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Modelling Chloride Transport in Alkali-Activated Slags

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Abstract

The service-life of steel-reinforced concrete structures is primarily determined by the ability of the concrete cover to resist chloride ingress. With limited literature available on the ingress of chloride into alkali-activated slags (AAS) under service conditions, it is critical that this is described by appropriate models. This paper describes an interactive software framework to relate chloride ingress into AAS with the chemistry of the concrete cover, by considering the chloride binding capacity and porosity of the binder as a function of time, based on thermodynamic calculations of the phase assemblage as a function of slag and activator composition. This provides a major step towards developing the ability to predict the ingress of chlorides in alkali-activated concretes from a sound theoretical basis, which is essential in providing confidence in the durability of these materials in essential infrastructure applications.

Keywords: Thermodynamic Calculations (B); Diffusion (C); Chloride (D); Alkali Activated Cement (D); Durability (C).

28 **1 Introduction**

29 The service life of steel reinforced concrete structures in the presence of chlorides is often
30 described by the classical model proposed by Tuutti [1]. The model can be broadly categorised
31 into the transport process (*initiation phase*), the breakdown of steel passivity (*onset of*
32 *corrosion*), and the time between the onset of corrosion and the end of serviceability
33 (*propagation phase*). The duration of the initiation phase is primarily a function of the
34 chemistry of the hydration products forming in the binder and their ability to bind chloride
35 ions, the pore structure of the cement matrix, the pore solution chemistry and its ionic strength
36 [2], while the onset of corrosion is governed by the local characteristics of the steel-concrete
37 interface (SCI) – pore solution chemistry and its pH, the chloride concentration and the
38 chemical composition of the steel surface [3,4]. The duration of the propagation phase is
39 determined by the ability of the SCI to sustain stable pit growth and a reduction in the cross
40 section of the steel reinforcement [3,4].

41 In the case of Portland cement (PC) based steel-reinforced concretes, a significant amount
42 of research has been carried out to gain an understanding of the initiation phase, the onset of
43 corrosion and the propagation phase. However, some critical questions regarding the onset of
44 corrosion in PC based systems remain unanswered, particularly those pertaining to the
45 influence of the SCI [3].

46 Alkali-activated slag (AAS) binders are less well understood than PC, and there remains a
47 significant need to improve the understanding of the long-term performance of AAS when used
48 in steel-reinforced concrete structures, as field data spanning decades or more are very limited.
49 The initiation phase, or the time taken for chloride ingress through the cover of AAS concretes,
50 has been observed in some instances to be notably longer than in PC based systems, and this
51 has been attributed to denser microstructures, higher chloride binding capacity, and/or higher
52 ionic strength of the pore solutions in AAS [5–7], but remains incompletely understood. The
53 extent of chloride binding in AAS has been found to depend on the chemical composition of
54 slag used, the phase assemblage evolution formed upon activation, and the alkalinity of the
55 resulting pore solution [8]. The pore solution of AAS is highly reducing due to the presence of
56 reduced sulfur species supplied by the slag, which at high concentrations has also been
57 observed to alter both the passivation capability and the surface chemistry of the steel
58 reinforcement [9] from those encountered in PC based concretes. The breakdown of passivity
59 and the subsequent propagation of steel corrosion in concrete structures has been associated
60 with the concept of a chloride ‘threshold’ value [10], but as is the case for PC, the available
61 data on the chloride ‘threshold’ value for AAS are very scattered.

62 The various parameters that control the initiation, onset of corrosion and propagation phases
 63 are highly convoluted and inter-dependent. Therefore, any predictive service life model needs
 64 to consider the influence of the concrete cover characteristics on the transport processes, as
 65 well as the conditions prevailing at the SCI for corrosion to initiate and propagate. This study
 66 provides an underpinning framework focused on the first of these two points, by coupling
 67 thermodynamic simulations predicting the chemistry of the concrete cover with numerical
 68 modelling of chloride diffusion and binding.

69

70

71 2 Developing a modelling framework

72 A framework for predicting chloride ingress into AAS based concretes was developed in the
 73 MATLAB software environment. The MATLAB script, which is provided as Supporting
 74 Information accompanying this paper, incorporates the thermodynamic data generated for
 75 various chemistries of commercial blast furnace slags and activators (discussed in detail in
 76 Section 2.1), the transport and chloride binding properties of AAS (discussed in detail in
 77 Section 2.2) and then calculates the chloride profiles for a specified AAS concrete for the first
 78 70 years. The script works from input data provided by the user regarding the composition of
 79 the slag and the activator of interest, concentration of the chloride exposure solution, and the
 80 concrete cover depth. To investigate the application of the proposed model, several slag
 81 compositions were selected from the literature [7,11] and are shown in Table 1.

82

83 Table 1: The chemical compositions of various slags considered in this study, expressed as
 84 wt. % of oxides in this table regardless of the true oxidation state of each element. Data for
 85 M01, M05, M06, and M14 are from [7], and those for M08, M11, and M13 are from [11].

	M01	M05	M06	M08	M11	M13	M14
CaO	42.9	42.3	41.3	35.8	34.6	33.4	33.9
SiO₂	31.6	32.3	36.0	38.2	37.1	36.4	37.4
Al₂O₃	14.6	13.3	11.3	12	11.5	11.3	9.0
Fe₂O₃	1.1	0.6	0.3	1.6	1.8	1.4	0.4
MgO	1.2	5.2	6.5	7.7	10.5	13.2	14.3
Na₂O	0.2	0	0.3	0.4	0.4	0.5	0.4
K₂O	0.3	0.3	0.4	1.2	1.1	1.0	0.5
MnO	0.3	0.2	0.3	1.5	1.5	1.4	1.0
SO₃	2.0	2.9	0.7	1.4	1.2	0.4	0.7

86

87

88 **2.1 Chemistry of AAS paste in the concrete cover**

89 Thermodynamic modelling simulations conducted in this study for slags activated using
90 various activators including NaOH, Na₂SiO₃, Na₂O·2SiO₂, Na₂CO₃ and Na₂SO₄ follow very
91 similar procedures to those described by Myers et al. [12–14]. To establish a look-up database
92 for use in further simulations, the masses and volumes of each stable solid phase and the
93 chemical compositions of the aqueous solutions simulated by using the GEMS-Selektor
94 software, were tabulated and stored in MATLAB (hereafter referred to as the ‘GEMS
95 calculated database’) for a large number of slag compositions. This database is then
96 interrogated directly for calculation of the total chloride binding capacity of the cementitious
97 constituent of each concrete simulated. Additionally, this database included the properties of
98 the modelled C-(N-)A-S-H gel solid solution for each combination of slag and activator, such
99 as composition, density and molar volume. The full database is also presented as
100 Supplementary Information accompanying this paper.

101 To ensure that the range of chemistries studied here span those that are relevant to AAS, the
102 SiO₂ contents within the simulated slags were fixed at 30 and 40 wt.%, and the effective SO₃
103 was fixed at 2 wt.% but represented as sulfide; the sulfur was specified as S²⁻ and charge-
104 balanced by H⁺. The minor species Na, K and Mn were neglected, and given the passive nature
105 of Fe within slags [15], Fe was excluded from the simulations. The remaining species were
106 specified within the pseudo-ternary system CaO-Al₂O₃-MgO. For fixed quantities of SiO₂ and
107 SO₃, the molar quantities of CaO, Al₂O₃, and MgO were calculated and normalised to constitute
108 the remainder of the slag. Within the pseudo-ternary CaO-Al₂O₃-MgO sub-system, the range
109 $0.5 \leq \text{CaO} \leq 1$, $0 \leq \text{Al}_2\text{O}_3 \leq 0.5$, and $0 \leq \text{MgO} \leq 0.5$ (on a molar basis) was covered in the
110 simulation, using a step size of 0.02 in each constituent to span this part of the pseudo-ternary
111 sub-system.

112 The simulations were carried out at extents of slag reaction from 10 to 60 %, with a step
113 size of 5 %, to ensure coverage of early age and long-term characteristics of AAS. Unreacted
114 slag at each extent of reaction was considered to be inert in the Gibbs energy minimisation
115 protocol. The w/b ratio (water/binder, where the anhydrous activator components are
116 considered part of the binder) was fixed at 0.40 for these simulations. The dosage of the
117 activator was set to 8 g activator/100 g slag for activation by Na₂CO₃ and Na₂SO₄ [12,16], 4.75
118 g activator/100 g slag for NaOH [17], 10.24 g activator/100 g slag for Na₂SiO₃ (modulus:
119 SiO₂/Na₂O molar ratio = 1.0) [18], and 13.4 g activator/100 g slag for Na₂O·2SiO₂ (modulus =
120 2) [17]. The activator doses for NaOH, Na₂SiO₃ and Na₂O·2SiO₂ activated slags are slightly
121 higher than those reported in the literature. A predominantly N_{2(g)} atmosphere was used for the

122 simulations to provide an oxygen-depleted environment to prevent sulfur oxidation,
 123 representing undamaged concrete.

124 Simulations were carried out using the Gibbs energy minimisation software GEM-Selektor
 125 version 3.2 [19,20] (<http://gems.web.psi.ch/>), with the CEMDATA14 database [21]
 126 supplemented by additional phases as described below. Thermodynamic data for solid phases,
 127 aqueous species/complexes, and gases considered in this study are listed the Supplementary
 128 Information. The aqueous and gas phase models were represented by the Truesdell-Jones
 129 version of the extended Debye-Hückel equation (Eq. 1) and the ideal gas equation of state,
 130 respectively [12].

$$131 \log_{10}(\gamma_j) = \frac{-A_\gamma z_j^2 \sqrt{I}}{1 + a B_\gamma \sqrt{I}} + b_\gamma I + \log_{10} \frac{x_{jw}}{X_w} \quad (\text{Eq. 1})$$

132 where, γ_j and z_j are the activity coefficient and the charge of the j^{th} aqueous species,
 133 respectively, I is the ionic strength of the aqueous phase, A_γ ($\text{kg}^{0.5} \text{mol}^{-0.5}$) and B_γ ($\text{kg}^{0.5} \text{mol}^{-0.5} \text{cm}^{-1}$)
 134 are electrostatic parameters that depend on the temperature and pressure, and x_{jw} (mol)
 135 and X_w (mol) are the molar quantities of water and total aqueous phase, respectively. The
 136 average ionic radius (\bar{a} , Å) and the parameter for short-range interactions of charged species
 137 (b_γ , kg/mol) were specified according to [22], and set to 3.31 and 0.098 kg/mol respectively,
 138 representing NaOH-dominated solutions.

