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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

properties on calcium and chloride adsorption. The density of the surface functional groups was determined by analysing the structure of C-S-H and C-A-S-H through ²⁷Al and ²⁹Si MAS NMR. 22

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The surface sites of \equiv SiOH and \equiv AlOH are available in C-A-S-H whereas C-S-H has \equiv SiOH groups 23

24 for ionic adsorption. We found that the incorporation of aluminium decreases the number of total

26 understand the C-A-S-H/solution interface, a triple-layer surface complexation model was

adsorption sites in C-A-S-H. Furthermore, the site density increased with Ca/(Si+Al). To

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

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

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36 **1. Introduction**

37 The characteristics of the cement paste matrix and concrete—such as porosity, tortuosity, the composition of cement hydrates, and the properties of calcium silicate hydrate (C-S-H), which is the 38 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 (Ca₄Al₂(SO₄)(OH)₁₂·6H₂O) and forms Friedel's salt 42 (Ca₄Al₂Cl₂(OH)₁₂·4H₂O). 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 chloride in the pore solution [5-8]. It has been reported that a partial replacement of ordinary 46 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].

53 Numerous experimental and modelling studies have reported the interaction of chloride with cement hydrates [2-8, 10-16]. It is widely accepted that the formation of Friedel's salt occurs through the 54 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 that the H₂O-SiO₂ and CaO-SiO₂ ratios of C-S-H significantly affect the chloride adsorption on its 58 59 surface [5]. De Weerdt'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]. Elakneswaran et al. highlighted that the chloride adsorption on C-S-H occurs via calcium-adsorbed 65 66 surface sites and proposed a double layer surface complexation model to predict chloride adsorption in hydrated OPC [8, 10]. In addition, the model is coupled with a reactive transport equation to 67 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.

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Alumina-rich SCMs increase the incorporation of aluminium in C-S-H and form calcium aluminosilicate hydrate (C-A-S-H) phase [17-21]. The surface chemistry of C-A-S-H is significantly different from that of conventional C-S-H and thus has an impact on the ionic adsorption behaviour. Only a few studies have been conducted on the ionic adsorption on the C-A-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 (\equiv SiOH). At high pH, the \equiv SiOH group deprotonates to \equiv SiO⁻ and calcium can compensate for the 80 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 ≡AlOH surface functional 83 groups in C-A-S-H, in addition to \equiv 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

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

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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 Ca(OH)₂ (special grade 98 reagent manufactured by Kanto Chemical Co.) and SiO₂ (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, Ca(OH)₂, SiO₂, and CaAl₂O₄ were 102 mixed for the target of Ca/(Si+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 N₂ 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.

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

	T (T (T '4' 1	T '4' 1	τ.'.' 1
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

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111 **2.2 Experimental procedure**

C-S-H and C-A-S-H were characterised by a Rigaku X-ray generator with CuKa radiation, and the 112 measurement conditions were tube voltage 40 kV, scanning range of 5 to 70 ° (20), sampling width 113 of 0.02 ° (20), and scan speed of 6.5 ° / min. A fluorescent X-ray analyser element monitor 114 EA1200VX manufactured by Hitachi High-Tech Science was used to determine the solid 115 116 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 specific surface areas of C-S-H and C-A-S-H were measured using the Brunauer-Emmett-Teller 120 121 (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

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 124 titrating the solution with 0.25 mol/L NaOH. The suspension was equilibrated for one day and was 125 stirred for three minutes using an ultrasonic cleaner before titration. The ²⁹Si MAS NMR 126 127 experiment was conducted on MSL 400 9.4 T BRUKER at 79.48 MHz. The Q₈M₈ (Si (CH₃)₈Si₈O₂) 128 manufactured by Wako Pure Chemical Industries was used as a reference material for the measurement. The measurement conditions for each sample were 90 $^{\circ}$ pulse length of 5 μ s for ²⁹Si 129 recycling delay of 45 s and 2000 scans and 4 kHz of the number of rotations. The Win-nut program 130 was used for the analysis of ²⁹Si MAS NMR data. A JEOL ECA-700 was used to obtain ²⁷Al 131 spectra, where AlCl₃ • 6H₂O was used as a reference material. The measurement conditions for the 132 27 Al spectra were 90 ° pulse length of 2.09 µs, delay time of 30 s, 2880 scans, and 18 kHz of 133 spinning rates with 3.2 mm MAS probe. The number of scans for CASH-1.5 was set to 5760 times, 134 135 as it was considered to have a small amount of Al uptake. All spectra were deconvoluted using the 136 Delta program.

