



Title	Hydration study of slag-blended cement based on thermodynamic considerations
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Citation	Construction and building materials, 124, 615-625 https://doi.org/10.1016/j.conbuildmat.2016.07.138
Issue Date	2016-10-15
Doc URL	http://hdl.handle.net/2115/71657
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Type	article (author version)
File Information	Slag-Hydration_Manuscript-Revised.pdf



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1 **Hydration study of slag-blended cement based on thermodynamic**
2 **considerations**

3

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22

23 **Abstract**

24 Thermodynamic calculations, using the geochemical code PHREEQC coupled with empirical
25 equations for kinetics of cement hydration and slag reaction, were carried out to predict the
26 compositions of the hydrate assemblage and pore solutions of hydrating Portland cement and

27 cement blended with slag and the blended cement containing limestone. The predicted compositions
28 of hydration products and element concentrations in pore solutions compared well with
29 experimental data reported in literature. The calculation results showed the varying Ca/Si and Al/Si
30 ratios of calcium aluminosilicate hydrate (C-A-S-H)* in the hydration products due to hydration
31 and slag addition. Limitations on the equation for reaction of slag and the importance of a C-A-S-H
32 solid solution model in prediction of hydration products are discussed.

33

34 **Keywords:** Thermodynamic Calculations; Slag-blended Cement; Hydration Products; Pore
35 Solution; PHREEQC

36

37 1. INTRODUCTION

38

39 A partial replacement of Portland cement (PC) by supplementary cementitious materials (SCMs) or
40 innovative low-carbon cement-based materials can substantially reduce CO₂ emissions associated
41 with PC production [1]. Several studies have focused on developing SCMs from a variety of waste
42 and by-product materials, in addition to common SCMs such as fly ash, ground granulated
43 blast-furnace slag, and silica fume [2]. Further, novel cement systems/concrete are being developed
44 through alkaline activation of aluminosilicates or innovative uses of waste materials [3]. Some of
45 these novel cements are in use on a limited scale in some parts of the world; however, their short-
46 and long-term performance as compared to conventional PC needs to be established for their
47 large-scale application [1]. More investigation on the properties and performance of SCMs or novel
48 cements is necessary for their successful usage as partial or complete replacement of PC in
49 concrete.

50

51 Knowledge of hydrating cement and the cementitious behaviour and pozzolanic characteristics of

* Cement chemistry shorthand notations: A = Al₂O₃, C = CaO, S = SiO₂, and H = H₂O

52 SCMs are important for better understanding of the properties and performance of the materials in
53 concrete. It is also essential in terms of materials selection for concrete and for predicting properties
54 and the durability and structural performance of concrete. The properties of hydrated PC and
55 blended cement can be determined by laboratory experiments. However, it is difficult to depend
56 entirely on experimental methods to determine the properties owing to the variety of SCMs used
57 and the time it takes to perform these experiments. On the other hand, thermodynamic or
58 mathematical models significantly reduce the reliance on laboratory experiments and help to predict
59 hydration processes and materials properties.

60

61 Thermodynamic models in cementitious systems would make it possible to predict the composition
62 of the hydrate assemblage and the aqueous phase composition based on information about the
63 starting materials. Rothstein [4] studied the saturation indexes of solid phases in hydrating PC
64 during the first 28 days of hydration using thermodynamic analysis of the element concentrations
65 and compared the calculated saturation indexes with the supersaturation of phases found in previous
66 work. Lothenbach and associates [5-12] made significant contributions to the thermodynamic
67 calculations for cementitious materials to better understand cement hydration processes. Their work
68 facilitated prediction of the composition of solid and liquid phases during hydration as a function of
69 hydration time and simulation of the phase changes in cementitious materials in contact with ionic
70 solutions. A thermodynamic model developed using the Gibbs free energy minimisation program
71 GEMS-PSI (available at <http://gems.web.psi.ch/>) coupled with kinetic equations for the dissolution
72 of clinker minerals successfully predicted the solid-phase assemblage and pore solution
73 composition of hydrated PC [7] and PC-containing limestone [7 and 9]. The model was extended to
74 allow calculations in the temperature range of 0–100 °C [10]; it was also applied to various cements
75 [8] and mineral admixtures [5 and 12]. In addition to thermodynamic models, several hydration
76 models in cementitious materials have been proposed to simulate the hydration reaction of cement
77 and slag and also to predict the evolution of hydration products [13-14]. It is recognised that a

78 partial or complete replacement of PC with slag reduces the Ca/Si ratio of calcium silicate hydrate
79 (C-S-H) and also forms calcium aluminosilicate hydrate (C-A-S-H) [2, and 15-16]. The
80 incorporation of aluminium in C-S-H of PC has also been reported in previous studies [2 and 16].
81 However, details of these aspects have not yet been taken into account in existing models for
82 predicting the composition of the hydrate assemblage and pore solution chemistry. A model that
83 includes Al incorporation and various Ca/Si ratios of C-S-H is thus important for better prediction
84 of the solid products and aqueous phase compositions formed in PC and slag-blended systems.

85

86 In this study, chemical thermodynamic calculations were carried out to predict the solid-phase
87 assemblages and pore solution composition of hydrating PC and slag as a function of hydration time.
88 An integrated model that coupled PHREEQC [17-18] with empirical expressions for dissolution of
89 clinker minerals and reactions of slag was developed, in which, the reactions among solids, aqueous
90 solutions, and solid solutions were considered simultaneously at each hydration time step. Various
91 calculation features built into PHREEQC including phase-equilibrium, speciation, and solid
92 solutions, allowed the performance of a variety of geochemical calculations at higher ionic strengths
93 as well, using an incorporated Pitzer model [19]. A solid solution that consists of various C-S-H and
94 C-A-S-H gels as end-members was considered to account for the changing Ca/Si ratio and
95 aluminium uptake in the gels [15 and 20]. The results of thermodynamic calculations in terms of
96 solid-phase composition and concentration of elements in the pore solution were compared with the
97 experimental data in literature for hydrating PC, cement blended with slag, and blended cement
98 containing limestone.

99

100 **2. MODEL DESCRIPTION**

101 **2.1. Thermodynamic model**

102

103 In this study, a phase-equilibrium module in PHREEQC was employed to carry out thermodynamic

104 equilibrium calculations [17-18]. When a pure phase is no longer in equilibrium with a solution, it
 105 will dissolve or precipitate. The equilibrium reactions are expressed by the mass-action equation as
 106

$$107 \quad K_p = \prod_i (\gamma_i c_i)^{n_{i,p}} \quad (1)$$

108
 109 where K_p is the thermodynamic equilibrium constant for phase p , γ_i is the activity coefficient of ion i
 110 ($-$), c_i is the concentration of ion i (mol/L), and $n_{i,p}$ is the stoichiometric coefficient of ion i in phase
 111 p ($-$). The thermodynamic equilibrium constant, K_p , at a given temperature T (K) can be expressed
 112 as

$$113 \quad K_p = \exp\left(-\frac{\Delta_r G_T^0}{RT}\right) \quad (2)$$

114
 115
 116 where $\Delta_r G_T^0$ is the standard Gibbs energy of reaction at temperature T and R is the universal gas
 117 constant (8.31451 J/(mol K)). The standard Gibbs energy of reaction is expressed as

$$118 \quad \Delta_r G_T^0 = \sum \Delta_f G_{T,products}^0 - \sum \Delta_f G_{T,reactants}^0 \quad (3)$$

119
 120
 121 where $\Delta_f G_T^0$ is the Gibbs free energy of formation for a species at a given temperature T . The
 122 equilibrium constant ($\log K_p$) and the standard heats of reaction ($\Delta_r H^0$), which is used in the Van't
 123 Hoff equation (Appelo and Postma 2009) to determine temperature dependence of the equilibrium
 124 constant, for the dissolution reactions of phases used in the simulation are tabulated in **Table 1**. The
 125 name of the phase (defined by dissolution reaction, $\log K_p$, and $\Delta_r H^0$, as given in **Table 1**), the
 126 specified saturation index (which has a value of zero for equilibrium), and the amount of the phase
 127 were the input parameters for the phase-equilibrium module in PHREEQC.

128

129 **Table 1** Thermodynamic properties of the phases at 25°C used in the calculations [10, 15, and 18]

Phase	Reactions	$\log K_p$	$\Delta_r H^0$	Ref.
Anhydrite	$\text{CaSO}_4 \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}$	-4.36	-1.71	[18]
Brucite	$\text{Mg}(\text{OH})_2 + 2\text{H}^+ \leftrightarrow \text{Mg}^{2+} + 2\text{H}_2\text{O}$	17.07	-115.66	[10]
C_3AH_6	$\text{Ca}_3\text{Al}_2(\text{OH})_{12} + 12\text{H}^+ \leftrightarrow 3\text{Ca}^{2+} + 2\text{Al}^{3+} + 12\text{H}_2\text{O}$	82.22	-595.76	[10]
C_3FH_6	$\text{Ca}_3\text{Fe}_2(\text{OH})_{12} + 12\text{H}^+ \leftrightarrow 3\text{Ca}^{2+} + 2\text{Fe}^{3+} + 12\text{H}_2\text{O}$	73.65	-516.96	[10]
Calcite	$\text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$	-8.48	-2.297	[18]
CASH_5CA	$(\text{CaO})_{1.25}(\text{Al}_2\text{O}_3)_{0.125}(\text{SiO}_2):1.625\text{H}_2\text{O} + 3.25\text{H}^+ \leftrightarrow 1.25\text{Ca}^{2+} + 0.25\text{Al}^{3+} + \text{H}_4\text{SiO}_4 + 1.25\text{H}_2\text{O}$	22.00	-141.58	[15]
CASH_INFCA	$(\text{CaO})(\text{Al}_2\text{O}_3)_{0.15625}(\text{SiO}_2)_{1.1875}:1.65625\text{H}_2\text{O} + 2.9375\text{H}^+ \leftrightarrow \text{Ca}^{2+} + 0.3125\text{Al}^{3+} + 1.1875\text{H}_4\text{SiO}_4 + 0.75\text{H}_2\text{O}$	16.60	-110.67	[15]
CSH_T2C	$(\text{CaO})_{1.5}(\text{SiO}_2):2.5\text{H}_2\text{O} + 3\text{H}^+ \leftrightarrow 1.5\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 2\text{H}_2\text{O}$	25.88	-127.10	[15]
CSH_T5C	$(\text{CaO})_{1.25}(\text{SiO}_2)_{1.25}:2.5\text{H}_2\text{O} + 2.5\text{H}^+ \leftrightarrow 1.25\text{Ca}^{2+} + 1.25\text{H}_4\text{SiO}_4 + 1.25\text{H}_2\text{O}$	18.74	-83.46	[15]
CSH_Jen	$(\text{CaO})_{1.667}(\text{SiO}_2):2.1\text{H}_2\text{O} + 3.334\text{H}^+ \leftrightarrow 1.667\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 1.767\text{H}_2\text{O}$	29.60	-148.44	[10]
CSH_TobH	$(\text{CaO})(\text{SiO}_2)_{1.5}:2.5\text{H}_2\text{O} + 2\text{H}^+ \leftrightarrow \text{Ca}^{2+} + 1.5\text{H}_4\text{SiO}_4 + 0.5\text{H}_2\text{O}$	13.18	-47.83	[15]
Ettringite	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}:26\text{H}_2\text{O} + 12\text{H}^+ \leftrightarrow 6\text{Ca}^{2+} + 2\text{Al}^{3+} + 3\text{SO}_4^{2-} + 38\text{H}_2\text{O}$	57.73	-389.36	[10]
Gypsum	$\text{CaSO}_4:2\text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	-4.58	-0.109	[18]
Hemicarboaluminate	$\text{Ca}_4\text{Al}_2(\text{CO}_3)_{0.5}(\text{OH})_{13}:5.5\text{H}_2\text{O} + 13\text{H}^+ \leftrightarrow 4\text{Ca}^{2+} + 2\text{Al}^{3+} + 0.5\text{CO}_3^{2-} + 18.5\text{H}_2\text{O}$	87.88	-604.27	[10]
Hydrotalcite	$\text{Mg}_4\text{Al}_2(\text{OH})_{14}:3\text{H}_2\text{O} + 14\text{H}^+ \leftrightarrow 2\text{Al}^{3+} + 4\text{Mg}^{2+} + 17\text{H}_2\text{O}$	75.97	-607.91	[10]
Monocarboaluminate	$\text{Ca}_4\text{Al}_2(\text{CO}_3)(\text{OH})_{12}:5\text{H}_2\text{O} + 12\text{H}^+ \leftrightarrow 4\text{Ca}^{2+} + 2\text{Al}^{3+} + \text{CO}_3^{2-} + 17\text{H}_2\text{O}$	71.54	-533.14	[10]
Monosulfoaluminate	$\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12}:6\text{H}_2\text{O} + 12\text{H}^+ \leftrightarrow 4\text{Ca}^{2+} + 2\text{Al}^{3+} + \text{SO}_4^{2-} + 18\text{H}_2\text{O}$	73.68	-553.08	[10]
Portlandite	$\text{Ca}(\text{OH})_2 + 2\text{H}^+ \leftrightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O}$	22.79	-129.66	[10]
Stratlingite	$\text{Ca}_2\text{Al}_2\text{SiO}_2(\text{OH})_{10}:3\text{H}_2\text{O} + 10\text{H}^+ \leftrightarrow 2\text{Ca}^{2+} + 2\text{Al}^{3+} + \text{H}_4\text{SiO}_4 + 11\text{H}_2\text{O}$	51.42	-408.12	[10]