139 The thermodynamic dataset for solid phases (as indicated in the Supplementary
 140 Information) includes the ideal solid solution models CNASH_ss [14] and MA-OH-LDH_ss
 141 [13], for the calcium-alkali aluminosilicate hydrate and the hydrotalcite-group layered double
 142 hydroxide (LDH) solid solutions, respectively. In addition, zeolites such as natrolite
 143 ($\text{Na}_{0.4}\text{Al}_{0.4}\text{Si}_{0.6}\text{O}_2 \cdot 0.4\text{H}_2\text{O}$) and Ca-heulandite ($\text{Ca}_{0.111}\text{Al}_{0.222}\text{Si}_{0.778}\text{O}_2 \cdot 0.667\text{H}_2\text{O}$) have been
 144 considered in the thermodynamic simulations and are consistent with experimentally
 145 determined phase assemblages in AAS. All other zeolites mentioned in [13] were suppressed as
 146 they were not observed in initial trial simulations.

147 As mentioned earlier, thermodynamic simulations were conducted for slags either
 148 containing 30 wt. % or 40 wt. % SiO_2 . So, the MATLAB input script selects the type of slag
 149 to use from the database, initially based on the bulk SiO_2 content and the activator type selected
 150 by the user. Therefore, slags with ≥ 35 wt. % SiO_2 were represented by the database entries
 151 with 40 wt. % SiO_2 , and those with < 35 wt. % SiO_2 were assumed to be similar to those
 152 containing 30 wt. % SiO_2 . Based on the mole fractions of CaO, MgO and Al_2O_3 present, the
 153 SiO_2 content and the activator, the MATLAB script extracts data for the hydrate phase
 154 assemblage from the tabulated ‘GEMS calculated database’ at the selected degree of hydration.

155 In this study, the sulfur content of the slag, the w/b ratio used to formulate the AAS binder and
 156 the paste volume were kept constant, although these parameters do represent scope for future
 157 model extension.

158 2.2 Chloride binding and diffusion

159 The transport of chloride within concrete under saturated conditions is primarily driven by
 160 diffusion, and this is the mechanism described here; other forms of transport such as migration
 161 and capillary suction are not considered. Under saturated conditions, the transport of chloride
 162 ions can be assumed [23] to occur via the evaporable water in the concrete (w_e – defined in
 163 volume fraction terms), which is considered to be the volume of water in the pore solution of
 164 the concrete. So, the flux (J_{Cl} , in $\text{kg/m}^2 \cdot \text{s}$) of chloride ions through the concrete at depth x from
 165 the surface can be described by Fick's first law (Eq. 2):

$$166 \quad J_{Cl} = -D_{Cl}^* \frac{\partial C_f}{\partial x} = -D_{Cl} \cdot w_e \cdot \frac{\partial C_f}{\partial x} \quad (\text{Eq. 2})$$

167 where, D_{Cl} (m^2/s) is the effective diffusion coefficient when the chloride concentration is
 168 expressed in terms of kg/m^3 of concrete, and D_{Cl}^* (m^2/s) is the effective diffusion coefficient
 169 when the chloride concentration is expressed in kg/m^3 of pore solution. The free chloride
 170 concentration is represented by C_f (kg/m^3) and the negative sign indicates the difference
 171 between the direction of the concentration gradient and the direction of transport. By applying
 172 mass conservation in saturated concrete, and substituting Eq. 2 into Eq. 3, the change in the
 173 total chloride concentration (C_t , in kg/m^3 of concrete) with respect to time (t) can be expressed
 174 as a function of the change in free chloride concentration as a function of the distance within
 175 the concrete cover, and is articulated as Fick's second law (Eq. 4) [23,24] when D_{Cl} is assumed
 176 to be uniform throughout the cover concrete:

$$177 \quad \frac{\partial C_t}{\partial t} = - \frac{\partial J_{Cl}}{\partial x} \quad (\text{Eq. 3})$$

$$178 \quad \frac{\partial C_t}{\partial t} = \frac{\partial}{\partial x} (D_{Cl} \cdot w_e \cdot \frac{\partial C_f}{\partial x}) = D_{Cl} \cdot w_e \cdot \frac{\partial^2 C_f}{\partial x^2} \quad (\text{Eq. 4})$$

179 The total chloride concentration can be expressed as a function of the free chloride
 180 concentration, bound chloride content (C_b), and the total evaporable water as Eq. 5 [25]:

$$181 \quad C_t = C_b + w_e C_f \quad (\text{Eq. 5})$$

182 Substitution of Eq. 5 into Eq. 4 allows consideration of the influence of chloride binding on
 183 the diffusion of free chloride ions within the concrete matrix, and the modified equation for
 184 Fick's second law can be expressed as Eq. 6:

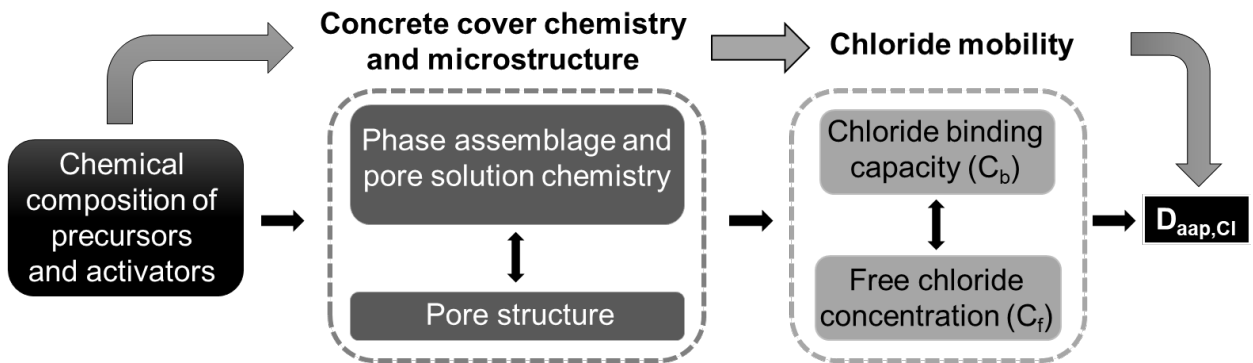
$$185 \quad \frac{\partial C_f}{\partial t} = D_{app,Cl} \cdot \frac{\partial^2 C_f}{\partial x^2} \quad (\text{Eq. 6})$$

186 and,

$$187 \quad D_{app,Cl} = \frac{D_{Cl}}{1 + \frac{1}{w_e} \frac{\partial C_b}{\partial C_f}} \quad (\text{Eq. 7})$$

188 where, $D_{app,Cl}$ is the apparent chloride diffusion coefficient (m^2/s) and $\partial C_b/\partial C_f$ is the chloride
 189 binding capacity of the concrete cover [23]. As highlighted in Eq. 7, $D_{app,Cl}$ can thus be
 190 described (Figure 1) as a function of the chloride binding capacity of the concrete cover. The
 191 chloride binding capacity of the cementitious hydrates is dependent on the hydrate phase
 192 assemblage, which in turn is a function of the chemistry of the slag and the activating solution,
 193 and the degree of hydration. Additionally, as highlighted in Figure 1, $D_{app,Cl}$ can also be
 194 influenced by the evolving pore structure of the concrete cover (pore geometry, tortuosity of
 195 the bulk paste and the ITZ, connectivity), but these effects fall out of the scope of this study.

196



197

198 Figure 1: A simple schematic of the factors influencing the effective chloride diffusion
 199 coefficient in concrete under saturated conditions.

200

201 The extent of chloride binding for a particular phase assemblage can be described as a
 202 function of free chloride concentration via chloride binding isotherms (when determined at a
 203 given temperature), using functional forms such as the Langmuir [24] and Freundlich isotherms
 204 (Eq. 8) [23,26].

$$205 \quad C_b = \alpha C_f^\beta \quad (\text{Eq. 8})$$

206 where, α and β are empirical constants and their values depend on the chemistry of the
 207 binder. Tang and Nilsson [25] observed that the Langmuir functional form was only valid for

208 free chloride concentrations less than 0.05 M as it cannot extend beyond the formation of an
 209 adsorbed monolayer, but for free chloride concentrations greater than 0.01 M, the use of a
 210 Freundlich isotherm was deemed more appropriate [25]. Therefore, the Freundlich adsorption
 211 isotherm was used to fit experimental data [7] in this study, and to quantify the binding capacity
 212 and apparent chloride diffusion coefficient of AAS; this is revisited later. Eq.8 can be
 213 differentiated with respect to C_f to give Eq. 9:

$$214 \quad \frac{\partial C_b}{\partial C_f} = \alpha \beta C_f^{\beta-1} \quad (\text{Eq. 9})$$

215 Substituting Eq. 9 into Eq. 7, Eq.10 is obtained:

$$216 \quad D_{app,Cl} = \frac{D_{Cl}}{1 + \frac{1}{w_e} \alpha \beta C_f^{\beta-1}} \quad (\text{Eq. 10})$$

