



Title	Hydration of ferrite-rich Portland cement: Evaluation of Fe-hydrates and Fe uptake in calcium-silicate-hydrates
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1 **Hydration of Ferrite-Rich Portland Cement: Evaluation of Fe-Hydrates and Fe**  
2 **Uptake in Calcium-Silicate-Hydrates**

3

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27 **Abstract**

28 The hydration process in ferrite-rich cement (FC) and its pore structure have been investigated by  
29 experimental and thermodynamic modelling techniques. X-ray diffraction (XRD)/Rietveld analysis,  
30 thermogravimetry (TG), and mercury intrusion porosimetry (MIP) were performed to study the  
31 hydration process, pore volume-pore size distributions, and Fe uptake in calcium-silicate-hydrate (C-  
32 S-H). Similar phases were found in both FC and ordinary Portland cement (OPC). The hydration  
33 degree of FC was higher at the early stage compared with that of OPC; however, the hydration of  
34 OPC exceeded that of FC after 14 days because the high amount of C<sub>2</sub>S in OPC promoted the late  
35 hydration. The XRD-TG results revealed relatively similar Fe uptake by C-S-H in both FC and OPC.  
36 The thermodynamic model confirmed the formation of a high amount of Fe phases in FC. Moreover,  
37 the model predictions agreed well with the experimental results, demonstrating the accuracy of the  
38 proposed model for FC.

39  
40 **Keywords:** Ferrite-rich cement (FC); hydration; Fe phases; calcium-silicate-hydrate (C-S-H);  
41 thermodynamic modelling

42  
43 **1. Introduction**

44 Concrete is the second most used material in the world after water [1]. Due to the significant increase  
45 in the demand and production of cementitious materials, (the worldwide production has  
46 approximately doubled between 2005–2015 [2]), the global CO<sub>2</sub> emissions increase daily, thereby  
47 posing several environmental risks. Cement manufacturing plants are responsible for approximately  
48 8–9% of anthropogenic CO<sub>2</sub> emissions and approximately 1 tonne of CO<sub>2</sub> are produced during the  
49 production of 1 tonne of cement [3-5]. In addition, high amount of thermal energy is required for the  
50 production process (approximately 4.7 million British Thermal Unit per 1 tonne of cement) [2].  
51 Recently, there have been considerable developments to reduce CO<sub>2</sub> emission and to increase energy  
52 savings in the cement and concrete industry. It includes the developments of supplementary

53 cementitious materials, production of alternative clinkers with reduced amounts of limestone in the  
54 raw mix, alternative fuels and renewable energy sources, and process optimisation [3, 5-7].

55

56 Very recently, the reduction of the firing temperature of the clinker has been proposed and  
57 investigated to reduce energy consumption and CO<sub>2</sub> emission [8-9]. In this process, the clinker has  
58 been produced alternatively, by reducing the firing temperature of the clinker by 100 °C, which varies  
59 from the production of conventional ordinary Portland cement (OPC) wherein the burning  
60 temperature of the clinker is 1450 °C. The clinker burnt at 1350 °C consists of higher amount of ferrite  
61 (C<sub>4</sub>AF) (approximately twice) and lower amounts of belite (C<sub>2</sub>S) (approximately half) compared to  
62 those in OPC. This novel cement produced on the aforementioned low-temperature basis is called  
63 ferrite-rich Portland cement (FC). It should be noted that the same raw materials as used for OPC  
64 have been used to produce FC, but the ratio of the raw materials has been adjusted to achieve the  
65 target mineral composition of FC. Further, it has been demonstrated that the FC can reduce  
66 approximately 5 % of CO<sub>2</sub> emission compared to OPC during the clinkering process [8]. Although  
67 the FC has been proven to be an eco-friendly alternative to OPC, the number of studies on the subject  
68 are very limited [10-12], providing insufficient information on the hydration process, evolution of  
69 mechanical properties and performance of FC, which restricts the commercialisation, industrial  
70 applications and particularly the developments of numerical models.

71

72 The application of thermodynamic models coupled with an accurate database have gained significant  
73 momentum to accurately investigate the hydration process of a large variety of cement pastes with  
74 wide range of variables such as temperature, water to cement ratio and relative humidity [13-16].  
75 Basically, chemical behaviours of numerous minerals and phases existing in the hydrated cement are  
76 thermodynamically well defined. However, the necessary thermodynamic data for Fe phases are still  
77 very limited. Besides, the experimental characterisation of Fe phases is complicated, as the signals  
78 from Fe phases in hydrated cement significantly overlap with those of the Al analogues using typical

79 techniques such as X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning  
80 electron microscopy [13, 17]. The identification of amorphous Fe phases in the hydrated cement  
81 matrix is also difficult using conventional techniques. In addition, Fe(III) could partly substitute  
82 Al(III)-bearing hydrates such as Fe-ettringite, Fe-monosulfate, Fe-monocarbonate, Fe-hemicarbonate  
83 and Fe-siliceous hydrogarnet depending on the presence of calcium, sulphate or carbonate during  
84 cement hydration [13, 18-19]. As experimentally demonstrated by Dilnesa et al [13], Fe/Al-siliceous  
85 hydrogarnet ( $C_3(A,F)S_{0.84}H_{4.32}$ ) is more stable than Fe-containing AFm phases and Fe-ettringite in  
86 OPC. Moreover, the leaching of Ca from C-S-H and the low Ca/Si ratio induce the uptake of  $Fe^{3+}$   
87 ions in the place vacated by calcium [20-21]. However, a recent study showed that the uptake of  $Fe^{3+}$   
88 ions occurs highly at high Ca/Si ratios (1.2 and 1.5) of synthesised C-S-H [19]. At high Ca/Si ratios,  
89 the presence of  $Fe^{3+}$  ions is witnessed in the interlayer of C-S-H phases. On the other hand, the uptake  
90 of  $Fe^{3+}$  ions by the interlayer is eliminated at a low Ca/Si ratio (0.8), instead, leading to the formation  
91 of Ca-Si-rich complex on the surface of C-S-H. With all the above contrast observations, the  
92 mechanism of Fe(III) uptake by C-S-H is poorly understood and remains ambiguous.

93

94 In our previous work [10], we have studied the hydration behaviour of FC and compared it with that  
95 of OPC. However, we did not identify or quantify the Fe-hydrates in the cements. Therefore, the  
96 objectives of this study were (i) to investigate the hydration process of FC and quantify Fe-hydrates  
97 and (ii) to evaluate Fe uptake by C-S-H. All the experimental results were synergistically used to  
98 verify the coupled thermodynamic model developed in our previous work [22] to predict the  
99 hydration products including the Fe-siliceous hydrogarnet and Fe uptake by C-S-H (C-F-S-H).

100

## 101 **2. Materials and methods**

### 102 **2.1 Experimental procedure**

103 OPC and ferrite-rich Portland cements were used in this study. The physical properties and the  
104 mineral composition of the cements are tabulated in **Table 1**, and the chemical composition of oxide

105 and the proportions of raw materials are given in Table 1 of ref. [10]. The cement was mixed with  
106 distilled water at a water to cement ratio of 0.5. The mixture was stirred manually until the bleeding  
107 stopped. Further, it was cast into cylindrical moulds and sealed-cured at 20 °C. The samples that  
108 reached the predetermined curing time (1, 6, and 12 h and 1, 2, 3, 7, 14, 28, 91 and 182 days) were  
109 ground and immersed in acetone for 1 h to stop the hydration. Thereafter, the samples were removed  
110 from the acetone solution by suction filtration using an aspirator. Finally, the samples were kept in  
111 an oven at 40 °C until they reached a constant mass. The prepared samples were ground and powdered  
112 for XRD and TG measurements. The selective dissolution experiment was performed according to  
113 the method proposed by Dilnesa et al. [13]. In the selective dissolution method, 5 g of a crushed  
114 hydrated cement sample was stirred for 2 h using a magnetic stirrer in a beaker containing 300 mL  
115 methanol and 20 g salicylic acid. The suspension was allowed to settle for approximately 15 min and  
116 then it was vacuum-filtered through 0.08-mm filter paper. Thereafter, the samples were dried at 90 °C  
117 for 45 min in an electric furnace. The XRD/Rietveld analysis was performed to determine the  
118 quantities of hydration products and un-hydrated clinker minerals. Rigaku MultiFlex X-ray generator  
119 with CuK $\alpha$  radiation was used for XRD measurements while Siroquant Version 4.0, manufactured  
120 by Sietronics, was adopted for quantitative Rietveld analysis. The TG-differential thermal analysis  
121 (DTA) was conducted using TG/DTA7220 manufactured by HITACHI under an N<sub>2</sub> flow  
122 environment. The waiting time before the measurement for stabilising the apparatus was 50 min. The  
123 temperature was raised at a rate of 5 °C/min from 20 to 1000 °C and was maintained for 10 min and  
124 then reduced at a rate of 50 °C/min. Approximately 10 mg of the sample was weighed and used for  
125 measurements. Mercury intrusion porosimetry (MIP) was conducted using Shimadzu Auto Pore IV  
126 9500 with a pressure range of 0.5–60000 psi. The samples were cut into cubes (3 mm) after curing  
127 and immersed in acetone for 24 h. Thereafter, the samples were vacuum-dried for 24 h before  
128 conducting MIP measurements.

129

130

131 **Table 1:** Physical properties and mineral composition of cements used

Cement	OPC	FC
Blaine specific surface area (cm <sup>2</sup> /g)	3220	3220
Density(g/cm <sup>3</sup> )	3.19	3.20
LoI	0.80	0.76
C <sub>3</sub> S	57.6	59.1
C <sub>2</sub> S	18.0	8.6
C <sub>3</sub> A	9.0	8.5
C <sub>4</sub> AF	9.3	17.2
Gypsum	3.02	2.78

132

## 133 2.2 Modelling approach

134 The hydrate assemblage of OPC and FC as a function of hydration time was calculated using the  
 135 thermodynamic model, which couples IPhreeqc module [23] for thermodynamic equilibrium and  
 136 Microsoft Excel for solving cement hydration. The thermodynamic properties of cement hydrates  
 137 including Fe-containing phases were collected from Cemdata18 [24-25]. The data were converted to  
 138 PHREEQC format [22] and used along with PHREEQC default thermodynamic database [26]. The  
 139 uptake of Fe by C-S-H can be expressed by the distribution coefficient,  $R_d$ , which can be defined as  
 140 follows with reference to the alkali adsorption on C-S-H [27]:

141

$$142 \quad R_d(\text{mL/g}) = \frac{\text{Fe in solid C-S-H}}{\text{Fe concentration in solution}} \quad (1)$$

143

144 where *Fe in solid C-S-H* is the amount of Fe uptake by 1 g of C-S-H (mmol/g), and *Fe concentration*  
 145 *in solution* is the equilibrium concentration of Fe (mmol/mL).

146

147

### 148 3. Results and discussion

#### 149 3.1 Characterisation of cements and Fe-hydrates

150 **Fig. 1** shows the hydration reaction of each clinker mineral and the total hydration degree of cement  
151 determined by XRD/Rietveld analysis. The hydration degree of  $C_3S$  and  $C_3A$  are similar in both  
152 cements, and they are fully hydrated after 28 days. However, the hydrations of  $C_2S$  and  $C_4AF$  in OPC  
153 are higher than those in FC. The difference becomes remarkable from 91 days for  $C_2S$  and 14 days  
154 for  $C_4AF$ . The change in the proportions of the clinker minerals affects their hydration degree. These  
155 differences did not alter the total hydration degree of cement (**Fig. 1. (E)**). FC shows higher hydration  
156 degree up to 7 days, and the high amount of  $C_2S$  contributes to the increase in the late hydration of  
157 OPC.

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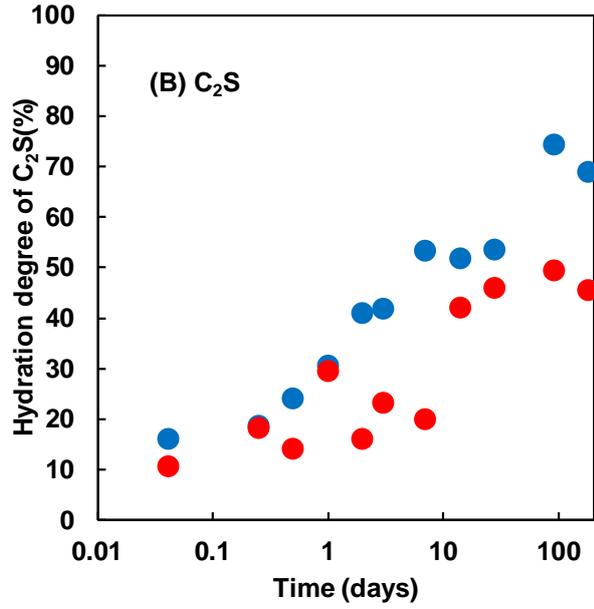
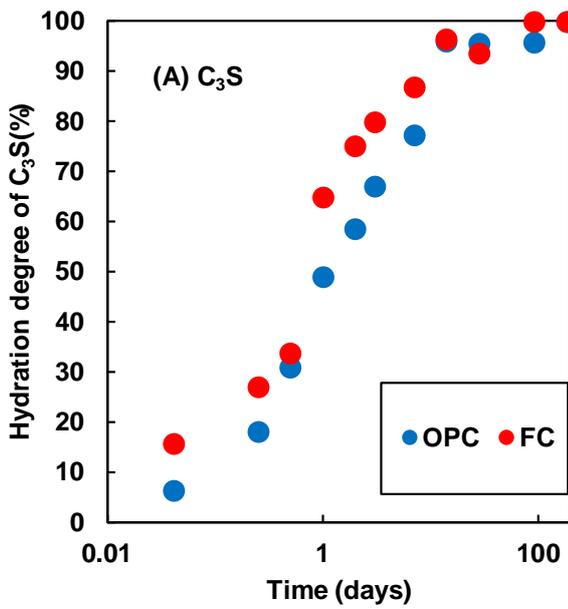
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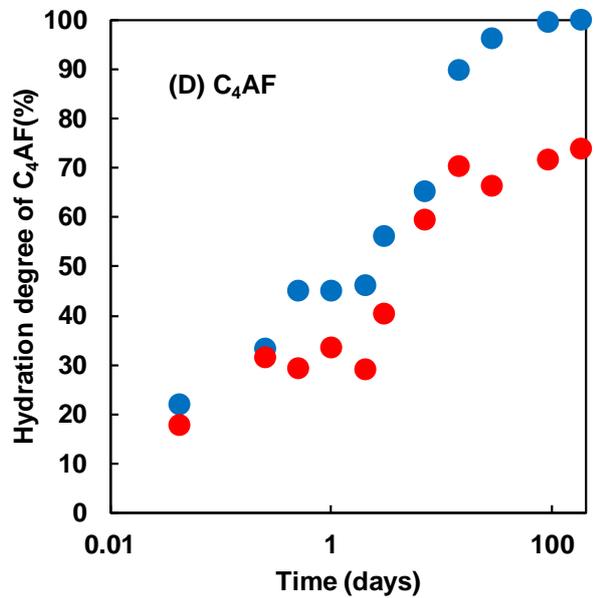
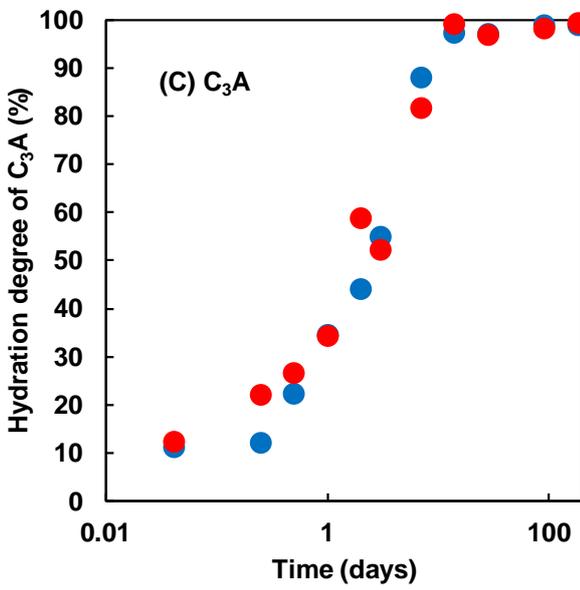
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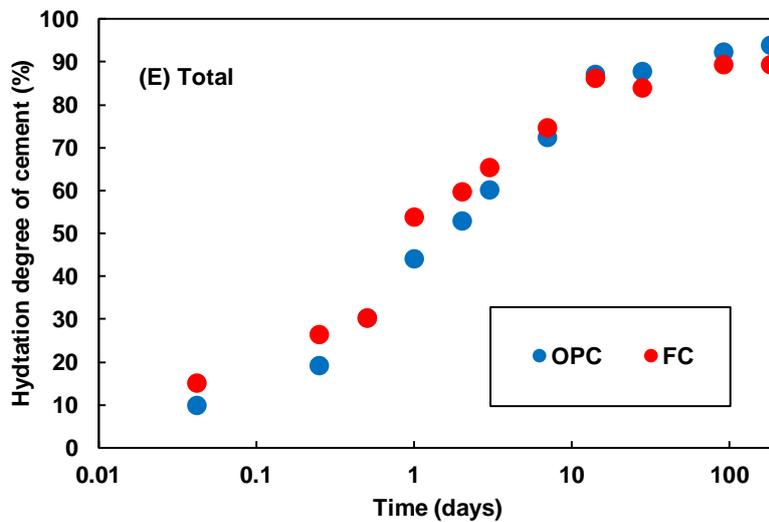
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172 **Fig. 1.** Hydration of clinkers and cements as a function of time from the XRD/Rietveld analysis

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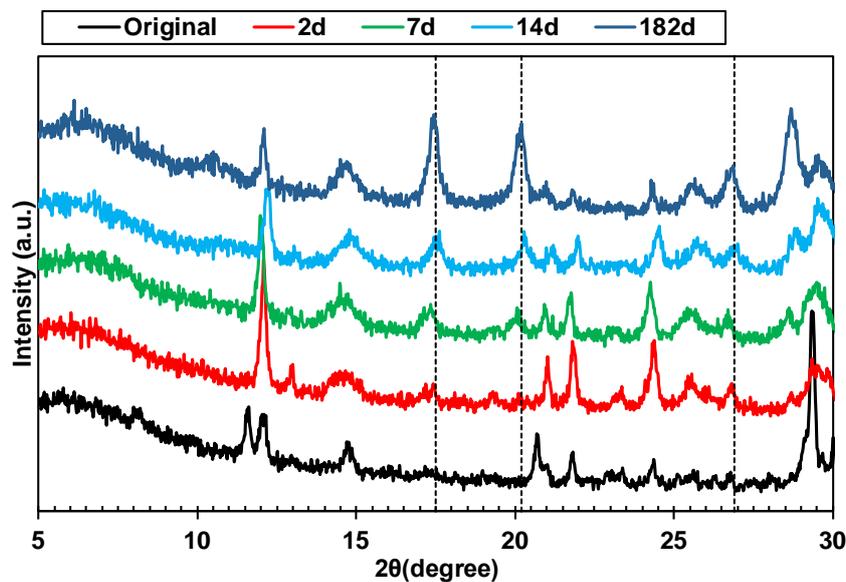
174 Lothenbach et al. have reported that Fe-siliceous hydrogarnet is the only Fe-containing phase  
175 expected to form during the hydration of Portland cements; thus, the presence of other Fe-containing  
176 phases in the hydrated cement system can be negligible [24]. To quantify the formed Fe-siliceous  
177 hydrogarnet, the selective dissolution was conducted. **Fig. 2** shows the XRD pattern of the sample  
178 after the selective dissolution treatment. The peak of siliceous hydrogarnet at approximately  $17.5^\circ/2\theta$   
179 and additional peak at  $20.2^\circ/2\theta$  and  $26.9^\circ/2\theta$  indicated by dotted line can be observed after 7 days of  
180 hydration. However, the poor crystallinity of siliceous hydrogarnet makes it difficult to quantify by  
181 Rietveld analysis. Therefore, TG/differential thermal gravimetry (DTG) was used to quantify the  
182 formed siliceous hydrogarnet. **Fig. 3** shows the TG/DTG curves before and after the selective  
183 dissolution treatment of FC hydrated for 28 days. The mass reduction and the remaining phases can  
184 be observed after selective dissolution. In particular, the portlandite peak at approximately  $400^\circ\text{C}$  to  
185  $450^\circ\text{C}$  disappears, and the peak of siliceous hydrogarnet is confirmed at approximately  $200^\circ\text{C}$  to  
186  $300^\circ\text{C}$ . These results are consistent with those reported by Dilnesa et al. [13] and proved that the  
187 selective dissolution is an effective method to quantify the Fe-containing phases in the hydrated  
188 cement. As shown in XRD and DTG results, the peak of C-S-H and AFm phases remain after the  
189 selective dissolution, but they do not overlap with the peak of siliceous hydrogarnet to quantify. From  
190 the mass loss, the amount of formed siliceous hydrogarnet was calculated, and the results are shown  
191 in **Fig. 4** as a function of hydration time. For the calculation, it was assumed that the chemical  
192 composition of Fe-siliceous hydrogarnet as  $\text{Ca}_3\text{FeAl}(\text{SiO}_4)_{0.84}(\text{OH})_{8.64}$ . Approximately 10–12% of Fe-  
193 siliceous hydrogarnet was formed in the hydrated cements, primarily at the early stages of hydration.  
194 The hydration degree of ferrite correlates to the formation of Fe-siliceous hydrogarnet, and the high  
195 content of ferrite in FC leads to the formation of a high amount of Fe-siliceous hydrogarnet at the  
196 same hydration time. As reported in ref. [13, 16-17], the cement hydration produces iron hydroxides  
197 during the first hours and then siliceous hydrogarnet after 1 day and longer. The results (**Fig. 4**)

198 showed that the amount of formed Fe-siliceous hydrogarnet is almost constant after 14 days of  
199 hydration.

200

201 The measured porosity and pore size distribution for hydrated cement are shown in **Fig. 5**. OPC and  
202 FC hydrated for 7 and 182 days are shown in **Fig. 5** as an example. At an early age, FC has a lower  
203 amount of pore volume and large amount of smaller pore compared to OPC, but this trend is reversed  
204 at the later stages of hydration. Furthermore, the porosity of both cements is similar in the hydration  
205 period of 14–28 days. The hydration degrees of clinker minerals, mainly  $C_2S$  and  $C_4AF$ , affect the  
206 microstructure of the hydrated cement paste. The late hydration reaction of high-content  $C_2S$  in OPC  
207 contributes to the lesser and denser pore structure compared with that of FC. This difference will  
208 contribute to the change in mechanical properties of the hydrated cement paste.

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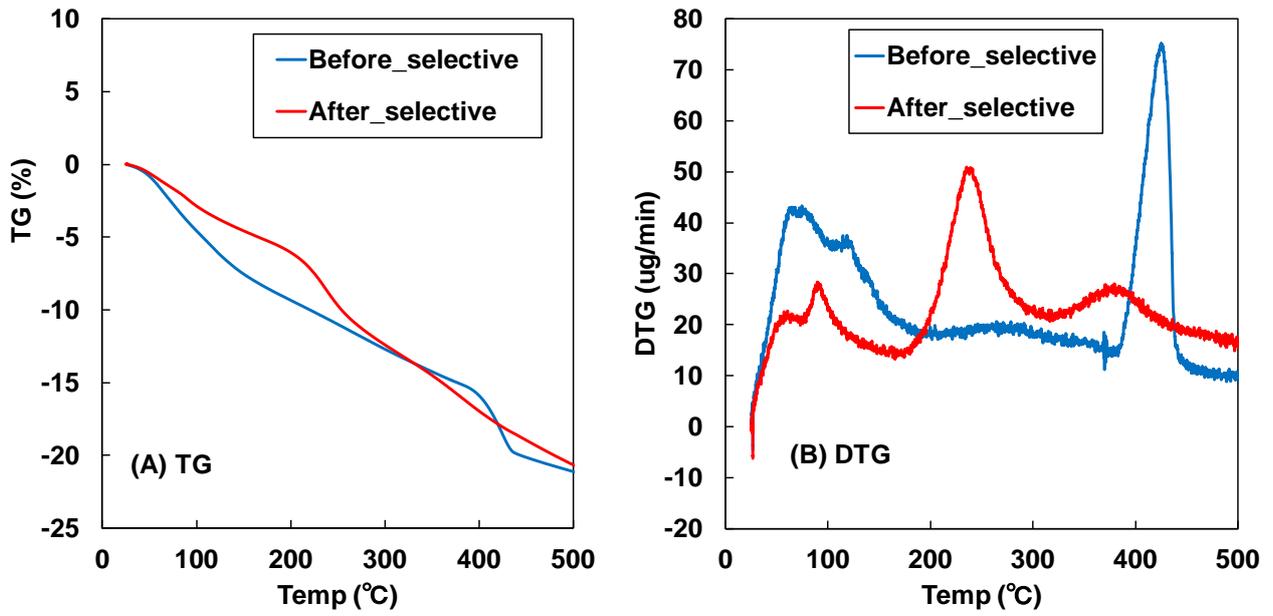


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**Fig. 2.** XRD patterns of OPC after selective dissolution

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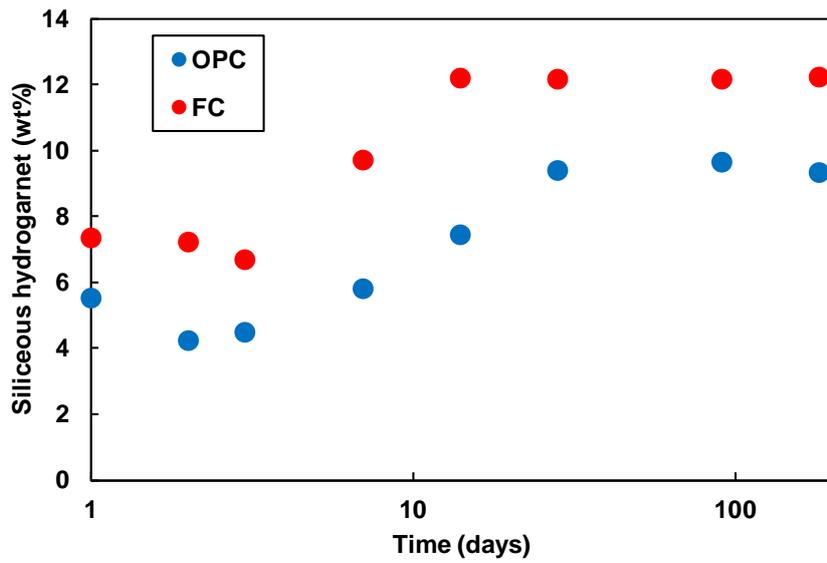


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**Fig. 3.** Effect of selective dissolution after 28 days of hydration of FC. (A) TG; (B) DTG

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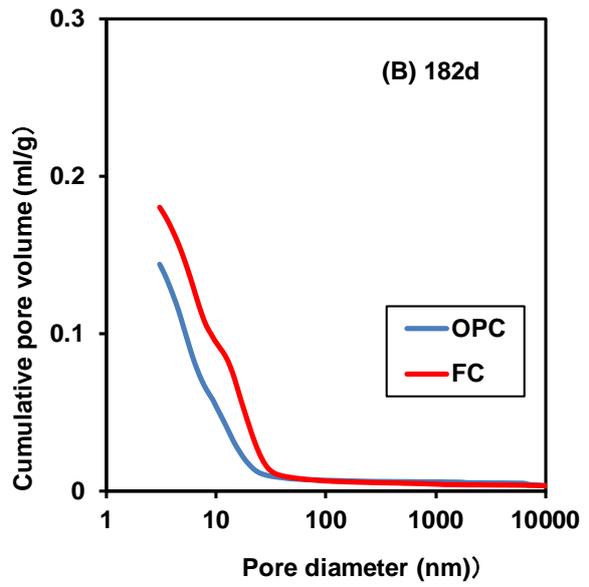
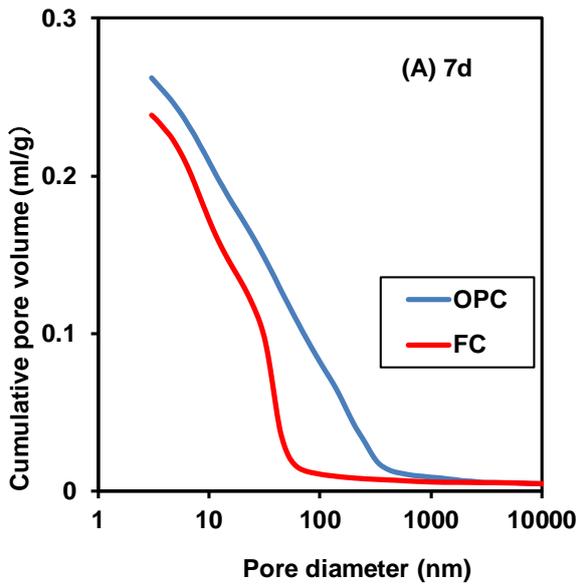
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**Fig. 4.** Amount of siliceous hydrogarnet in the hydrated cements

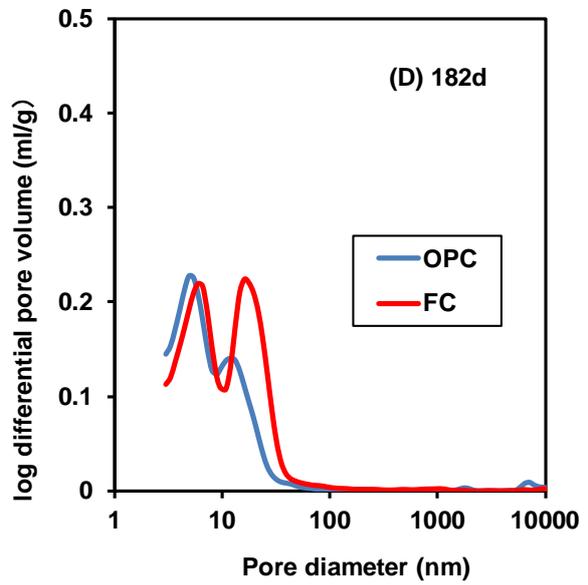
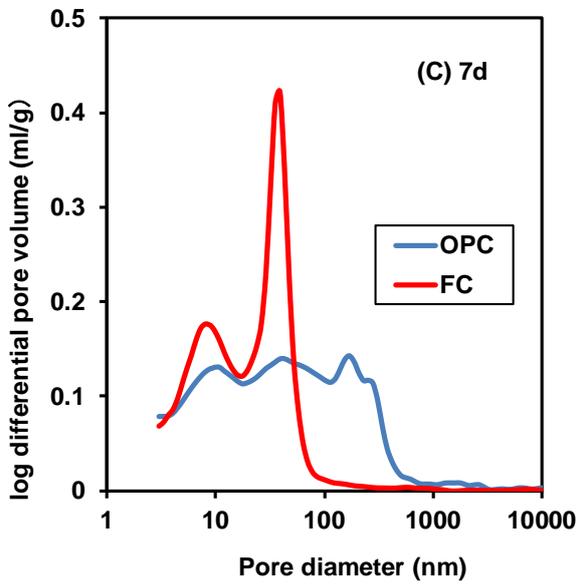
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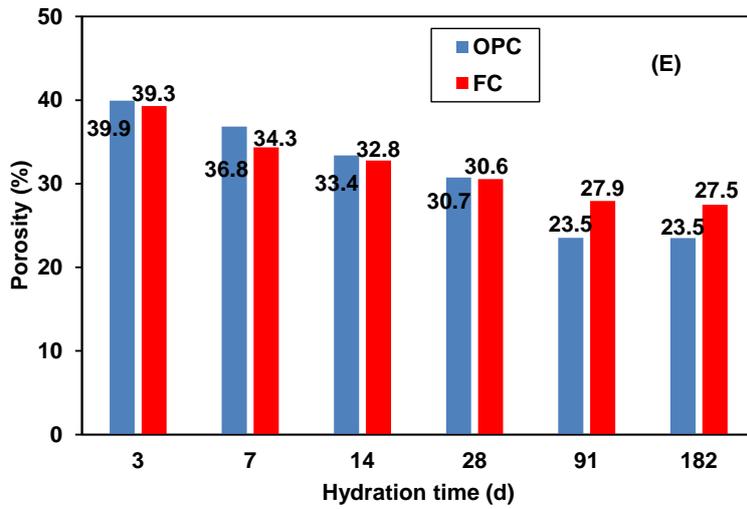
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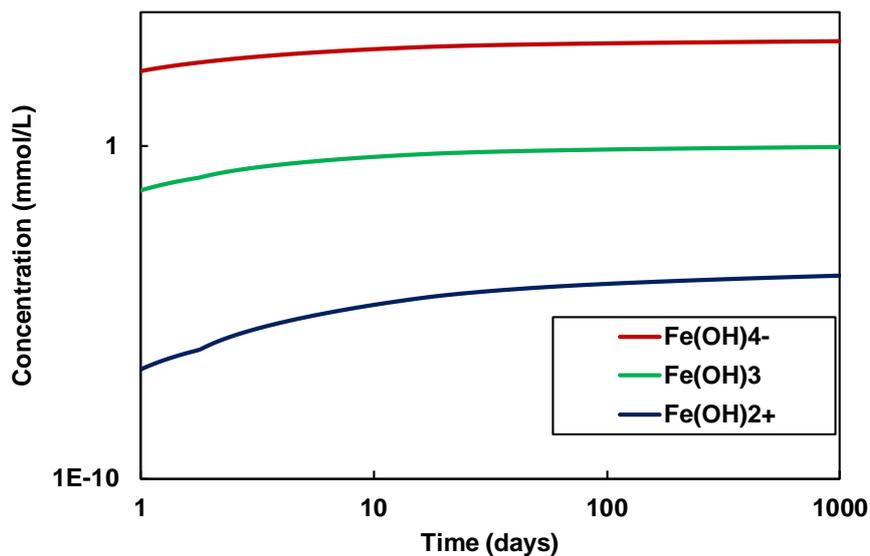
**Fig. 5.** Cumulative pore volume, pore size distribution and total porosity of OPC and FC

### 226 3.2 Incorporation of Fe in C-S-H

227 The recent research on Fe uptake has been focused on the synthetic C-S-H [19], and there is a lack of  
228 results or report on Fe incorporation in C-S-H in the hydrated cement. Many studies have shown that  
229 the amount of Fe ions in the pore solution is negligible [15, 22]. To find the state of Fe ions in the  
230 pore solution after the hydration of  $C_4AF$ , a thermodynamic calculation was performed considering  
231 various Fe ions and complexes and without considering any Fe-containing hydrate formation. The  
232 results show that  $Fe(OH)_4^-$  is primarily found in the high-pH pore solution of the hydrated cement  
233 (**Fig. 6**), similar to producing  $Al(OH)_4^-$  in high-pH solution [19]. Therefore, Fe ions released from the  
234 hydration of  $C_4AF$  form  $Fe(OH)_4^-$  and produce Fe-containing phases or incorporate into C-S-H.  
235 Therefore, with the results shown in **Fig. 4**, the amount of Fe taken by C-S-H can be calculated as

$$236 \quad M_{C-(F-)S-H} = M_{Fe \text{ dissolved}} - M_{Siliceous-Hydrogarnet} \quad (2)$$

