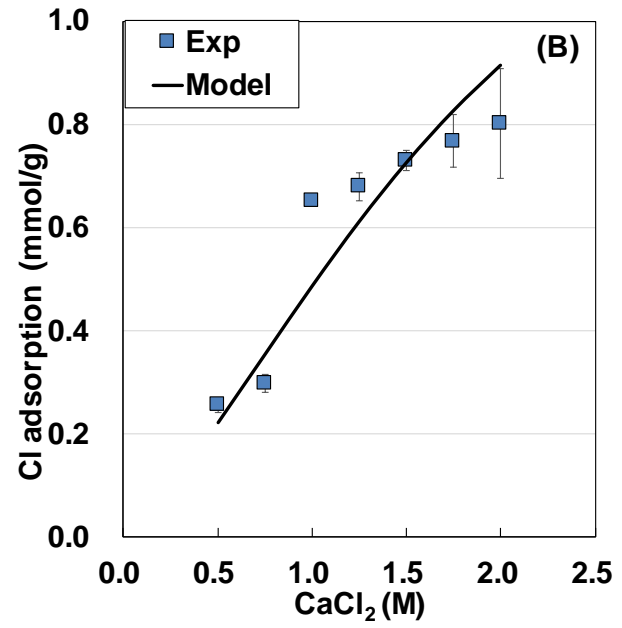
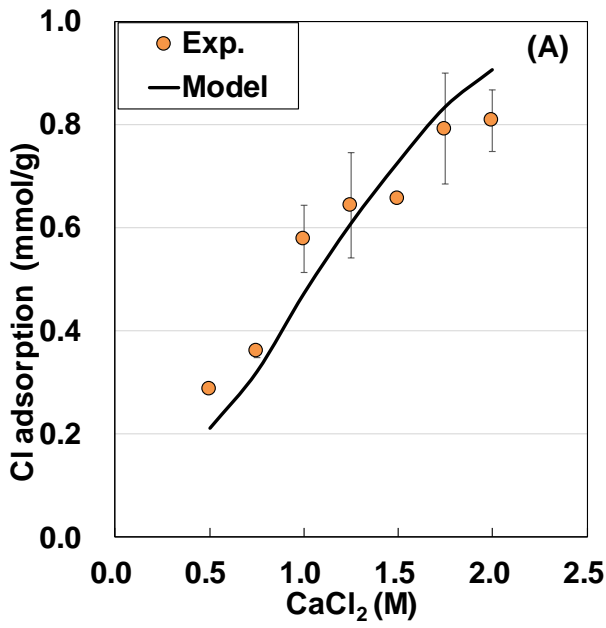
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Fig. 13. Comparison of the predicted and measured calcium adsorption on C-A-S-H with (A) Ca/(Si+Al) of 0.8; (B) Ca/(Si+Al) of 1.0; (C) Ca/(Si+Al) of 1.5. (D) Comparison of the measured calcium adsorption on C-A-S-H with different Ca/(Si+Al) ratios.