217 Both long- and short-term tests have been used to quantify chloride ingress within concrete
 218 structures; however, one of the most accepted methods is the rapid chloride migration (RCM)
 219 test, NT Build 492 [27], developed by Tang [28]. The RCM test is a short-term test and gives
 220 the value of non-steady state migration coefficient (D_{nssm} or D_{RCM}) and details of the test can
 221 be found in [27,28]. The DuraCrete guidelines [29,30] use $D_{RCM}(t)$ as an input parameter to
 222 define the service life of concrete structures, implying that this should be equivalent to $D_{app,Cl}$
 223 values obtained using bulk diffusion tests. However, in the case of PC-based concretes, several
 224 authors [28,31–33] have found the value of D_{RCM} to be slightly higher than $D_{app,Cl}$, and it is
 225 possible that the short-term RCM test underestimates the extent of chloride binding in cement
 226 matrices. This has been found to be true in the case of AAS mortars as well [6], where the ratio
 227 of the non-steady state migration and apparent diffusion coefficients ($D_{RCM}/D_{app,Cl}$) was found
 228 to be approximately 100. Therefore, the value of D_{Cl} in Eq. 10 in this study was assumed to be
 229 the mean D_{nssm} (0.5×10^{-12} m²/s) obtained using the NT Build 492 test on Na₂SiO₃-activated
 230 M6 mortars cured for 28 days, reported in [7] and [6], implying that D_{nssm} obtained using NT
 231 Build 492 does not take into account the influence of chloride binding. The value of D_{Cl} was
 232 assumed to be the same for all AAS considered in this study. The experimentally observed
 233 D_{nssm} values for AAS mortars [7] were considered to be true for AAS concretes as well, on the
 234 assumption that the aggregate volume fraction (or the interfacial transition zone (ITZ)) has
 235 negligible influence on $D_{app,Cl}$ [34]. Future evolution of the model is envisaged to include a
 236 more sophisticated treatment of aggregate volume and ITZ effects, but that is beyond the scope
 237 of the current work.

238 AAS binders are characterised by the formation of C-(N-)A-S-H gel as the major reaction
 239 product, and secondary reaction products including hydrotalcite-like Mg-Al-OH-LDH phases
 240 and AFm-group phases. As an initial assumption, the total binding capacity of AAS can be

241 approximated by the sum of the individual binding capacities of its constituent hydrate phases
 242 (Eq. 11).

$$243 \left(\frac{\partial C_b}{\partial C_f} \right)_{binder}^{total} = \left[\left(\frac{\partial C_b}{\partial C_f} \right)_{C-(N-)A-S-H} + \left(\frac{\partial C_b}{\partial C_f} \right)_{Mg-Al-OH-LDH} + \left(\frac{\partial C_b}{\partial C_f} \right)_{strätlingite} + \dots \right] \quad (\text{Eq. 11})$$

244 According to Eq. 11, if the amounts and the individual chloride binding capacity of each of
 245 the reaction products are known, a theoretical value for the total chloride binding capacity of
 246 AAS could be calculated. Ke [7] calculated the individual chloride binding capacities of the C-
 247 (N-)A-S-H gel, hydrotalcite-like Mg-Al-OH-LDH phase and strätlingite, under pH conditions
 248 relevant to the pore solution chemistry of AAS. Substituting Eq. 11 into Eq. 7, $D_{app, Cl}$ can be
 249 represented by Eq. 12:

$$250 D_{app, Cl} = \frac{D_{Cl}}{1 + \frac{1}{w_e} \left[\left(\frac{\partial C_b}{\partial C_f} \right)_{C-(N-)A-S-H} + \left(\frac{\partial C_b}{\partial C_f} \right)_{Mg-Al-OH-LDH} + \left(\frac{\partial C_b}{\partial C_f} \right)_{strätlingite} + \dots \right]} \quad (\text{Eq. 12})$$

251 Based on the individual binding isotherms obtained by Ke [7] (reproduced in Figure 2), the
 252 total chloride binding capacity of each AAS composition in this study was considered to be the
 253 sum of the individual binding capacities of the C-(N-)A-S-H gel, hydrotalcite-like Mg-Al-OH-
 254 LDH phase, and the AFm phase strätlingite. The latter phase is predicted extensively in
 255 thermodynamic simulations of AAS, although less often observable as a crystalline phase by
 256 X-ray diffractometry [35,36]. Additional phases formed in smaller quantities in AAS, such as
 257 monocarbonate-AFm, monosulfate-AFm, ettringite, Ca-heulandite, natrolite, katoite and
 258 brucite, were not included in the calculations of chloride binding. Various authors have
 259 determined chloride binding isotherms for synthetic AFm phases [37–39], however, they are
 260 not considered in this study primarily because the experimental setup used to calculate the
 261 binding isotherms could neither represent the alkalinity nor the ionic strength of the pore
 262 solutions of AAS.

263

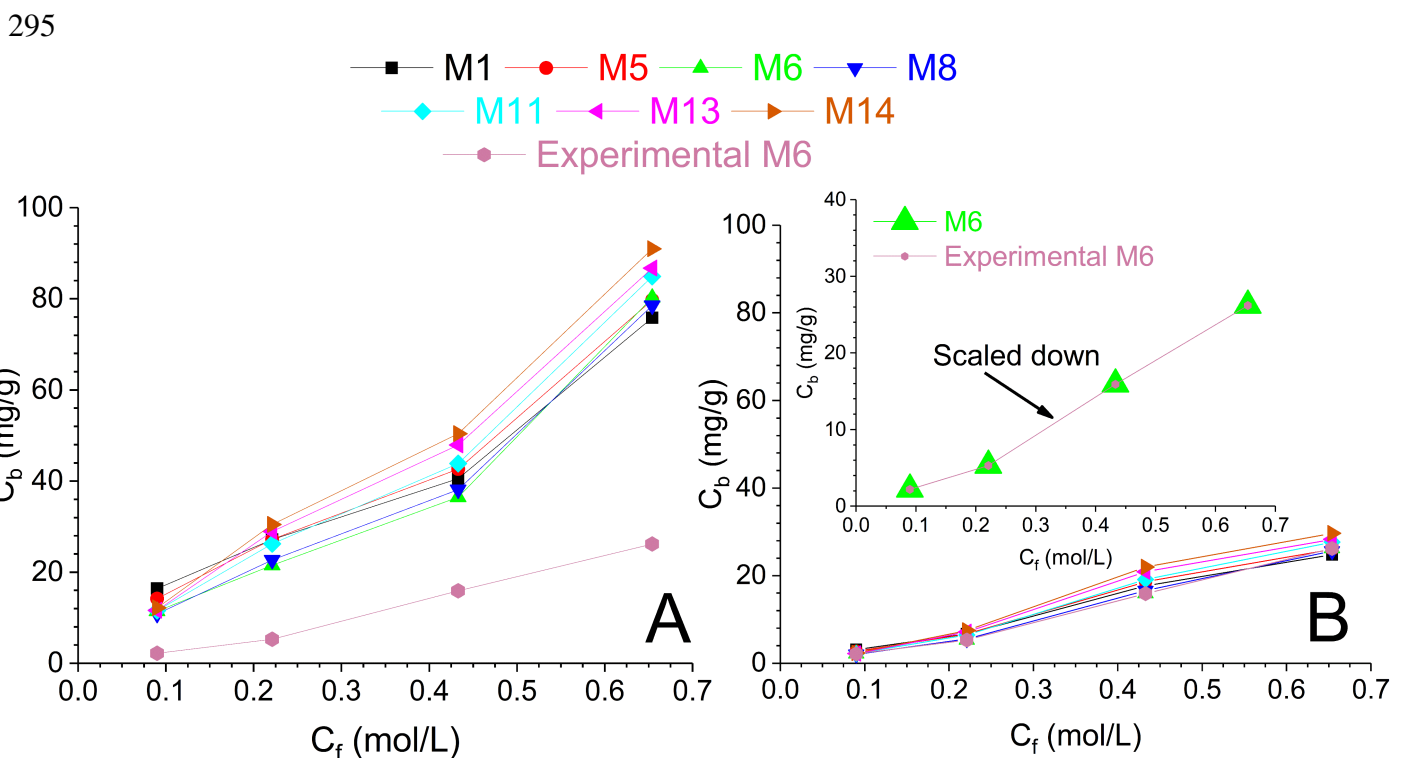
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265 Figure 2: Chloride binding isotherms for synthetic phases formed in AAS, C-(N-)A-S-H gel,
266 hydrotalcite-like Mg-Al-OH-LDH phase and strätlingite; data from Ke [7]. The experimental
267 methods used to determine bound and free chloride are detailed in [7,8]. It must be noted that
268 chloride binding in AAS could occur via the physical adsorption of chloride on the surface of
269 the different reaction products and ionic exchange with the interlayer anionic species present
270 in some reaction products [7,8].

271

272 Ke [7] reported the experimental chloride binding capacity of Na_2SiO_3 - and Na_2CO_3 -
273 activated slag (composition M6, Table 1). In the current study, the experimentally determined
274 binding isotherm for Na_2SiO_3 -activated M6 from that work [7] is also assumed to be valid for
275 slag M6 activated using the other activators discussed (NaOH , $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$, Na_2CO_3 , and
276 Na_2SO_4), due to the lack of experimental binding isotherms in the literature for various AAS.
277 In addition, Ke [7] compared the theoretical (Eq. 11) and experimental chloride binding
278 isotherms, and observed the theoretical values to be 3 to 6 times higher than experimental
279 observation. This overestimation was attributed to the higher crystallinity of the synthetic
280 phases used for measuring the individual chloride binding isotherms [7]. It is also possible that

281 surface blocking by neighbouring hydrate phases influences these results, when comparing
 282 finely-dispersed synthetic powders to hydrated pastes. Based on the quantities of C-(N-)A-S-
 283 H gel, hydrotalcite-like Mg-Al-OH-LDH phase and strätlingite predicted by the
 284 thermodynamic simulations as described in Section 2.1, the total chloride binding isotherm for
 285 each AAS considered in this study was calculated as the sum of the individual chloride binding
 286 capacities of each of these phases (as shown in Figure 3A) in proportions corresponding to a
 287 slag reaction extent of 60 %. This methodology was followed in scaling down the theoretical
 288 binding isotherms of activated M6 binders to match the experimentally determined values. In
 289 the absence of any experimental information to indicate otherwise, the theoretical binding
 290 isotherms for all other activated slags (M1, M5, M8, M11, M13 and M14) and for all activators
 291 were also scaled down by the same factor (as shown in Figure 3B). In reality it is likely that
 292 the scaling factors between synthetic phases and real pastes will depend on the slag and
 293 activator chemistry, but given that no data currently exist to describe this dependence, it is
 294 neglected in the current work.



297 Figure 3: (A) Chloride binding isotherms calculated through the use of simulated solid phase
 298 assemblages for Na_2SiO_3 -activation of all slags considered in this study at 60% reaction
 299 extent, and the individual binding capacity of each of the reaction products, compared with
 300 the experimental data from [7]. (B) Scaling down of the theoretical chloride binding
 301 isotherms to match experimental data, defining the apparent diffusion coefficients as a
 302 function of the free chloride concentration.

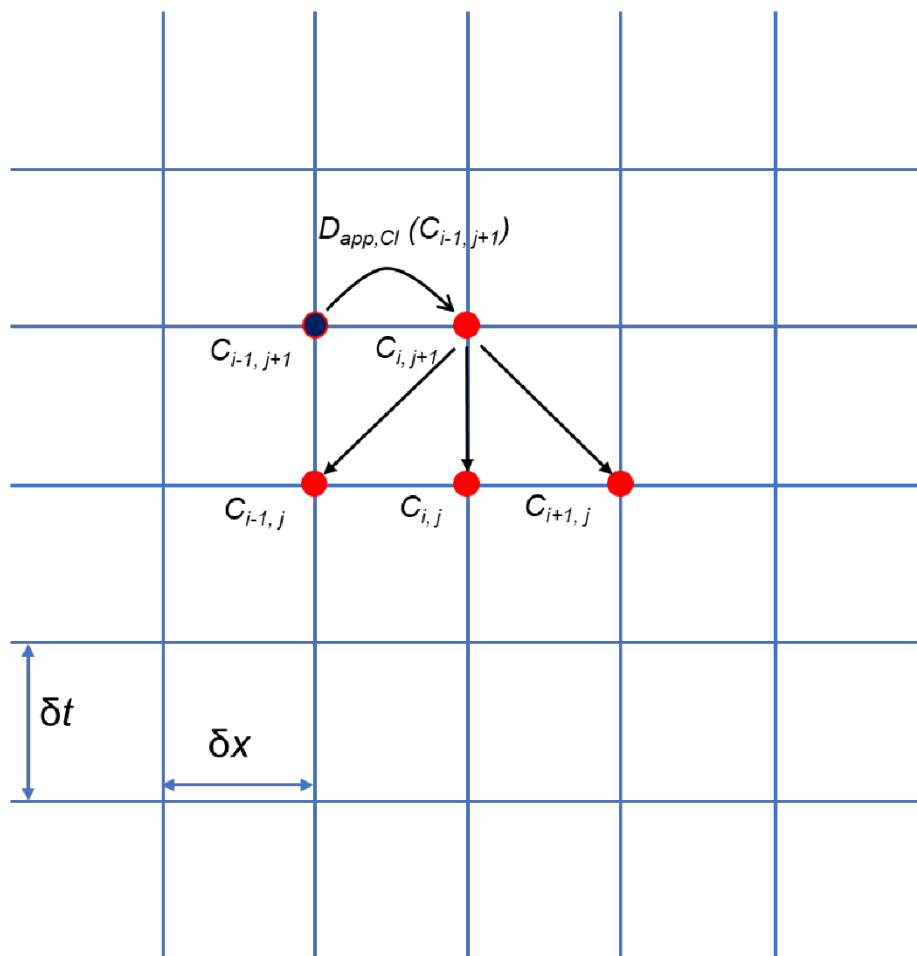
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304 To model the diffusion of chloride in saturated concretes, considering $D_{app,Cl}$ as a function
 305 of C_f , Eq. 7 was solved numerically as a space-time problem using the explicit finite difference
 306 method [40], in one spatial dimension with time and space steps set to approximately 1 day and
 307 1 mm, respectively. To take into account the non-linear nature of $D_{app,Cl}(C_f)$, the value of $D_{app,Cl}$
 308 was set to depend on the free chloride concentration at the previous spatial step for any given
 309 time step, and was calculated individually at each space-time step using the calculated binding
 310 parameters of the Freundlich isotherm. It is assumed that the timescales of the chloride binding
 311 and chloride diffusion processes can be fully decoupled from each other, as the kinetics of
 312 chloride binding are rapid compared to the kinetics of diffusion - i.e., the adjustment of the
 313 bound/free chloride ratio to small changes in chloride concentration per timestep is assumed to
 314 be essentially instantaneous [41].

315 Figure 4 shows the finite difference propagation model used. It is important to note that the
 316 calculated Freundlich adsorption isotherm is only validated for free chloride concentrations
 317 lower than 0.654 M, as binding isotherms for higher free chloride concentrations do not exist
 318 in the literature. For a concrete with thickness L , the initial and boundary conditions used to
 319 solve Eq. 7 numerically are described by Eq. 13:

$$\begin{aligned}
 320 \quad & \text{For } t \geq 0, & C_f = C_o & \quad \text{at } x = L \\
 321 \quad & & C_f = C_s & \quad \text{at } x = 0 & \quad \quad \quad (\text{Eq. 13}) \\
 322 \quad & \text{For } t = 0, & C_f = C_o & \quad \text{at } x > 0
 \end{aligned}$$

323 where, C_o is the chloride concentration present in the concrete prior to exposure to a salt
 324 solution (defined in wt.% of the binder; set to zero for the simulations presented here), and C_s
 325 is the concentration of chloride in the exposure salt solution (0.60 M Cl^-). The maximum
 326 thickness (L) of the concrete was set to be 70 mm. It must be noted that the surface chloride
 327 concentration for each AAS was assumed to be constant, and the influence of leaching [30] (or
 328 any other factors that could potentially lead to a reduction in the near-surface alkalinity) on the
 329 chloride binding capacity of the hydrate phases was not considered in this study. Based on the
 330 total amount of evaporable water content in each of the AAS phase assemblages, the surface
 331 chloride concentration was calculated in terms of wt.% of binder.



332

333 Figure 4: Schematic diagram of the explicit fine difference method employed in this study to
 334 describe the ingress of chloride as a space-time problem. The values of δx and δt were set to 1
 335 mm and 0.9125 days, respectively, making the grid (x vs. t) size $70 \times 28,000$, representing a
 336 cover depth of 70 mm and 70 years of service-life. The explicit fine difference method was
 337 solved using a loop function over space and time, with the boundary conditions described in
 338 Eq. 13. $D_{app,Cl}$ was calculated based on the Freundlich isotherm, binder chemistry, and free
 339 water content, and expressed as a function of the free chloride concentration ($c_{i-1,j+1}$) of the
 340 previous space step $i - 1$. The free chloride concentration ($c_{i,j+1}$) at time step $(j + 1)$ was thus
 341 calculated on the basis of free chloride concentrations ($c_{i,j}$, $c_{i-1,j}$, and $c_{i+1,j}$) at the previous
 342 time step j at locations i , $i - 1$ and $i + 1$, using the assumption of separation of time-scales
 343 between the binding (fast) and diffusion (slow) processes.

344

345 **3 Results and Discussion**

346 **3.1 Chemistry of the concrete cover**

347 Figure 5 shows the influence of MgO content in the slag and the type of activator on the
348 simulated solid phase assemblages of AAS at 60 % extent of slag reaction. Irrespective of the
349 nature of the activator and of the MgO content in the slag, the hydration products of AAS are
350 dominated by a C-(N-)A-S-H gel (Figure 5), however, the bulk MgO content in the slag
351 significantly influences the chemistry of the C-(N-)A-S-H gel. The Ca/Si ratio in the C-(N-)A-
352 S-H gel for all AAS systems studied, at 60 % extent of slag reaction, was calculated to be
353 between 0.80 and 1.07. Lower MgO content in the slag leads to a higher Al content in the C-
354 (N-)A-S-H gel; during the reaction of MgO-rich slags, much of the Al is consumed in the
355 formation of secondary hydration products such as hydrotalcite-like phases [18], resulting in
356 low Al/Si ratios in the C-(N-)A-S-H gel, Figure 5.

357 In NaOH-activated slags, the secondary reaction products were Mg-Al-OH-LDH, katoite
358 (C_3AH_6) and strätlingite (C_2ASH_8). At low MgO contents, for example in slags M1 and M5,
359 the secondary hydration products are dominated by the formation of katoite and strätlingite.
360 However, at higher slag MgO content, hydrotalcite-like Mg-Al-OH-LDH phase dominates the
361 secondary hydration products, with trace katoite and strätlingite. The presence of katoite in this
362 study was only observed for Ca-rich slags with $Ca/Si \geq 1.14$ (M1, M5 and M6) and this
363 observation aligns well with the literature [12,42,43]. Strätlingite is also a minor constituent
364 observed in NaOH-activated slags with low MgO contents [44], and its stability in C-(A-)S-H
365 systems at low temperatures (around 20 °C) was confirmed by Okoronkwo and Glasser [45].
366 Trace quantities of natrolite ($Na_{0.4}Al_{0.4}Si_{0.6}O_2 \cdot 0.4H_2O$) and brucite ($Mg(OH)_2$) were predicted
367 to form in slags containing high amounts of MgO; M13 and M14, respectively. The prediction
368 of brucite in the solid phase assemblages of slags activated using NaOH, and also Na_2SiO_3 and
369 $Na_2O \cdot 2SiO_2$ in this study (see below), is in contradiction with experimental observations for
370 AAS [11,17,43,46–49]. This could possibly be explained by the lack of thermodynamic data
371 for MgO-SiO₂-H₂O (magnesium silicate hydrate or M-S-H) phases in the CEMDATA14
372 database used in this study, as there is not another stable Mg-containing phase available to take
373 up this element once the capacity to form Mg-Al-OH-LDH has been exhausted by consumption
374 of all available Al.