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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 measurement using a Zetasizer Nano series. The equilibrium time for the suspension in Ca(OH)₂ 139 140 solution was one day, whereas two days were adopted for the CaCl₂ solution. The ionic strength of the solution was adjusted by NaNO₃ and kept constant at 20 mmol/L. The suspension was stirred 141 142 for 3 min using an ultrasonic cleaner before measurement at 25 °C. The average of five measurements was used as the zeta potential value. A batch experiment was performed with 143 144 Ca(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 Ca(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 µm 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

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

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158 **2.3 Modelling approach**

159 The geochemical code PHREEOC was used for the speciation, thermodynamic equilibrium, and surface complexation modelling calculations [25-26]. The charge-distribution-multi site 160 complexation model (CD-MUSIC) available in PHREEQC was adopted for the surface 161 162 complexation reaction between C-S-H/C-A-S-H and ionic species [27-28], as illustrated in Fig. 1. The surface has three planes: the 0-, 1-, and 2-planes. The surface groups of C-S-H/C-A-S-H are 163 located at the 0-plane, and the diffuse layer begins at the 2-plane. The potential at the 0-plane is the 164 surface potential, and the zeta potential can be directly compared with the potential at the 2-plane. 165 The CD-MUSIC model requires the capacitance of the layers and change in charge at three layers 166 167 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].



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Fig. 1. Schematic of the electrical triple-layer used in the CD-MUSIC model.

175 **3. Results and discussion**

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

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

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.

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

Sample ID	Target	Measured	Target	Measured
	Ca/(Si+Al)	Ca/(Si+Al)	Al/Si	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

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

208





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

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

Information about the number of layers was used to estimate the surface site density of C-S-H and 215 216 C-A-S-H. It was assumed that the structure of C-S-H and C-A-S-H is close to tobermorite-type crystal structure [19], and the C-S-H has surface functional group of ≡SiOH, whereas C-A-S-H 217 218 possesses both ≡SiOH and ≡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 silica and aluminium. The area occupied by the dimer is 41.123Å² and is constant regardless of the 220 221 Ca/(Si+Al) ratio [30-31]. Nonat proposed that the layered structure of C-S-H was a $60 \times 30 \times 5$ nm elliptical cylinder [32]. Based on the above information and the results shown in Fig. 4, the density 222 of surface sites presents in Q^1 and Q^2b can be calculated using the equations given below: 223

224

225
$$N_{s-Q^1} = \frac{S_{ellipse}}{S_{unit}} \times \frac{MCL}{2} \times \frac{1}{2} \times \frac{Q^1}{MCL} \times \frac{1}{S_{ellipse}} \times 2N_{lamella}$$

226 (1)

227
$$N_{s-Q_b^2} = \frac{S_{ellipse}}{S_{unit}} \times \frac{MCL}{2} \times \frac{1}{2} \times \frac{2 \times Q_b^2}{MCL} \times \frac{1}{S_{ellipse}} \times 2N_{lamella}$$

228 (2)

229

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





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



243 The total sites determined in section 3.1 were divided further into strong and weak sites, where the weak sites were easy to dissociate, while the strong sites were difficult to dissociate. Charukov et al. 244 performed a simulation based on the different degrees of dissociation in Q¹ and Q²b, each of which 245 exists at a ratio of 1:1 [33]. A similar approach was adopted in this study to estimate the density of 246 weak and strong sites. In the silicate chain, Q²b exists only on the flat surface and is distributed to 247 sites with different dissociation ratios of 1:1. However, Q^1 exists on both flat surface and edge, and 248 the surface area ratio between the end surface and the layer surface can be calculated based on the 249 layered structure proposed by Haas et al. [30]. The Q^1 sites on the flat surface can form a hydrogen 250 bond and are considered to be strong sites, whereas the sites at the edge surface are less affected by 251 252 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 ≡SiOH and ≡AlOH surface sites are dissociated in the alkaline solution as
256 follows:

