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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

cement blended with slag and the blended cement containing limestone. The predicted compositions of hydration products and element concentrations in pore solutions compared well with experimental data reported in literature. The calculation results showed the varying Ca/Si and Al/Si ratios of calcium aluminosilicate hydrate (C-A-S-H)^{*} in the hydration products due to hydration and slag addition. Limitations on the equation for reaction of slag and the importance of a C-A-S-H 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 innovative low-carbon cement-based materials can substantially reduce CO₂ emissions associated 40 with PC production [1]. Several studies have focused on developing SCMs from a variety of waste 41 42 and by-product materials, in addition to common SCMs such as fly ash, ground granulated blast-furnace slag, and silica fume [2]. Further, novel cement systems/concrete are being developed 43 44 through alkaline activation of aluminosilicates or innovative uses of waste materials [3]. Some of these novel cements are in use on a limited scale in some parts of the world; however, their short-45 and long-term performance as compared to conventional PC needs to be established for their 46 47 large-scale application [1]. More investigation on the properties and performance of SCMs or novel cements is necessary for their successful usage as partial or complete replacement of PC in 48 49 concrete.

50

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

^{*} Cement chemistry shorthand notations: $A = Al_2O_3$, C = CaO, $S = SiO_2$, and $H = H_2O_3$

52 SCMs are important for better understanding of the properties and performance of the materials in concrete. It is also essential in terms of materials selection for concrete and for predicting properties 53 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 and the time it takes to perform these experiments. On the other hand, thermodynamic or 57 58 mathematical models significantly reduce the reliance on laboratory experiments and help to predict 59 hydration processes and materials properties.

60

Thermodynamic models in cementitious systems would make it possible to predict the composition 61 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 and compared the calculated saturation indexes with the supersaturation of phases found in previous 65 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 models in cementitious materials have been proposed to simulate the hydration reaction of cement 76 77 and slag and also to predict the evolution of hydration products [13-14]. It is recognised that a

partial or complete replacement of PC with slag reduces the Ca/Si ratio of calcium silicate hydrate (C-S-H) and also forms calcium aluminosilicate hydrate (C-A-S-H) [2, and 15-16]. The incorporation of aluminium in C-S-H of PC has also been reported in previous studies [2 and16]. However, details of these aspects have not yet been taken into account in existing models for predicting the composition of the hydrate assemblage and pore solution chemistry. A model that includes Al incorporation and various Ca/Si ratios of C-S-H is thus important for better prediction 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 C-A-S-H gels as end-members was considered to account for the changing Ca/Si ratio and 94 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

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

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

108

109 where K_p is the thermodynamic equilibrium constant for phase p, γ_i is the activity coefficient of ion i110 (-), 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

114
$$K_p = \exp\left(-\frac{\Delta_r G_T^0}{RT}\right)$$
 (2)

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

119
$$\Delta_r G_T^0 = \sum \Delta_f G_{T, products}^0 - \sum \Delta_f G_{T, reac \tan ts}^0$$
(3)

120

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

Phase	Reactions	$\log K_p$	$\triangle_r H^0$	Ref.
Anhydrite	$CaSO_4 \leftrightarrow Ca^{2+} + SO_4^{2-}$	-4.36	-1.71	[18]
Brucite	$Mg(OH)_2 + 2H^+ \leftrightarrow Mg^{2+} + 2H_2O$	17.07	-115.66	[10]
C ₃ AH ₆	$Ca_{3}Al_{2}(OH)_{12} + 12H^{+} \leftrightarrow 3Ca^{2+} + 2Al^{3+} + 12H_{2}O$	82.22	-595.76	[10]
C ₃ FH ₆	$Ca_{3}Fe_{2}(OH)_{12} + 12H^{+} \leftrightarrow 3Ca^{2+} + 2Fe^{3+} + 12H_{2}O$	73.65	-516.96	[10]
Calcite	$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$	-8.48	-2.297	[18]
CASH_5CA	$\begin{array}{rl} (CaO)_{1.25}(Al_2O_3)_{0.125}(SiO_2):1.625H_2O & + \\ 3.25H^+ \leftrightarrow 1.25Ca^{2+} + 0.25Al^{3+} + H_4SiO_4 & + \\ 1.25H_2O \end{array}$	22.00	-141.58	[15]
CASH_INFCA	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	16.60	-110.67	[15]
CSH_T2C	$(CaO)_{1.5}(SiO_2):2.5H_2O + 3H^+ \leftrightarrow 1.5Ca^{2+} + H_4SiO_4 + 2H_2O$	25.88	-127.10	[15]
CSH_T5C	$(CaO)_{1.25}(SiO_2)_{1.25}:2.5H_2O + 2.5H^+ \leftrightarrow$ $1.25Ca^{2+} + 1.25H_4SiO_4 + 1.25H_2O$	18.74	-83.46	[15]
CSH_Jen	$(CaO)_{1.667}(SiO_2):2.1H_2O + 3.334H^+ \leftrightarrow$ $1.667Ca^{2+} + H_4SiO_4 + 1.767H_2O$	29.60	-148.44	[10]
CSH_TobH	$(CaO)(SiO_2)_{1.5}:2.5H_2O + 2H^+ \leftrightarrow Ca^{2+} + 1.5H_4SiO_4 + 0.5H_2O$	13.18	-47.83	[15]
Ettringite	$Ca_{6}Al_{2}(SO_{4})_{3}(OH)_{12}:26H_{2}O + 12H^{+} \leftrightarrow 6Ca^{2+}$ $+ 2Al^{3+} + 3SO_{4}^{2-} + 38H_{2}O$	57.73	-389.36	[10]
Gypsum	$CaSO_4{:}2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2 H_2O$	-4.58	-0.109	[18]
Hemicarboaluminate	$\begin{array}{rll} Ca_{4}Al_{2}(CO_{3})_{0.5}(OH)_{13}:5.5H_{2}O &+& 13H^{+} &\leftrightarrow \\ 4Ca^{2+} + 2Al^{3+} + 0.5CO_{3}^{2-} + 18.5H_{2}O \end{array}$	87.88	-604.27	[10]
Hydrotalcite	$\begin{array}{rcl} Mg_4Al_2(OH)_{14}{:}3H_2O &+& 14H^+ \ \leftrightarrow \ 2Al^{3+} &+\\ 4Mg^{2+} + 17H_2O \end{array}$	75.97	-607.91	[10]
Monocarboaluminate	$\begin{aligned} & \operatorname{Ca_4Al_2(CO_3)(OH)_{12}:5H_2O} + 12H^+ \leftrightarrow 4\operatorname{Ca^{2+}} + \\ & 2\operatorname{Al^{3+}} + \operatorname{CO_3^{2-}} + 17H_2O \end{aligned}$	71.54	-533.14	[10]
Monosulfoaluminate	$\begin{aligned} & \operatorname{Ca_4Al_2(SO_4)(OH)_{12}:6H_2O} + 12H^+ \leftrightarrow 4\operatorname{Ca^{2+}} + \\ & 2\operatorname{Al^{3+}} + \operatorname{SO_4^{2-}} + 18H_2O \end{aligned}$	73.68	-553.08	[10]
Portlandite	$Ca(OH)_2 + 2H^+ \leftrightarrow Ca^{2+} + 2H_2O$	22.79	-129.66	[10]
Stratlingite	$\begin{aligned} Ca_2Al_2SiO_2(OH)_{10}:3H_2O \ + \ 10H^+ &\leftrightarrow \ 2Ca^{2+} \ + \\ 2Al^{3+} + H_4SiO_4 \ + \ 11H_2O \end{aligned}$	51.42	-408.12	[10]

2.2. Cement hydration model

the hydration degree of each cement clinker mineral as a function of time. The model is described in 134 135 detail elsewhere [7, 9, and 21]; the main equations are briefly described here. Parrot and Killoh [21] derived a set of empirical equations to describe the hydration rate, R_t^m , of an individual clinker 136 mineral *m* at time t ($m = C_3S$, C_2S , C_3A , C_4AF): 137 138 139 Nucleation and growth 140 $R_{t,1}^{m} = \frac{K_{1}}{N_{1}} \left[1 - \alpha_{t}^{m} \right] \left\{ -\ln(1 - \alpha_{t}^{m}) \right\}^{(1-N_{1})}$ 141 (4) 142 143 Diffusion 144 $R_{t,2}^{m} = \frac{K_{2} \left(1 - \alpha_{t}^{m}\right)^{\frac{2}{3}}}{1 - \left(1 - \alpha_{t}^{m}\right)^{\frac{1}{3}}}$ 145 (5)146 Hydration shell formation 147 148 $R_{t,3}^{m} = K_{3} (1 - \alpha_{t}^{m})^{N_{3}}$ 149 (6)150 The associated empirical parameters in the equations are tabulated in Table 2 as reported by 151 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 152 the controlling rate. The hydration degree of clinker mineral m at the time t, α_t^m , is calculated from 153

In this study, the cement hydration model proposed by Parrot and Killoh [21] was used to estimate

154 the hydration degree of the mineral at the previous time step (α_{t-1}^{m}) , the time interval (Δ_t) , and

155 hydration rate of the clinker mineral at the previous time step (R_{t-1}^{m}) as

157
$$\alpha_{t}^{m} = \alpha_{t-1}^{m} + \Delta t \cdot \min\left(R_{t-1,1}^{m}, R_{t-1,2}^{m}, R_{t-1,3}^{m}\right) \cdot \beta_{w/c} \cdot \lambda_{RH} \cdot \frac{A}{A_{0}} \cdot \exp\left[\frac{E_{a}^{m}}{R}\left(\frac{1}{T_{0}} - \frac{1}{T}\right)\right]$$
(7)

158 where,

159 $\beta_{w/c} = \left[1 + 3.333 \times \left(H^m \times w/c - \alpha_{t-1}\right)\right]^4 \qquad \text{if} \quad \alpha_t > H^m \times w/c$

160
$$\beta_{w/c} = 1$$
 if $\alpha_t \le H^m \times w/c$ (8)

161
$$\lambda_{RH} = \left(\frac{RH - 0.55}{0.45}\right)^4$$
 (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 (m²/kg), A^0 is the reference surface area of cement (385 m²/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
$$\alpha_{t} = \frac{f^{C_{3}S}\alpha_{t}^{C_{3}S} + f^{C_{2}S}\alpha_{t}^{C_{2}S} + f^{C_{3}A}\alpha_{t}^{C_{3}A} + f^{C_{4}AF}\alpha_{t}^{C_{4}AF}}{f^{C_{3}S} + f^{C_{2}S} + f^{C_{3}A} + f^{C_{4}AF}}$$
(10)

173

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

176 Table 2 Parameters adapted to calculate the hydration degree of the clinker minerals as a function177 of time [9-10]

	C_3S	C_2S	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
Н	1.8	1.35	1.60	1.45
E _a (J/mol)	41570	20785	54040	34087

179 3. SIMULATION RESULTS AND VERIFICATIONS

180 **3.1. Ordinary Portland cement system**

181 **3.1.1. Modelling approach**

182

PHREEQC was coupled (using the IPhreeqc module [22]) with Excel[®] to carry out thermodynamic 183 calculations in each time step. PHREEQC performs speciation and batch-reaction calculations to 184 185 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 minerals were carried out in Excel[®] and the necessary data were transferred to PHREEQC as input 187 188 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.
- 198 \diamond Na₂O and K₂O, which are present as minor components in the clinker minerals, and total MgO
- 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 \diamond Gypsum and calcite react continuously to reach equilibrium with the pore solution.

207

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

212

213
$$Rd_{K} = 0.20C_{K}^{-0.76}$$
 (11)

- 214
- 215 where C_K is the concentration of K⁺.
- 216

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

218

The predicted phase changes as a function of time for Ordinary Portland Cement (OPC) paste (using the input parameters given in **Table 3**) are shown in **Fig. 1**(A). The model predicts the complete dissolution of the available gypsum in the cement within the first 7 h of hydration and the gradual increase in the amount of C-A-S-H end-members and portlandite with time. The presence of CSH_TobH and CASH_INFCA end-members in C-A-S-H solid solution is negligible. Magnesium present in the cement is predicted as brucite at an early age and then converted to hydrotalcite after 0.5 days of hydration. The model also calculates the continuous dissolution of calcite present in the cement to form monocarboaluminate, and some monocarboaluminate transforms to hemicarboaluminate. The predicted phases in the hydrated OPC (after 7 days or longer of hydration time) include C-A-S-H gel solid solution, portlandite, ettringite, hydrotalcite, and AFm phases such as monocarboaluminate and hemicarboaluminate, in addition to un-hydrated clinker minerals. The chemical composition data for end-members of the C-A-S-H gel solid solution are used to predict the Ca/Si and Al/Si ratios of the gel (**Fig. 1**(B)). The predicted ratios of hydrating OPC are $1.48 \le Ca/Si \le 1.53$ and $0.003 \le Al/Si \le 0.049$.