375 In Na_2SiO_3 -activated and $Na_2O \cdot 2SiO_2$ -activated slags (Figure 5B and Figure 5C,
376 respectively), the secondary hydration products are the hydrotalcite-like Mg-Al-OH-LDH
377 phase, natrolite, strätlingite, Ca-heulandite, katoite and brucite. Similar to the observations
378 made for NaOH-activated slags, the quantity of Mg-Al-OH-LDH formed was strongly
379 dependent on the slag MgO content (Figure 5B, C). In slags containing 30 wt. % SiO₂ and low

380 bulk MgO contents (M1 and M5) activated using Na_2SiO_3 and $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$, strätlingite was
381 the major secondary reaction product, with minor and trace quantities of katoite, respectively,
382 also being present. Ca-heulandite was only predicted to form in slags containing 40 wt. % SiO_2
383 and high MgO contents (M6 to M14), and was more pronounced in $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ -activated slags
384 (Figure 5B and Figure 5C), due to the higher Si content provided by this activator. Similarly,
385 natrolite was also predicted to form for slags containing 40 wt. % SiO_2 and high MgO contents
386 (M6 to M13). As mentioned above, brucite is also predicted to form in trace quantities in
387 Na_2SiO_3 - and $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ -activation of slags containing a high level of MgO (M14).

389 Figure 5: Influence of bulk MgO content in slags, and the type of activator in the
 390 simulated solid phases when the extent of slag reacted is 60 %. The values in square [] and
 391 curly brackets { } within the navy-blue background indicate the calculated Ca/Si and Al/Si
 392 ratios in the C-(N-)A-S-H gel, respectively. $C_4A\bar{C}H_{11}$ = monocarbonate-AFm, $C_4A\bar{S}H_{12}$ =
 393 monosulfate-AFm, Mg-Al-OH-LDH = hydrotalcite-like phase, C-(N-)A-S-H gel = calcium
 394 (alkali) aluminosilicate hydrate gel.

395

396 In Na_2CO_3 -activated slags (as shown in Figure 5D), the hydrotalcite-like phase (Mg-Al-OH-
 397 LDH), natrolite, monocarbonate-AFm ($C_4A\bar{C}H_{11}$) and calcite ($CaCO_3$) were predicted to form.
 398 Additionally, in slags with 40 wt. % SiO_2 and extremely high bulk MgO content (M13 and
 399 M14), brucite and Ca-heulandite were observed to form. Similar to NaOH, Na_2SiO_3 , and
 400 $Na_2O \cdot 2SiO_2$ -activated slags, the formation of hydrotalcite-like phase was dependent on the
 401 extent of slag reaction and the bulk MgO content of the slag. The formation of natrolite was
 402 predicted for all slags considered in this study, and it indicates the coexistence of C-(N-)A-S-
 403 H and N-A-S-H type gels [46]. Monocarbonate-AFm is predicted to form in Na_2CO_3 -activated
 404 slags, as observed experimentally [16], and its formation was closely associated with the bulk
 405 MgO and SiO_2 content in the slag (Figure 5D), being preferred in slags with lower MgO and/or
 406 lower SiO_2 contents. Additionally (as seen in Figure 5D), in slags with high bulk MgO content
 407 and ~40 wt. % SiO_2 (M13 and M14), Ca-heulandite and brucite were predicted to form in trace
 408 quantities. Unlike NaOH, Na_2SiO_3 and $Na_2O \cdot 2SiO_2$ -activated slags, katoite and strätlingite
 409 were not predicted to form in Na_2CO_3 activation.

410 In Na_2SO_4 -activated slags (Figure 5E), the secondary reaction products were ettringite
 411 ($C_6A\bar{S}_3H_{32}$), monosulfate-AFm ($C_4A\bar{S}H_{12}$), hydrotalcite-like Mg-Al-OH-LDH, strätlingite,
 412 natrolite, brucite and Ca-heulandite. Ettringite has been observed experimentally to be the
 413 major secondary reaction product in Na_2SO_4 -activated slags [50–53], and is primarily
 414 responsible for the higher solids volume of these binders than other activated slags. Ettringite
 415 was stable for the entire range of slags (M1 to M14) studied here (Figure 5E), but more
 416 prevalent for slags with higher bulk SiO_2 content. In contrast, for lower- SiO_2 slags,
 417 monosulfate-AFm and strätlingite were observed to be the most stable secondary reaction
 418 products. The hydrotalcite-like phase was much less prevalent for slags with low MgO contents
 419 and with 30 wt. % SiO_2 (M1 and M5) when compared to their higher SiO_2 and higher MgO
 420 counterparts (M6 to M14). Natrolite and Ca-heulandite were predicted to be minor products,
 421 and small amounts of brucite were again predicted to form in slags with very high bulk MgO
 422 contents (M13 and M14).

423

424 3.2 Chloride diffusion

425 Based on the simulated solid and aqueous phase assemblages at 60 % extent of slag reaction
426 from Section 3.1, chloride binding isotherms for each AAS were calculated, so they could be
427 utilised to calculate the apparent chloride diffusion coefficient as a function of the free chloride
428 concentration, and to estimate the ingress of chloride in each of these binders.

429 3.2.1 *Influence of chloride binding*

430 Figure 6 shows a representative example depicting the influence of chloride binding on the
431 calculated chloride ingress profiles; in this instance, for concretes made from Na₂SiO₃-
432 activated M6 at various ages of exposure. As mentioned in Section 2.2, it must also be noted
433 that the migration coefficient (D_{nsm}) obtained in [7] was assumed to underestimate chloride
434 binding occurring within AAS, and therefore has been considered to be the value to be used
435 when there is no chloride binding. Chloride binding significantly retards the transport of
436 chloride towards the steel-concrete interface, and its importance can be clearly seen in chloride
437 profiles modelled at later ages (Figure 6D). Chloride binding decreases the concentration of
438 free chloride ions in the pore solution that are available to diffuse through the material
439 [28,54,55]. Therefore, the use of D_{nsm} as a parameter to characterise the ingress of chloride
440 may lead to underestimation of the service life of concrete structures based on AAS.

441 One of the major advantages of relating the $D_{app,Cl}$ to the binding capacity of each of the
442 reaction products present in a concrete structure, is the avoidance of the mathematically
443 problematic usage of an empirically derived time-dependent diffusion coefficient together with
444 Fick's equations, as is used by many service-life guidelines [29,30]. Table 2 shows the
445 calculated binding constants of the Freundlich adsorption isotherm, and the thermodynamically
446 estimated evaporable water content expressed as volume % of the total binder (i.e., the volume
447 % of the binder that is H₂O in the pore solution, from the thermodynamic simulations presented
448 as Supplementary Information, assuming negligible difference in the effective volume of pore
449 solution in the binder between pastes and concretes), which are used to derive a relationship
450 between $D_{app,Cl}$ and the free chloride concentration for various AAS compositions when the
451 extent of slag reaction is 60 %. The values of α and β Freundlich adsorption isotherm
452 parameters obtained by fitting the chloride binding isotherms are only validated for free
453 chloride concentrations up to 0.654 M, which is the limit of the experimental data set used [7].
454 The binding parameter β calculated for all activated slags was greater than 1, which suggests
455 that much of the chloride binding in AAS occurs via chemisorption rather than physical
456 adsorption in the concentration range for which data are available [56,57].

457

458 Table 2: Fitted chloride binding constants (Freundlich isotherm parameters) and the
 459 evaporable water contents (un-bound H₂O) that were used to determine $D_{app,Cl}$ for each space
 460 and time step, for each slag and activators assessed at 60 % extent of slag reaction.

NaOH			Na ₂ SiO ₃			Na ₂ O·2SiO ₂			
<i>A</i>	<i>β</i>	Evaporable water (vol.%)	<i>α</i>	<i>β</i>	Evaporable water (vol.%)	<i>α</i>	<i>β</i>	Evaporable water (vol.%)	
M1	0.29	1.22	36.6	0.85	1.08	32.5	1.32	1.03	30.8
M5	0.27	1.33	35.5	0.67	1.17	32.6	1.05	1.11	31.3
M6	0.46	1.28	36.8	0.46	1.28	36.7	0.46	1.28	36.7
M8	0.56	1.26	35.7	0.44	1.29	36.0	0.45	1.29	35.9
M11	0.40	1.36	36.5	0.48	1.31	35.0	0.48	1.30	35.0
M13	0.42	1.37	35.5	0.49	1.32	34.0	0.49	1.32	34.2
M14	0.41	1.37	35.2	0.51	1.32	33.9	0.47	1.31	34.8

Na ₂ CO ₃			Na ₂ SO ₄			
<i>α</i>	<i>β</i>	Evaporable water (vol.%)	<i>α</i>	<i>β</i>	Evaporable water (vol.%)	
M1	0.25	1.22	29.8	0.85	1.06	26.4
M5	0.36	1.28	30.3	0.61	1.20	26.1
M6	0.46	1.28	38.1	0.46	1.28	26.9
M8	0.46	1.29	37.8	0.45	1.29	26.1
M11	0.51	1.31	37.3	0.51	1.30	26.0
M13	0.52	1.32	36.3	0.43	1.31	26.3
M14	0.53	1.32	36.4	0.36	1.27	27.3

461

462 Figure 6 also compares the influence of using a constant value of $D_{app,Cl}$, calculated based on
 463 the maximum chloride binding capacity of a binder (blue dotted line), and the $D_{app,Cl}$ dependent
 464 on the free chloride concentration, calculated based on the Freundlich adsorption isotherm (red
 465 dashed line). As seen in Figure 6, using a fixed diffusion coefficient and assuming the highest
 466 chloride binding capacity (calculated using the Freundlich adsorption isotherm) to be true for
 467 all concentrations of free chloride and through the entire depth of the concrete cover
 468 overestimates the extent of chloride binding when the free chloride concentration is low, and
 469 also overestimates the time taken for chloride to reach a potentially damaging concentration at
 470 the depth of the first steel reinforcing element.