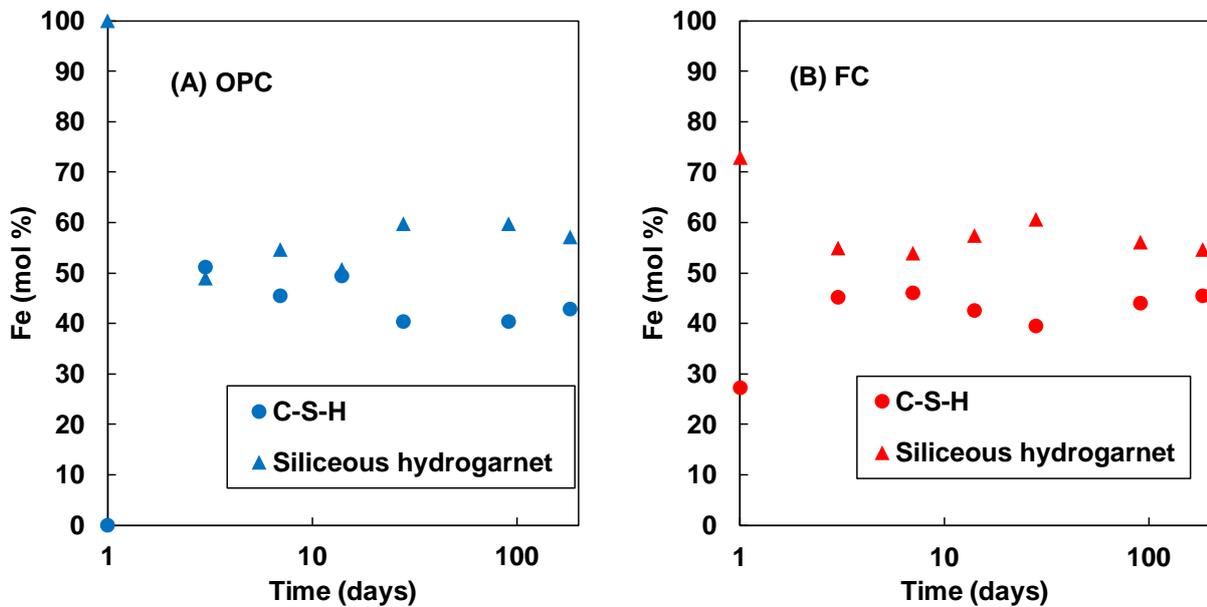
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239 where  $M_{C-(F-)S-H}$  is the Fe uptake by C-S-H (mol),  $M_{Fe \text{ dissolved}}$  is the amount of Fe released from the  
240 hydration of  $C_4AF$  (mol), and  $M_{Siliceous-Hydrogarnet}$  is the Fe in Fe-Siliceous hydrogarnet (mol).



241  
242 **Fig. 6.** Calculated concentrations of Fe complexes as a function of hydration time in OPC

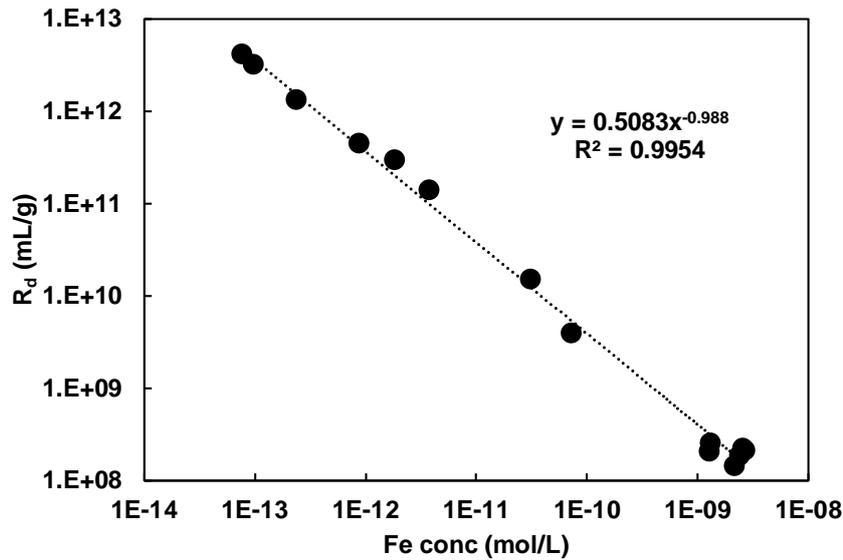
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244 The calculated mol percentages of Fe in C-S-H and Fe-siliceous hydrogarnet as a function of  
 245 hydration time for both cements are shown in **Fig. 7**. Initially, the released Fe from C<sub>4</sub>AF forms as  
 246 Fe-siliceous hydrogarnet, and then the released Fe incorporates into C-S-H. Both cements show a  
 247 nearly equal amount of Fe uptake by C-S-H. The Fe incorporation into C-S-H was considered by the  
 248 distribution ratio,  $R_d$ , together with thermodynamic calculations. The calculated  $R_d$  values as a  
 249 function of Fe concentration is shown in **Fig. 8**. The distribution coefficient decreases with increase  
 250 of Fe concentration and follows power approximation, as proposed for alkalis [28]. In the construction  
 251 of the model, it is desirable to have a single equation for adsorption irrespective of cement type.  
 252 Therefore, in **Fig. 8**,  $R_d$  values of both cements have been used to drive the equation. The results  
 253 indicate the decrease of Fe uptake by C-S-H with the increase in Fe concentration. Mancini et al. have  
 254 reported a relationship between sorbed Fe and aqueous solution Fe from the sorption experiment on  
 255 synthesised C-S-H with Ca/Si ratio of 0.8 and 1.5, and their results showed that  $R_d$  depends neither  
 256 on the composition of C-S-H nor the pH of the solution [19]. In this study,  $R_d$  does not depend on  
 257 cement type, but it relates to the equilibrated Fe concentration in the pore solution.  
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 261

**Fig. 7.** State of Fe in (A) OPC; (B) FC



**Fig. 8.** Relationship between distribution coefficient and concentration of Fe

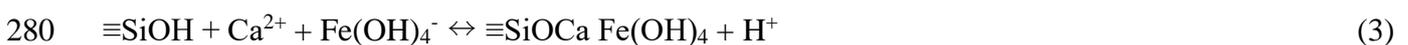
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265 Various mechanisms have been proposed for aluminium incorporation into C-S-H, including the  
 266 substitution of Si atom at bridging sites (Q<sup>2</sup>B) of the aluminosilicate chains or cross-linked sites (Q<sup>3</sup>),  
 267 exchange with interlayer calcium ions, and surface complexation reactions [29-30]. A similar  
 268 mechanisms can be considered for the uptake of Fe by C-S-H. Mancini et al. have analysed the uptake  
 269 mechanism based on <sup>29</sup>Si NMR and EXAFS data and showed that the coordination of Fe into C-S-H  
 270 depends on its Ca/Si [19]. As shown in **Fig. 6.**, Fe (III) exists mainly as Fe(OH)<sub>4</sub><sup>-</sup>, and the possible  
 271 exchange with interlayer calcium would not easily occur. Furthermore, the Fe sorption by C-S-H  
 272 depends on the equilibrium concentration, and therefore, the surface complexation is the main  
 273 mechanism for the uptake of Fe by C-S-H. Hass et al. have proposed surface complexation  
 274 mechanism for aluminium uptake through Al(OH)<sub>4</sub><sup>-</sup> [31], and Fe(OH)<sub>4</sub><sup>-</sup> can adsorb on C-S-H in a  
 275 similar way as aluminium. The hydrated cement pore solution has a high-pH and high Ca  
 276 concentration, which is responsible for the positive surface charge on C-S-H through a high  
 277 concentration of calcium adsorbed surface specie, ≡SiOCa<sup>+</sup> [31-32]. It is believed that Fe(OH)<sub>4</sub><sup>-</sup> can  
 278 adsorb on ≡SiOCa<sup>+</sup> as follows:

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### 282 **3.3 Thermodynamic model and verification**

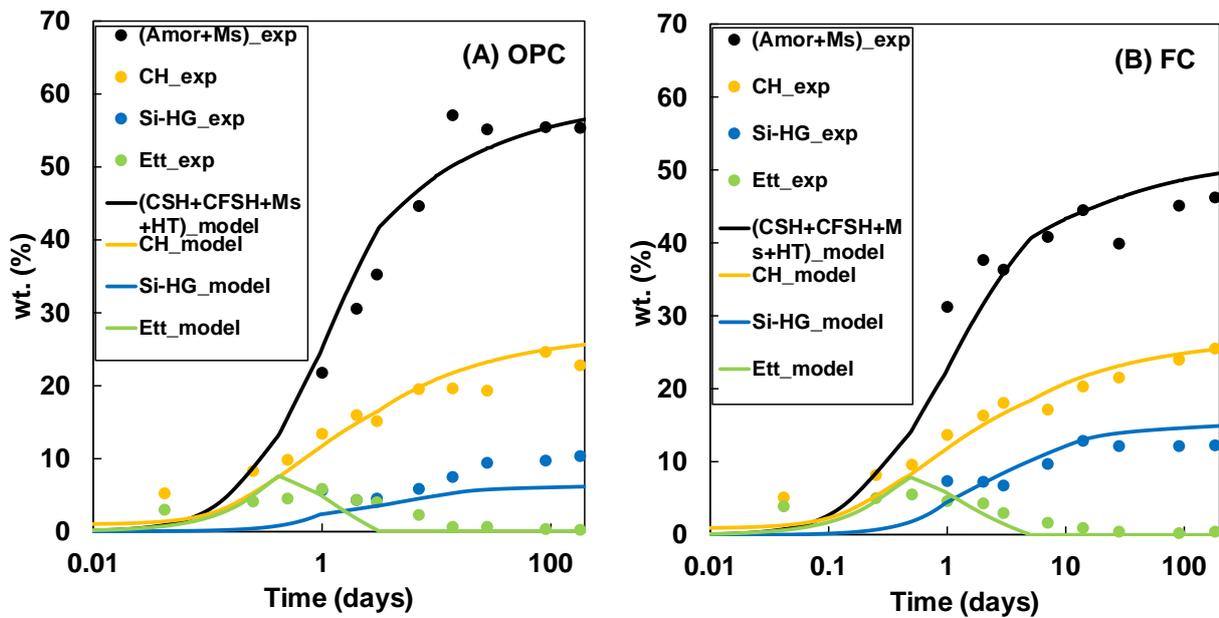
283 The coupled thermodynamic model developed in our previous study was used to predict the hydrate  
284 assemblage as a function of hydration time [10, 22]. The relationship derived in **Fig. 8.** was  
285 incorporated into the model to account for Fe uptake by C-S-H in the hydration of cement. The  
286 chemical composition of  $(\text{CaO})_{1.667}(\text{SiO}_2): 2.1\text{H}_2\text{O}$  with known thermodynamic properties [24-25]  
287 was assumed for C-S-H. The model predictions were compared with the experimental results in **Fig.**  
288 **9** for Fe-siliceous hydrogarnet and other products. It should be noted that experimental results of  
289 amorphous and poorly crystalline monosulfate [33] were compared with the addition of the modelling  
290 results of C-S-H, Fe incorporated C-S-H, monosulfate, and hydrotalcite which was very small  
291 quantity in the hydration product and difficult to quantify accurately by XRD/Rietveld analysis.  
292 Despite some variation in OPC, the modelling results of Fe-siliceous hydrogarnet and other hydrates  
293 reproduced well the experimental data of both types cement. Both cements produce nearly the equal  
294 amount of portlandite and ettringite, but the higher proportion of belite produces more C-S-H in OPC  
295 than in FC, and more ferrite in FC produces high Fe-siliceous hydrogarnet. The composition of  
296 calculated phase assemblage in terms of weight percentage for both cements are shown in **Fig. 10.**  
297 Approximately 2 % of Fe incorporated C-S-H [C-(F)-S-H] was produced in the matured hydrated  
298 cement. The amount of formed C-(F)-S-H is very small relative to the ferrite hydration product of Fe-  
299 siliceous hydrogarnet and thus, its effect in the physical properties of the paste could be negligible.

300

301 The molar volume of each hydration products including Fe-siliceous hydrogarnet helps to estimate  
302 the porosity of cement paste. The capillary porosity was calculated by deducting the volume of  
303 hydration products and un-hydrated cement, and chemical shrinkage from the initial volume of paste  
304 [34]. In the thermodynamic model, the C-S-H was divided into low density (LD) and high density  
305 (HD) C-S-H, and the porosity associated with the C-S-H was calculated as gel porosity [34]. As  
306 shown in **Fig. 5**, the MIP technique measures the porosity for the pore diameter above 3 nm, which

307 includes capillary porosity and a part of gel porosity. Therefore, it is appropriate to compare MIP  
 308 results with the summation of capillary porosity and LD C-S-H gel porosity. The comparison is shown  
 309 in **Fig. 11** for both cements as a function of hydration period. The modelling results show a relatively  
 310 good agreement with the measured data.