233

Table 3 Chemical composition and Blaine surface area of OPC and mixing conditions as input to

235	the model, adap	pted from ref.	[9]
-----	-----------------	----------------	-----

Phase composition (g/100 g)		Minor components in the clinker phases			
-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	Mixing conditions			
-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				
$-K_2SO_4$	1.33	Blaine surface area (m ² /kg)	413		
* Total MgO					

236



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

The simulated hydration products of OPC paste for the input parameters listed in Table 3 were 243 244 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 amount, and lack of data concerning the structure. Therefore, the total amorphous content (C-S-H + 247 248 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 comparison of computed elements concentration in the pore solution of hydrating OPC (for the 255 256 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 ions in pore solution is compared with another experimental data [25] to give further validation to 260 the proposed model. The simulated concentration of Na, K, and Ca elements and pH of pore 261 262 solution are compared with experimental values of hydrating OPC with varying w/c ratios in Fig. 4. It can be seen that the concentration of ions are predicted well though some discrepancies are 263 264 observed for pH at 1 and 3 days.



265

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



Fig. 3. Comparison of simulated pore solution concentration changes with experimental data [9] for

271 hydrating OPC



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

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 the cement replacement by slag of 20-60% for up to 2 years of hydration, to a function. The 290 291 influence of temperature, using the Arrhenius equation, and the surface area of the slag were included in the equation. The derived equation for the reaction degree of slag in percentage, α_{sg} , can 292 293 be described as follows:

294

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

where,

297
$$A = -0.16 \times r_{sg} + 12.81 \tag{13}$$

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

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

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

301

302 where r_{sg} is the replacement ratio of slag (%), SA_{sg} is the Blaine value of slag (cm²/g), and E_{sg} is the

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





Fig. 5. Comparison of calculated reaction degree of slag using Eq. (12) with published ([26], #[27], *[28], [29], and #[30]) experimental data. The dotted lines show $\pm 10\%$ deviation from y = x line. Notation: ()-xx-yD: Reference-slag replacement ratio-curing period in days. Two types of slag in ref. (Lumley *et al.*, 1996) are used.

3.2.2. Simulation results and experimental data verification

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 shown in Fig. 6(A) for the input parameters given in Table 3 and the composition of slag tabulated 317 in Table 4. The predicted monocarboaluminate, which is formed through the dissolution of calcite, 318 319 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%, has C-A-S-H solid solution, monosulfoaluminate, hydrotalcite, and monocarboaluminate, in 321 322 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

Mineral composition (wt. %)		Glass composition (wt. %)		
-Anhydrite	3.1	-SiO ₂	30.80	
-Glass	96.9	$-Al_2O_3$	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	



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



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

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

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

347

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 underestimates the amount of C-S-H/C-A-S-H in the hydrating slag-blended cement. Further, both 354 355 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 hemicarboaluminate in the hydrates but the model did not predict it (Fig. 9). The element 357 358 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 solution are consistent with experimental observations, and also the model predicts well the 360 361 decrease of alkali concentration in the pore solution with increasing slag proportions as observed in the experiment. 362



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





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







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

377

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

The calculated results show the same kind of hydration products, such as C-A-S-H, portlandite, ettringite, hydrotalcite, and AFm phases, as observed in the experiments for hydrating Portland 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
	Experimental	Predicted	Experimental	Predicted	(days)
OPC*	≈ 1.80	1.48	≈ 0.05	0.05	400
OPC: $slag = 60:40^{\#}$	≈ 1.55	1.47	≈ 0.15	0.06	400

407

A series of simulations were performed to evaluate the significance of the C-A-S-H solid solution in 408 409 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

In contrast, another simulation was performed in which phase-equilibrium model with only
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 model can be used. However, poor agreement was found for the OPC containing slag, where 423 424 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 order to predict precisely the hydration products in the blended cement. Despite some discrepancies 426 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 427 428 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



Fig. 11. Comparison of predicted portlandite weight percentage with experimental data [9 and 33] considering (A) C-A-S-H solid solution model and (B) without C-A-S-H solid solution model, but considered only the CSH_Jen phase for C-S-H. Notation: AA-xD-6M/4M/J: Binder-curing period in days-six end-members (CSH_Jen, CSH_T2C, CASH_5CA, CSH_T5C, CASH_INFCA and CSH_TobH) or four end-members (CSH_Jen, CSH_T2C, CASH_5CA, and CSH_T5C) solid solution for C-A-S-H or considered only the CSH_Jen phase.

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 hydration products, such as C-A-S-H, portlandite, ettringite, hydrotalcite, and AFm phases, and 447 448 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 and the concentrations in the pore solution agreed well with the experimental results, but a proper 455 456 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.

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