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258
$$\equiv XOH \rightleftharpoons \equiv XO^- + H^+$$
 $K_{OH} = \frac{(\equiv XO^-)*(a_{H^+})}{(\equiv XOH)}exp\left(-\frac{\Delta z_iF\psi_i}{RT}\right)$

259 (3)

- 260 X: Si or Al
- 261

where K_{OH} is the intrinsic equilibrium constant for dissociation, (=*XOH*), (=*XO*) are concentrations of the surface species of surface sites (mol/m²), a_{H^+} is the activity of H^+ (mol/L), ψ_i is the potential at the 0-, 1-, or 2-plane (V), Δz_i is the charge distribution, *R* is the universal gas constant equal to 8.31451 J/(mol·K), and *T* is the absolute temperature (K).

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

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

- 272 (4)
- 273

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

277

The titration experimental results from Eq. (4) were fitted to the surface complexation modelling 278 279 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-A-S-H samples in NaOH solution. The estimated equilibrium constant for the dissociation of 283 284 surface sites as a function of Ca/Si is shown in Fig. 7 and presented in Table 3. The determined pK_{OH} for weak and strong sites were 6.6 and 13.0, respectively, irrespective of Ca/Si or aluminium 285 incorporation into the C-S-H. The results indicated that the surface of C-S-H/C-A-S-H was affected 286 by the presence and ionisation of weak sites in NaOH solution, and not by the strong sites. The 287 288 estimated equilibrium constants are comparable to the results reported in the literature; Pointeau et 289 al. reported 7.6 for both strong and weak ≡SiOH sites [34], Hass and Nonat reported 7.7 for ≡SiOH [30], Elakneswaran et al reported 12.7 for ≡SiOH [8], Viallis-Terrisse et al. reported 12.3 [31] and 290 291 Pointeau et al. reported 12.0 for \equiv SiOH sites [13].



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







Fig. 7. Determined dissociation equilibrium constant for strong and weak sites: (A) \equiv SiOH sites in C-S-H; (B) \equiv SiOH sites in C-A-S-H; (C) \equiv AlOH sites in C-A-S-H.

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

$$308 \equiv XOH + Ca^{2+} \rightleftharpoons \equiv XOCa^{+} + H^{+} \qquad K_{Ca} = \frac{(\equiv XOCa^{+})*(a_{H^{+}})}{(\equiv XOH)*(a_{Ca^{2+}})} exp\left(-\frac{\Delta z_{i}F\psi_{i}}{RT}\right)$$

- 309 (5)
- 310

$$311 \equiv XOH + Ca^{2+} + OH^{-} \rightleftharpoons \equiv XOCaOH + H^{+} \quad K_{CaOH} = \frac{(\equiv XOCaOH)*(a_{H^{+}})}{(\equiv XOH)*(a_{Ca^{2+}})*(a_{OH^{-}})} exp\left(-\frac{\Delta z_{i}F\psi_{i}}{RT}\right)$$

- 312 (6)
- 313 X: Si or Al

where K_{Ca} and K_{CaOH} are the intrinsic equilibrium constants for calcium adsorption, ($\equiv XOCa^+$) and ($\equiv XCaOH$) are the concentrations of the surface species of surface sites (mol/m²), and a_{Ca2+} is the activity of Ca²⁺ (mol/L).

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The experimental data for the C-S-H/C-A-S-H in Ca(OH)₂ solution were fitted to the modelling results to estimate K_{Ca} and K_{CaOH} . An example of such fitting is shown in **Fig. 8**. Furthermore, the change in the determined equilibrium constant with Ca/Si is shown in **Fig. 9** and presented in **Table** 3. As observed for the dissociation of sites in the NaOH solution (**Fig. 7**), the weak sites significantly influence the adsorption of calcium ions. Moreover, the equilibrium constant of =AlOH is nearly equal to that of =SiOH.

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

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Fig. 9. Determined equilibrium constant of calcium absorption for strong and weak, (A) ≡SiOH
sites in C-S-H; (B) ≡SiOH sites in C-A-S-H; (C) ≡AlOH sites in C-A-S-H. Note: pKCa and
pKCaOH for strong site of CSH-0.8 and CASH-0.8 are identical values and overlap in the figure.