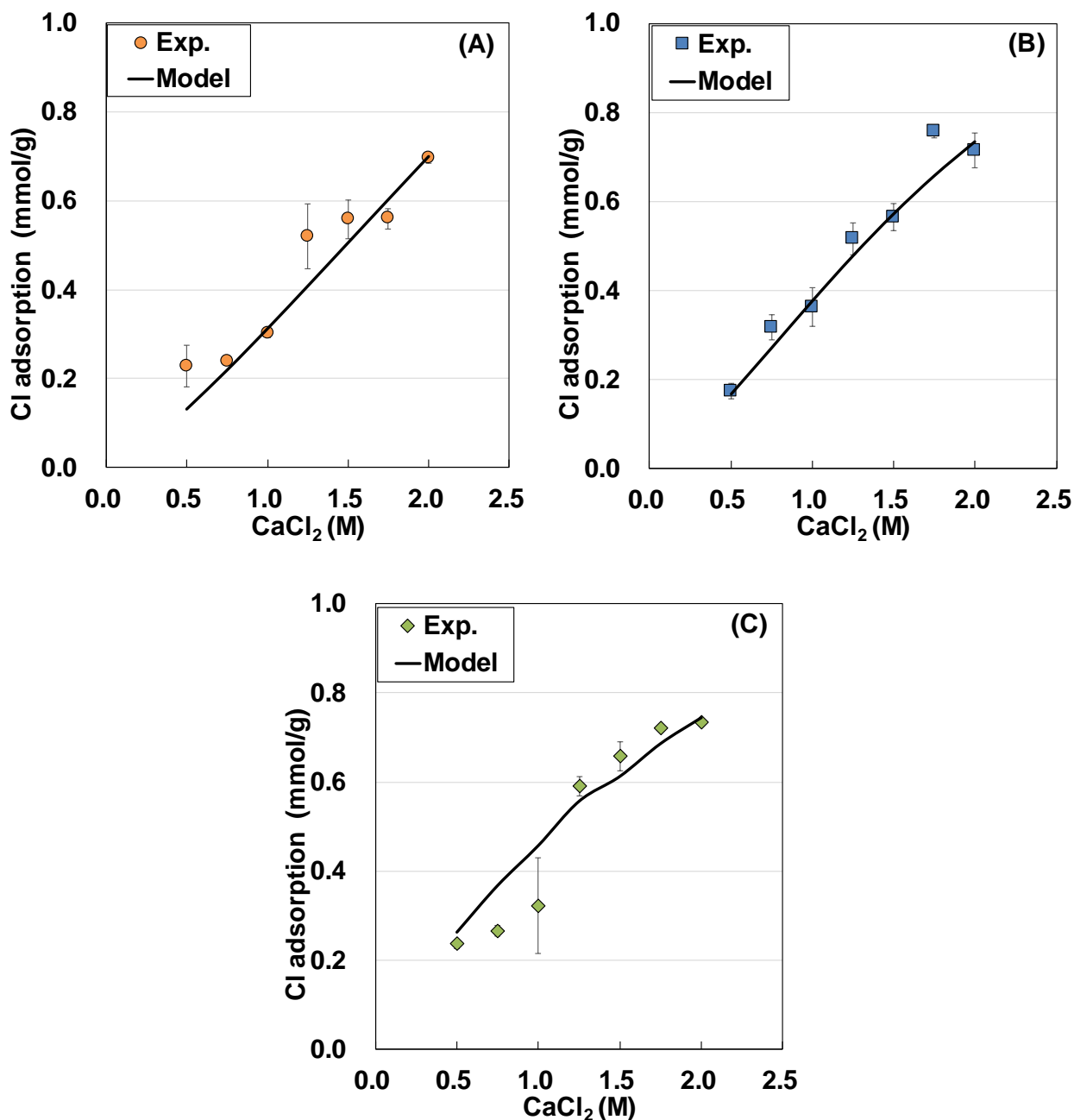
408

409

410 **Fig. 14.** Comparison of the predicted and measured chloride adsorption on C-S-H with (A) Ca/Si of
 411 0.8; (B) Ca/Si of 1.0; (C) Ca/Si of 1.5.

412

413



414

415

416 **Fig. 15.** Comparison of the predicted and measured chloride adsorption on C-A-S-H with (A)
 417 Ca/(Si+Al) of 0.8; (B) Ca/(Si+Al) of 1.0; (C) Ca/(Si+Al) of 1.5.

418

419 4. Conclusions

420 The electrostatic interaction of calcium and chloride ions on C-S-H and C-A-S-H was evaluated by
 421 experiments and a triple-layer surface complexation model. C-S-H and C-A-S-H were characterised
 422 to determine the surface functional groups and their densities: C-S-H possesses strong and weak
 423 $\equiv\text{SiOH}$ sites, whereas C-A-S-H has strong and weak $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ sites. The chemical

424 composition of C-S-H/C-A-S-H affects the site density, which increases with the Ca/(Si+Al) ratio,
425 but aluminium substitution decreases the site density at each Ca/(Si+Al) ratio. The CD-MUSIC
426 triple-layer model built-in PHREEQC was used to understand the interaction of pH, calcium, and
427 chloride ions with C-S-H and C-A-S-H. The equilibrium constants for the dissociation and
428 adsorption of calcium and chloride were derived by fitting the experimental data to the modelling
429 results. Moreover, the effect of the Ca/(Si+Al) ratio and aluminium incorporation on the
430 equilibrium constant were evaluated. It was found that weak sites have high affinity for hydroxyl,
431 calcium, and chloride ions. The validity of the determined site density and equilibrium constant
432 values were tested against the batch adsorption experimental data. The modelling results agree well
433 with the experimental data for both C-S-H and C-A-S-H, as a function of calcium or chloride
434 concentration. Aluminium incorporation in C-S-H did not influence the calcium adsorption, but it
435 reduced chloride adsorption in each Ca/Si ratio.

436

437 **Acknowledgments**

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439 Grants-in-Aid for Scientific Research (KAKENHI) Grant No. 18K0429708.