471 For example, for a cover depth of 20 mm and the chloride ‘threshold’ value of 0.2 wt. % of
472 binder, the influence of chloride binding on the predicted initiation time for a steel-reinforced
473 concrete structure based on Na₂SiO₃-activated M6 can be determined using the model
474 presented here. A previous publication [9] by some of the authors of this study shows that the
475 chloride ‘threshold’ value for steel immersed in simulated pore solutions of AAS is highly
476 dependent on the concentration of sulfide, and additionally, chloride ‘threshold’ values for steel
477 embedded in AAS mortars/concretes are not available in the literature. Therefore, the chloride
478 ‘threshold’ value of 0.2 wt. % of binder assumed in this section is only for demonstrative
479 purposes and does not in any way suggest that the chloride threshold value for AAS concretes
480 is the abovementioned value. This is quite a low value to assume for a chloride threshold in
481 reinforced concrete, which is done solely for purposes of conservatism.

482 In the case of no chloride binding and $D_{app,Cl}$ being set equal to D_{nms} , the initiation time
483 (defined as the time to reach 0.2 wt. % Cl⁻ at a depth of 20 mm) was found to be ~15 years,
484 compared to ~70 years when assuming the maximum binding capacity to hold for the entire
485 depth of the concrete cover and using a fixed diffusion coefficient. However, when $D_{app,Cl}$ was
486 related to the free chloride concentration (according to calculated binding isotherms), the
487 initiation time was ~50 years. Logically, the most appropriate way of determining the ingress
488 of chloride would be to relate the $D_{app,Cl}$ to the free chloride concentration by the use of
489 experimentally observed chloride binding isotherms. Unfortunately, experimental chloride
490 profiles for multi-year exposure of reinforced AAS to chloride under saturated conditions (as
491 required for pure diffusional mass transport) are not available in the open literature, and
492 therefore, the direct validation of the modelling results with experimental data was not possible.

493

494

495 Figure 6: Influence of chloride binding on the chloride ingress profiles calculated for
496 Na_2SiO_3 -activated M6 at (A) 1 year, (B) 5 years, (C) 10 years and (D) 50 years. The solid
497 lines represent the case of no binding, with the apparent diffusion coefficient assumed to be
498 the migration coefficient obtained from NT Build 492 [7]. The red dashed lines represent the
499 case when the apparent diffusion coefficient was calculated using the free chloride
500 concentration (based on the Freundlich adsorption isotherm) at the preceding space step for
501 any given time step. The dotted blue lines represent the scenario when the apparent diffusion
502 coefficient was kept constant and calculated using only the maximum chloride binding
503 capacity of the AAS paste.

504

505

506

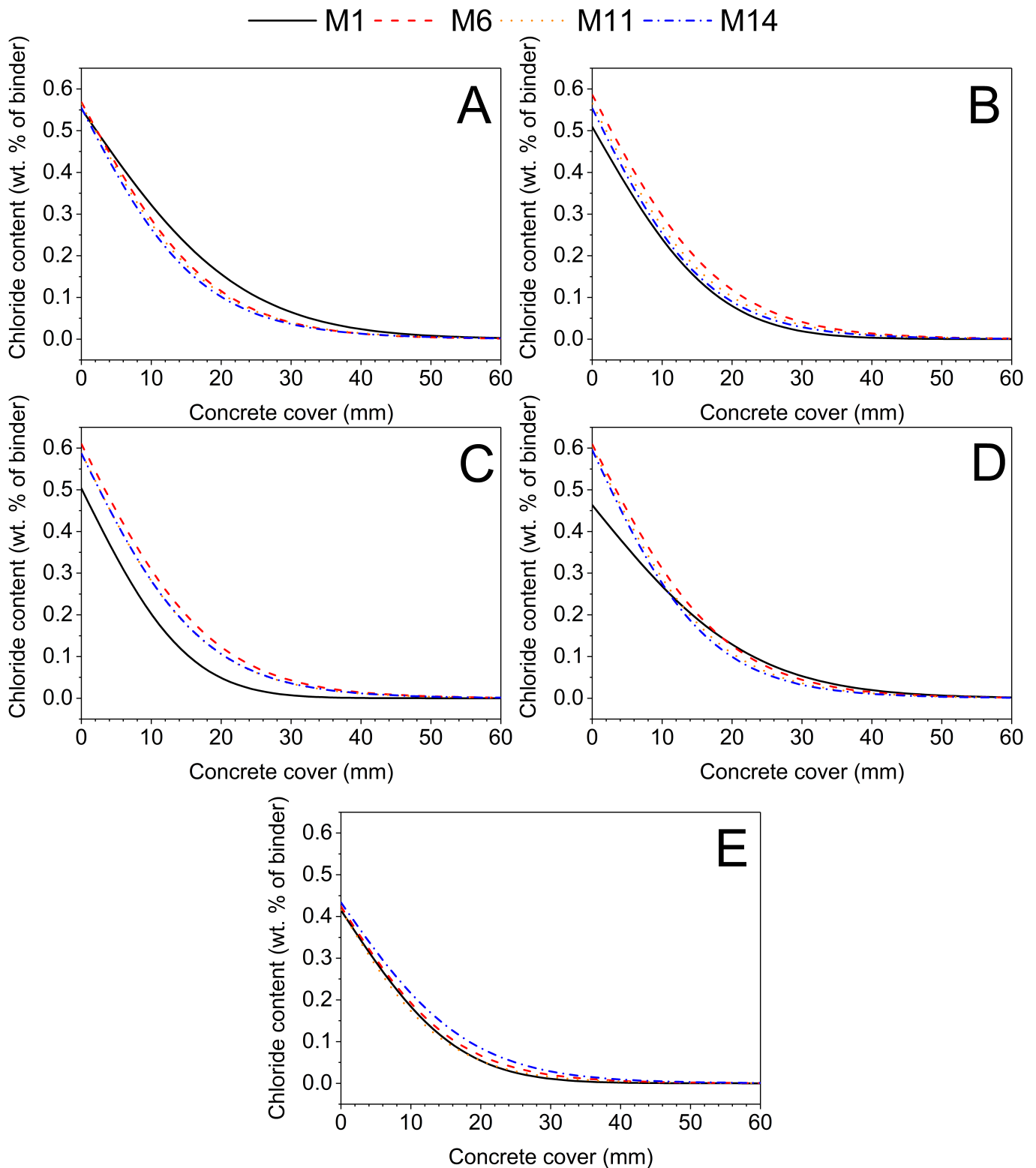
507

508 3.2.2 *Influence of slag composition*

509 Figure 7 shows the influence of the slag composition on chloride ingress after 25 years of
510 exposure to 3.5 wt.% (0.6 M) NaCl solution, calculated for activation of four selected slags by
511 NaOH (Figure 7A), Na₂SiO₃ (Figure 7B), Na₂O·2SiO₂ (Figure 7C), Na₂CO₃ (Figure 7D) and
512 Na₂SO₄ (Figure 7E).

513 In the case of NaOH-activated slags (Figure 7A), an increase in the bulk MgO content of
514 the slag leads to retardation in the chloride ingress, indicating a higher chloride binding
515 capacity for NaOH-activated slags with higher MgO content. In slags with lower MgO content
516 and higher CaO content, as in the case of NaOH-activated M1, the chloride binding capacity
517 of the binder is primarily governed by the amounts of strätlingite and C-(N-)A-S-H gel formed.
518 However, in the case of intermediate and high MgO slags, as in NaOH-activated M6, M11 and
519 M14, the precipitation of greater amounts of hydrotalcite-like Mg-Al-OH LDH (Figure 7A)
520 increases the total chloride binding capacity, thereby retarding the ingress of chloride.

521 According to the quantities of each reaction product (Figure 5A) and the individual binding
522 isotherms of C-(N-)A-S-H gel, hydrotalcite-like Mg-Al-OH LDH phase and strätlingite
523 obtained experimentally by Ke [7], as shown in Figure 2, at relatively high or low
524 concentrations of free chloride, the total binding capacity of the binder would be primarily
525 dominated by the C-(N-)A-S-H gel. However, at intermediate concentrations of free chloride,
526 much of the chloride binding is due to ion-exchange and physical adsorption to Mg-Al-OH
527 LDH and strätlingite (Figure 2). This is true for all of the NaOH-activated slags. For constant
528 exposure to 3.5 wt. % NaCl solution, the calculated near-surface chloride content was found to
529 only marginally change for all NaOH-activated slags shown in Figure 7A. This is primarily
530 due to the similar amounts of evaporable water calculated (as observed in Figure 7A) for each
531 of the binders at 60 % extent of slag reaction.



533 Figure 7: Influence of the slag composition on chloride ingress profiles calculated for (A)
 534 NaOH, (B) Na_2SiO_3 , (C) $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, (D) Na_2CO_3 and (E) Na_2SO_4 activated M1, M6, M11
 535 and M14 at 25 years of exposure to 0.6 M NaCl solution.

536

537 Unlike NaOH-activated slags, in the case of Na_2SiO_3 - and $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ -activated slags (Figure
538 7B and Figure 7C, respectively) chloride ingress was found to be the slowest in the case of slag
539 M1, when compared to M6, M11 and M14. Figure 7B reveals that at high concentrations of
540 free chloride the extent of chloride binding (depending on the slope, $\Delta c/\Delta x$, of the chloride
541 ingress profiles) is slightly higher in the case of Na_2SiO_3 -activated M1 when compared to
542 Na_2SiO_3 -activated M6, M11 and M14, with the inverse being true at intermediate and low
543 concentrations of free chloride. However, the binding capacity was found to be much higher at
544 all concentrations of free chloride in the case of $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ -activated M1 (Figure 7C), when
545 compared to $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ -activated M6, M11 and M14. In both Na_2SiO_3 - and $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ -
546 activated M1, the lower rates of chloride ingress could be attributed to the higher amounts of
547 strätlingite predicted to form (Figure 5B and Figure 5C). Therefore, in slags with low MgO and
548 high Al_2O_3 contents (e.g. slag M1) activated using Na_2SiO_3 and $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$, the extent of
549 chloride binding is strongly influenced by the chloride ion-exchange and chloride adsorption
550 capabilities of the AFm-type phases present. Much of the chloride binding in Na_2SiO_3 and
551 $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ -activated M1 was due to the C-(N-)A-S-H gel and strätlingite, and only a small
552 percentage of the total bound chloride was due to the hydrotalcite-like Mg-Al-OH LDH phase
553 as this was present in only very low quantities in this particular AAS.

