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## Hydration of Calcium [Alumino] Ferrite with Limestone

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### ABSTRACT

Ferrite has the lowest embodied CO<sub>2</sub> among the four major phases found in Portland cement, so increasing the ferrite content of the clinker would improve its CO<sub>2</sub> footprint. Ferrite hydration is known to depend on the cooling regime during the production, Al/Fe ratio, and minor element uptake, and thus, their effects have to be fully understood to increase the composition of this phase in the Portland cement and assure their good hydration properties. Here, ferrites with different Al/Fe ratios (0, 0.5, 1, and 2), and minor elements (Zn) has been synthesized at two different burning temperatures, 1250 °C and 1350 °C and hydrated in presence of excess CaCO<sub>3</sub> for 1 and 3 days. The ferrite with Al/Fe = 0 did not form any hydration product after 3 days of hydration, while Al-monocarbonate was the only hydration product in the other systems. The hydration kinetics increased with Al/Fe ratio, and when the burning temperature was increased. Comparing XRD and TGA data, the Al-monocarbonate formed from the ferrite with Al/Fe = 2 was found to be more amorphous than other ferrites. ZnO doping up to 2 wt.% had no prominent effect on hydration, implying that raw materials with Zn can be utilised in high-ferrite cement. These results indicate that high-ferrite limestone cement could be a promising solution to reduce cement the CO<sub>2</sub> emission.

**KEYWORDS:** *Limestone, Ferrite, Monocarbonate, Hydration, ZnO doping*

### 1. Introduction

Portland cement (PC) generates ~8% of anthropogenic CO<sub>2</sub> emissions (Monteiro et al., 2017), and one of the ways to reduce CO<sub>2</sub> footprint of cement includes designing PC clinker containing a higher ferrite (Ca<sub>2</sub>Fe<sub>2-x</sub>Al<sub>x</sub>O<sub>5</sub>, x = 0 - 1.4) content as it lowers the clinkering temperature by ~100°C and requires less limestone calcination because of less calcium content (Gartner, 2004). Currently, high ferrite cement is already being used in oil-well cement and sulphate-attack-resistant cement. However, the reactivity of ferrite is less than alite and tricalcium aluminate, thus one of the drawbacks of high-ferrite cements is their lower early-age strength. The reactivity of ferrite is known to be affected by the Al/Fe ratio and synthesis conditions (sintering temperature, cooling rate) as well as the presence of minor elements in the raw materials, such as Zn, Mg, Cr, Ti, and Mn. Out of these elements, Mg, Ti, and Cr generally reduce the ferrite reactivity. The presence of Mn has been shown to improve ferrite reactivity through an increase in the initial dissolution (Zhong et al., 2022), but the effect of Zn is still debated. <sup>27</sup>Al MAS NMR and Raman spectroscopy indicated that in the presence of Zn, the Fe speciation changes from [FeO<sub>4</sub>] to [FeO<sub>6</sub>] (Zhang et al., 2019) and DFT showed that an increase in effective charge of Fe in the presence of Zn is responsible for higher reactivity (Tao et al., 2020). Most of the studies investigate the ferrite hydration process only in the presence of calcium sulphates, as calcium sulphate is well-known to react with ferrite to form monosulphate or ettringite. However, the cement industry is currently rapidly moving towards producing Portland Limestone Cement (PLC) containing up to 15% limestone. Limestone is expected to react with ferrites because it reacts with tricalcium aluminates, but there is no detailed study in the literature about the hydration kinetics and hydration products formed when ferrites react with calcium carbonate.

In this paper, we have synthesised ferrites with four different Al/Fe ratios, two different burning temperatures, and ZnO doped at four different quantities. The ferrites were hydrated in presence of excess limestone to evaluate their hydration product formation using X-ray diffraction and thermal analysis.

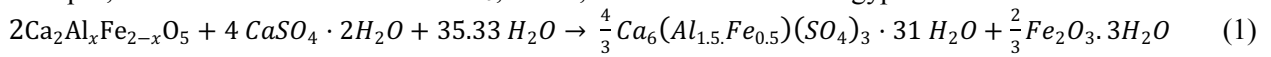
Briefly, we found that ferrites ( $x \geq 0.5$ ) react with calcite to form Al-monocarbonate, and the reactivity of ferrite increases with increasing Al/Fe ratio, or increasing sintering temperature from 1250 °C to 1350 °C.

## 2. Materials and Methods

### 2.1. Ferrite synthesis and its hydration

Ferrites with different Al/Fe ratio, ZnO doping, and burning temperatures (Table 1) were synthesized by mixing CaCO<sub>3</sub> (Sigma-Aldrich, 99.5%), Al<sub>2</sub>O<sub>3</sub> (Acros Organics, 99%), Fe<sub>2</sub>O<sub>3</sub> powders (Sigma-Aldrich, >96%) and ZnO powders (Sigma-Aldrich, 99.9%) in a ball mill for ~10 minutes and compressing them into pellets. The pellets were introduced in a Carbolite 1600 furnace using platinum crucibles at 900 °C and heated to a final burning temperature of 1250 or 1350 °C at 5 °C/min and were held at the final burning temperature for one hour. The pellets were subsequently water quenched while still in the platinum crucible to avoid direct contact with water. Finally, the pellets were ground into powder passing through a 63-micron sieve using mortar and pestle. The ferrite samples were subsequently characterised using X-ray diffraction to ensure their purity.

Previous studies (Fukuhara et al., 1981) evaluated the hydration reaction of C<sub>4</sub>AF and gypsum, as shown in Eq. 1, where 2 mols of Ca<sub>2</sub>Al<sub>x</sub>Fe<sub>2-x</sub>O<sub>5</sub>,  $x = 1$ , react with 4 mols of gypsum and 35.33 mols of water.



In this paper, the synthesised ferrites (Ca<sub>2</sub>Al<sub>x</sub>Fe<sub>2-x</sub>O<sub>5</sub>) were mixed with CaCO<sub>3</sub> and water at 2:8:43.33 molar ratio to form Fe-carbonate-Aft, C<sub>6</sub>(A<sub>0.75</sub>F<sub>0.25</sub>)C<sub>3</sub>H<sub>31</sub>, where C̄ represents CO<sub>3</sub>. Twice the minimum required amount of CaCO<sub>3</sub> was used to encourage the formation of C<sub>6</sub>(A<sub>0.75</sub>F<sub>0.25</sub>)C<sub>3</sub>H<sub>31</sub>. Although the existence of this compound has not been proven, a very similar compound, called carbonate-ettringite with chemical formula Ca<sub>6</sub>Al<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>(OH)<sub>12</sub>·26H<sub>2</sub>O has been observed in the past (Barnett et al., 2001).

**Table 1: Ferrite Test Sample Matrix**

| Sample Name                        | 0AF1350 | 0.5AF1350 | 1AF1350 | 2AF1350 | 1AF0.5Zn1350 | 1AF1Zn1350 | 1AF2Zn1350 | 1AF1250 |
|------------------------------------|---------|-----------|---------|---------|--------------|------------|------------|---------|
| Burning Temperature                | 1350    | 1350      | 1350    | 1350    | 1350         | 1350       | 1350       | 1250    |
| Extra ZnO added (wt.% of raw meal) | 0       | 0         | 0       | 0       | 0.5          | 1.0        | 2.0        | 0       |
| Al/Fe                              | 0       | 0.5       | 1       | 2       | 1            | 1          | 1          | 1       |

### 2.2. Characterisation of clinkers and hydration products

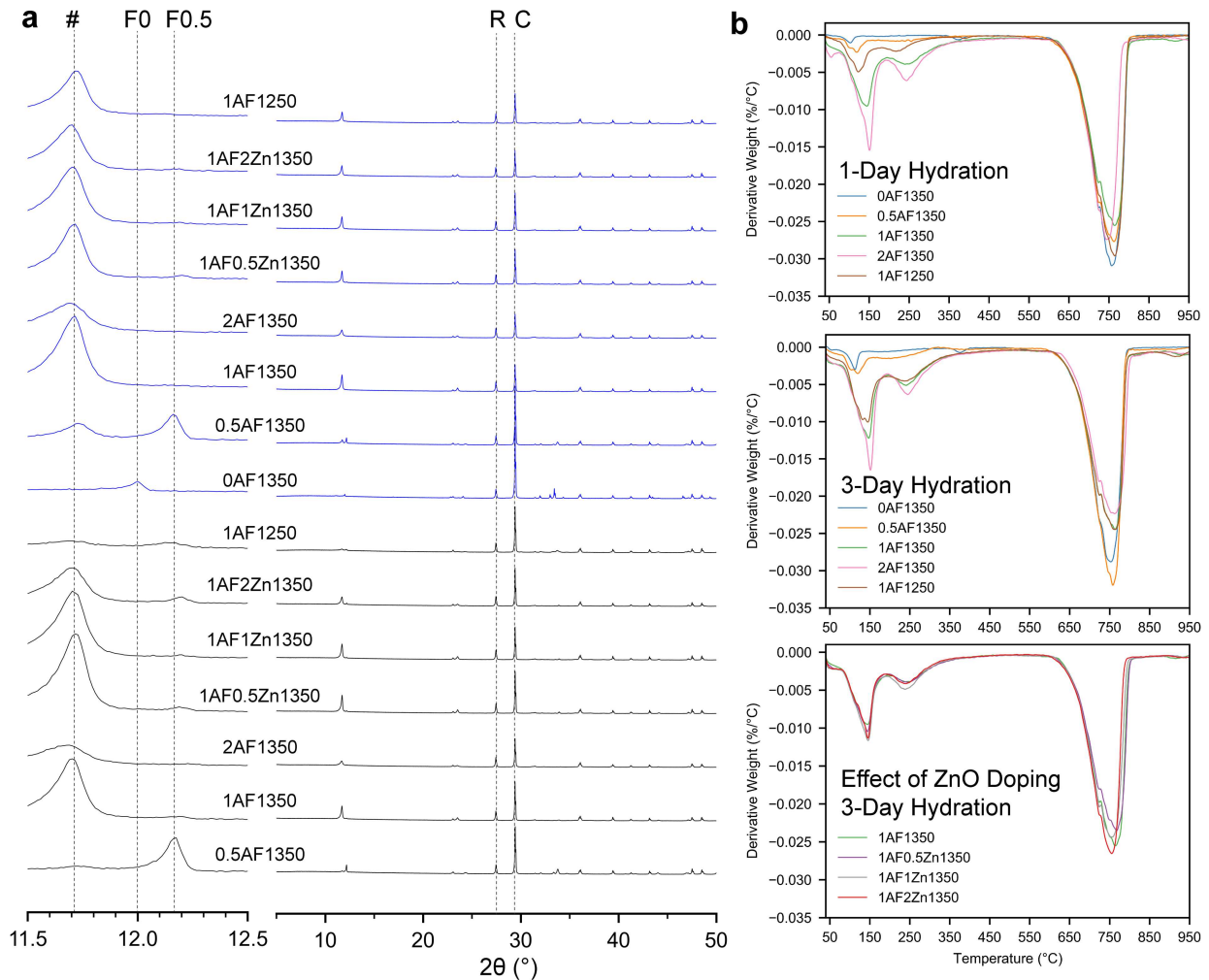
X-ray diffraction patterns of the un-hydrated and hydrated ferrites were obtained using a Panalytical Xpert<sup>3</sup> that operates using a Cu source ( $K\alpha \sim 1.5406 \text{ \AA}$ ) at 45 kV and 40 mA and a PIXcel1D-Medipix3 detector. The samples were backloaded into a 16 mm dia. sample holder rotating at 4 s per revolution. For the hydrated samples, ~20% rutile (Alfa Aesar, 99.5%) by mass was added as an internal standard and  $2\theta$  values ranged from 5 to 80° with a step size of 0.013°, with a ¼° divergence slit and a ⅛° anti-scatter slit with a total scan time of ~2.5 h. Thermogravimetric analysis of the hydrated samples was performed using a Pyris 1 TGA with alumina crucible in between 40 and 1000 °C at 10 °C/min using 10±0.5 mg samples with 20 mL/min nitrogen flow. The derivative of the weight loss was calculated using cubic spline regression.

## 3. Results and Discussions

The X-ray diffraction data (Figure 1a) showed that no AFt or hydrogarnet phases formed in any of our samples as no peaks below  $2\theta = 10^\circ$  or at around  $17^\circ$  were observed. Even though there is no existing detailed crystal structure of Fe-carbonate-Aft in the literature, the crystal structure of Fe-carbonate-Aft can be expected to be similar to Fe-ettringite, and thus the samples are expected to have a peak at around  $2\theta = 9^\circ$  (Fe-ettringite's (100) peak location is at  $9.139^\circ$ ) had Fe-carbonate-Aft formed. The XRD detected only one hydrated phase, Al-monocarbonate with 11 mols of water (Al-Mc,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$ ), in all the samples. As the lattice parameter is expected to change by less than 1% when Fe completely replaces

Al in Al-monocarbonate, the formula of the hydrate could be  $3\text{CaO}\cdot y\text{Al}_2\text{O}_3\cdot(1-y)\text{Fe}_2\text{O}_3\cdot y\text{CaCO}_3\cdot 11\text{H}_2\text{O}$  ( $y>0$ ). However, we are confident that the hydration product is not Fe-monocarbonate with 12 mols of water ( $3\text{CaO}\cdot\text{Fe}_2\text{O}_3\cdot\text{CaCO}_3\cdot 12\text{H}_2\text{O}$ ) as it is rhombohedral, and Al-Mc, with 11 mols of water is triclinic, leading to different diffraction patterns (Dilnesa et al., 2011). SEM-EDS measurements will be performed in the future to determine the Al/Fe ratio in the monocarbonate.