440

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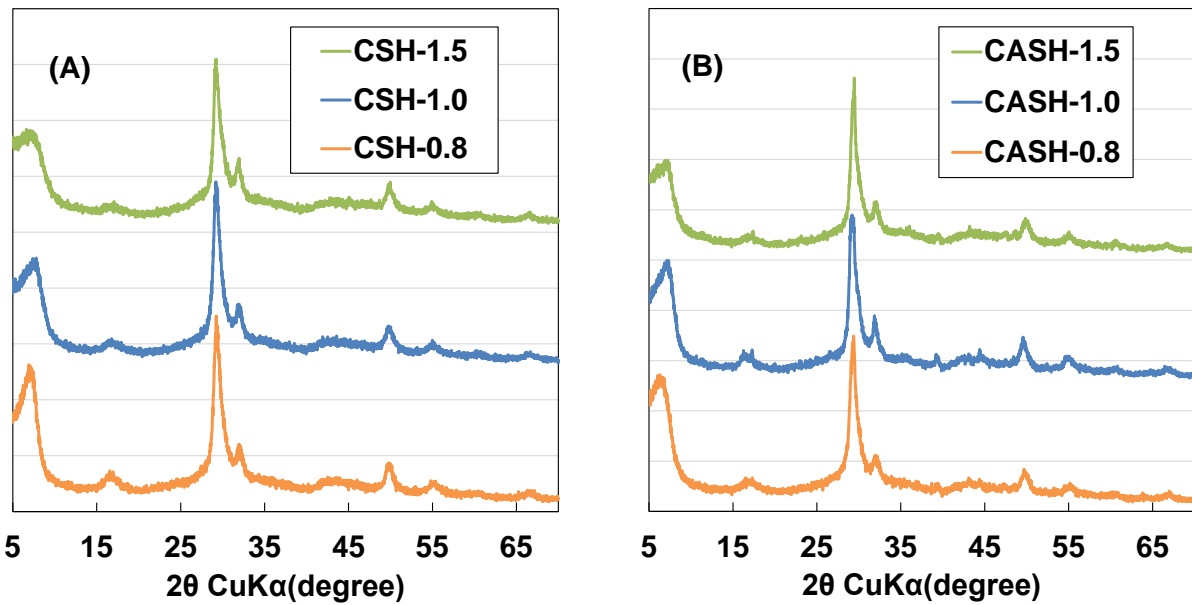
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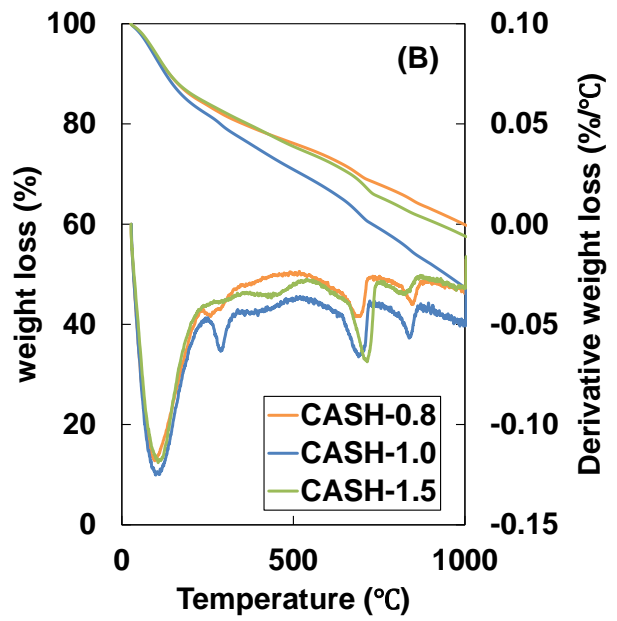
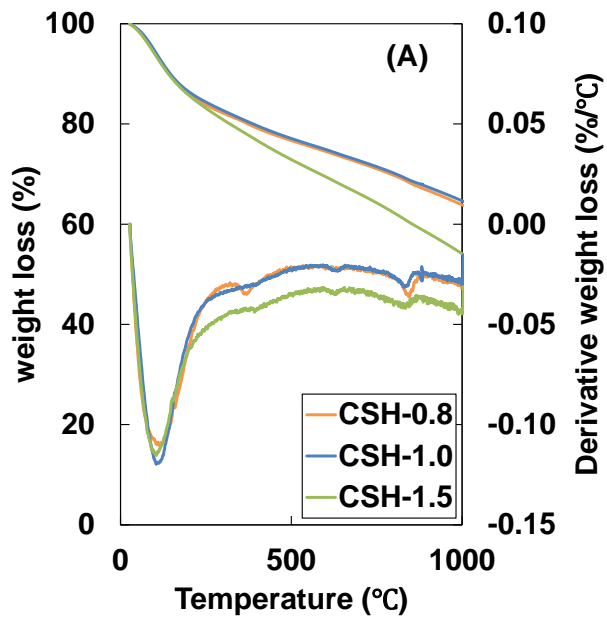
534 Appendix A