554 In the cases of Na_2SiO_3 - and $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ -activated M6, M11 and M14, chloride binding
555 only took place in the C-(N-)A-S-H gel and hydrotalcite-like Mg-Al-OH LDH phase, as
556 strätlingite is not predicted to form. Similar to the observations in Figure 7A, chloride binding
557 was found to be the highest for slags (among M6, M11 and M14) containing higher bulk MgO
558 contents, and consequently these show slower chloride ingress. The surface chloride
559 concentration was found to be much lower for Na_2SiO_3 - and $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ -activated M1, when
560 compared to the Na_2SiO_3 and $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ -activated M6, M11 and M14, primarily due to the
561 lower volume of evaporable water (Figure 5B,C).

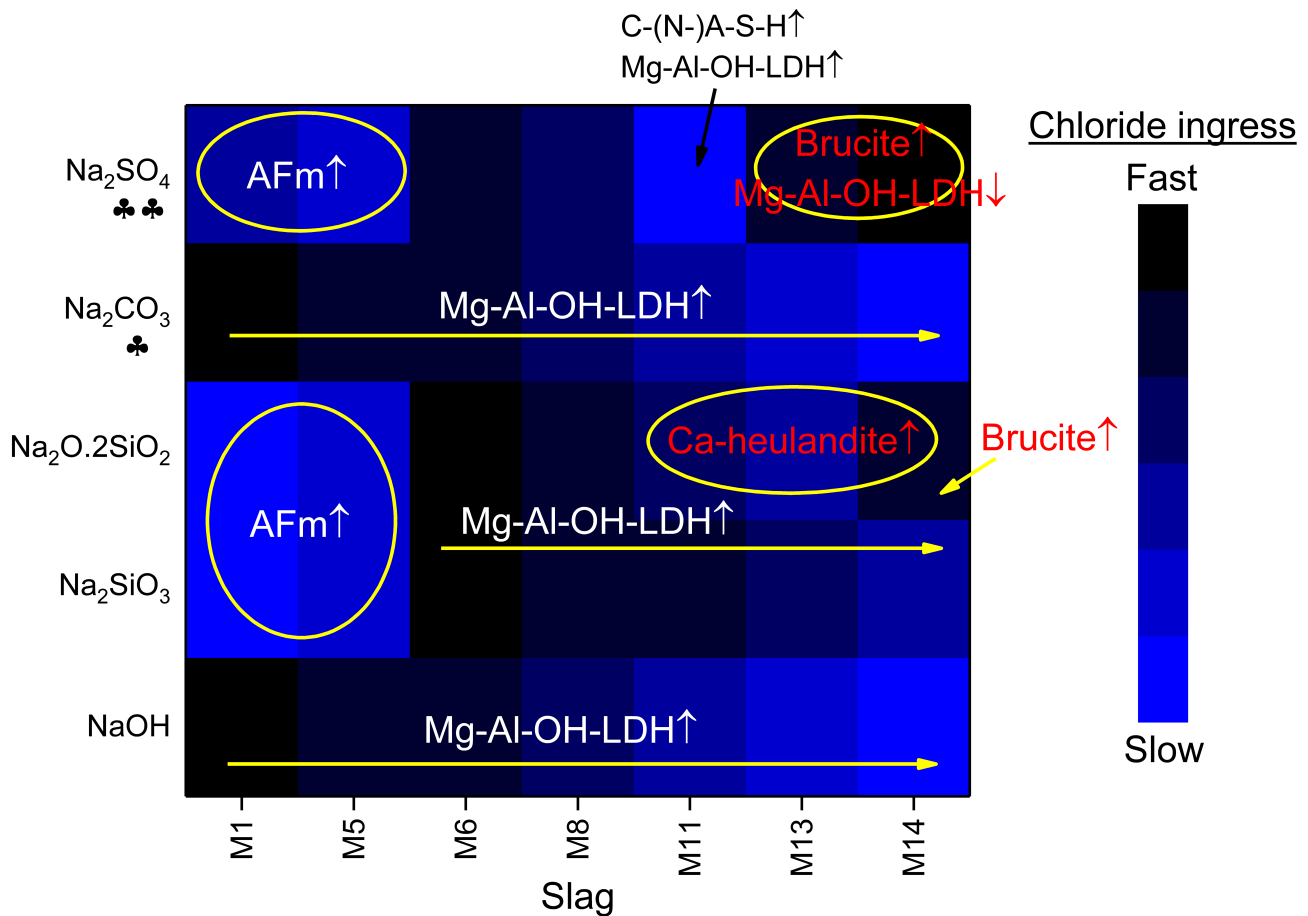
562 In the case of Na_2CO_3 -activated slags (Figure 7D), the extent of chloride binding was
563 proportional to the bulk MgO content in the slag and thus the amount of hydrotalcite-like Mg-
564 Al-OH-LDH phases. Na_2CO_3 -activated M14 exhibited the slowest chloride ingress, followed
565 by Na_2CO_3 -activated M11, Na_2CO_3 -activated M6 and Na_2CO_3 -activated M1. In Na_2CO_3 -
566 activated slags, chloride binding occurs only due to the presence of the C-(N-)A-S-H gel and
567 the hydrotalcite-like Mg-Al-OH LDH phase, as no strätlingite was predicted to be formed
568 (Figure 5D). However, in the cases of Na_2CO_3 -activated M1 and M6, where monocarbonate-
569 AFm forms as a major and minor reaction product (Figure 5D) respectively, the total chloride
570 binding capacity could be underestimated in these calculations because chloride binding by

571 monocarbonate was not considered in the absence of binding isotherm data for the relevant pH
572 range. Ke et al. [58] investigated the chloride binding capacity of Na₂CO₃-activated slags, and
573 observed the transformation of monocarbonate to two polymorphs of Friedel's salt via the
574 partial exchange of interlayer CO₃²⁻ by Cl⁻ in the AFm structure [58–60]. Therefore, chloride
575 binding isotherms for monocarbonate and full characterisation of these anion exchange
576 equilibria (which will also involve competition from hydroxide ions and from various sulfur-
577 containing anions) in simulated pore solutions representative of AAS are required to accurately
578 predict the chloride ingress in these binders. Additionally, in carbonate-bearing pore solutions,
579 the binding capacity of the hydrotalcite-like phase Mg-Al-OH-LDH phase has been observed
580 to be reduced due to the higher affinity of the hydrotalcite-like phase to incorporate divalent
581 ions (CO₃²⁻) instead of monovalent ions [8,61]. Therefore, in Na₂CO₃-activated slags where
582 the pore solution contains CO₃²⁻, the extent of chloride binding due to hydrotalcite-like Mg-Al-
583 OH LDH phase is possibly overestimated in these calculations.

584 For Na₂SO₄-activated slags (Figure 7E), the amount of chloride binding decreases with an
585 increase in bulk MgO content in slag (except for Na₂SO₄-activated M11). Significant amounts
586 of strätlingite are predicted to form in Na₂SO₄-activated M1 (Figure 5E), which might
587 contribute to its higher chloride binding capacity when compared to Na₂SO₄-activated M6 and
588 M14. As mentioned earlier for the case of monocarbonate, the chloride binding capacities of
589 additional phases formed during Na₂SO₄ activation of slags, such as monosulfate and ettringite,
590 have not been considered. The transformation of monosulfate to Friedel's salt in PC based
591 binders is well known [38,39], but chloride binding isotherms in simulated pore solution
592 compositions representative of AAS do not exist in the literature. The ability of ettringite to
593 bind chloride ions has also been debated in the literature [37,39,62]. Therefore, the calculations
594 of the total chloride binding capacity of Na₂SO₄-activated M1 conducted in this study can
595 plausibly be assumed to be underestimated, which means that predictions of the time at which
596 the chloride threshold will be exceeded would be conservative. Na₂SO₄-activated slag M11
597 exhibited the slowest chloride ingress among all the Na₂SO₄-activated slags due to the higher
598 amounts of C-(N-)A-S-H gel and hydrotalcite like Mg-Al-OH-LDH phases formed in these
599 binders in comparison to Na₂SO₄-activated slags M1, M6, and M14, and consequentially
600 leading to a higher chloride binding capacity. Additionally, the lower chloride binding capacity
601 of Na₂SO₄-activated slag M14 is due to the precipitation of brucite, which was not considered
602 to contribute towards chloride binding. The near-surface chloride concentration in the case of
603 Na₂SO₄-activated slags in Figure 7E is much lower than those observed for other activators in
604 Figure 7A-D due to the lower amount of evaporable water within these binders, because of the
605 precipitation of voluminous ettringite in these binders, Figure 5E.

606 Figure 8 ranks the chloride ingress in various AAS binders as a function of slag chemistry
607 for each activator. In the case of NaOH- and Na₂CO₃-activated slags, the rate of chloride ingress
608 is correlated to the MgO content and the amounts of Mg-Al-OH LDH type phases formed.
609 However, in the case of Na₂CO₃-activated slags, it must be noted that the influence of
610 monocarbonate phases and the presence of minor quantities of CO₃²⁻ (aq.) species in the pore
611 solution, have not been considered to influence chloride binding. In the case of Na₂SiO₃- and
612 Na₂O·2SiO₂-activated slags, M1 and M5 slags were found to have the slowest ingress of
613 chloride due to the formation of strätlingite and their chloride binding capability. For slags M6-
614 M14, the rate of chloride ingress is determined primarily by the amounts of Mg-Al-OH LDH
615 phase formed. In Na₂O·2SiO₂-activated M11, M13 and M14 the precipitation of Ca-heulandite
616 and brucite influence the chloride binding capacity of the binder. In Na₂SO₄ activated slags,
617 the chloride binding capacities of monosulfate and ettringite have not been taken into account.
618 The rate of chloride ingress in low MgO containing slags (M1 and M5) is primarily influenced
619 by the presence of AFm, whereas in slags containing intermediate and high MgO (M6-M14),
620 chloride ingress is dependent on the amounts of C-(N-)A-S-H gel and Mg-Al-OH LDH formed.

