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A numerical model including thermodynamic equilibrium, kinetic control and surface complexation in order to explain cation type effect on chloride binding capability of concrete

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Abstract

The impact of cation type, sulphate and pH on chloride binding is studied using a numerical model combining thermodynamic equilibrium, kinetics and surface complexation. First, the model is validated by comparing numerical and experimental results obtained on a CEM II concrete material exposed to $NaCl$, KCl , $MgCl_2$ and $CaCl_2$ solutions. Then, the numerical results are discussed to improve our understanding of the differences in chloride binding capability generally observed in the literature. A strong coupling between cation, pH and sulfate affecting chloride binding is highlighted. After six months of exposure, chloride binding due to Kuzel's salt formation has little effect on chloride binding capability whatever the chloride salt solution. The results also confirm the existence of a relationship between pH and chloride binding capability previously observed experimentally in the literature. When some sulfate ions are present in the chloride solution, they reduce

the chloride binding capability because of the sulfate absorption process on C-S-H.

Keywords: Concrete; Chloride binding; Thermodynamic equilibrium; Kinetic control; Surface complexation; Cation type.

1. Introduction

Chloride diffusion is one of the major cause of reinforcement corrosion in concrete exposed to seawater or de-icing salts. Many authors consider that corrosion initiation stage of steel reinforcement in concrete depends on the chloride threshold value which can be expressed in a number of different ways, such as: total chloride content in relation to the weight of cement (or concrete) (1), free chloride contents (2), $[Cl^-]/[OH^-]$ (3; 4). To predict the chloride concentration threshold value in cementitious materials, the performance-based approach Fib model code (5) requires the consideration of the empirical chloride binding isotherm. **In this model, based on the analytical solution of the Fick's second law,** the chloride binding isotherm is therefore one of the most significant input data of the Fib model code.

A survey of the literature reveals that a considerable amount of effort has been devoted in the last decade to the study of chloride binding in cementitious materials. Page et al. (6), for instance, show that the OH^- concentration (or pH) arising from the external environment significantly affects chloride binding. Tritthart (7) and Sandberg et al. (8) both experimentally demonstrate that lower pH values give higher chloride ions binding, which may be accounted for by a competition among OH^- and Cl^- ions for

the sorption sites of hydrated cement (7). Moreover, Roberts (9) and Zhu et al. (10) consider that an increase in pore solution pH enhances the solubility of chloroaluminate salt (Friedel's salt, Kuzel's salt) consequently reducing chloride binding due to chloroaluminate salt formation.

Furthermore, Arya et al. (11), Page et al. (6), Delagrave et al. (12), Zhu et al. (10), DeWeerd et al. (13) and Song et al. (14) experimentally observe that cations associated to chloride salts affect chloride binding capability. These authors note that the maximum chloride binding capability is reached when the cementitious materials are exposed to a $CaCl_2$ solution. In a more detailed manner, Zhu et al. (10) and Song et al. (14) experimentally describe that the binding capability of chloride decreases in the order $Ca^{2+} > Mg^{2+} > Na^+ \approx K^+$ when the cementitious samples are exposed to $CaCl_2$, $MgCl_2$, $NaCl$ and KCl solutions, respectively. Wowra et al. (15) find that the Ca^{2+} cations sorption onto C-S-H surfaces increases the positive charge and in turn the chloride binding in the double electrical layer. Moreover, according to Delagrave et al. (12), the nature of the associated cation significantly affects chloroaluminate solubility and accessibility of chloride ions to sorption sites. On the basis of experimental results, Yuan et al. (16) suggest that, in the presence of Na^+ , cementitious materials have higher pH value than with Ca^{2+} and Mg^{2+} . Zhu et al. (10) demonstrate that Na^+ and K^+ may increase the pH value of pore solutions. These arguments imply that pore solution pH affects chloride binding capability.

However, DeWeerd et al. (13) experimentally prove that the relationship between the decrease in pore solution pH and the increase in chloride binding for exposure solutions like $MgCl_2$ or $CaCl_2$ is not valid when the SO_4^{2-}

ions concentration is significant. Byfors (17) and Wowra et al. (15) have previously shown that an increase in sulfate ion concentration causes a sharp decrease in chloride binding capability. DeWeerd et al. (13) suggest that one reason might be the chloride sorption process onto C-S-H and the chloride binding due to the chloroaluminate salt formation capacity. C-S-H indeed, when exposed to $MgSO_4$ and $MgCl_2$, fixes more SO_4^{2-} ions than Cl^- ions, leading to the decreased chloride sorption onto C-S-H. The SO_4^{2-} ions react with the AFm phase to precipitate ettringite which is more stable than the chloroaluminate salts (Friedel's salt, Kuzel's salt) and as a result chloride binding due to chloroaluminate salt formation decreases.

The experimental studies mentioned above emphasize the coupling effect of three different factors affecting chloride binding capability: cation of chloride salt, solution pH and sulfate concentration. It is, however, interesting to verify and confirm the arguments proposed through a numerical investigation. The numerical study presented in this paper is carried out through the development of a numerical model, its validation through the comparison with the experimental results found in the literature and the analysis of the chloride binding mechanism in a final section.

A number of chloride transport models are found in the literature: some models based on Fick's second law or on the multispecies ionic transport equations (18), (19) and (20), or physically and chemically coupled model (21). These models use global binding isotherms to determine the total chloride amounts as a function of the free chloride amounts. However, isotherms parameters must be calibrated on the basis of experimental data (19).

Numerical models must describe simultaneously chloride sorption and

71 binding due to the chloroaluminate salt formation. Chloride sorption can be
72 described using a surface complexation model considering the surface charge
73 and the double electrical layer. Chloride binding due to the chloroaluminate
74 salt formation is described by chloroaluminate precipitation/dissolution us-
75 ing thermodynamic equilibrium and kinetic control. The aim of this paper
76 is to investigate the factors affecting chloride binding in concretes exposed
77 to chloride and other ions. A reactive transport model including thermody-
78 namic equilibrium, kinetic control and surface complexation modelling that
79 has been previously described for chloride ingress and external sulphate at-
80 tack (22; 23) is used.

81 First, the governing equations used to simulate the reactive transport
82 model in saturated cementitious materials are presented: transport equa-
83 tions, surface complexation describing interaction on mineral surfaces, prin-
84 ciple of thermodynamic equilibrium and kinetic laws. Then, the model input
85 data of the model are discussed: parameters of solid species under kinetic
86 constraints, surface complexation parameters, original mineralogical com-
87 position of hydrated cement, exposure conditions and numerical procedure,
88 sorption reaction in thermodynamic database. Finally, the modelled results
89 are compared with some experimental data from the literature to validate
90 the numerical model.