535

536 **Fig. A1.** XRD pattern of (A) C-S-H and (B) C-A-S-H

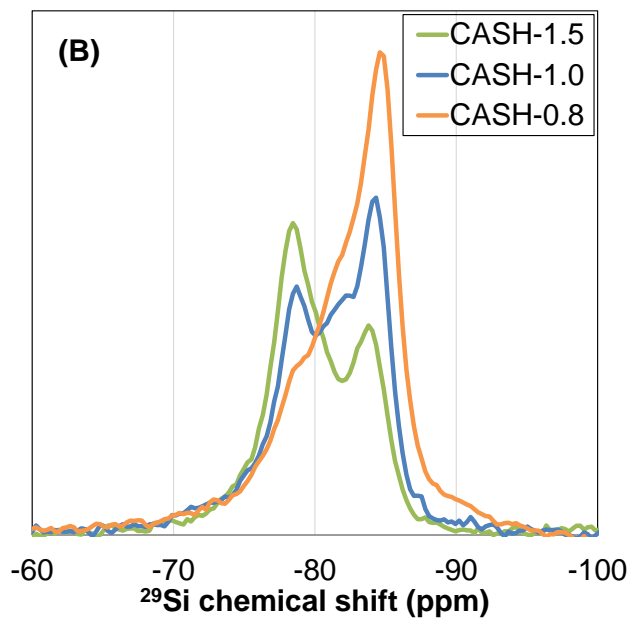
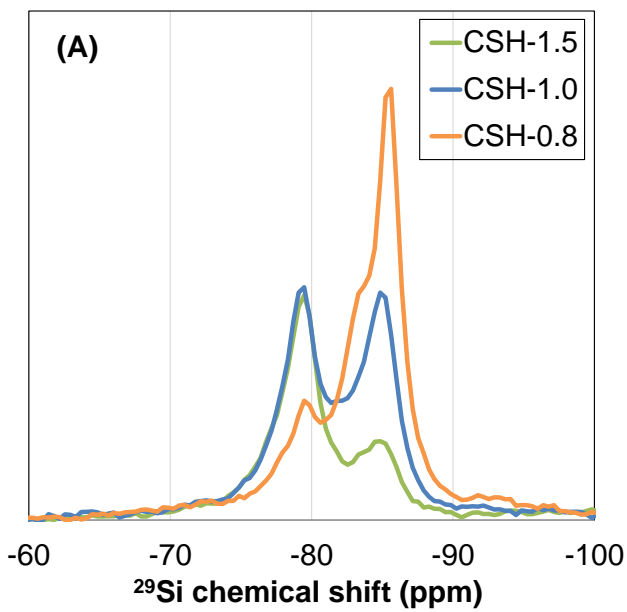
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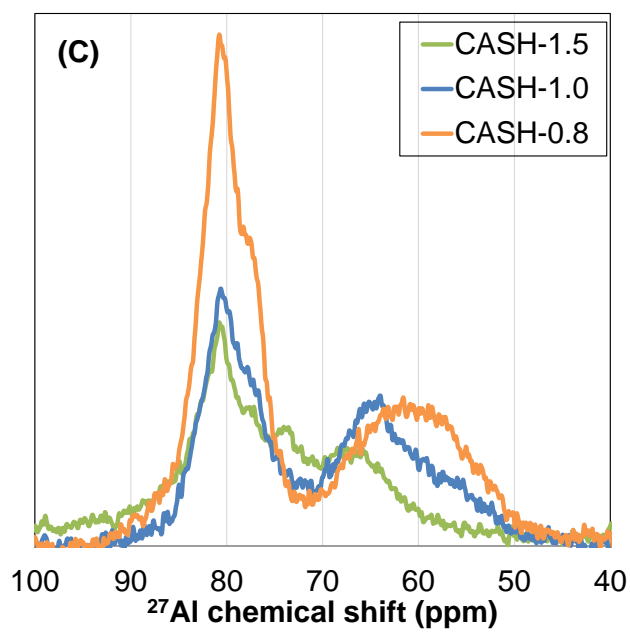
538

539 **Fig. A2.** TGA of (A) C-S-H and (B) C-A-S-H

540



541



542

543 **Fig. A3.** (A) ²⁹Si NMR of C-S-H; (B) ²⁹Si NMR of C-A-S-H; and (C) ²⁷Al NMR of C-A-S-H

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: