In-situ hydration studies of $C_4AF$ at early ages in the presence of other phases

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The ferrite phase, $C_4AF$ in cement nomenclature, also called brownmillerite, is the major iron-containing phase in Ordinary Portland Cement (OPC) and in iron rich belite calcium sulfoaluminate cements. The term “ferrite” usually refers to a solid solution with a wide range of composition with the general formula $Ca_2(Al_yFe_{2-y})O_5$, where $y$ can vary from 0 to about 1.33 [1]. In cement chemistry the ideal composition $C_4AF$ (4CaO·Al$_2$O$_3$·Fe$_2$O$_3$), is used to describe the ferrite phase in Portland cement.

The hydration of pure brownmillerite with water initially forms metastable C-(A,F)-H hydrates which eventually convert to a hydrogarnet phase $C_3(A,F)H_6$ (katoite) over time. The addition of calcium sulfates to $C_4AF$ inhibits the direct hydration of $C_4AF$ to $C_3(A,F)H_6$. Ettringite (AFt) is the most commonly hydration product observed under these conditions. In addition, ettringite could decompose to an AFm monosulfoaluminate hydrate [2].

The aim of this work is to better understand the early age hydration of tetracalcium aluminoferrite phase in the presence of other phases at early ages in order to understand “eco-cement” performances. Chiefly, we want to determine the hydration kinetic and mechanisms of this phase using different reaction media.

Firstly, $C_4AF$ in the presence of water hydrates to form mainly a hydrogarnet-type phase $C_3(A,F)H_6$. The hydration of ferrite with w/s ratio of 1.0
yielded $C_3A_{0.84}F_{0.16}H_6$ as single crystalline phase. Its crystal structure has been determined by the Rietveld method. Figure 1 shows the Rietveld synchrotron X-ray powder diffraction plot for this sample.

Secondly, we have observed that the presence of sulfates strongly modifies ferrite hydration behavior. The hydration of $C_4AF$ in the presence of gypsum gives AFt and, once gypsum is completely dissolved, crystalline AFm starts to precipitate. Figure 2 shows a selected range of the SXRPD raw patterns for $C_4AF_{st}$-$C_4A_3S_{g}$-1.0 (sample with $C_4AF$, gypsum and ye’elimite) recorded at different time of hydration, with the main peaks due to a given phase labelled.

Finally, the effect of w/s ratio has also been studied for this sample. Results indicate that higher amounts of water favour the formation of AFm. A summary of the results for the hydration of $C_4AF$ will be discussed.

Figure 1. Rietveld Synchrotron X-Ray Powder Diffraction plot for $C_3A_{0.84}F_{0.16}H_6$. The tic marks are the Bragg reflections: $C_3A_{0.84}F_{0.16}H_6$ (lower row); Quartz, internal standard (upper row).
Figure 2. Selected range of the SXRPD raw patterns for $C_4AF$ with ye’elimite and gypsum (w/s=1.0) recorded at different time of hydration, with the main peaks due to a given phase labelled. AFt: circle; AFm: star; Qz: triangle; gypsum: rhombus; C$4$AF: inverted triangle and ye’elimite: square.

REFERENCES


Cement nomenclature: $C$=CaO, $A$=Al$_2$O$_3$, $F$= Fe$_2$O$_3$, $S$=SO$_3$ and $H$=H$_2$O.