130

131 **2.2. Cement hydration model**

132

133 In this study, the cement hydration model proposed by Parrot and Killoh [21] was used to estimate
134 the hydration degree of each cement clinker mineral as a function of time. The model is described in
135 detail elsewhere [7, 9, and 21]; the main equations are briefly described here. Parrot and Killoh [21]
136 derived a set of empirical equations to describe the hydration rate, R_t^m , of an individual clinker
137 mineral m at time t ($m = C_3S, C_2S, C_3A, C_4AF$):

138

139 Nucleation and growth

140

$$141 \quad R_{t,1}^m = \frac{K_1}{N_1} [1 - \alpha_t^m] \{-\ln(1 - \alpha_t^m)\}^{(1-N_1)} \quad (4)$$

142

143 Diffusion

144

$$145 \quad R_{t,2}^m = \frac{K_2(1 - \alpha_t^m)^{2/3}}{1 - (1 - \alpha_t^m)^{1/3}} \quad (5)$$

146

147 Hydration shell formation

148

$$149 \quad R_{t,3}^m = K_3(1 - \alpha_t^m)^{N_3} \quad (6)$$

150

151 The associated empirical parameters in the equations are tabulated in **Table 2** as reported by
152 Lothenbach *et al.* [9-10]. The minimum among above the rates ($R_{t,1}^m, R_{t,2}^m, R_{t,3}^m$) is considered to be
153 the controlling rate. The hydration degree of clinker mineral m at the time t , α_t^m , is calculated from
154 the hydration degree of the mineral at the previous time step (α_{t-1}^m), the time interval (Δt), and
155 hydration rate of the clinker mineral at the previous time step (R_{t-1}^m) as

156

$$157 \quad \alpha_t^m = \alpha_{t-1}^m + \Delta t \cdot \min(R_{t-1,1}^m, R_{t-1,2}^m, R_{t-1,3}^m) \cdot \beta_{w/c} \cdot \lambda_{RH} \cdot \frac{A}{A_0} \cdot \exp\left[\frac{E_a^m}{R} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \quad (7)$$

158 where,

$$159 \quad \beta_{w/c} = \begin{cases} [1 + 3.333 \times (H^m \times w/c - \alpha_{t-1})]^4 & \text{if } \alpha_t > H^m \times w/c \\ 1 & \text{if } \alpha_t \leq H^m \times w/c \end{cases} \quad (8)$$

$$161 \quad \lambda_{RH} = \left(\frac{RH - 0.55}{0.45}\right)^4 \quad (9)$$

162

163 where H^m is the critical degree of the clinker mineral m , w/c is the water to cement ratio, α_{t-1} is the
 164 total hydration degree of cement at the previous time step, A is the Blaine surface area of cement
 165 (m^2/kg), A^0 is the reference surface area of cement ($385 \text{ m}^2/\text{kg}$), E_a^m is the apparent activation
 166 energy of clinker mineral m (J/mol), T_0 is the reference temperature (293.15 K), and RH is the
 167 relative humidity. The adapted values for H^m and E_a^m are based on the work by Lothenbach *et al.*
 168 [9-10], given in **Table 2**.

169

170 The total hydration degree of cement, α_t , relative to the total clinker content at time t is expressed by

171

$$172 \quad \alpha_t = \frac{f^{C_3S} \alpha_t^{C_3S} + f^{C_2S} \alpha_t^{C_2S} + f^{C_3A} \alpha_t^{C_3A} + f^{C_4AF} \alpha_t^{C_4AF}}{f^{C_3S} + f^{C_2S} + f^{C_3A} + f^{C_4AF}} \quad (10)$$

173

174 where f^m is the relative mass fraction of the cement clinker mineral m .

175

176 **Table 2** Parameters adapted to calculate the hydration degree of the clinker minerals as a function
 177 of time [9-10]

	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
K ₁	1.5	0.5	1	0.37

N_1	0.7	1	0.85	0.7
K_2	0.05	0.006	0.04	0.015
K_3	1.1	0.2	1	0.4
N_3	3.3	5	3.2	3.7
H	1.8	1.35	1.60	1.45
E_a (J/mol)	41570	20785	54040	34087

178

179 3. SIMULATION RESULTS AND VERIFICATIONS

180 3.1. Ordinary Portland cement system

181 3.1.1. Modelling approach

182

183 PHREEQC was coupled (using the IPhreeqc module [22]) with Excel[®] to carry out thermodynamic
184 calculations in each time step. PHREEQC performs speciation and batch-reaction calculations to
185 calculate the solution composition and the kind and amount of precipitated phases based on a
186 thermodynamic dataset and input parameters. The calculations on the dissolution rate of clinker
187 minerals were carried out in Excel[®] and the necessary data were transferred to PHREEQC as input
188 parameters. The thermodynamic properties for various phases and minerals found in cement system
189 were collected from CEMDATA07 [10] and others [15], and the data were converted into a format
190 suitable for PHREEQC; the data are given in **Table 1**. The converted data, together with the
191 PHREEQC default thermodynamic database [18], were used in in this study for every calculation.
192 The following assumptions were considered to determine the compositions of the solid phases and
193 pore solutions using the coupled model:

194 ✧ Free lime and alkali sulphates are dissolved completely as the cement comes into contact with
195 water. Ca, O as OH, Na, K, and S are released into the pore solution.

196 ✧ Cement clinker minerals are dissolved according to Eqs. (4) – (9) as a function of time and
197 release Ca, Si, O as OH, Al, and Fe into the pore solution.

198 ✧ Na_2O and K_2O , which are present as minor components in the clinker minerals, and total MgO
199 are dissolved by the total hydration degree of the cement and release Na, K, Mg, and O as OH

200 into the pore solution.

201 ✧ Gypsum and calcite react continuously to reach equilibrium with the pore solution.

202 ✧ The elements released into the pore solution form minerals and phases through thermodynamic
203 equilibrium.

204 ✧ An ideal solid solution of six end-members (CASH_5CA, CASH_INFCA, CSH_T2C,
205 CSH_T5C, CSH_Jen, and CSH_TobH, as given in **Table 1**) is assumed for C-S-H and
206 C-A-S-H.

207

208 The alkalis are released from readily soluble alkalis sulphates and the dissolution of the clinker
209 minerals. It is well known that a part of the released alkalis are taken up by C-A-S-H gel, and a
210 distribution ratio (Rd_{Na}) of 0.45 mL/g is used for Na^+ uptake by C-A-S-H gel while the distribution
211 ratio of K^+ (Rd_K) is expressed as follows [23]:

212

$$213 \quad Rd_K = 0.20C_K^{-0.76} \quad (11)$$

214

215 where C_K is the concentration of K^+ .

216

217 **3.1.2. Simulation results and experimental data verification**

218

219 The predicted phase changes as a function of time for Ordinary Portland Cement (OPC) paste
220 (using the input parameters given in **Table 3**) are shown in **Fig. 1(A)**. The model predicts the
221 complete dissolution of the available gypsum in the cement within the first 7 h of hydration and the
222 gradual increase in the amount of C-A-S-H end-members and portlandite with time. The presence
223 of CSH_TobH and CASH_INFCA end-members in C-A-S-H solid solution is negligible.
224 Magnesium present in the cement is predicted as brucite at an early age and then converted to
225 hydrotalcite after 0.5 days of hydration. The model also calculates the continuous dissolution of

226 calcite present in the cement to form monocarboaluminate, and some monocarboaluminate
 227 transforms to hemicarboaluminate. The predicted phases in the hydrated OPC (after 7 days or
 228 longer of hydration time) include C-A-S-H gel solid solution, portlandite, ettringite, hydrotalcite,
 229 and AFm phases such as monocarboaluminate and hemicarboaluminate, in addition to un-hydrated
 230 clinker minerals. The chemical composition data for end-members of the C-A-S-H gel solid
 231 solution are used to predict the Ca/Si and Al/Si ratios of the gel (**Fig. 1(B)**). The predicted ratios of
 232 hydrating OPC are $1.48 \leq \text{Ca/Si} \leq 1.53$ and $0.003 \leq \text{Al/Si} \leq 0.049$.

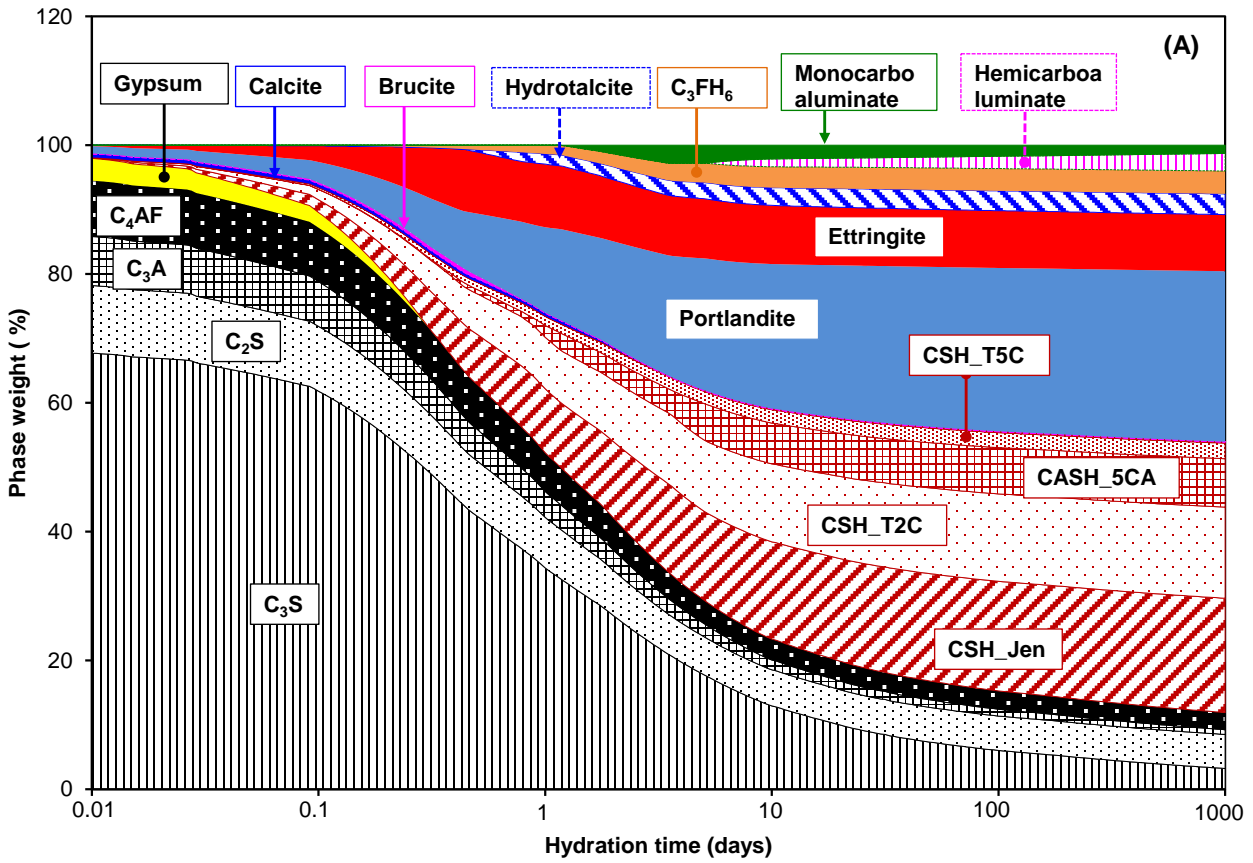
233

234 **Table 3** Chemical composition and Blaine surface area of OPC and mixing conditions as input to
 235 the model, adapted from ref. [9]

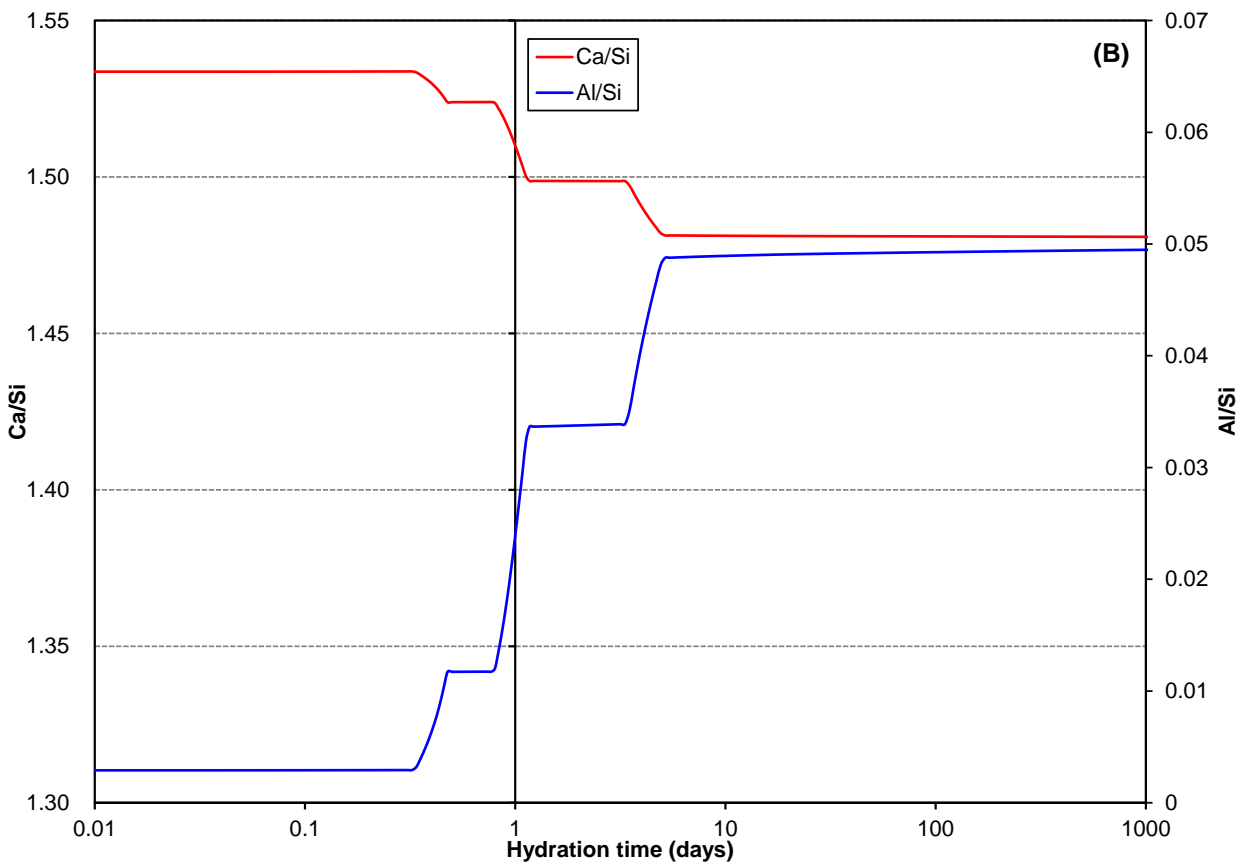
<i>Phase composition (g/100 g)</i>		<i>Minor components in the clinker phases</i>	
-Alite	66.5	-Na ₂ O	0.33
-Belite	10.3	-K ₂ O	0.06
-Aluminate	7.5	-MgO	1.8*
-Ferrite	8.5	<i>Mixing conditions</i>	
-CaO_Free	0.93	-w/c	0.4
-Calcite	0.6	-Temp (°C)	20
-Gypsum	3.1	-RH (%)	1.0
-Na ₂ SO ₄	0.21		
-K ₂ SO ₄	1.33	Blaine surface area (m ² /kg)	413

236 * Total MgO

237



238



239

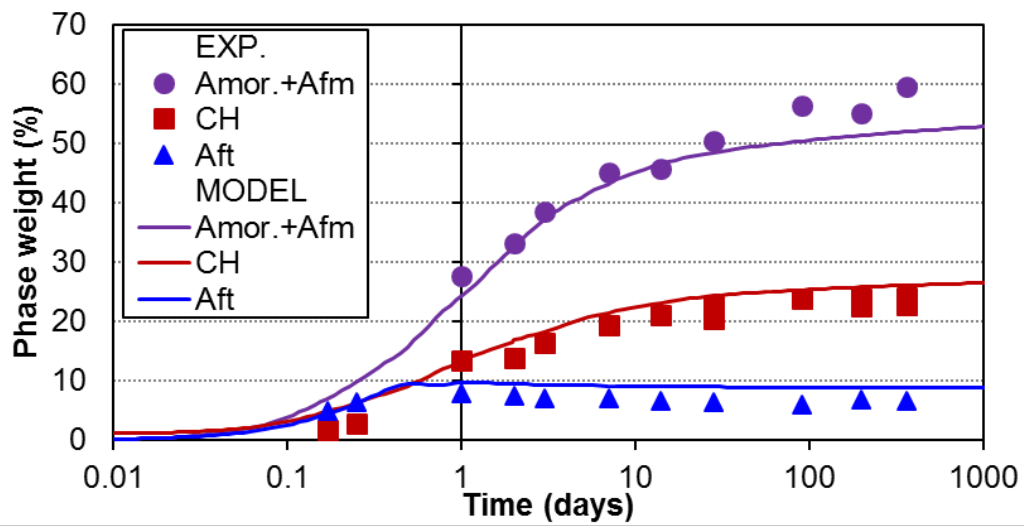
240 **Fig. 1.** Simulated phase (A), Ca/Si and Al/Si ratios of C-A-S-H (B) changes as a function of
 241 hydration time for OPC

242

243 The simulated hydration products of OPC paste for the input parameters listed in **Table 3** were
244 compared with the experimental data available in the literature [9], shown in **Fig. 2**. As reported by
245 Matschei [24] and validated by Lothenbach *et al.* [9], the AFm phases determined by XRD (X-ray
246 Diffraction) are certainly underestimated owing to their poor crystalline structure, relatively low
247 amount, and lack of data concerning the structure. Therefore, the total amorphous content (C-S-H +
248 amorphous AFm) from XRD measurement was compared with the summation of C-S-H and
249 monosulfoaluminate from the current simulation. As illustrated in **Fig. 2**, the predicted hydration
250 products of OPC are consistent with both the qualitative and quantitative experimental results as a
251 function of hydration time.

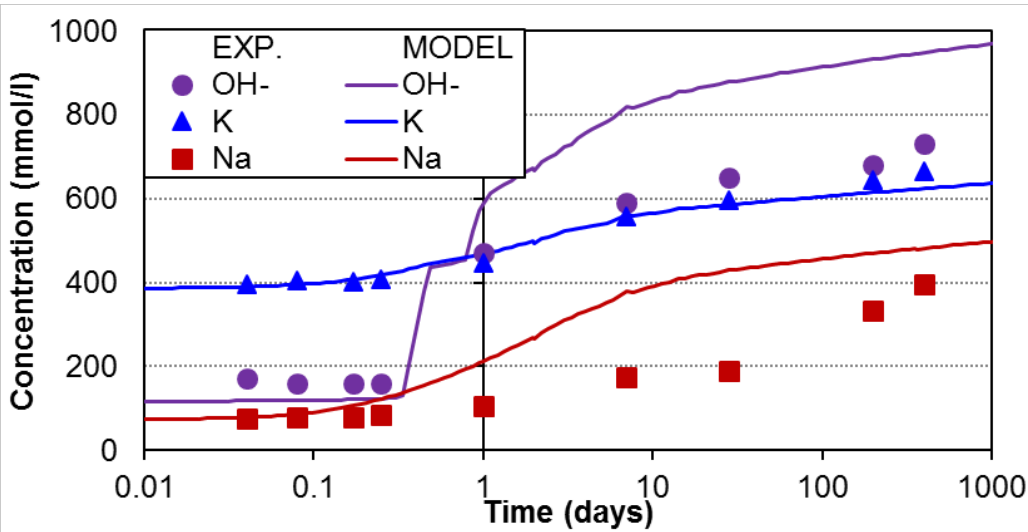
252

253 The ionic concentration in the pore solution was calculated based on the release and uptake of
254 alkalis as well as the thermodynamic equilibrium between the phases and the pore solution. The
255 comparison of computed elements concentration in the pore solution of hydrating OPC (for the
256 input parameters of **Table 3**) with experimentally determined ones [9] are shown in **Fig. 3**. The
257 model predicts reasonably well the changes of major elements such as Na, K, OH, Ca, S, Al, and Si
258 with hydration time, but the model cannot predict the presence of other elements such as Li, Sr, Ba,
259 Cr, and Mo, even though they can be detected in the experiments. The simulated concentration of
260 ions in pore solution is compared with another experimental data [25] to give further validation to
261 the proposed model. The simulated concentration of Na, K, and Ca elements and pH of pore
262 solution are compared with experimental values of hydrating OPC with varying w/c ratios in **Fig. 4**.
263 It can be seen that the concentration of ions are predicted well though some discrepancies are
264 observed for pH at 1 and 3 days.

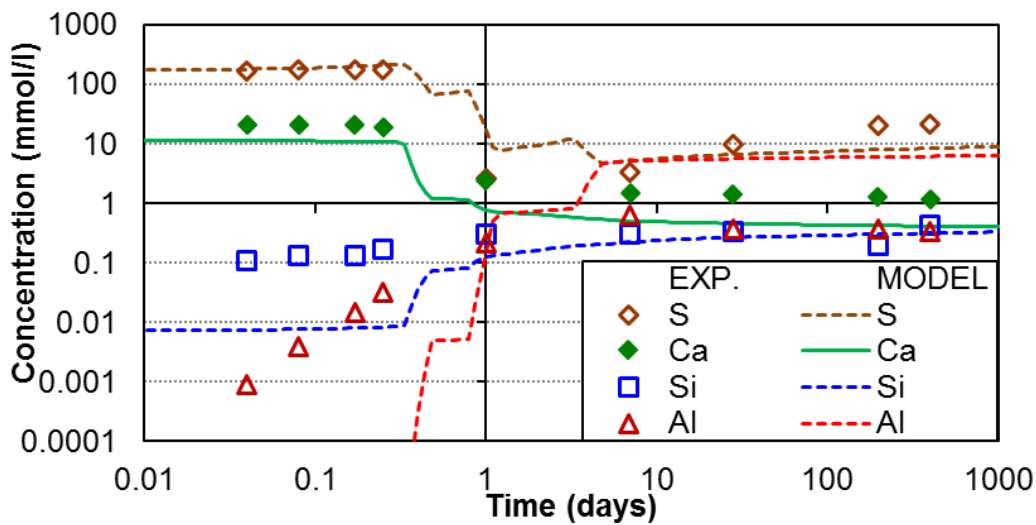


265

266 **Fig. 2.** Comparison of simulated portlandite, ettringite, and amorphous + Afm changes with
 267 experimental data [9] for hydrating OPC



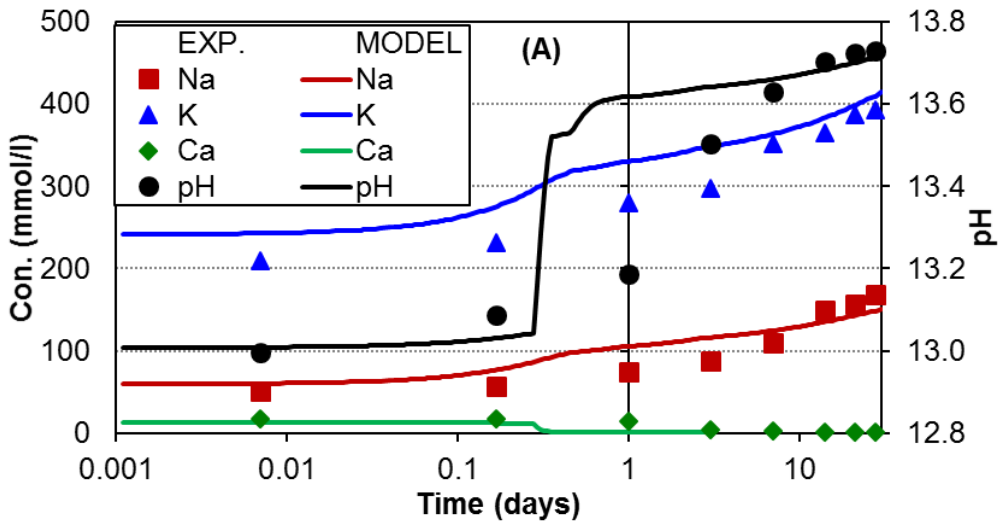
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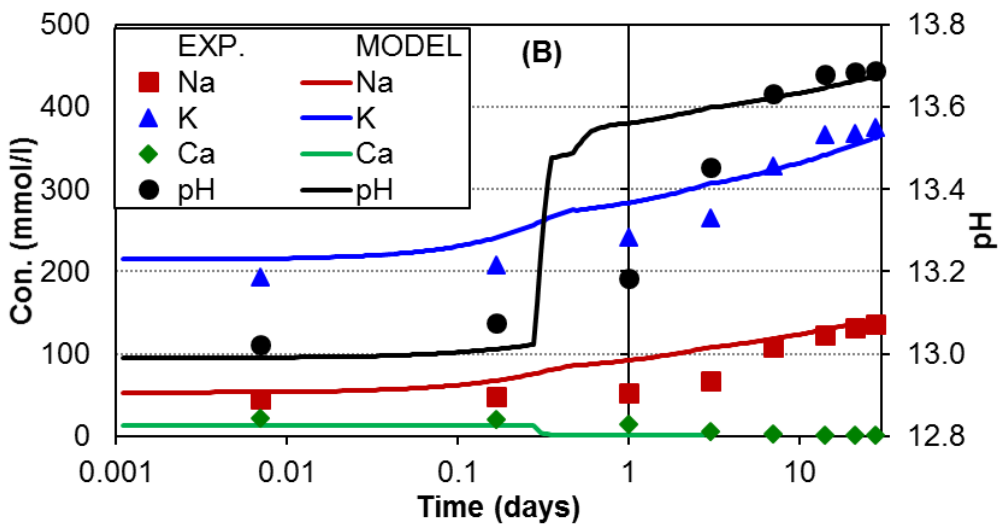
269

270 **Fig. 3.** Comparison of simulated pore solution concentration changes with experimental data [9] for
 271 hydrating OPC

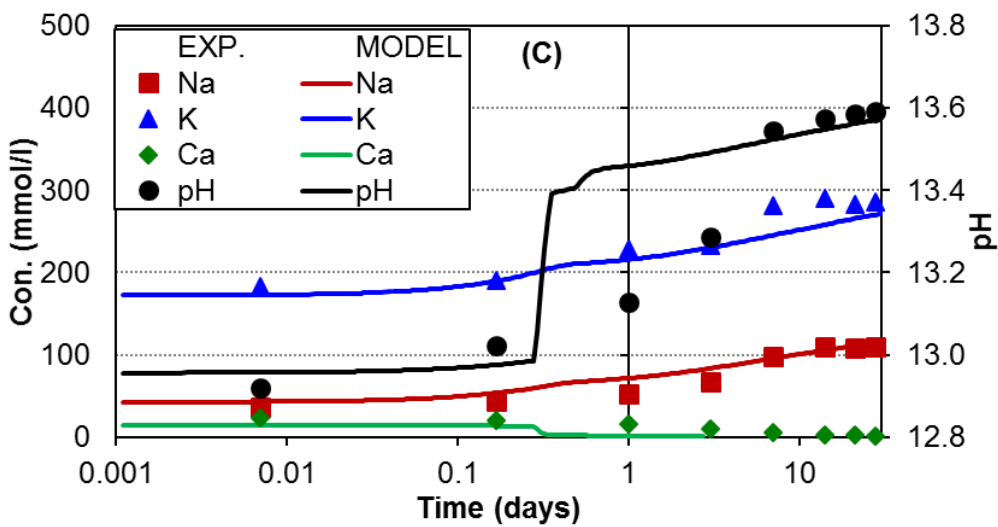
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273



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275

276 **Fig. 4** Comparison of simulated pore solution concentration changes with experimental data [25] for
277 hydrating OPC with w/c of (A) 0.4, (B) 0.45, and (C) 0.56

278

279 3.2. Slag cement system

280 3.2.1. Modelling approach

281

282 The coupled thermodynamic model described in **section 3.1.1**, including the solid solution model
283 for C-S-H and C-A-S-H considered for the OPC system, with the same database and information
284 relevant to cement hydration was also used to model the slag cement system. Thermodynamic
285 calculations were performed for the dissolution of clinker minerals and the reaction of slag at every
286 time step. The ions released as result of cement clinker dissolution and the reaction of the glass
287 phase of slag determined the kind and amount of the formed phases and the composition of
288 C-A-S-H. An equation to describe the degree of slag reaction was derived by fitting the various
289 experimental data (**Fig. 5**) available in the literature [26-30], which included the reaction degree for
290 the cement replacement by slag of 20–60% for up to 2 years of hydration, to a function. The
291 influence of temperature, using the Arrhenius equation, and the surface area of the slag were
292 included in the equation. The derived equation for the reaction degree of slag in percentage, α_{sg} , can
293 be described as follows:

294

$$295 \quad \alpha_{sg} = [A \times \ln(t) + B] \times S_{sg} \times \exp\left[-\frac{E_{sg}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (12)$$

296 where,

$$297 \quad A = -0.16 \times r_{sg} + 12.81 \quad (13)$$

$$298 \quad B = 0.33 \times r_{sg} + 4.30 \quad (14)$$

$$299 \quad S_{sg} = \frac{SA_{sg}}{4000} \quad (15)$$

$$300 \quad E_{sg} = 400 \times r_{sg} + 32200 \quad (16)$$

301

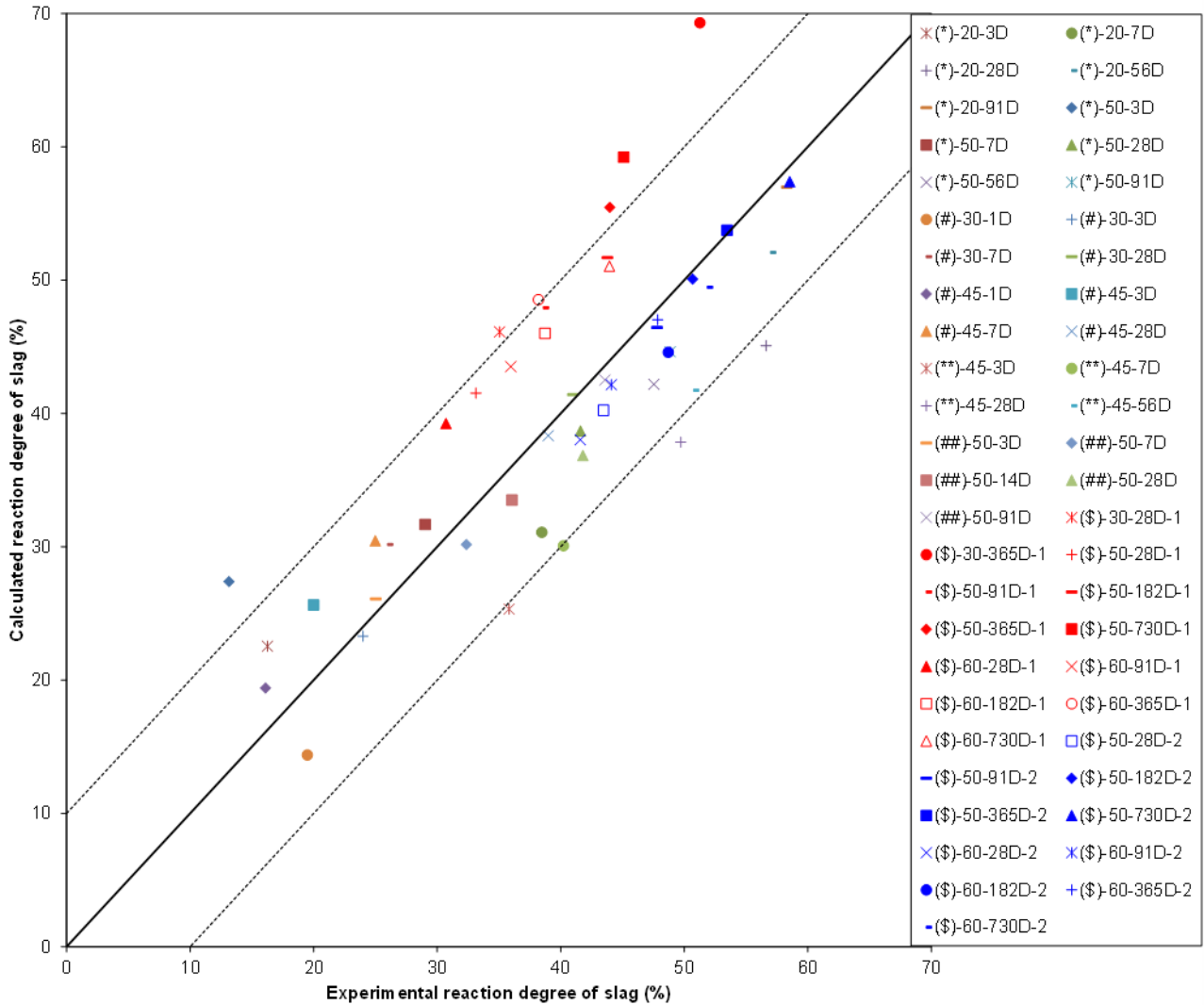
302 where r_{sg} is the replacement ratio of slag (%), SA_{sg} is the Blaine value of slag (cm^2/g), and E_{sg} is the

303 activation energy of slag (J/mol), which was calculated from an equation given in ref. [31].

304

305 A distribution ratio of 0.45 mL/g is used for both Na⁺ and K⁺ uptake by C-A-S-H gel in the cement

306 blended with slag system in order to predict ionic concentration in the pore solution.



307

308 **Fig. 5.** Comparison of calculated reaction degree of slag using Eq. (12) with published (\$[26],

309 ##[27], **[28], *[29], and #[30]) experimental data. The dotted lines show ±10% deviation from y

310 = x line. Notation: ()-xx-yD: Reference-slag replacement ratio-curing period in days. Two types of

311 slag in ref. (Lumley *et al.*, 1996) are used.

312

313 3.2.2. Simulation results and experimental data verification

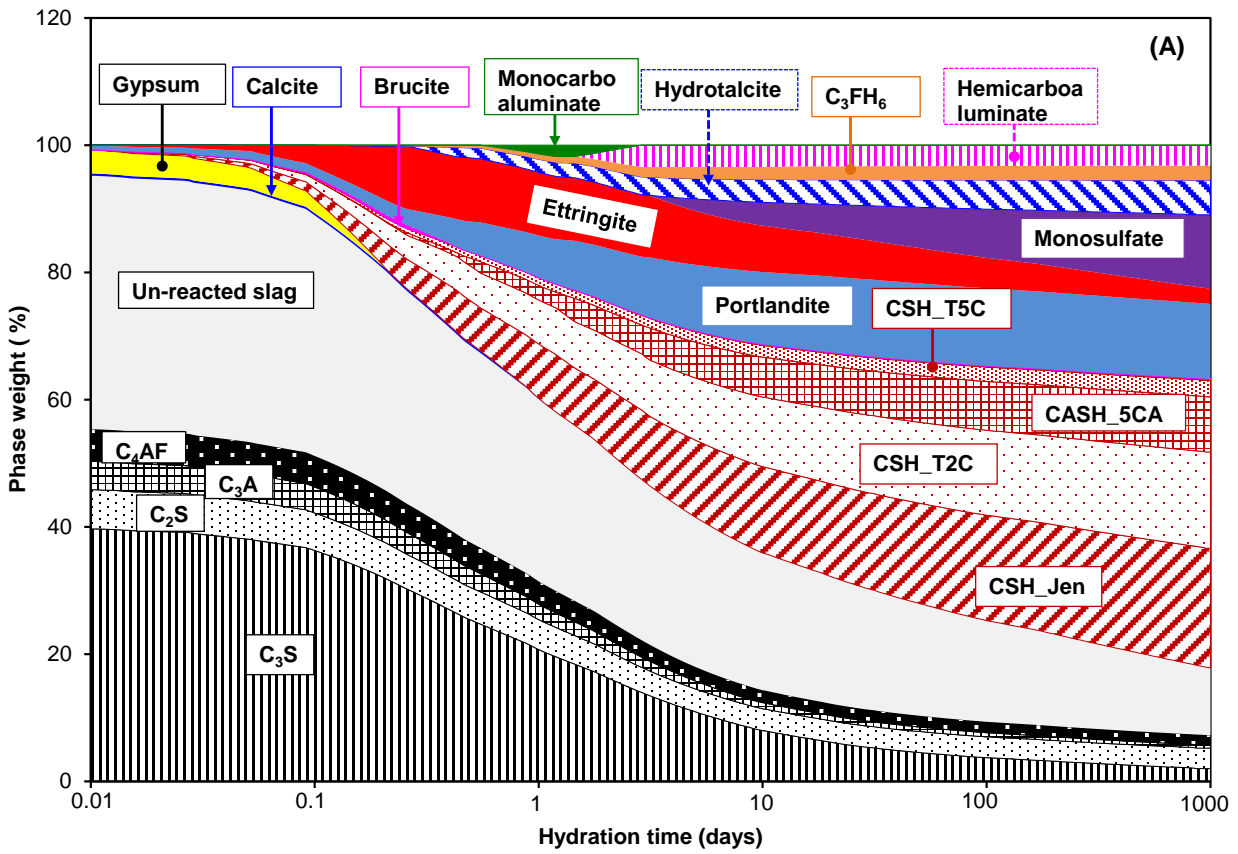
314

315 The calculated composition of hydrates and the remaining un-reacted slag and clinker of the slag
 316 cement system, which consists of 60% OPC and 40% slag, as a function of hydration time are
 317 shown in **Fig. 6(A)** for the input parameters given in **Table 3** and the composition of slag tabulated
 318 in **Table 4**. The predicted monocarboaluminate, which is formed through the dissolution of calcite,
 319 is completely changed to hemicarboaluminate after approximately 7 days of hydration, thus
 320 destabilising ettringite. The hydrated slag cement, with a degree of slag reaction of more than 70%,
 321 has C-A-S-H solid solution, monosulfoaluminate, hydrotalcite, and monocarboaluminate, in
 322 addition to decreasing trend of portlandite and ettringite as the main hydration products. The
 323 calculated Ca/Si and Al/Si ratios of C-A-S-H as a function of hydration time are shown in **Fig. 6(B)**.

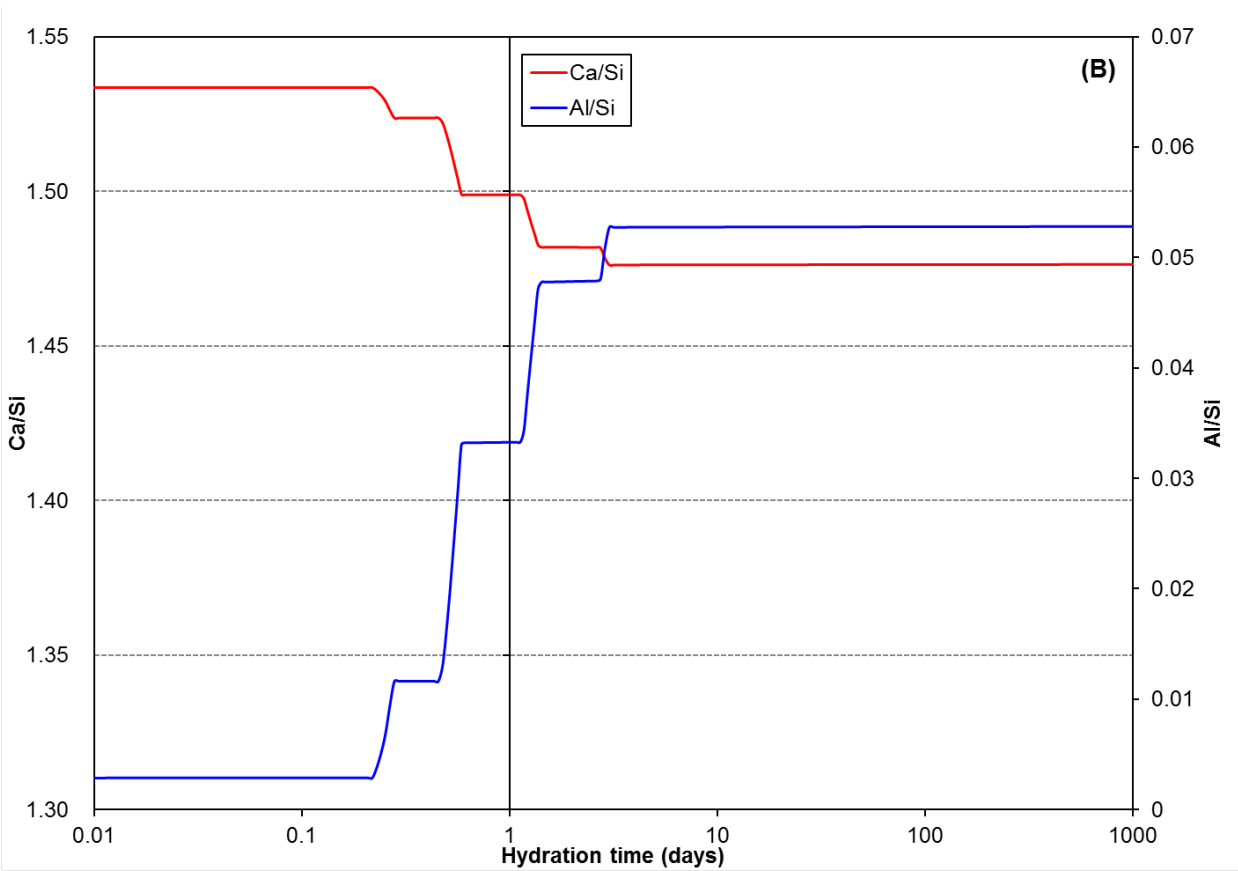
324 **Table 4** Mineral composition of slag and chemical composition of glass in the slag

<i>Mineral composition (wt. %)</i>		<i>Glass composition (wt. %)</i>	
-Anhydrite	3.1	-SiO ₂	30.80
-Glass	96.9	-Al ₂ O ₃	13.80
Total	100.0	-Fe ₂ O ₃	0.29
		-CaO	44.00
		-MgO	6.00
		-SO ₃	3.45
		-Na ₂ O	0.23
		-K ₂ O	0.28
		Total	98.85