The samples synthesised at 1350 °C and with  $\text{Al/Fe} \geq 1$  were almost fully hydrated just after 1 day of hydration as no ferrite peaks were visible in the XRD data. The 0.5AF1350 and 1AF1250 show a considerable increase in Al-monocarbonate peak intensity from 1 to 3 days of hydration. The 1AF1250 clinker sample had a smaller crystallite size and more disorder than the 1AF1350 clinker, which might explain the lower reactivity. The sample with  $\text{Al/Fe} = 0$  on the other hand, does not show any reactivity as no hydrated products were detected in the XRD data. The lower reactivity of ferrite with  $\text{Al/Fe} = 0$  is expected as previously it took ~7-days for a mix of  $\text{C}_2\text{F}$  and  $\text{CaCO}_3$  in a highly alkaline solution to form Fe-hemicarbonate, and about 180 days to start forming Fe-monocarbonate (Dilnesa et al., 2011). In general, for all the samples, an increase in the Al-monocarbonate peak was accompanied by a decrease in the calcite and ferrite peaks. However, for  $\text{Al/Fe} = 2$ , even though the calcite peak intensity was lower than the  $\text{Al/Fe} = 1$  samples for both 1 and 3-days of hydration, implying a greater reactivity, the Al-monocarbonate peak intensity was not higher than the  $\text{Al/Fe} = 1$  samples, indicating “amorphous AFm” formation (Lothenbach et al., 2008). In terms of the effect of ZnO addition, there were no obvious trends in the Al-monocarbonate peak intensity.



**Figure 1. XRD and TGA results of the hydration products. (a) XRD patterns of hydration products of ferrites with  $\text{CaCO}_3$  after 1-day (black) and 3-day (blue) hydration (#: Al-monocarbonate, F0: ferrite with  $\text{Al/Fe} = 0$ , F0.5: ferrite with  $\text{Al/Fe} = 0.5$ , R: rutile, and C: calcite). (b) DTG curves of the hydration products.**



### 3.2. Thermal Analysis

The thermal analysis of the hydrated samples (Figure 1b) mostly confirmed the XRD observations. The twin-peaks in the DTG data commonly associated with Al-monocarbonate were observed in the DTG data, where Al-monocarbonate loses five interlayer water molecules in between 50 and 200 °C, and six water molecules from the octahedral layer in between 200 and 300 °C (Lothenbach et al., 2008). The 0AF1350 sample showed minimal water mass loss indicating little hydration product formation, and the amount of mass loss related to Al-monocarbonate increased with the Al/Fe ratio, including Al/Fe = 2, further indicating that there is more amorphous AFm formation in the 2AF1350 sample compared to other samples. Further, the DTG peak area of the 0.5AF1350 and 1AF1250 increased from 1 day to 3-day of hydration implying continual hydration process between 1 and 3-day for those samples, whereas the DTG peak did not change a lot in between 1 and 3 days for 1AF1350 and 2AF1350 samples showing the hydration reaction was mostly completed within 1 day. Finally, there was no pronounced effect and trends of ZnO doping on the hydration product formation in general, however, the sample with 1% ZnO doping showed a slight increase in DTG peak area. As Zn-doping did not change the ferrite reactivity, raw materials containing minor amounts of Zn can be used in cement with high ferrite content.

### 4. Conclusions

Ferrites with different Al/Fe ratios, sintering temperatures, and ZnO doping were synthesised and hydrated in presence of excess CaCO<sub>3</sub> in this paper, and the hydration product was characterised using TGA and XRD. Four major conclusions were drawn from the experiments — first, Al-monocarbonate forms when ferrites with Al/Fe = 0.5, 1 and 2 react with excess calcium carbonate, with the reaction kinetics accelerating with Al/Fe ratio, and the hydration reaction being almost completed just after 1-day hydration for Al/Fe = 1 and 2, when a sintering temperature of 1350°C is used. No AFt or hydrogarnet phases were observed in the XRD data. Second, the hydration kinetics is slower when a sintering temperature of 1250 °C is used instead of 1350 °C for ferrite with Al/Fe = 1, as the hydration reaction was continued between 1 day and 3 days for the sample synthesised at 1250 °C. Third, the Al-monocarbonate formed from the ferrite with Al/Fe = 2 is potentially more amorphous and/or contains more disorder than other ferrite samples. Finally, ZnO doping did not alter the hydration product formation and hydration kinetics prominently showing that Zn containing raw materials can be utilised for high ferrite cements. These results indicate that high-ferrite limestone cement could be a promising solution to reduce cement CO<sub>2</sub> emission by reducing both clinker factor and clinker carbon footprint.

### Acknowledgements

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