621 It must be noted that the formation of strätlingite (or similar AFm phases) when low MgO
622 and high Al₂O₃ slags (particularly M1) are activated using Na₂SiO₃, Na₂O·2SiO₂ and Na₂SO₄,
623 as predicted in this study and others [12,13], is not in agreement with the X-ray diffractograms
624 reported elsewhere including [18]. Instead, gismondine has been observed to form in these
625 slags [18] when activated with Na₂SiO₃, and monosulfoaluminate AFm when activated with
626 Na₂SO₄ [36]. This discrepancy can be attributed to the lack of reliable thermodynamic data for
627 gismondine in the thermodynamic database. Therefore, it could possibly be the case that the
628 extent of chloride binding and the ingress of chloride in Na₂SiO₃-, Na₂O·2SiO₂- and Na₂SO₄-
629 activated M1 is overestimated, if these other potential phases have lower chloride binding
630 potential than strätlingite, but there are no available data to enable this to be assessed in detail.



6.

632 Figure 8: A schematic summarising the main parameters that influence chloride ingress in
 633 AAS concretes formulated using a wide range of GGBS and activators. Notes as marked on
 634 the graphic: * In Na_2CO_3 -activated GGBS, the influence of CO_3^{2-} ions in the pore solution
 635 and $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$ on chloride binding is not considered. ** In the case of Na_2SO_4 -activated
 636 GGBS, chloride binding by ettringite or $\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}$ has not been taken into account.

637

638 4 Limitations and further development of the model

639 The model presented here is a significant step forward in linking AAS phase assemblage
 640 evolution and chloride binding to chloride transport. However, its extension is certainly
 641 possible, and several points have been identified where the existing body of data and literature
 642 require further development, to enable enrichment of the model and its use in the accurate
 643 prediction of service life for steel-reinforced structures based on AAS:

- 644 • Most importantly, the value of D_{Cl} in Eq. 7 was assumed to be the same for all AAS
 645 binders, and was based on the D_{nsm} values observed experimentally [7,58]. However,
 646 in principle these values should vary for each of the slags and activators considered in

647 this study. Therefore, more experimental data are required to accurately separate the
648 influence of chloride binding capacity and microstructure (pore structure –
649 connectivity, tortuosity – and ITZ) on the $D_{app,Cl}$ (Eq. 7). Additionally, a better
650 understanding of the influence of aggregates on chloride diffusion in AAS needs to be
651 established and incorporated into the framework.

- 652 • Another major assumption made in this study was the scaling down of the theoretically
653 calculated chloride binding isotherms to match the experimental binding isotherms for
654 a particular AAS. The factor used for scaling down the theoretical chloride binding
655 isotherms was extended to all slags and activators used. Most likely, this would be
656 different for each of the slags, and therefore extensive experimental work needs to be
657 carried out to draw empirical correlations between the activator used, the slag
658 composition and the binding capacity of mortars/concretes based on AAS.
- 659 • Chloride binding isotherms for additional aluminate phases, particularly in the AFm
660 and AFt families, need to be experimentally determined in simulated pore solutions
661 representative of AAS, to ensure that the contributions of all phases identified in AAS
662 towards chloride binding are considered. Extension of the isotherms to higher chloride
663 concentrations would also be desirable.
- 664 • The phase assemblage database created in this study only considered slags with either
665 30 wt. % or 40 wt. % SiO₂, a constant SO₃ content of 2 wt. %, and fixed w/b ratios.
666 However, a larger database for various SiO₂ and SO₃ contents and variable w/b ratio is
667 needed to increase the accuracy in prediction of the chemistry of the binder. All
668 parameters used in this study to quantify chloride binding and ingress relate to the solid
669 and aqueous phase assemblages when the extent of slag reaction is 60 %. The extent of
670 reaction could be extended from low values (representing early age) to 100 %, and its
671 evolution while the concrete is in service integrated into the model.
- 672 • In the case of Na₂CO₃-activated slags, the influence of carbonate ions in the pore
673 solution on the binding capacity of individual hydrate phases needs to be systematically
674 understood.
- 675 • The alkalinity in this study was assumed to be constant with respect to space and time,
676 and therefore the influence of carbonation and leaching were not considered.
677 Experimental data are required to empirically draw a relationship between the chloride
678 binding capacity and a reduction in pH of the pore solution due to carbonation and
679 leaching.

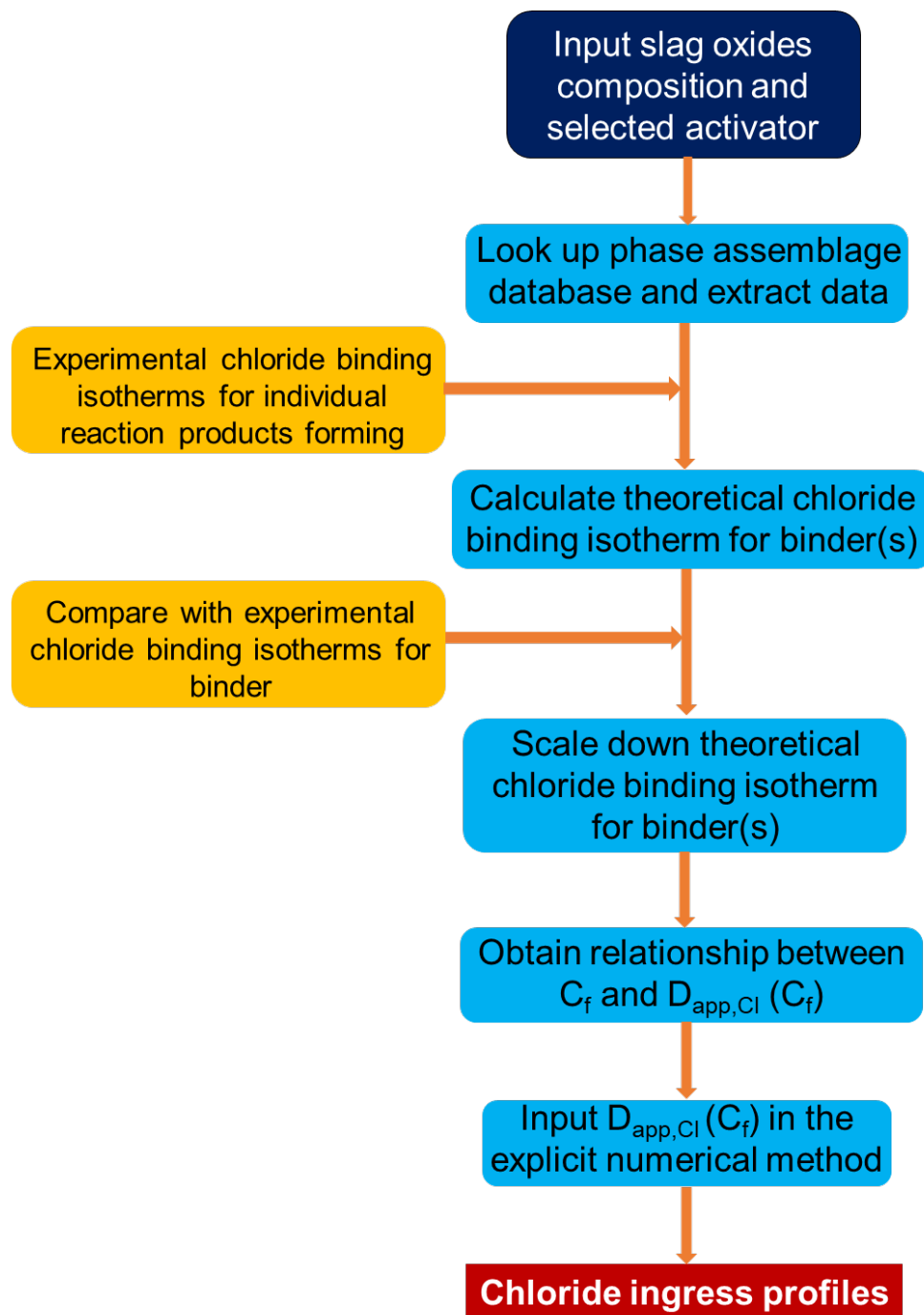
- 680 • The chloride ingress profiles obtained using this modelling framework need to be
681 validated by comparing with field data or laboratory data.

682

683 **5 Conclusions, and further model development and implementation**

684 This study provides the first ever modelling framework allowing the user to input the
685 composition of the slag and the activator of interest to estimate the chemistry of the concrete
686 cover, which can then be used to estimate the total chloride binding capacity of the binder
687 within the concrete, and thus predict the time required for chloride to diffuse to the steel-
688 concrete interface, as shown in Figure 9. This predictive modelling framework negates the need
689 to use a mathematically ‘incorrect’ solution to Fick’s second law, with a varying diffusion
690 coefficient ($D_{app}(t)$) and the empirically derived age exponent. However, it would be necessary
691 to point out that the model in its current state is conservative in nature (and only applicable for
692 submerged structures) and several areas requiring more attention have been identified (Section
693 4) to enable enrichment of the framework.

694



695

696 Figure 9: Schematic of the model developed in this study to calculate the ingress of chloride
 697 in steel-reinforced concrete structures based out of AAS. Additional information regarding
 698 chloride ‘threshold’ value needs to be experimentally determined to enable the modelled
 699 chloride ingress profiles to be used to estimate the service life of steel-reinforced AAS
 700 concretes.

701

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711

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