

## **FE INCORPORATION IN CEMENT HYDRATES: EXPERIMENTS AND THERMODYNAMIC MODELING**

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### **Abstract**

Current understanding of the state of Fe during the hydration of cement is very limited and further studies are necessary to find out the possible incorporation of Fe in cement hydrates. Moreover, it is important to understand the hydration reaction and properties development of ferrite-rich cement. Our previous study [1] reported the hydration reaction and properties of ferrite-rich Portland cement by various experimental techniques and thermodynamic modelling and compared with ordinary Portland cement. However, we could not quantify the Fe-containing hydrates in the cements and the uptake of Fe by C-S-H. Therefore, the objective of this study is to quantify the Fe-containing hydrates during the hydration of ordinary Portland cement and ferrite-rich Portland cement. Ordinary Portland cement and ferrite-rich Portland cement were hydrated for 3 months and the hydration products were quantified with XRD/Rietveld analysis. The selective dissolution was used to determine the amount of Fe-containing phases. It was found that Fe-siliceous hydrogarnet was the primary Fe-containing phase. From the hydration of ferrite and amount of formed Fe-siliceous hydrogarnet, the Fe uptake in C-S-H was determined. The distribution ratio for Fe uptake in C-S-H and chemical composition of Fe-siliceous hydrogarnet were incorporated into the thermodynamic model to predict the hydration reaction of ordinary Portland cement and ferrite-rich Portland cement and the results were compared with experimental data of XRD/Rietveld analysis and selective dissolution. The successful agreement of the experimental results with the model demonstrates the state of Fe in the hydrated cements.

Keywords: Hydration, thermodynamic modelling, C-S-H, Fe-siliceous hydrogarnet

### **1. INTRODUCTION**

It has been reported that the ferrite phase contributes significantly the sintering of the clinker, and the contribution of clinker components to its burnability is in the order of

$C_4AF > C_3A > C_2S > C_3S$  [2-3]. A low-burning-temperature clinker, which sinters at 1350 °C that is approximately 100 °C lesser than temperature required for the ordinary Portland Cement (OPC) clinker, was produced by increasing the  $C_4AF$  and decreasing the  $C_2S$  proportions while targeting a strength equal to that of the conventional OPC [3]. The cement produced using the low-burning-temperature-clinker is called ferrite-rich Portland cement (FC). The manufacturing process of this cement may release 5% lesser  $CO_2$  than that of OPC, thus demonstrating a potential to substitute the OPC [3-4].

Gartner and Myers [5] has reported that higher proportion of ferrite in the cement delays the compressive strength development and admixtures are necessary to enhance the ferrite hydration and thus later strength development [6]. The hydration of ferrite phase induces to form Fe-containing phases [7-8]. However, it is difficult to conclude the kind of Fe-containing phases actually formed in the hydrated cement. In our previous study [1], we have investigated the hydration behaviour of ferrite-rich Portland cement and compared with OPC. However, that study did not identify and quantify the Fe-containing phases in the hydration of cements. Therefore, the present study focuses on the quantification of Fe-containing phases by experiment and compared the data with the hydration model. In addition, a possible Fe incorporation into C-S-H is also investigated.

## 2. MATERIALS AND METHODS

The ordinary Portland cement (OPC) and ferrite-rich Portland cement (FC) were used in the experiments. The physical properties and the mineral composition by Bogue analysis are listed in Table 1, and the chemical composition of oxide and the proportions of raw materials are given in Table 1 of ref. [1]. The cement paste with a water to cement ratio of 0.5 was prepared and cured at 20 °C under sealed-condition. The samples that reached the predetermined curing time (1, 6, and 12 h and 1, 2, 3, 7, 14, 28, and 91 days) were ground and immersed in acetone for 1 h to stop hydration. Thereafter, the samples were removed from the acetone solution by suction filtration using an aspirator. Finally, the samples were kept in an oven at 40 °C until they reached a constant mass. The prepared samples were ground and powdered for XRD and TG measurements. The XRD was performed using a Rigaku MultiFlex X-ray generator with  $CuK\alpha$  radiation for the samples blended with 10 wt. % of corundum ( $\alpha-Al_2O_3$ ). Siroquant Version 4.0, manufactured by Sietronics, was used for quantitative Rietveld analysis. In the Rietveld analysis, monoclinic and triclinic  $C_3S$ ,  $\alpha$ - and  $\beta$ - $C_2S$ , cubic  $C_3A$ ,  $C_4AF$ , Gypsum, Bassanite, Portlandite, Ettringite, Monosulfoaluminate (simply called monosulfate), and Corundum ( $\alpha-Al_2O_3$ ) were assigned as targets. HITACHI TG/DTA 7220 analyser was used for TG/DTA measurements in nitrogen atmosphere and the measurements were performed at a heating rate of 5 °C/min up to 1000 °C. The selective dissolution experiment was conducted to estimate the Fe-containing phases. According to ref. [8], the phases of  $C_3S$ ,  $C_2S$ , portlandite, C-S-H, ettringite, and monosulfoaluminate will dissolve and ferrite, siliceous-hydrogarnet, and hydrotalcite will remain in the selective dissolution process. The hydrated cement paste of 5 g was dissolved with 300 mL of methanol and 20 g of salicylic acid for 2 hours. Thereafter, the suspension was allowed to settle for 15 minutes and then vacuum filtered thorough 0.08 mm filter paper. The remaining solid was dried at 90 °C for 45 minutes before the solid analysis.

The coupled thermodynamic model developed in our previous work [9] was used to predict the hydrate assemblage of OPC and FC. The thermodynamic properties of various phases including Fe-containing hydrates and minerals in the cement system were collected from

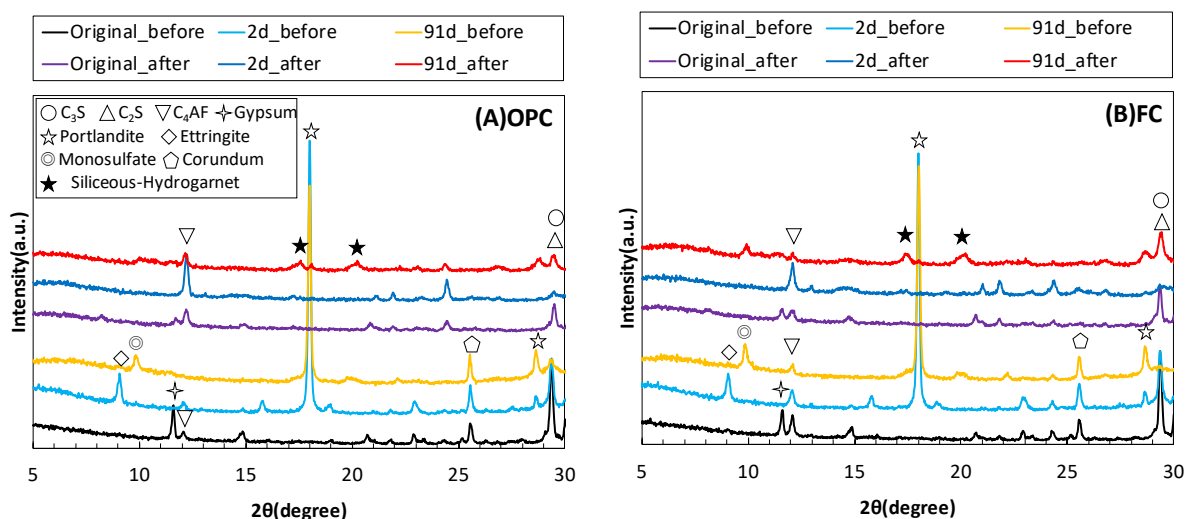
Cemdata18 [10-11], and the data were converted into a format suitable for PHREEQC. The converted data by Elakneswaran [9] along with the PHREEQC default thermodynamic database [12] were used for the calculations.

**Table 1: Physical properties and chemical composition of cements used**

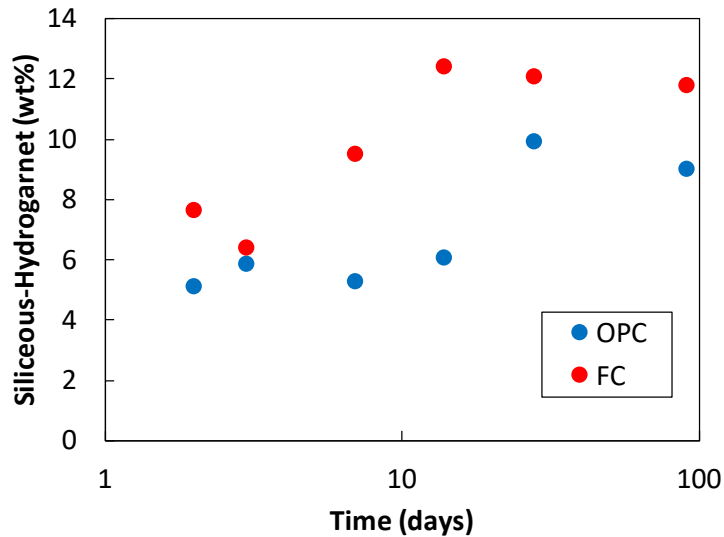
Cement	OPC	FC
Blaine specific surface area (cm <sup>2</sup> /g)	3220	3220
Density(g/cm <sup>3</sup> )	3.19	3.20
C <sub>3</sub> S	57.6	59.1
C <sub>2</sub> S	18.0	8.6
C <sub>3</sub> A	9.0	8.5
C <sub>4</sub> AF	9.3	17.2

### 3. RESULTS AND DISCUSSION

Figure 1 shows the effect of selective dissolution on the dissolution of hydrates in both OPC and FC. Although a very small amount of monosulfate and portlandite was observed, the siliceous-hydrogarnet was the main hydration product after the selective dissolution, which is consistent with previous study [8]. It is confirmed that the hydration of both cements produces the siliceous-hydrogarnet from the early age. The chemical composition of siliceous-hydrogarnet was assumed as  $\text{Ca}_3\text{FeAl}(\text{SiO}_4)_{0.84}(\text{OH})_{8.64}$  based on the results reported in a previous study [8]. The quantity of siliceous-hydrogarnet remained after selective dissolution was determined by TG and the results are shown in Figure 2 for both cement as a function of hydration time. The data shows that the amount of formed siliceous-hydrogarnet becomes stable after 28 days of hydration. Furthermore, the hydration of ferrite-rich cement forms higher amount of siliceous-hydrogarnet.

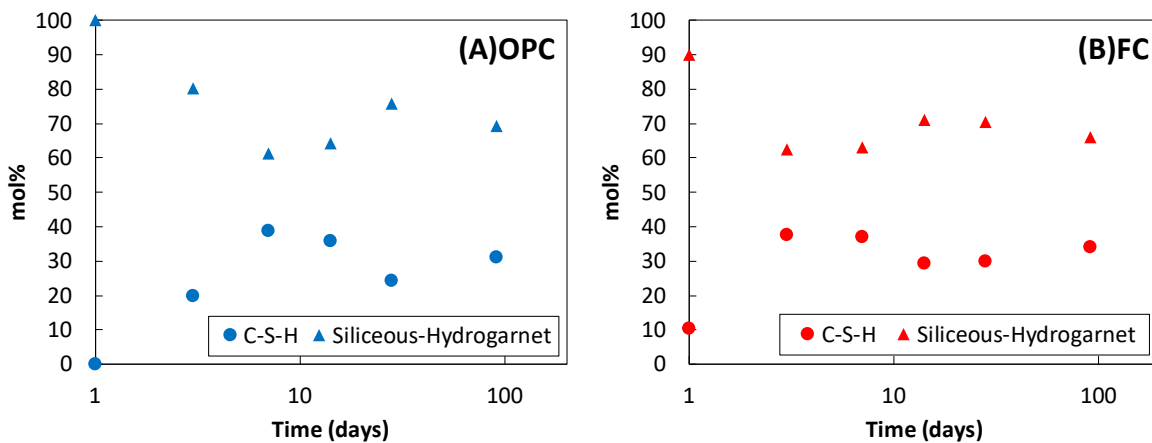


**Figure 1: XRD patterns of (A) OPC; (B) FC before and after selective dissolution**



**Figure 2: Amount of siliceous-hydrogarnet in the hydrated cements**

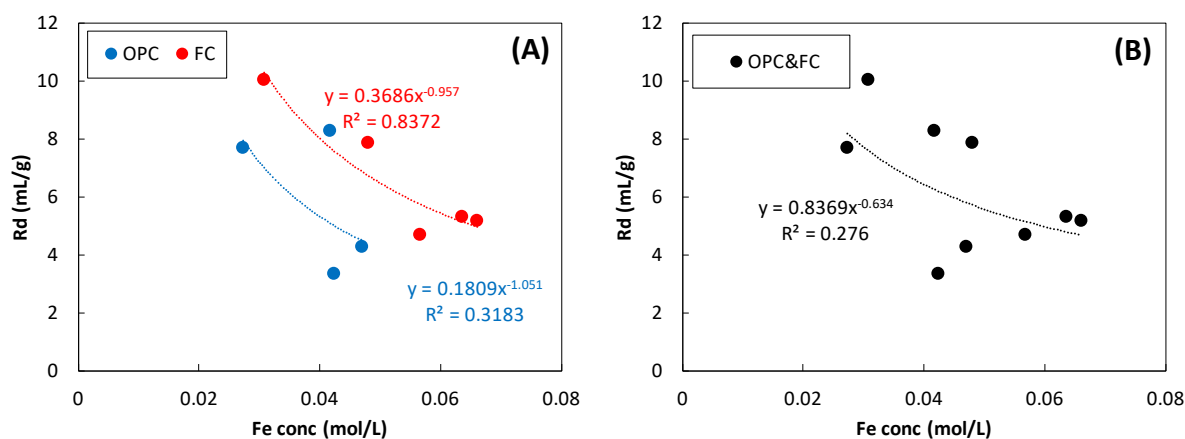
Fe ions from the ferrite hydration together with aluminium accumulates as siliceous-hydrogarnet, however the Fe ions could accommodate in the C-S-H as well. Mancini et al. has recently highlighted that Fe can incorporate into synthesized C-S-H [13]. Herein, the quantity of Fe incorporate into C-S-H was calculated from the hydration reaction of ferrite and the amount of formed siliceous-hydrogarnet. It has been reported that the concentration of Fe ions in the pore solution is negligible, which leads to determine the amount of Fe uptake by C-S-H. Figure 3 shows Fe incorporation into the siliceous-hydrogarnet and C-S-H as a function of hydration time for both cements. A part of released Fe ions as a result of ferrite hydration incorporates into C-S-H and others precipitates as siliceous-hydrogarnet. After 7 days of hydration, the amount of Fe taken by C-S-H and siliceous-hydrogarnet is reached to a steady state for both cements. A lower hydration degree of ferrite in FC compared to OPC show a nearly equal Fe in the siliceous-hydrogarnet and C-S-H.



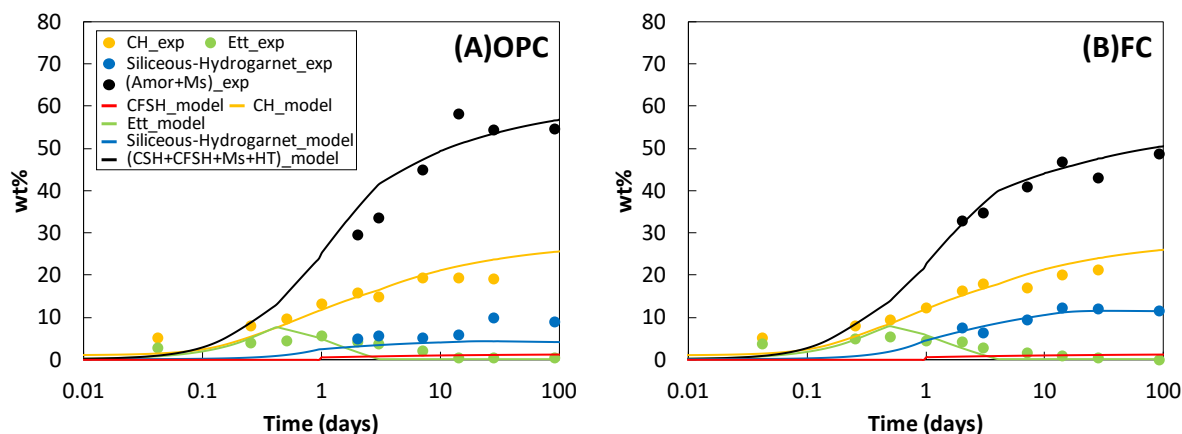
**Figure 3: The state of Fe in (A) OPC; (B) FC**

The results reported in Figure 3 is an evident in the Fe uptake by C-S-H, but it is difficult to propose a mechanism for uptake as the studies on Fe incorporation into C-S-H are very limited. In this study, the same approach used for  $\text{Na}^+$  or  $\text{K}^+$  incorporation [14-15] into C-S-H is adopted to quantify Fe uptake by C-S-H. The distribution ratio ( $R_d$ ) for the uptake is determined and the results are shown in Figure 4. The estimated  $R_d$  is a function of Fe concentration and each of OPC and FC show different function for  $R_d$  (Figure 4 (A)). The value of  $R_d$  tends to decrease as the Fe concentration increases. Further, for the same concentration of Fe,  $R_d$  of FC is higher than that of OPC, indicating higher uptake of Fe in ferrite-rich cement. Figure 4(B) shows the  $R_d$  relationship irrespective of cement type. From the reported relationship of  $R_d$  for alkalis and for the development of model, it is desirable to have a single relationship for  $R_d$  regardless of cement type. Although the coefficient of determination ( $R^2$ ) is low, the relationship derived in Figure 4 (B) is adopted in the hydration model.

The coupled thermodynamic model proposed in our previous study is used to predict hydrate assemblage as a function of hydration time. The model uses chemical composition of cements and mixing conditions as input parameter for the prediction of phase-assemblage composition. The model is applied to predict the hydration of ferrite-rich cement in our previous study [1] and found that Fe-siliceous-hydrogarnet is the main and stable Fe containing phase which forms from the early age. The experimental results obtained in this study is consistent with the model estimation. Furthermore, the experimentally quantified Fe-siliceous-hydrogarnet is compared with model prediction together with other phases in Figure 5 for both cements. Considering the crystallinity of AFm phases, the summation of total amorphous and monosulfate from the experimental results is compared with the addition of modelling results of C-S-H, Fe-incorporated C-S-H (C-F-S-H), monosulfate, and hydrotalcite. Despite some variation in OPC, the predicted Fe-siliceous-hydrogarnet and other hydrates agree well experimental data for both cements. The amount of Fe incorporated C-S-H (C-F-S-H) can be calculated from the moles of Fe uptake by C-S-H given in Figure 3. The modelling results of C-F-S-H are also plotted in Figure 5, which is less than 2% in total weight of hydrated OPC or FC where FC produces slightly higher than OPC.



**Figure 4: The relationship between distribution coefficient and concentration of Fe: (A) depend on cement type; (B) independent of cement type**



**Figure 5: Comparison of calculated hydrates with quantitative value determined by XRD Rietveld analysis and TG/DTA for (A) OPC and (B) FC**

#### 4. CONCLUSIONS

In this paper, a combination of experimental and modelling study is conducted to quantify Fe-containing hydrates and Fe-uptake by C-S-H. Based on the results, the following conclusion are made:

- Fe-siliceous-hydrogarnet starts to form from the early age and continue with hydration time, but it reaches to a steady state after 28days of hydration. The high amount of ferrite in FC enhances its formation.
- Hydration of ferrite and the formed Fe-siliceous-hydrogarnet lead to determine Fe uptake in C-S-H. Fe from ferrite hydration can incorporate into C-S-H in addition to the formation of Fe-siliceous-hydrogarnet.
- The distribution ratio ( $R_d$ ) for Fe uptake in C-S-H is determined as function of  $Fe^{3+}$  concentration. A constant relationship is assumed for both cements.
- The thermodynamic model predicts well the hydration reaction of FC. The experimentally determined Fe-siliceous-hydrogarnet agrees satisfactorily with predicted results.
- The hydration model estimates around 2% of Fe incorporated C-S-H (C-F-S-H) in the hydration products.

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