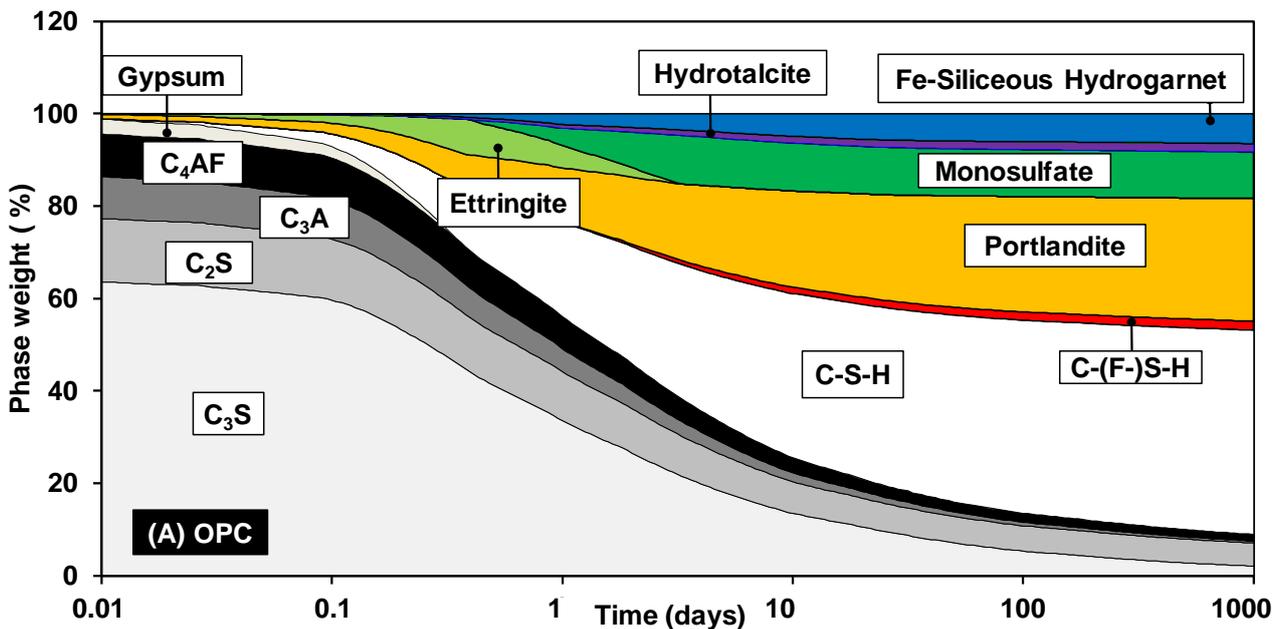
311



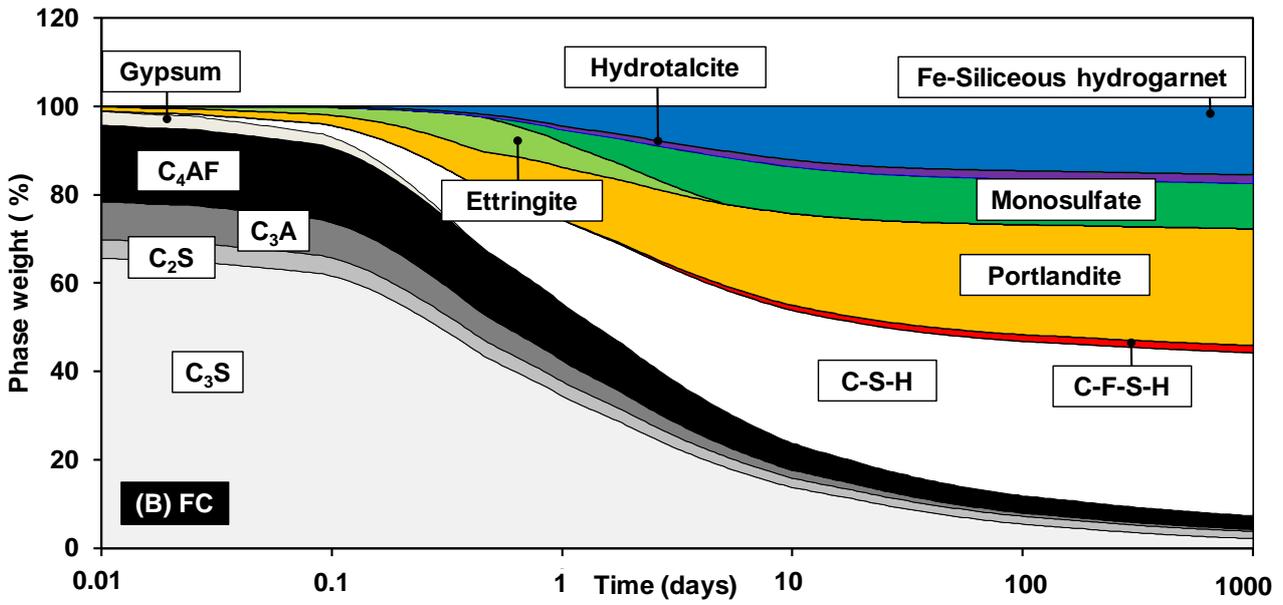
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313 **Fig. 9.** Comparison of calculated hydrates with the quantitative values determined by XRD Rietveld  
 314 analysis and TG/DTA for (A) OPC and (B) FC

315



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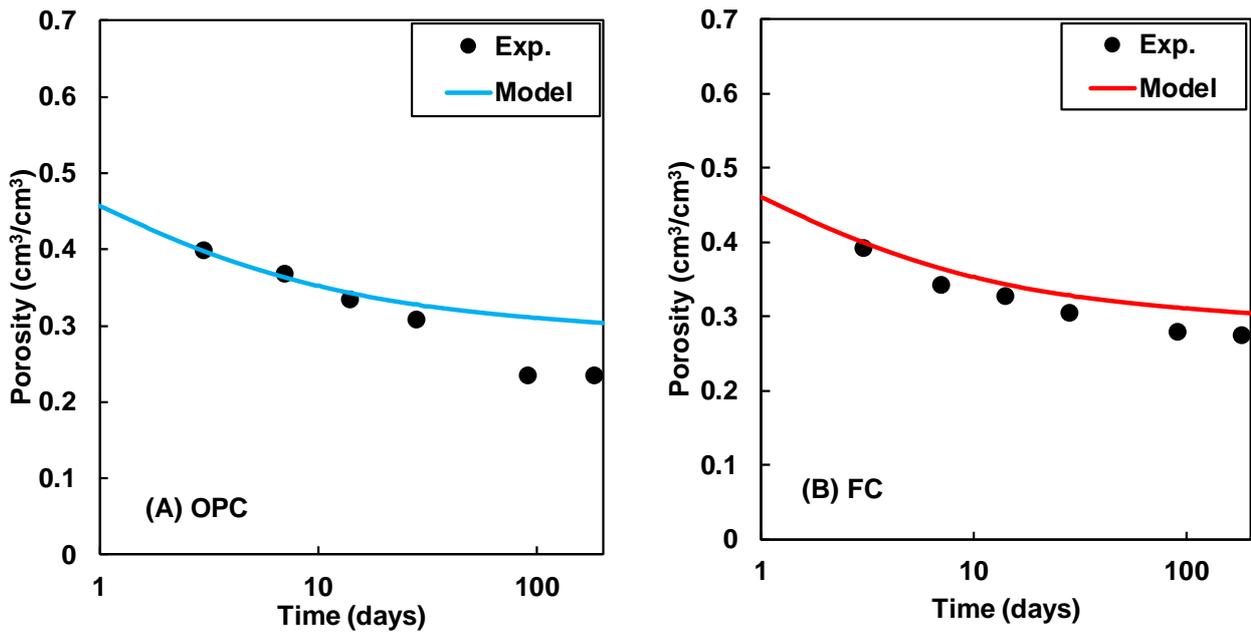


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318

Fig. 10. Calculated mass of hydrates as a function of hydration time for (A) OPC and (B) FC

319



320

321

Fig. 11. Comparison of porosity for (A) OPC and (B) FC

322

#### 323 4. Conclusions

324

High proportion of ferrite and low of belite in ferrite-rich cement lower their individual hydration

325

degree compared to those in OPC, but not the total hydration of cements. Moreover, their proportions

326

influence the microstructure of the hydrated cement: FC produces denser microstructure at an early

327 age compared to OPC, whereas it is the opposite at a later age. Fe-siliceous hydrogarnet was the main  
328 Fe-containing phase in the hydration of the ferrite phase and was quantified by selective dissolution  
329 approach. Fe-siliceous hydrogarnet was formed starting from the initial stages of hydration and  
330 reached a steady state in approximately 14 days. A high amount of ferrite present in FC enhances the  
331 formation of Fe-siliceous hydrogarnet. Fe uptake by C-S-H was estimated from the hydration of  
332 ferrite and the amount of formed Fe-siliceous hydrogarnet. A distribution coefficient ( $R_d$ ) was  
333 calculated for the uptake and was related to the equilibrium concentration of Fe ions in the pore  
334 solution. Fe(III) ions exist as  $\text{Fe}(\text{OH})_4^-$  in the high-pH pore solution of the hydrated cement, and C-  
335 S-H uptakes  $\text{Fe}(\text{OH})_4^-$  via surface complexation reactions. The distribution coefficient ( $R_d$ ) equation  
336 was incorporated into the thermodynamic model to predict the hydration products. The  
337 experimentally determined Fe-siliceous hydrogarnet and other hydration products agree well with the  
338 predicted results for both types of cements. Furthermore, the thermodynamic model predicted that  
339 approximately 2 wt.% of Fe was incorporated in C-S-H. Finally, the model efficiently predicted  
340 porosity development, and the predicted results were compared with the experimental MIP data.

341

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