325



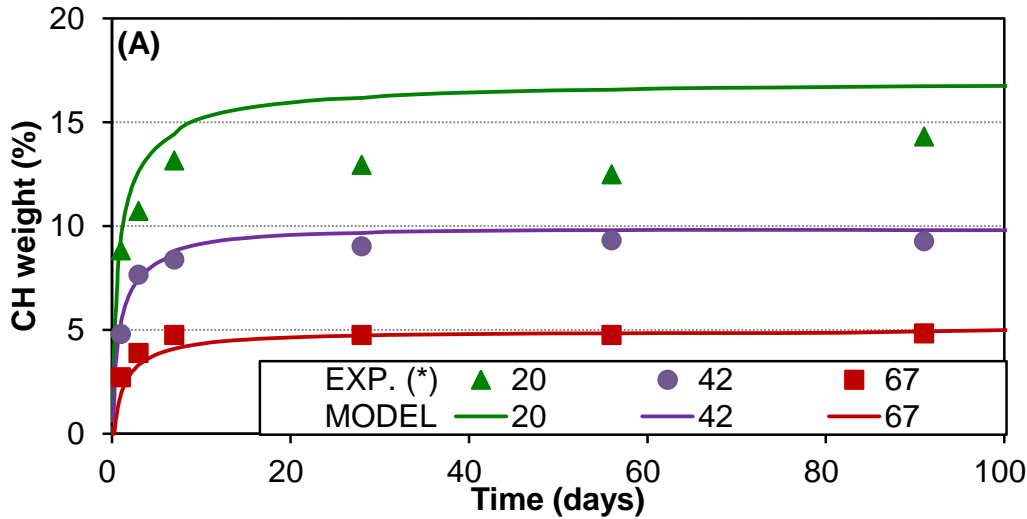
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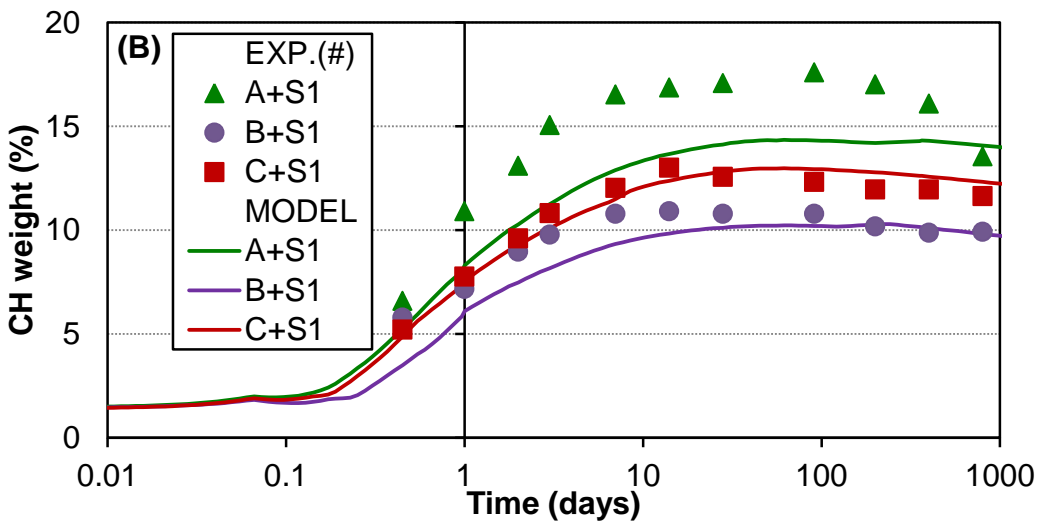
327

328 **Fig. 6.** Simulated phase (A), Ca/Si and Al/Si ratios of C-A-S-H (B) changes as a function of
 329 hydration time for cement blended with slag (OPC: slag = 60:40)

330



331



332

333 **Fig. 7.** Comparison of simulated portlandite changes with experimental data (*[32] and #[33]) for
334 (A) various slag replacement ratios and (B) a constant replacement of 40% slag with various types
335 of Portland cement as a function of hydration time for cement blended with slag

336

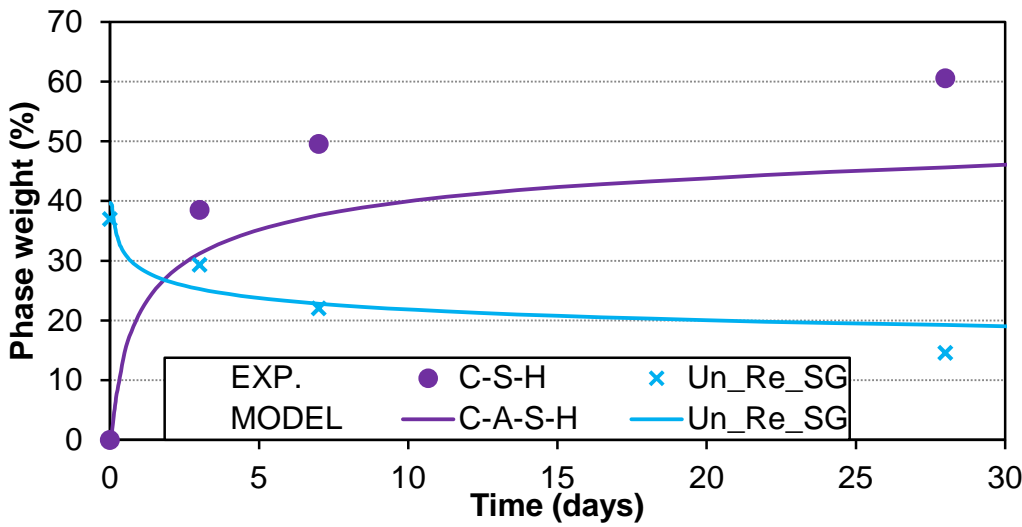
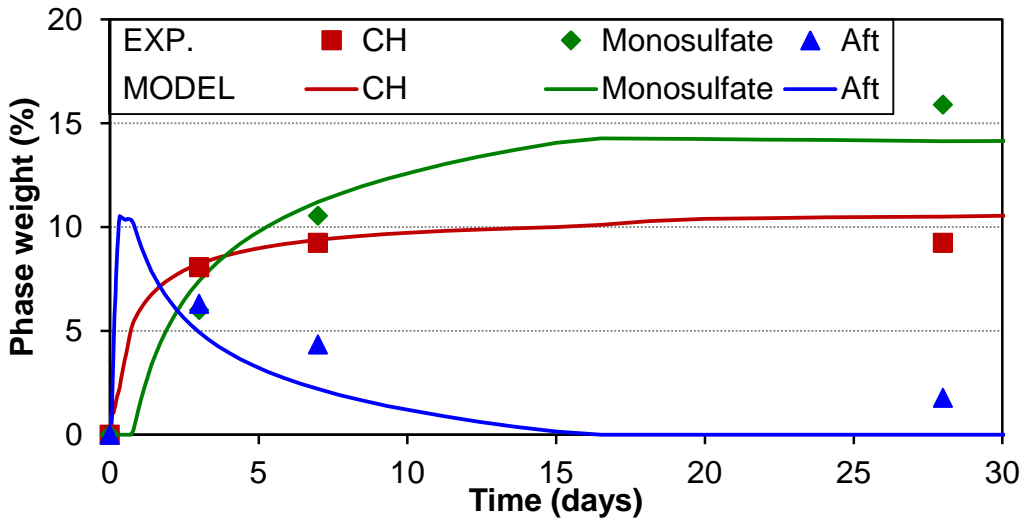
337 **Fig. 7** compares the portlandite weight percentage predicted by the model and that determined by
338 experiments [32-33] as a function of hydration time. The influence of the slag replacement ratio on
339 the consumption of portlandite is shown in **Fig. 7(A)** while the effect of the chemical composition
340 of Portland cement on the portlandite formation of the slag cement system is given in **Fig. 7(B)**. The
341 same composition of cement and slag and the mixing conditions as those given in ref. [32-33] were
342 adopted in the simulation. In addition to a consistent trend between the predicted and measured
343 values, the calculated portlandite content agrees very well with experimental results except for a

344 mixture containing 20% slag (20 in **Fig. 7 (A)**) and white cement blended with slag (A+S1 in **Fig.**
345 **7(B)**). The portlandite has not completely consumed by slag hydration, even for a high replacement
346 of slag and a long hydration time.

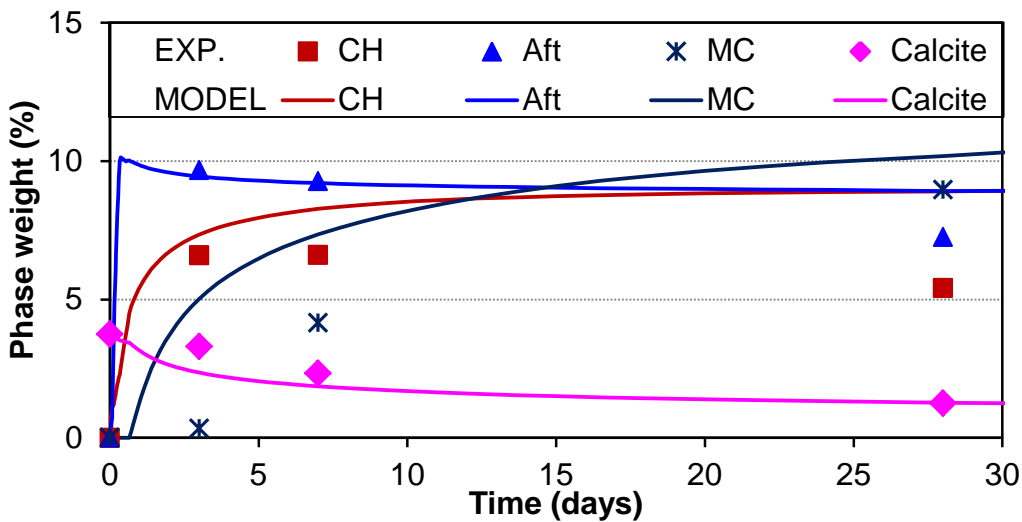
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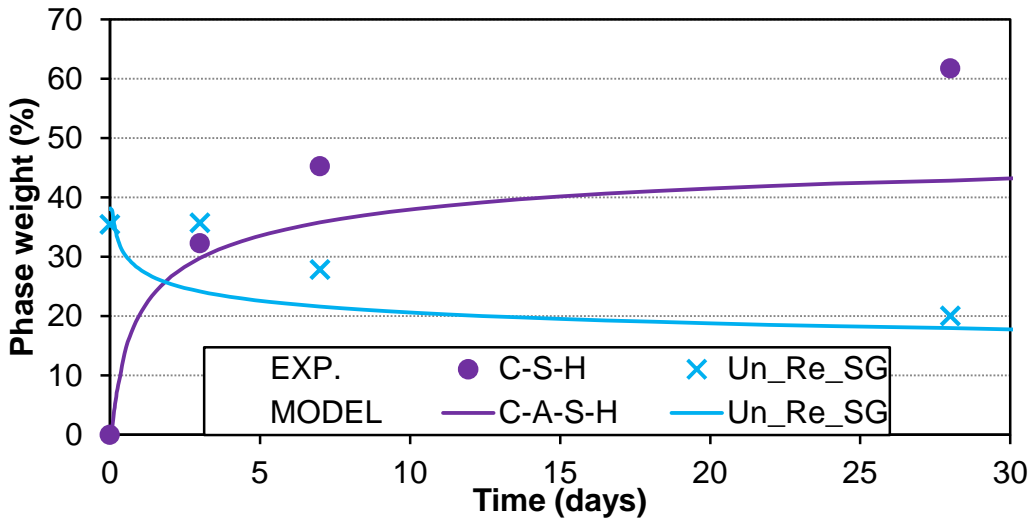
348 The main hydrates of the slag-blended cement (OPC:slag = 60:40) and slag and limestone-blended
349 cement (OPC:slag:LS = 57.7:38.5:3.8) were predicted using the same details as those used in the
350 experiment [34] as input, and the results are compared to XRD/Rietveld data in **Fig. 8** and **Fig. 9**
351 respectively. The calculated phase changes show the same tendency as the measured data. The
352 predicted portlandite, ettringite, monosulfoaluminate, monocarboaluminate, calcite, and un-reacted
353 slag weight percentage show good agreement with experimental values, but the model slightly
354 underestimates the amount of C-S-H/C-A-S-H in the hydrating slag-blended cement. Further, both
355 the XRD results and the model predictions agree on the absence of monosulfoaluminate in the
356 hydrated slag and limestone-blended cement, whereas the experimental results show the presence of
357 hemicarboaluminate in the hydrates but the model did not predict it (**Fig. 9**). The element
358 concentration predicted in the pore solution of the hydrating slag-blended cement is compared with
359 experimentally determined values [35-36] in **Fig. 10**. The predicted dominant elements in the pore
360 solution are consistent with experimental observations, and also the model predicts well the
361 decrease of alkali concentration in the pore solution with increasing slag proportions as observed in
362 the experiment.

363



366 **Fig. 8.** Comparison of simulated portlandite (CH), monosulfate, ettringite (Aft), C-S-H/C-A-S-H
 367 and un-reacted slag (Un_Re_SG) changes with experimental data [34] as a function of hydration
 368 time for cement blended with slag (OPC: slag = 60:40)

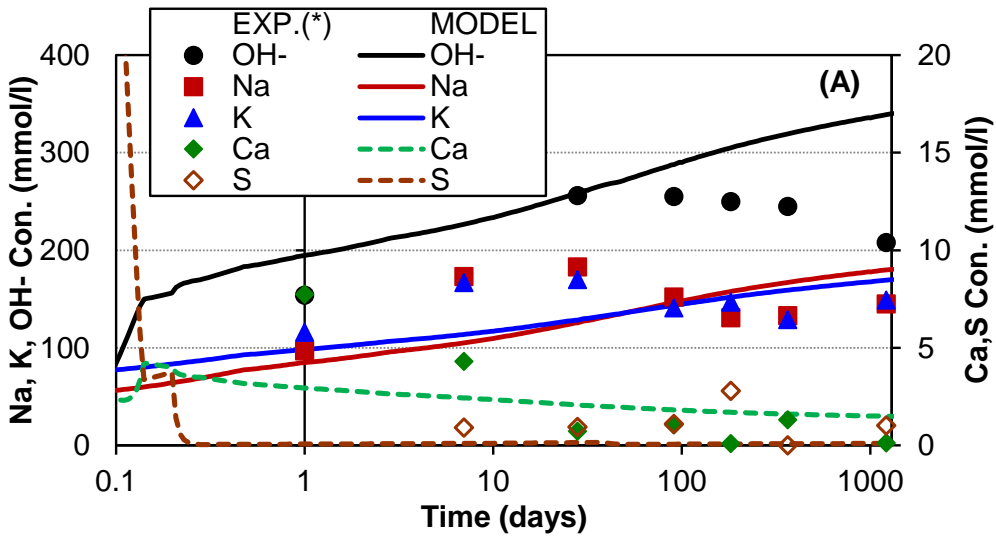




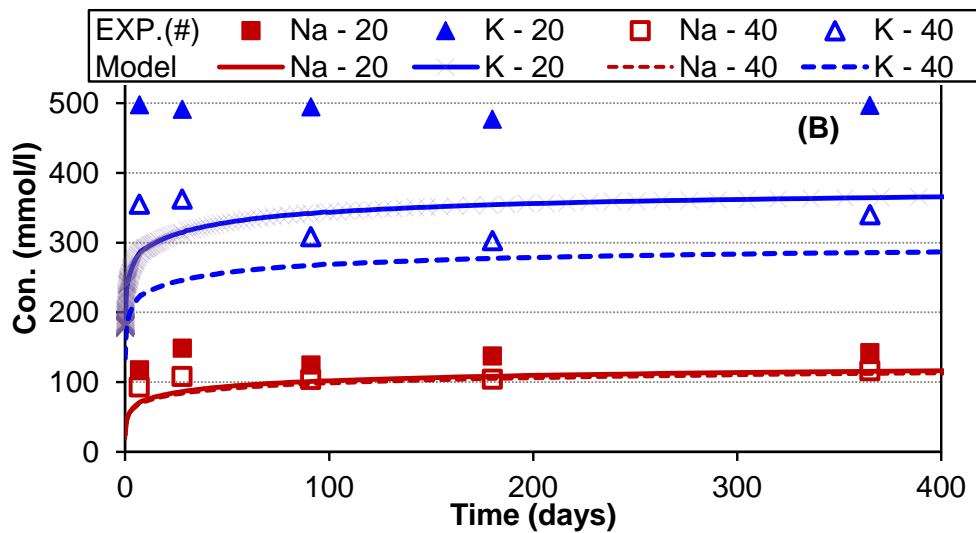
370

371 **Fig. 9.** Comparison of simulated portlandite (CH), ettringite (Aft), monocarboaluminate (MC),
 372 calcite, C-S-H/C-A-S-H and un-reacted slag (Un_Re_SG) changes with experimental data [34] as a
 373 function of hydration time for cement blended with slag and limestone (OPC: slag: LS = 57.7: 38.5:
 374 3.8)

375



376



377

378 **Fig. 10.** Comparison of simulated pore solution/alkali concentration changes with experimental data
 379 (*[35]; #[36]) for (A) cement blended slag (OPC: slag = 50:50) and (B) cement containing 20% and
 380 40% of slag

381

382 4. DISCUSSION

383

384 As demonstrated by the agreement between the experimental data and simulations results in slag
 385 cement systems, the approach used here can be applied to predict the compositions of the hydrate
 386 assemblage and pore solution. It should be noted that most of the slags used as supplementary
 387 cementitious materials have rather similar chemical compositions and high amorphous content.
 388 Different experimental results [32-36], which did not consider in the deriving equation (Eq. (12))
 389 for slag reaction, have used to verify the hydration in slag-blended cement systems (**Fig. 7–Fig. 10**).
 390 This suggests a wider applicable range for the derived equation. However, the suitability of using
 391 this derived equation for a high replacement of cement by slag needs to be assessed because the
 392 equation was obtained for replacement levels of up to 60% slag.

393

394 The calculated results show the same kind of hydration products, such as C-A-S-H, portlandite,
 395 ettringite, hydrotalcite, and AFm phases, as observed in the experiments for hydrating Portland
 396 cement and cement blended with slag. Furthermore, the predicted quantities of the phases agree

397 well with the experimental values. The predicted Ca/Si and Al/Si ratios of C-A-S-H in hydrated
 398 OPC and slag-blended cements are compared with experimental data in **Table 5**. The distribution
 399 among four end-members of the initially selected six end-members determines the Ca/Si ratio of
 400 C-A-S-H, and the fraction of the CASH_5CA member controls the Al/Si ratio because the presence
 401 of the CASH_INFCA member is negligible. The consideration of low Ca/Si ratio of C-S-H as
 402 end-members of C-A-S-H solid solution in OPC decreases its Ca/Si ratio, whereas the low amount
 403 of CASH_5CA decreases the Al/Si ratio in slag-blended cement.

404

405 **Table 5** Comparison between predicted and experimental Ca/Si and Al/Si ratios of C-A-S-H in
 406 hydrated OPC and blended cements. Experimental data from ^{*}[2, 12, and 33] and [#][33]

	Ca/Si		Al/Si		Time (days)
	Experimental	Predicted	Experimental	Predicted	
OPC [*]	≈ 1.80	1.48	≈ 0.05	0.05	400
OPC: slag = 60:40 [#]	≈ 1.55	1.47	≈ 0.15	0.06	400

407

408 A series of simulations were performed to evaluate the significance of the C-A-S-H solid solution in
 409 terms of precisely predicting the hydration products. The simulated portlandite weight percentage in
 410 the OPC and slag-blended cement was compared with experimental measurements in **Fig. 11** as an
 411 example. The simulation results for the case with six end-members of the C-A-S-H solid solution
 412 are shown in **Fig. 11(A)**, along with the results of four end-members (without CASH_INFCA and
 413 CSH_TobH). The predicted results using four end-members of the solid solution match exactly with
 414 those using six end-members because the fractions of CASH_INFCA and CSH_TobH are
 415 insignificant (**Fig. 1(A)** and **Fig. 6(A)**). Both the predicted and the measured results are very close
 416 to the $y = x$ line for the OPC and blended cement, indicating the importance of six or four
 417 end-members of the C-A-S-H solid solution.

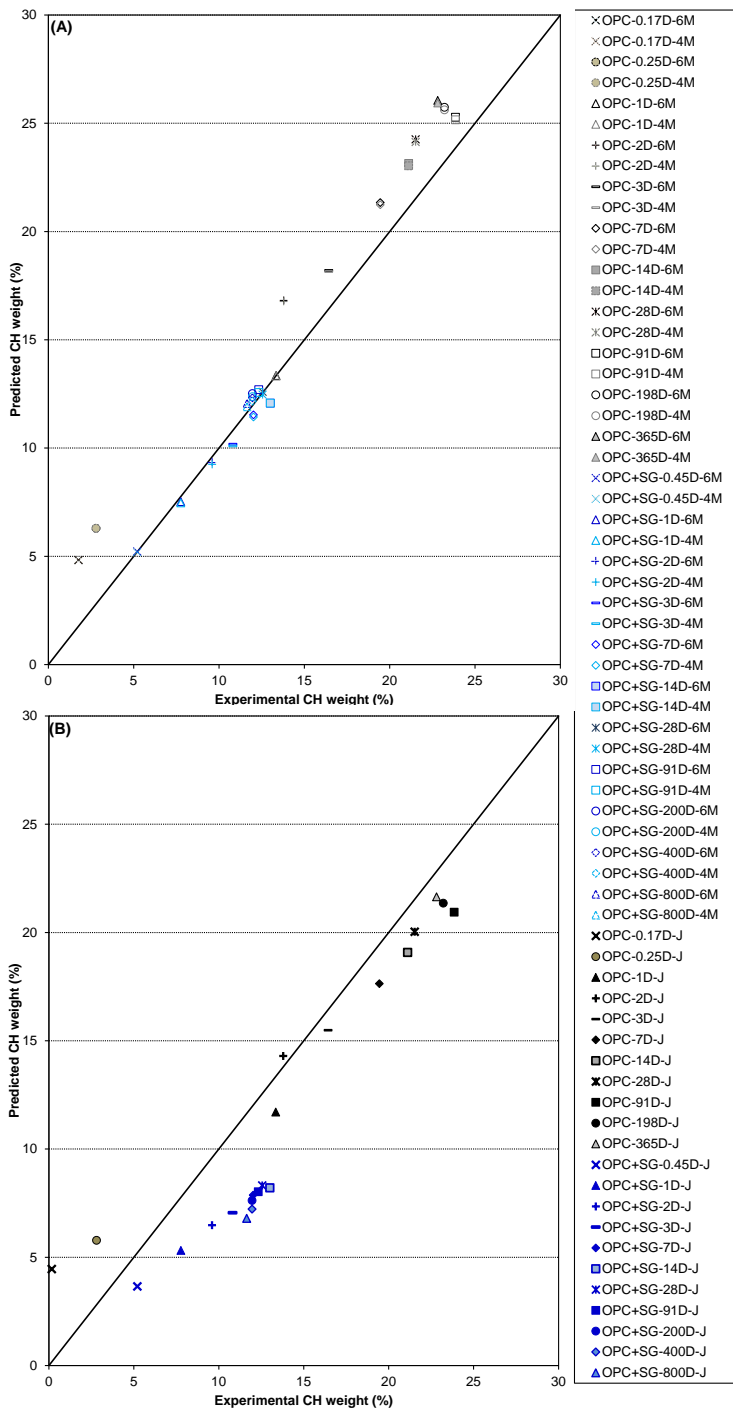
418

419 In contrast, another simulation was performed in which phase-equilibrium model with only
 420 CSH_Jen was assumed for C-S-H instead of the C-A-S-H solid solution model (**Fig. 11(B)**). The

421 modelled results are consistent with the experimental values for OPC, as observed in the case of the
422 solid solution, which suggests that either a C-A-S-H solid solution or a CSH_Jen phase-equilibrium
423 model can be used. However, poor agreement was found for the OPC containing slag, where
424 incorporation of the CSH_Jen phase-equilibrium model underestimated the portlandite content in
425 the blended cement. Therefore, it is important to consider the C-A-S-H solid solution model in
426 order to predict precisely the hydration products in the blended cement. Despite some discrepancies
427 in the Ca/Si or Al/Si ratio of C-A-S-H, the C-A-S-H solid solution model is more suitable for
428 predicting the hydration products of both OPC and slag-blended cement. Future research on the
429 thermodynamic models and laboratory experiments on C-A-S-H and the inclusion of other phases
430 as end-members would enable us to predict Ca/Si and Al/Si ratios in the blended cements more
431 accurately.

432

433



434

435 **Fig. 11.** Comparison of predicted portlandite weight percentage with experimental data [9 and 33]

436 considering (A) C-A-S-H solid solution model and (B) without C-A-S-H solid solution model, but

437 considered only the CSH_Jen phase for C-S-H. Notation: AA-xD-6M/4M/J: Binder-curing period in

438 days-six end-members (CSH_Jen, CSH_T2C, CASH_5CA, CSH_T5C, CASH_INFCA and

439 CSH_TobH) or four end-members (CSH_Jen, CSH_T2C, CASH_5CA, and CSH_T5C) solid

440 solution for C-A-S-H or considered only the CSH_Jen phase.

441

442 5. CONCLUSIONS

443

444 The composition of the hydrate assemblage and pore solution chemistry of OPC and slag-blended
445 cement as a function of hydration time were predicted using the PHREEQC integrated with
446 empirical expressions for the dissolution of clinker minerals and reactions of slag. The main
447 hydration products, such as C-A-S-H, portlandite, ettringite, hydrotalcite, and AFm phases, and
448 major elements in the pore solution, such as Na, K, OH, Ca, S, Al, and Si, were predicted for the
449 input of the chemical compositions of OPC and slag and mixing conditions. The considered solid
450 solution model for C-A-S-H explains the varying Ca/Si and Al/Si ratios due to hydration and the
451 addition of slag. The predicted results were verified with experimental data reported in the literature.
452 The types of phases in the model predictions for hydrating Portland cement, cement blended with
453 slag, and blended cement containing limestone were consistent with the experimental observations,
454 and both the calculated and measured quantities showed good agreement. The predicted elements
455 and the concentrations in the pore solution agreed well with the experimental results, but a proper
456 model for the uptake of alkalis by C-A-S-H is necessary for better predictions in slag-blended
457 cements. Comparing the simulated results considering the C-A-S-H solid solution model or not with
458 experimental data for portlandite as an example emphasised the significance of the solid solution
459 model in predicting the hydration products in slag-blended cement.

460

461 REFERENCES

462

- 463 1. M. S. Imbabi, C. Carrigan, S. McKenna, Trends and development in green cement and concrete
464 technology, *International Journal of Sustainable Built Environment* 1 (2012) 194–216.
- 465 2. B. Lothenbach, K. Scrivener, R.D. Hooton, Supplementary cementitious materials, *Cem. Concr.*
466 *Res.* 41 (2011) 1244–1256.
- 467 3. S. Miyahara *et al.* Durability and applications of environmental-friendly concrete with slag

- 468 and calcium activator, 5th *International Conference on Construction Materials (ConMat'15)*,
469 (2015).
- 470 4. D. Rothstein, J. J. Thomas, B. J. Christensen, H. M. Jennings, Solubility of Ca-, S-, Al-, and
471 Si-bearing solid phases in Portland cement pore solutions as a function of hydration time, *Cem.*
472 *Concr. Res.* 32 (2002) 1663–1671.
- 473 5. A. Gruskovnjak et al., Hydration mechanism of super sulphated slag cement, *Cem. Concr. Res.*
474 38 (2008) 983–992.
- 475 6. R. Loser, B. Lothenbach, A. Leemann, M. Tuchschnid, Chloride resistance of concrete and its
476 binding capacity - comparison between experimental results and thermodynamic modeling,
477 *Cement & Concrete Composites* 32 (2010) 34–42.
- 478 7. B. Lothenbach, F. Winnefeld, Thermodynamic modelling of the hydration of Portland cement,
479 *Cem. Concr. Res.* 36 (2006) 209–226.
- 480 8. B. Lothenbach, E. Wieland, A thermodynamic approach to the hydration of sulphate-resisting
481 Portland cement, *Waste Management* 26 (2006) 706–719.
- 482 9. B. Lothenbach, G. Le Saout, E. Gallucci, K. Scrivener, Influence of limestone on the hydration
483 of Portland cements, *Cem. Concr. Res.* 38 (2008) 848–860.
- 484 10. B. Lothenbach et al., Thermodynamic modelling of the effect of temperature on the hydration
485 and porosity of Portland cement, *Cem. Concr. Res.* 38 (2008) 1–18.
- 486 11. B. Lothenbach et al., Sulfate ingress in Portland cement, *Cem. Concr. Res.* 40 (2010) 1211–
487 1225.
- 488 12. K. De Weerd et al., Hydration mechanisms of ternary Portland cements containing limestone
489 powder and fly ash, *Cem. Concr. Res.* 40 (2011) 279–291.
- 490 13. Y. Elakneswaran and T. Ishida, Development and verification of an integrated physicochemical
491 and geochemical modelling framework for performance assessment of cement-based materials,
492 *Journal of Advanced Concrete Technology*, 12, (2014), 111–126.
- 493 14. B. Kolani et al., Hydration of slag-blended cements, *Cement & Concrete Composites* 34 (2012)

- 494 1009–1018.
- 495 15. R. J. Myers, S. A. Bernal, J. L. Provis, A thermodynamic model for C-(N-)A-S-H gel:
496 CNASH_{ss}. Derivation and validation, *Cem. Concr. Res.* 66 (2014) 27–47.
- 497 16. I. G. Richardson and G. W. Groves, Microstructure and microanalysis of hardened cement
498 pastes involving ground granulated blast-furnace slag, *J Mater Sci.*, 27, (1992), 6204–6212.
- 499 17. C. A. J. Appelo, D. Postma, *Geochemistry, groundwater and pollution*: CRC Press Taylor &
500 Francis Group, 2009.
- 501 18. D. L. Parkhurst, C. A. J. Appelo, A computer program for speciation, batch-reaction,
502 one-dimensional transport and inverse geochemical calculations, USGS report 1999.
- 503 19. K.S. Pitzer, Ion interaction approach: theory and data correlation, in: K.S. Pitzer (Ed.), *Activity*
504 *Coefficients in Electrolyte Solutions*, CRC Press, Boca Raton, 1991, pp. 75–153.
- 505 20. D.A. Kulik, Improving the structural consistency of C-S-H solid solution thermodynamic
506 models, *Cem. Concr. Res.* 41 (2011) 477–495.
- 507 21. L. J. Parrot, D. C. Killoh, Prediction of cement hydration, *British Ceramic Proceedings* 35
508 (1984) 41–53.
- 509 22. S. R. Charlton, D. L. Parkhurst, Modules based on the geochemical model PHREEQC for use in
510 scripting and programming languages, *Computers & Geosciences* 37 (2011) 1653–1663.
- 511 23. W. Chen and H. J. H. Brouwers, Alkali binding in hydrated Portland cement paste, *Cement and*
512 *Concrete Research*, 40, (2010), 716–722.
- 513 24. T. Matschei, B. Lothenbach, F.P. Glasser, The AFm phase in Portland cement, *Cem. Concr. Res.*
514 37 (2007) 118–130.
- 515 25. L.A Larbi, et al, The chemistry of pore fluid of silica fume-blended cement systems, *Cement*
516 *and Concrete Research*, 20, (1990), 506-516.
- 517 26. J. S. Lumley, R. S. Gollop, G. K. Moir, H. F. W. Taylor, Degrees of reaction of the slag in some
518 blends with Portland cements, *Cem. Concr. Res.* 26 (1996)139–51.
- 519 27. T. Sagawa, T. Nawa, Hydration of blast furnace slag cement and effect of water to cement ration

- 520 on hydration of blast furnace slag cement, *Cement Science and Concrete Technology* 60 (2006)
521 82–87. (In Japanese)
- 522 28. T. Sagawa, T. Ishida, Y. Luan, T. Nawa, Hydrate composition analysis and micro structure
523 characteristics of Portland cement-blast furnace slag system, *Journal of JSCE E* 66 (2010) 311–
524 324. (In Japanese)
- 525 29. E. Sakai, H. Imoto, M. Daimon, Hydration and strength development of blast furnace slag
526 cement, *Proceedings of JCI* 26 (2004) 135–140. (In Japanese)
- 527 30. N. Takamatsu, I. Maruyama, Study on volume deformation and hydration degree of blast
528 furnace slag replaced matrix, *Proceedings of JCI* 31 (2009) 187–192. (In Japanese)
- 529 31. S.J. Barnett, M.N. Soutsos, S.G. Millard, J.H. Bungey, Strength development of mortars
530 containing ground granulated blast-furnace slag: Effect of curing temperature and determination
531 of apparent activation energies, *Cem. Concr. Res.* 36 (2006)434–440.
- 532 32. T. Iyoda, Y. Dan, The effect of temperature on hydration rate of slag in blended cement,
533 *Proceeding of JSCE 333 committee symposium (2007)* II59–62. (In Japanese)
- 534 33. V. Kocaba, Development and evaluation of methods to follow microstructural development of
535 cementitious systems including slags, PhD thesis, ÉCOLE POLYTECHNIQUE FÉDÉRALE
536 DE LAUSANNE, 2009.
- 537 34. S. Hoshino, K. Yamada, H. Hirao, XRD/Rietveld analysis of the hydration and strength
538 development of slag and limestone blended cement, *Journal of Advanced Concrete Technology*
539 4 (2006) 357–367.
- 540 35. T. Maruya, Y. Matsuoka, Durability assessment of binders by analysing liquid and solid phase,
541 *JSCE* 478 (1993) 41–50 (In Japanese)
- 542 36. E. Schafer, “Einfluss der Reaktionen verschiedener Zementbestandteile auf den alkalihalt
543 der Porenlösung des Zementsteins”, *PhD thesis*, Clausthal University of Technology,
544 Clausthal-Zellerfeld, Germany, (2004).

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