91 **2. Reactive transport modeling and input data**

92 In this section the reactive transport modeling is exposed on several as-
93 pects, such as reactive transport equations, thermodynamic and complexa-
94 tion formation constants and kinetics of dissolution/precipitation. However,

the description of the model is intentionally reduced since it has been previously published and described in details for chloride transport in concrete (23) and external sulphate attack (22).

2.1. Reactive transport equations

The coupling of chemistry and transport in porous media was used to describe the mineral phases evolution in time and space. Toughreact, which is based on integral finite differences method, has been developed for this purpose by solving chemically reactive nonisothermal flows of multiphase fluids in porous media (24). A sequential iterative operator-splitting method is operated to solve the system.

In saturated condition without convection phenomena the main mechanism considered is diffusion which is coupled to chemistry according to the following equation:

$$\frac{\partial \phi C_j}{\partial t} = D_e \nabla (\nabla C_j) + q_j \quad (1)$$

where D_e is the effective diffusion coefficient of species j ($m^2.s^{-1}$) which value is the same for all species, ϕ the porosity and C_j the molar concentration of free species j in a pore solution ($mol.m^{-3}$ of solution). q_j is a source or sink term ($mol.m^{-3}.s^{-1}$) that denotes the removing or releasing species j and that is evaluated by chemical calculations. In this study, q_j combines sorption onto C-S-H surface (see paragraph 2.4), mineral dissolution/precipitation as explained in paragraphs 2.2 and 2.3 and aqueous complexation in solution.

Porosity can evolve with time by actualizing volume of each mineral species (25) that can precipitate or dissolve. Effective diffusion coefficient

can also evolve, as follows:

$$D_e^{n+1} = \frac{\phi^{n+1}}{\phi^n} D_e^n$$

115 where n labels the number of the time step.

116 2.2. Thermodynamic formation constants

117 The thermodynamic formation constants of species are taken from CEM-
118 DATA07 and Nagra/PSI TDB thermodynamic databases (26). The ther-
119 modynamic data are exposed in Table 1. C-S-H is supposed to be a mix
120 of tobermorite ($CaO/SiO_2 = 0.83$) and jennite ($CaO/SiO_2 = 1.67$). The
121 Helgeson-Kirham-Flowers (HKF) model (27) is used since it gives accurate
122 activity coefficient with dominance of $NaCl$ in the solution and when the
123 true ionic strength of the solution is close to 1 (24), as in this study.

124 At equilibrium, the activity product, Q_i , of the mineral species i must be
125 equal to its equilibrium constant, K_i . Q_i writes as follows:

$$Q_i = \prod_{j=1}^N (\gamma_j C_j)^{\nu_j} \quad (2)$$

126 where γ , C , ν and N are the activity coefficient, the concentration, the
127 stoichiometric coefficient and the number of the ionic species in the reaction,
128 respectively.

129 2.3. Mineral dissolution and precipitation kinetics

130 Several studies have shown that a pure thermodynamic approach does
131 not seem to be adapted for concrete exposed for several months (22; 23;
132 28; 29; 30). Moreover, for C-S-H the reactions can be very slow and even
133 irreversible.

Table 1: Equilibrium constants of mineral dissolution/precipitation reactions at 25°C

Phase reaction	$\log K_{T_0}$
Jennite+2.33 H^+ = 1.67 Ca^{2+} + $HSiO_3^-$ + 2.76 H_2O	-19.53
Tobermorite+0.66 H^+ = 0.83 Ca^{2+} + $HSiO_3^-$ + 1.16 H_2O	-0.63
Portlandite+2 H^+ = Ca^{2+} + 2 H_2O	-22.76
Monosulfoaluminate+12 H^+ = 4 Ca^{2+} + 2 Al^{3+} + SO_4^{2-} + 18 H_2O	-72.44
Ettringite+12 H^+ = 6 Ca^{2+} + 2 Al^{3+} + 3 SO_4^{2-} + 38 H_2O	-56.67
Hydrotalcite+14 H^+ = 4 Mg^{2+} + 2 Al^{3+} + 17 H_2O	-74.68
Kuzel's salts+12 H^+ = 4 Ca^{2+} + 2 Al^{3+} + 0.5 SO_4^{2-} + Cl^- + 18 H_2O	-73.24
Brucite+2 H^+ = Mg^{2+} + 2 H_2O	17.11
Chrysotile+4 H^+ = 3 Mg^{2+} + 2 $HSiO_3^-$ + 3 H_2O	-13.29
Sepiolite+2 H^+ = 4 Mg^{2+} + 6 $HSiO_3^-$ + 5 H_2O	-29.01

134 In this study, the expression of the kinetic law given by Lasaga et al. is
135 used (31):

$$r_i = \pm k_i A_{ms,i} \left| 1 - \left(\frac{Q_i}{K_i} \right) \right| \quad i = 1, \dots, N_q \quad (3)$$

136 where r indicates dissolution or precipitation (for positive and negative val-
137 ues, respectively), k is the rate constant ($mol.m^{-2}.s^{-1}$). A_{ms} is the specific
138 reactive surface area ($m^2.g^{-1}$). More details can be found in Xu et al. and
139 Steefel et al. (24; 25).

140 Table 2 exposes the kinetic parameters for each mineral species. Data are
141 taken from Baur et al. for Monosulfoaluminate, ettringite and C-S-H (32),
142 from Gali et al. for portlandite (33), from Tambach et al. for hydrotalcite
143 (34) and from Palandri and Kharaka for brucite, gibbsite and chrysotile (35).
144 Kuzel's salt is assumed to react instantaneously because of missing data. **It is**
145 **to note that the simulations are performed on concretes exposed to**
146 **chlorides during several months that is to say for short exposition**

time compared to concrete service life. The kinetics approach is of interest to know which mineral species is susceptible to precipitate during this transient problem. The precipitation of Kuzel's salt is observed (by the model thanks to the kinetics approach) first and at low chloride concentration, while Friedel's salt is observed later and for greater concentration (36).

Table 2: Parameters describing the kinetics of mineral reactions at 25°C where k is the dissolution rate constant ($\text{mol.m}^{-2}.\text{s}^{-1}$) and A_{ms} the mineral specific reactive surface area ($\text{m}^2.\text{g}^{-1}$). Precipitation mechanism and associated constants are assumed to be similar to dissolution

Minerals	A_{ms}	k	Ref
Jennite	41.0	2.75×10^{-12}	(32)
Tobermorite	41.0	2.75×10^{-12}	(32)
Ettringite	9.8	7.08×10^{-13}	(32)
Monosulfoaluminate	5.7	6.76×10^{-12}	(32)
Portlandite	16.5	2.24×10^{-8}	(33)
Hydrotalcite	9.8	1.00×10^{-09}	(34)
Kuzel's salt		<i>Instantaneous</i>	
Gibbsite	9.8×10^{-4}	3.16×10^{-12}	(35)
Brucite	9.8×10^{-4}	5.75×10^{-9}	(35)
Chrysotile	9.8×10^{-4}	10.0×10^{-12}	(35)
Sepiolite		<i>Instantaneous</i>	

2.4. Surface complexation formation constants

In cementitious materials, physical and chemical reactions between aqueous species and specific surface sites of mineral species can occur. These reactions mostly take place onto C-S-H (37; 38; 39). When the cementitious materials are exposed to boundary solutions, anions and cations move

158 through the material and reactions between the ions and the surface site of
 159 C-S-H (silanol $\equiv SiOH$) appears (40). A well-known model which is used in
 160 this study is the double diffuse layer model (see (41) for a complete descrip-
 161 tion).

Adsorption of X ions (Ca^{2+} , Na^+ , K^+ , Cl^- and SO_4^{2-} in the present study) onto the C-S-H surface can be described by the following mass action law:

$$K_{eq} = \frac{[\equiv SiOHX]}{[\equiv SiOH] \{X\}} \exp\left(\frac{-F\psi_0}{RT}\right) \quad (4)$$

162 where K_{eq} is the equilibrium constant. $\{X\}$ is the activity of X ions. ψ_0 is
 163 the potential at the surface (V). R is the molar constant ($8.354 J.mol^{-1}.K^{-1}$)
 164 and T is the absolute temperature (K).

165 The sorption of Ca^{2+} , Na^+ , K^+ , Cl^- and SO_4^{2-} ions on the C-S-H surface
 166 layer have been integrated in the database. They can be represented by
 167 sorption reactions (see Table 3). The equilibrium constants are taken from
 168 (40) for Na^+ , K^+ , Cl^- and Ca^{2+} . That of SO_4^{2-} is supposed to be equal to
 169 8.5. The equilibrium constants for Na^+ and K^+ are supposed to depend on
 170 C/S ratio of C-S-H whereas those for Ca^{2+} and Cl^- are not. Furthermore,
 171 the value of the specific surface site of C-S-H is supposed to be equal to 500
 172 $m^2.g^{-1}$ as suggested by Viallis et al. after calibration (37).

173 **3. Concrete properties**

174 The studied CEMII concrete is taken from the literature (14). The ce-
 175 ment composition and the concrete mix-design are given in Tables 4 and 5,
 176 respectively. After a 90-day curing period in saturated limewater at $20 \pm 1^\circ C$,

Table 3: Equilibrium constants of the surface complexation model.

Equation	$\log K_{T_0}$	Ref
$\equiv SiOH \leftrightarrow \equiv SiO^- + H^+$	-12.7	(40)
or $\equiv SiOH + OH^- \leftrightarrow \equiv SiO^- + H_2O$		
$\equiv SiOH + Ca^{2+} \leftrightarrow \equiv SiOCa^+ + H^+$	-9.4	(40)
$\equiv SiOH + Cl^- \leftrightarrow \equiv SiOHCl^-$	-0.35	(40)
$\equiv SiOH + Ca^{2+} + Cl^- \leftrightarrow \equiv SiOCaCl + H^+$	-9.8	^{a,b}
$\equiv SiOH + Ca^{2+} + SO_4^{2-} \leftrightarrow \equiv SiOCaSO_4^- + H^+$	-8.5	^{a,b}
$\equiv SiOH_{jennite} + Na^+ \leftrightarrow \equiv SiONa_{jennite} + H^+$	-13.745	(40)
$\equiv SiOH_{jennite} + K^+ \leftrightarrow \equiv SiOK_{jennite} + H^+$	-13.745	(40)
$\equiv SiOH_{tobermorite} + Na^+ \leftrightarrow \equiv SiONa_{tobermorite} + H^+$	-12.656	(40)
$\equiv SiOH_{tobermorite} + K^+ \leftrightarrow \equiv SiOK_{tobermorite} + H^+$	-12.656	(40)
Specific surface site of C-S-H $A_{cs} = 500 \text{ m}^2.g^{-1}$ (37)		
Sorption density of C-S-H $\Gamma_{C-S-H} = 8 \times 10^{-6} \text{ mol.m}^{-2}$ (42), (43)		
^a : Reaction on the C-S-H surface taken from (44)		
^b : Value of $\log K_{T_0}$ considered in the study		

177 some $\varnothing 100mm \times 50mm$ specimens were drilled out. The side and bottom
178 surfaces of the cylinder specimens were sealed with epoxy resin. An immer-
179 sion test was conducted to determine the penetration depth of chloride and
180 the chloride binding isotherms in saturated conditions at 20°C under labora-
181 tory conditions. The concrete properties and experimental data are detailed
182 in Song et al. (14).

Table 4: Chemical composition of cement, expressed as a percentage (%) (14).

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
Content	21.70	5.09	4.32	64.64	0.92	1.08	0.21	0.53

Table 5: Concrete mix-design ($kg.m^{-3}$) (14).

Cement	Water	Sand	Gravel	w/c
312	156	746	1118	0.5

183 The concrete is supposed to be completely hydrated. Its mineral com-
184 position is calculated using the the GEMS-software and CEMDATA07 and
185 Nagra/PSI TDB thermodynamic databases (26). The mineralogical compo-
186 sition is given in Table 6.

Table 6: Mineralogical content ($mol.dm^{-3}$ of concrete)

Minerals	Content
Jennite	0.9882
Tobermorite	0.1384
Ettringite	—
Monosulfoaluminate	0.0421
Portlandite	1.6011
Hydrotalcite	0.0178

187 Assuming that alkalis Na and K are fully dissolved as suggested by
188 Trotignon et al. (45), the initial chemical composition of the pore solution is
189 calculated using the Toughreact software (24) (Table 7).

Table 7: Initial composition of the pore solution in CEMII concrete ($mol.kg^{-1}$) calculated using Toughreact at 20°C.

	Concentration [mol/kg of pore solution]
Na^+	0.1366
K^+	0.2271
Ca^{2+}	0.2979×10^{-2}
Mg^{2+}	0.4057×10^{-10}
Al^{3+}	0.2348×10^{-3}
$HSiO_3^-$	0.1592×10^{-5}
SO_4^{2-}	0.2007×10^{-4}
pH	13.53

190 4. Results

191 4.1. Case study description

192 CEMII concrete is exposed to four different boundary solutions: 0.5
193 $mol.L^{-1}$ $NaCl$ solution, 0.5 $mol.L^{-1}$ KCl solution, 0.25 $mol.L^{-1}$ $MgCl_2$
194 solution and 0.25 $mol.L^{-1}$ $CaCl_2$ solution. In order to investigate the im-
195 pact of sulfate ions on chloride binding capability, solutions of 0.25 $mol.L^{-1}$
196 $MgCl_2 + 0.0276 mol.L^{-1}$ of $MgSO_4$ (SO_4^{2-} concentration in seawater) and
197 of 0.25 $mol.L^{-1}$ $MgCl_2 + 0.276 mol.L^{-1}$ of $MgSO_4$, respectively, are simu-
198 lated.

199 4.2. Numerical procedure

200 Only saturated concrete is considered during the simulations. Because
201 the numerical results are compared with experimental data obtained from
202 $\varnothing 100mm \times 50mm$ cylindrical specimens, one-dimensional calculations are
203 carried out. Indeed, during the immersion test, the side and bottom sur-
204 faces of the cylinder specimens are sealed with epoxy resin to ensure a one-
205 dimensional flow inside the cylinders as the top surface is exposed to the so-
206 lutions for six months. A simple regular mesh composed of one 1000-element
207 row is used, which represents 100 mm of the specimens. The reactive trans-
208 port code Toughreact (24) is used.

209 In the model proposed here, the only input data used to obtain chloride
210 binding isotherms are the chemical composition of cement and the concrete
211 mix-design. Porosity and effective diffusion data are additionally necessary
212 coefficient when the ion profiles as a function of depth and time are required
213 (22; 30; 23).

214 4.3. Chloride binding isotherms

215 Figures 1a,b,c and d display the chloride binding isotherms of concrete
216 after a 6-month exposure to 0.5 mol.L^{-1} of $NaCl$, 0.25 mol.L^{-1} of $CaCl_2$,
217 0.5 mol.L^{-1} of KCl and 0.25 mol.L^{-1} of $MgCl_2$ solutions, respectively. The
218 numerical chloride binding isotherms obtained are compared with the exper-
219 imental data previously found in the literature (14).

220 The equilibrium computation gives a pH of 8.1 for all the chloride so-
221 lutions. Further details on the pH calculation are given in (46). The fact
222 that the experimental chloride binding isotherms for each exposed solution
223 are successfully reproduced by the model confirms that the chloride binding

224 capability depends on the boundary solution type. The amount of bound
 225 chloride ions in concrete exposed to $NaCl$ and KCl solutions are equivalent.
 226 They are larger for concrete exposed to $CaCl_2$ and $MgCl_2$ solutions. The
 227 chloride binding capability as a function of the boundary solution type de-
 228 creases in the order: $Ca^{2+} > Mg^{2+} > Na^+ \approx K^+$. This result confirms the
 229 findings of Arya et al. (11), Page et al. (6), Delagrave et al. (12), Zhu et al.
 230 (10), DeWeerd et al. (13).

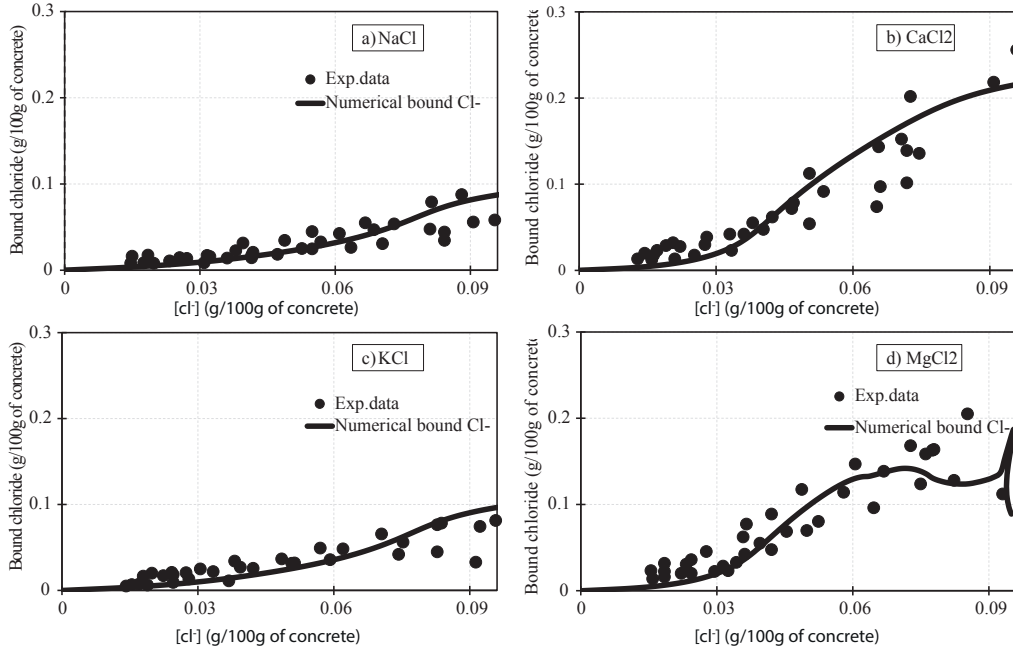


Figure 1: Chloride binding isotherm of CEM II concrete after 3 months of exposure to a) $0.5 \text{ mol.L}^{-1} NaCl$ solution, b) $0.25 \text{ mol.L}^{-1} CaCl_2$ solution, c) $0.5 \text{ mol.L}^{-1} KCl$ solution and d) $0.5 \text{ mol.L}^{-1} MgCl_2$ solution at 20°C (experimental data taken from the literature (14)).

231 5. Discussion

232 As discussed above, the model proposed in this paper can compute chlo-
233 ride absorption on C-S-H, chloride binding due to Kuzel's salt formation and
234 pH evolution. The following section provides some interpretive elements for
235 a better understanding of the evolution of chloride binding capability as a
236 function of boundary solution type. First, the chloride bound amount due
237 to Kuzel's salts precipitation and to surface complexation on C-S-H is high-
238 lighted. Then, the influence of cations associated with chloride from surface
239 complexation on C-S-H and its consequence in terms of pH is discussed. fi-
240 nally, additionally focus is made on magnesium and sulfate ions and their
241 effect on chloride binding capability.

242 5.1. Kuzel's salt formation and surface complexation on C-S-H

243 Chloride ions can be adsorbed and absorbed on C-S-H. The
244 adsorption on C-S-H are supposed to happen on two C-S-H sites
245 in the proposed model: $\equiv SiOH$ and $\equiv SiOCa^+$. Chloride ions
246 can also react with monosulfoaluminate to form Kuzel's salts. The
247 numerica results of sorption of chloride ions is shown on Figures
248 2a, b, c, d for concrete specimens exposed to $NaCl$, $CaCl_2$, KCl and
249 $MgCl_2$ solutions during six months, respectively.

250 The results show that the chloride quantity which reacts with
251 C-S-H is always greater than the quantity which reacts to form
252 Kuzel's salts. They also show that Kuzel's salts quantity is the
253 same whatever the boundary solution type, except for the high-
254 est chloride concentration when concrete is exposed to a $MgCl_2$

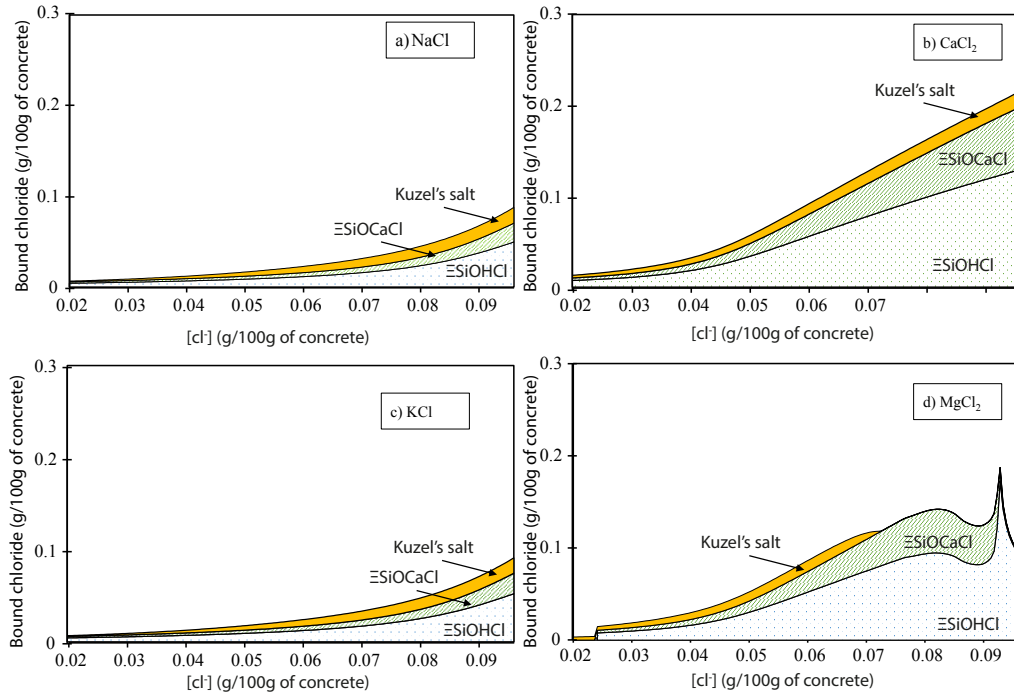


Figure 2: Chloride binding isotherm for CEM II concrete after a 6-month exposure to chloride sorption on C-S-H surface and chloride binding for a) $0.5 \text{ mol.L}^{-1} \text{ NaCl}$, b) $0.25 \text{ mol.L}^{-1} \text{ CaCl}_2$, c) $0.5 \text{ mol.L}^{-1} \text{ KCl}$ and d) $0.5 \text{ mol.L}^{-1} \text{ MgCl}_2$ solutions at 20°C , respectively. Contribution of Kuzel's salt formation and chloride sorption on C-S-H sites ($\equiv \text{SiOHCl}^-$, $\equiv \text{SiOCaCl}$)

255 **solution. This latter case is discussed in Section 5.3.**

256 5.2. Role of cation associated with chloride and pH

257 According to the chemical equations presented in Table 3, the reactions of
258 the chloride ions bound on C-S-H to form $\equiv SiOHCaCl$ or $\equiv SiOHCl-$ are
259 related directly or indirectly to pH. In the first case, the fixation of Cl^- and
260 Ca^{2+} releases H^+ . In the second case, Cl^- , Ca^{2+} and OH^- are competing
261 in order to react with $\equiv SiOH$. The reactions with Ca^{2+} and OH^- release
262 H^+ .

263 Figures 3a, b, c, d show Na^+ , K^+ , Ca^{2+} concentration and pH profiles
264 as a function of the free chloride concentration after a 6-month exposure,
265 respectively. As expected, Na^+ , K^+ and Ca^{2+} have the highest concentra-
266 tions within the concrete pore solutions exposed to $NaCl$, KCl and $CaCl_2$,
267 respectively. Regarding the other ions that are not present in the boundary
268 solutions, the profiles are equivalent whatever the exposed solution, except
269 Ca^{2+} in the concrete specimens exposed to the $MgCl_2$ solution (cf. Figure
270 3c). The role of $MgCl_2$ is discussed in Section 5.3.

271 These results reveal that the boundary solution types causing a large
272 amount of Ca^{2+} in the concrete pore solutions ($CaCl_2$ and $MgCl_2$) also lead
273 to a greater amount of bound chloride on C-S-H through the formation of
274 $\equiv SiOCaCl$ (cf. Figures 3c and 2). According to Le Chatelier's principle, a
275 higher Ca^{2+} amount increases the number of $\equiv SiOCa^+$ and, consequently,
276 leads to an increased positive and to a higher chloride ion amount bound on
277 this surface charge. This is consistent with Wowra et al.'s proposal (15).

278 Figure 3d shows that the pore solution pH of the concrete specimens
279 exposed to $CaCl_2$ and $MgCl_2$ solutions is lower than in the $NaCl$ and KCl

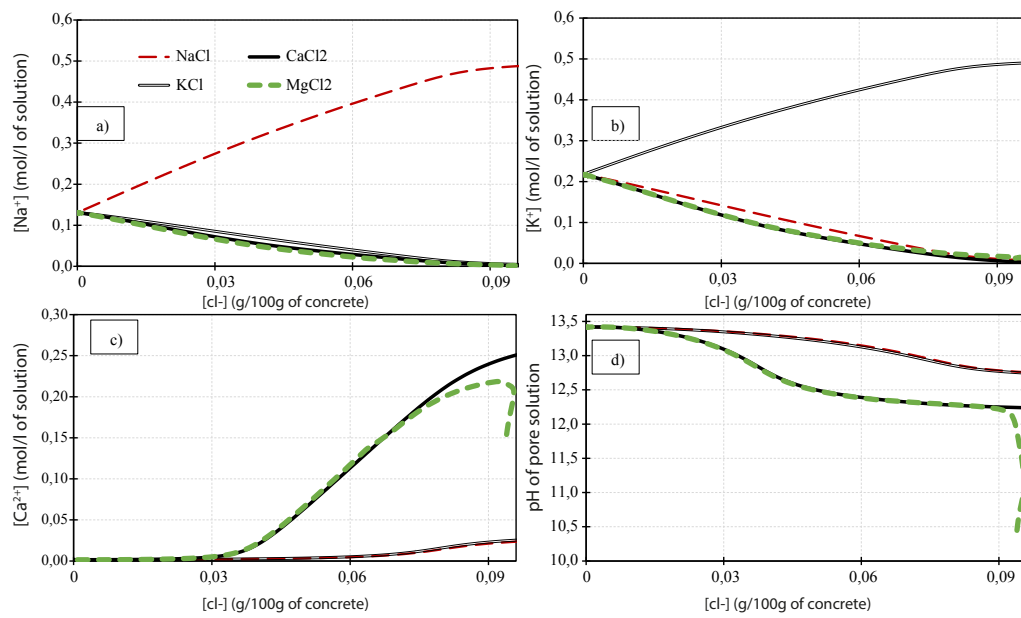


Figure 3: Concentration profile of CEM II concrete after six months of exposure to $NaCl$, $CaCl_2$, KCl and $MgCl_2$ solution at $20^\circ C$ respectively: a) Na^+ , b) K^+ , c) Ca^{2+} and d) pH.

280 solutions. This observation implies that the amount of chloride ion reacting
 281 with C-S-H to form $\equiv SiOHCl^-$ is larger for $CaCl_2$ and $MgCl_2$ solutions
 282 than for $NaCl$ and KCl solutions (cf. Figure 2). This proves that the pH-
 283 chloride binding capability relationship experimentally observed in (7; 8) is
 284 verified by the model. Indeed, the higher the OH^- concentration (higher
 285 pH) in pore solution is, the larger the number of $\equiv SiOH$ transformed into
 286 $\equiv SiO^-$ according to Le Chatelier's principle. Then, the amount of $\equiv SiOH$
 287 decreases and chloride binding capability on C-S-H decreases. This confirms
 288 OH^- and Cl^- competing for sorption on C-S-H.

289 In conclusion, the pore solution pH value directly affects chloride binding
 290 capability. It depends on the solid/pore solution equilibrium like portlandite
 291 dissolution/precipitation and Na^+ and K^+ concentrations. In all the cases
 292 studied, the Portlandite dissolution is numerically observed (cf. Figure 4).
 293 This is less pronounced for concrete exposed to the $CaCl_2$ solution because
 294 of higher Ca^{2+} concentrations. Nevertheless, the pH value is smaller. It
 295 may seem paradoxical considering the fact that the stronger the Portlandite
 296 dissolution, the higher the pH, but, because Na^+ and K^+ are stronger bases
 297 in the acid-base theory than Ca^{2+} and Mg^{2+} , the pore solution pH of the
 298 concrete exposed to $NaCl$ and KCl solutions is higher than with the $CaCl_2$
 299 and $MgCl_2$ solutions.

300 5.3. Role of magnesium

301 Figure 1 shows that the chloride binding isotherm with the $MgCl_2$ solu-
 302 tion behaves differently from the other solutions. With the $MgCl_2$ solution, a
 303 peak correspond with chloride binding capability appears for a chloride con-
 304 centration slightly lower than the maximal value, i.e. within the concrete. In

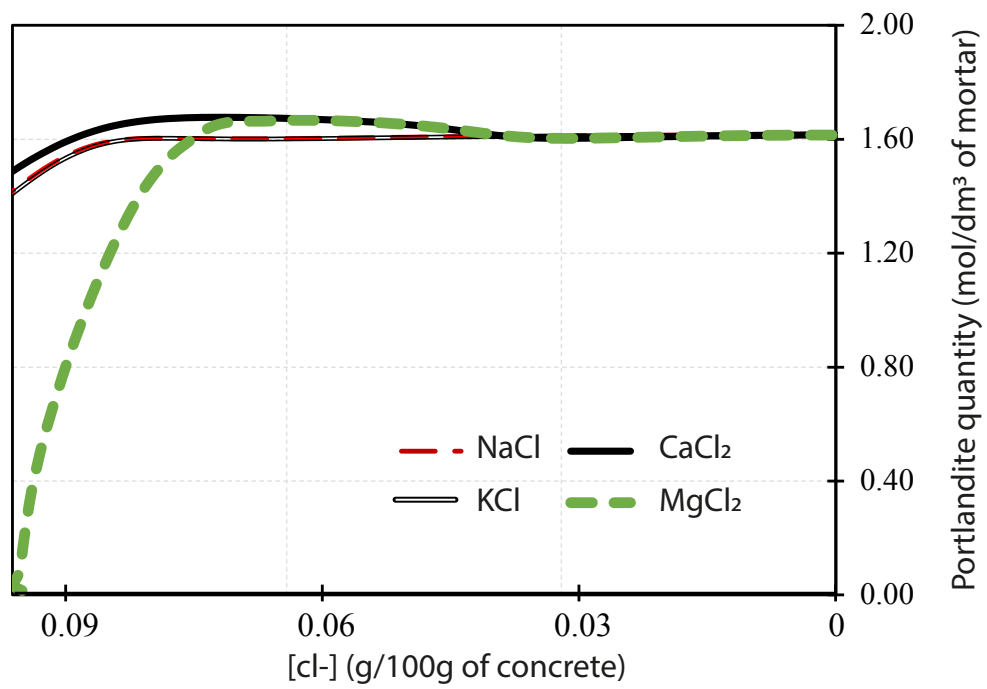


Figure 4: Portlandite amount as a function of depth for concrete specimens exposed to $NaCl$, KCl , $CaCl_2$ and $MgCl_2$ solutions after a 6-month exposure, respectively.

305 the meantime, the chloride binding capability is maximum on the concrete
306 surface exposed to $NaCl$, KCl and $CaCl_2$ solutions.

307 The previous section demonstrates the relationship between chloride bind-
308 ing capability and Ca^{2+} concentration and pH value, whereas Figure 2c shows
309 that the Ca^{2+} concentration in concrete decreases gradually from the exposed
310 surface towards the interior after a 6-month exposure. Moreover, the pore
311 solution pH on the surface with $MgCl_2$ exposure is the lowest of the four
312 solutions (cf. Figure 2d). An increased Mg^{2+} concentration in the exposed
313 solution indeed disturbs portlandite equilibrium and leads to the precipita-
314 tion of brucite (cf. Figure 5). C-S-H (jennite and tobermorite) is also dis-
315 solved and release $HSiO_3^-$, which reacts with Mg^{2+} to precipitate chrysotile.
316 The numerical observation of brucite and M-S-H (chrysotile) formation is
317 experimentally verified (47; 48; 49). C-S-H and portlandite dissolution also
318 release a large amount of Ca^{2+} into the pore solutions. The complete disso-
319 lution of Portlandite strongly affects the pH buffering system. Consequently,
320 with such low pH close to the exposed surface, chloride binding capability
321 increases. However, the C-S-H dissolution causes a decrease in the number
322 of surface charges $\equiv SiOHCl^-$, which reduces the ions binding capability of
323 C-S-H on the exposed surfaces.

324 Furthermore, Mg^{2+} , which progresses within the concrete reacts with
325 Al^{+3} coming from the monosulfoaluminate dissolution and precipitates hy-
326 drotalcite. As a result, the Al^{+3} concentration is no longer sufficient to
327 precipitate Kuzel's salt despite the high chloride concentration or ettringite
328 found just below the exposed surface. After a period of increase in the hy-
329 drotalcite amount, a small amount of ettringite and Kuzel's salt appears (cf.

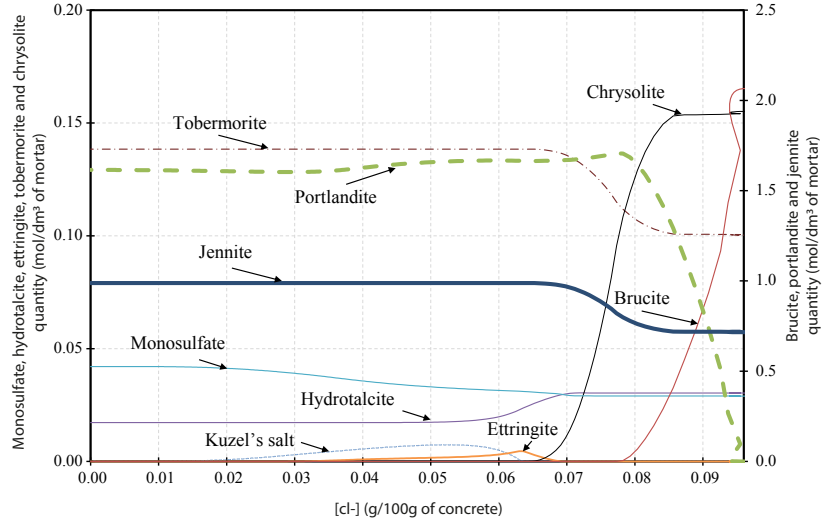


Figure 5: Mineral amount of CEM II concrete after six months of exposure in $MgCl_2$ solution at 20°C.

Figure 5). Hydrotalcite, ettringite and Kuzel's salt precipitation may be in competition with each other with high magnesium concentration.

For concrete specimens exposed to a $MgCl_2$ solution, Ca^{2+} leaching reduces the pH value and, in turn, chloride binding on $\equiv SiOH$ increases. This can be considered the most significant impact of the Mg^{2+} cation on chloride binding capability.

5.4. Role of sulfate

Figure 6 displays the comparison between the chloride binding isotherms within concrete specimens exposed to 0.5 M of $MgCl_2$ solutions containing 0, 0.0276 M of $MgSO_4$ and 0.2760 M of $MgSO_4$, respectively. The chloride binding capability is different depending on the concentration in the solution. In other words, the numerical results show that the higher SO_4^{-2} the

342 concentration, the weaker the chloride binding capability.

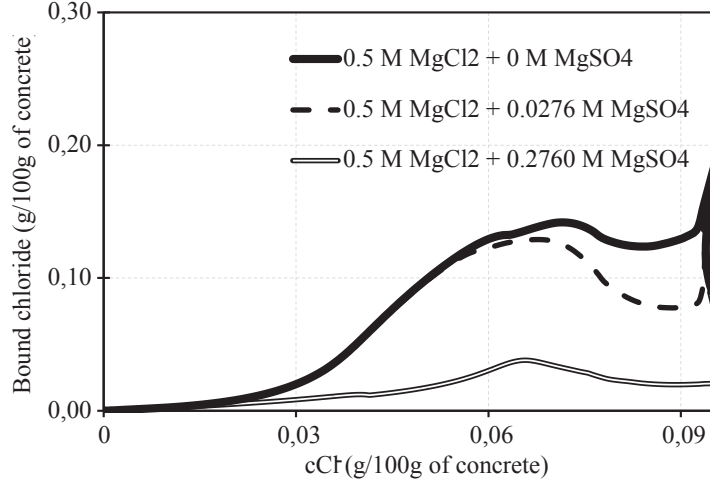


Figure 6: Chloride binding capability after six months of exposure in 0.5 M $MgCl_2$, 0.5 M $MgCl_2$ + 0.0276 M $MgSO_4$ and 0.5 M $MgCl_2$ + 0.2760 M $MgSO_4$ solution at 20°C, respectively.

343 This can be explained by the fact that the higher the $MgSO_4$ amount,
 344 the lower the pH value (cf. Figure 7a). A comparison between the results ob-
 345 tained with concrete specimens exposed to $MgCl_2$ solutions without $MgSO_4$
 346 and with 0.276 M of $MgSO_4$ shows this clearly. Another explanation is the
 347 number of chloride ions that can be adsorbed on C-S-H, which decreases
 348 as the amount of $MgSO_4$ increases, under all surface charge conditions:
 349 $\equiv SiOHCl^-$ or $\equiv SiOCaCl$ (cf. Figures 7b and c). The same tendency
 350 is also observed as regards Kuzel's salt formation (cf. Figure 7d).

351 However, Figure 8 shows that a large amount of sulfate is absorbed on the
 352 surface charge $\equiv SiOH$. Thus, a more negative surface charge $\equiv SiOCaSO_4^-$
 353 for the 0.5 M $MgCl_2$ + 0.2760 M $MgSO_4$ solution is released than the 0.5
 354 M $MgCl_2$ solution and the 0.5 M $MgCl_2$ + 0.0276 M $MgSO_4$ solution. In

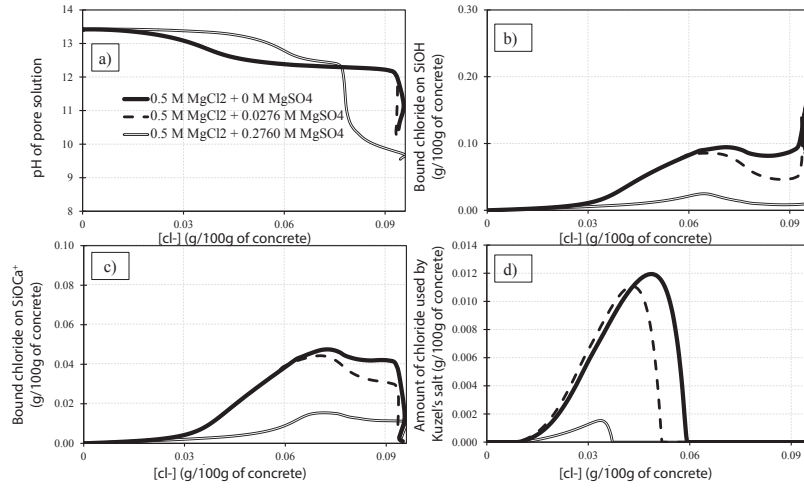


Figure 7: a) Pore solution pH and chloride binding on b) $\equiv SiOH$, c) $\equiv SiOCa^+$, d) Kuzel's salt formation after six months of exposure in 0.5 M $MgCl_2$, 0.5 M $MgCl_2$ + 0.0276 M $MgSO_4$ and 0.5 M $MgCl_2$ + 0.2760 M $MgSO_4$ solutions at 20°C, respectively.

355 addition, Cl^- and SO_4^{2-} start competing for sorption with Ca^{2+} on $\equiv SiOH$.
 356 Because of the charge balance condition and the competition between chlo-
 357 ride and sulfate, the number of negative surface charges $\equiv SiOHCl^-$ must
 358 decrease. This can only happen if the chloride binding capability decreases
 359 when the solution contains a significant amount of SO_4^{2-} .

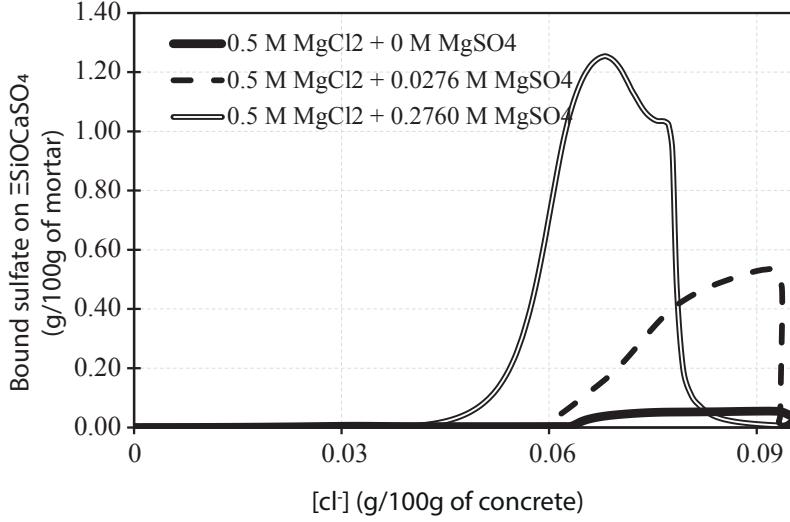


Figure 8: Sulphate binding on $\equiv SiOCaSO_4^-$

360 Chloride binding due to Kuzel's salt formation (cf. Figure 7d) is weakest
 361 when SO_4^{2-} concentration is highest. Ettringite formation then occurs at the
 362 expense of Kuzel's salt formation as shown in Figure 9. Results are differ-
 363 ent with the boundary solution without SO_4^{2-} . In contrast, the remaining
 364 mineral behaviors are similar. Consequently, for the 0.5 M $MgCl_2$ + 0.2760
 365 M $MgSO_4$ solution, Ca^{2+} leaching is not responsible for the low pH. The
 366 pH decrease is essentially due to the presence of SO_4^{2-} and to the adsorption
 367 reactions on C-S-H.

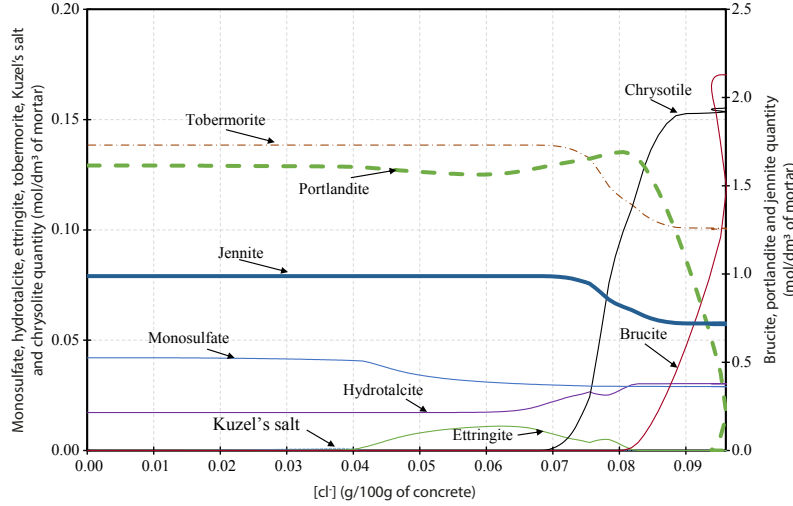


Figure 9: Mineral amount of CEM II concrete after six months of exposure in a 0.5 M $MgCl_2$ + 0.2760 M $MgSO_4$ solution at 20°C.

6. Conclusion

In this paper a physically and chemically based multiionic model considering thermodynamical reaction kinetics and surface complexation is proposed to investigate chloride binding capability of CEM II concrete exposed to different boundary chloride solutions. **Some chloride binding isotherms from the literature are compared with the numerical results for concrete exposed to $NaCl$, KCl , $CaCl_2$, $MgCl_2$. The presence of sulfate ions in the $MgCl_2$ boundary solution with two different concentrations is also studied.**

The results underline the influence of the cation type associated to the chloride boundary solution on the chloride binding capability. As observed in the literature, the chloride binding capability decreases in the order: $Ca^{2+} > Mg^{2+} > Na^+ \approx K^+$. In addition,

the numerical results show that the highest quantity of chloride that reacts is obtained by the sorption on $\equiv SiOH$, followed by the sorption on $\equiv SiOCa^+$. The chloride ions quantity that reacts to form Kuzel's salts is the smallest one. This latter numerical observation is true whatever the chloride salt solution and the type of cation associated with chloride. As regards the chloride salt solution without sulfate, the competition between H^+ (or indirectly pH) and Cl^- onto $\equiv SiOH$ presents the most significant effect on chloride binding capability. Indeed, the higher the pH is, the lower the chloride quantity is adsorbed on C-S-H. These conclusions also confirm the relationship between pH and chloride binding capability observed experimentally in the literature.

This study also shows that the leaching of Na^+ and K^+ for the concrete exposed to a $CaCl_2$ solution and the leaching of Na^+ , K^+ and Ca^{2+} for the concrete exposed to a $MgCl_2$ solution cause a local pH decrease and, thus, an increase in chloride binding capability. Regarding the $MgCl_2$ solution, the formation of hydrotalcite is enhanced and limits Kuzel's salt precipitation. The higher the Ca^{2+} concentration is, the higher the chloride amount absorbed on $\equiv SiOCa^+$.

Finally, the model is able to catch that when some sulfate ions are present in the chloride solution, they reduce chloride binding capability because of the sulfate absorption process on C-S-H. A more negatively charged surface $\equiv SiOCaSO_4^-$ and competition between Cl^- and SO_4^{2-} replace $\equiv SiOH$ in the presence of Ca^{2+} in the solution. This reaction releases H^+ and decreases the pH.

406 **These first results have to be confirmed with more experimental**
407 **data on several concretes and for other ionic species than chlorides**
408 **although data is missing in the literature.** In addition, on the basis of
409 the above study, it could be interesting to explore these findings and study
410 chloride binding capability of concrete exposed to seawater, in which different
411 cations and sulfate ions are present simultaneously.

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