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

$$339 \equiv XOH + Ca^{2+} + Cl^{-} \rightleftharpoons \equiv XOCaCl + H^{+} \quad K_{CaCl} = \frac{(\equiv XOCaCl) * (a_{H^{+}})}{(\equiv XOH) * (a_{Ca^{2+}}) (a_{Cl^{-}})} exp\left(-\frac{\Delta z_{i}F\psi_{i}}{RT}\right)$$

$$340 \quad (7)$$

$$341 \quad X: Si \text{ or } Al$$

where K_{CaCl} is the intrinsic equilibrium constant for chloride adsorption, (=*XOCaCl*) is the concentration of the surface species of surface sites (mol/m²), and a_{Cl} is the activity of Cl⁻ (mol/L).

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

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



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



Fig. 11. Determined equilibrium constant of chloride adsorption for strong and weak, (A) ≡SiOH

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

			Site density				
			(sites/nm ²)	рК _{ОН}	рК _{Са}	рК _{СаОН}	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
C511-1.0		strong site	4.12	13.0	7.1	6.8	7.3
CSH-1.5	SOH	weak site	1.13	6.6	5.8	3.7	5.7
	51011	strong site	5.14	13.0	7.9	6.9	8.0
	SiOH	weak site	1.22	6.6	5.8	3.5	5.7
CASH-08		strong site	2.02	13.0	6.8	6.8	6.5
		weak site	0.15	6.6	5.8	3.5	4.5
	non	strong site	0.15	13.0	6.8	6.8	6.0
	SiOH	weak site	1.07	6.6	5.8	3.5	5.7
CASH-10		strong site	2.89	13.0	7.3	6.9	7.5
CASII-1.0	AIOH	weak site	0.22	6.6	5.8	3.5	5.5
	non	strong site	0.22	13.0	7.3	6.9	7.5
	SiOH	weak site	1.06	6.6	5.8	3.5	5.7
CASH-1.5	51011	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

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

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

model successfully predicted calcium adsorption as a function of calcium concentration. As can be 374 seen from the model prediction, both Ca^{2+} and $CaOH^{+}$ adsorb on the surface sites, but the 375 adsorption of CaOH⁺ contributes at a high concentration of calcium. Therefore, both surface 376 377 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 decreases with an increase in the ratio (Fig. 12 (D) and Fig. 13 (D)). This is due to the equilibrium 379 380 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 AlOH sites. 384 Therefore, both ≡SiOH and ≡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

The surface complexation reactions given in Eqs. (3), (5), (6) and (7) were used to predict chloride 387 388 adsorption on C-S-H and C-A-S-H in CaCl₂ solution. A high concentration of CaCl₂ solution was 389 selected to enhance chloride adsorption on C-S-H and C-A-S-H, as reported in ref. [12] where 20-70% of chloride adsorption was observed when cement paste was exposed to CaCl₂ solutions. Both 390 the strong and weak of the \equiv SiOH and \equiv AlOH sites compete for chloride adsorption via the surface 391 392 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.



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-S402 H with different Ca/Si ratios.



405 Fig. 13. Comparison of the predicted and measured calcium adsorption on C-A-S-H with (A)
406 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
407 calcium adsorption on C-A-S-H with different Ca/(Si+Al) ratios.



Fig. 14. Comparison of the predicted and measured chloride adsorption on C-S-H with (A) Ca/Si of

0.8; (B) Ca/Si of 1.0; (C) Ca/Si of 1.5.



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.

419 **4.** Conclusions

The electrostatic interaction of calcium and chloride ions on C-S-H and C-A-S-H was evaluated by experiments and a triple-layer surface complexation model. C-S-H and C-A-S-H were characterised to determine the surface functional groups and their densities: C-S-H possesses strong and weak \equiv SiOH sites, whereas C-A-S-H has strong and weak \equiv SiOH and \equiv 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, but aluminium substitution decreases the site density at each Ca/(Si+Al) ratio. The CD-MUSIC 425 426 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 results. Moreover, the effect of the Ca/(Si+Al) ratio and aluminium incorporation on the 429 430 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

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534 Appendix A



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

537







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

Declaration of interests

 \boxtimes 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: