

In Situ Hydration of Sulfoaluminate Cement Mixtures Monitored by Synchrotron X-Ray Diffraction

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Abstract. Mixtures of calcium sulfoaluminate and Portland clinkers with gypsum were hydrated with deionized water. The pastes were introduced in 0.7 mm borosilicate capillary tubes and kept at 40 °C while diffraction patterns were collected every 35 s for approximately 3 hours with a monochromatic radiation of 12 keV at the XRD1 beamline of the Laboratório Nacional de Luz Síncrotron (LNLS) in Campinas, SP - Brazil. The main crystalline phases (C2S, C3S, ettringite, ye'elemite and gypsum) involved in the hydration were quantified by Rietveld analysis. The most noticeable fact was the absence of portlandite as a crystalline precipitate, most likely due to the capture of calcium ions to form ettringite.

Introduction

Calcium sulfoaluminate cement (CSAC) is known at least since the beginning of last century. The first reference in scientific literature about this type of compounds dates back to 1929 [1]. A few decades later a patent was granted in 1964 to A. Klein [2] - hence the alternative name given to the major component of calcium sulfoaluminate - Klein's compound. Subsequently the research and exploitation of this kind of materials was abandoned in the Western World but China, especially since 1970, continued with the research and development of these cements. Only in recent years this endeavor has been retaken in Europe [3] and has been considered as a viable alternative ecocement. The crescent pressure to reduce carbon dioxide emissions has led to find alternative products to the most widespread Portland cements. By comparison the production of 1 g of ordinary Portland cement (OPC) releases approximately 0.58 g of CO₂, while to produce the same amount of CSAC only 0.22 g of carbon dioxide is released. Another added advantage is the lower synthesis temperature in favor of CSAC (1250 °C vs 1450 °C) and, finally, the sulphoaluminate product is easier to grind [4]. Furthermore the synthesis process of these cements provides also an alternative way of recycling gypsum obtained as byproduct from other industries, since both the clinker synthesis process and its hydration require it [5].

Concerning the mechanical properties of concrete they are also superior; after 21 days of hydration the compressive strength can vary between 60 and 100 MPa, whereas OPC for the same period of time can attain approximately 40 MPa [6] and an adequate strength can be obtained in one day instead of four weeks in the case of Portland. This feature makes it appropriate for civil works that require short time to function such as motorway pavements repairs, airports runways and tunnels. Also due to its absence of shrinkage during setting traditionally has been used in combination with Portland cement to compensate this drawback [7-9].

Another distinct feature is its lower pH around 11, compared to 13 for Portland cement; this makes less likely to promote an alkali-silica reaction with aggregates different of sand such as glass fiber or even plain glass [10]. In addition it is chemically resistant to both sulfate attack and biological degradation by bacteria that might happen in sewage systems.

Besides its interesting mechanical properties, it exhibits a good behavior to encapsulate waste in natural rock deposits [11], since its pH is lower than in OPC and the crystal structure of hydrated products can accommodate heavy cations [12].

Synchrotron radiation is an interesting tool to study the hydration of cements in situ. In this respect an early work reported the formation of calcium sulfoaluminate phases with the help of an energy dispersive instrument [13]. These days the modern synchrotron sources allow rapid data collection in angle-dispersive mode; an example of in-situ hydration of calcium sulfoaluminate phases can be found in reference [14]. Within this frame of thought an attempt to elucidate some aspects of the hydration of mixtures of ordinary Portland and calcium sulfoaluminate cements is presented in this article.

Experimental

The hydration of calcium sulfoaluminate cement mixed with gypsum and Portland clinker was studied in situ by synchrotron X-ray diffraction at the XRD1 beamline of the LNLS synchrotron source [15]. The powder specimens were introduced in borosilicate glass capillary tubes of 0.7 mm of internal diameter and imbued with boiled deionized water. The capillaries were placed on the goniometer and the data collection was started after two minutes of mixing with water. The X-ray energy chosen to get an adequate flux for these short time acquisitions was 12 keV or more precisely 1.03326 Å, determined with polycrystalline corundum standard. Diffraction patterns were collected sequentially every 35 seconds for several hours at 40 °C with accuracy better than 0.1 °C, attained with the help of a hot air blower. The diffracted signal was collected with an array of twenty-four Mythen detectors situated at 760 mm from the capillary tube.

Data Processing

The diffraction patterns were analyzed with GSAS [16] Rietveld package to quantify, by the Rietveld method, the crystalline phases. The diffraction data were smoothed with a code written in Python by applying the Savitzky-Golay algorithm [17]. Further treatment of the XRD patterns was made with a series of scripts written in IDL [18] to get data conditioned to plot three-dimensional maps. The diffraction patterns sequence and their two-dimensional projections were computed using Transform [19]. The plotting of data in Fig. 2 was made with Origin 8 [20].

Results and Discussion

The series of diffraction patterns collected for one and half hour are shown in Fig. 1. In Fig. 2 the evolution of the relative proportions of crystalline phases can be seen. Non-crystalline phases such as CSH gel or Al(OH)₃ (gibbsite) are not taken in consideration.

The same Figure clearly shows that the ettringite formation happens in two stages, the second one starting after approximately forty minutes. It is also interesting to notice that this stages seem to coincide with the depletion of Ca₂SiO₄ (C2S) for the first stage and the depletion of Ca₃SiO₅ (C3S) for the second one.

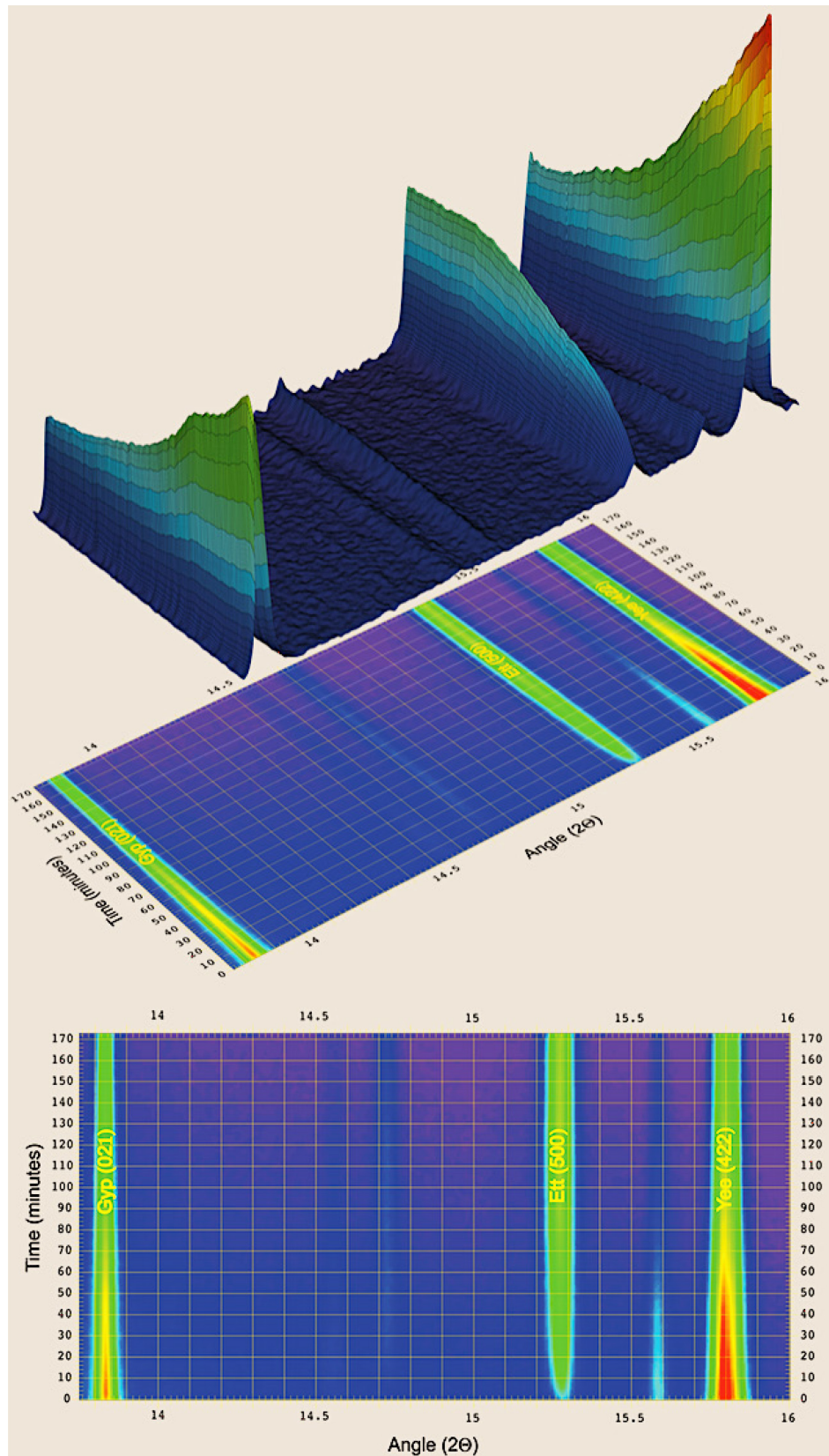


Fig. 1. Sequence of diffraction patterns in a pseudo- 3D fashion as a function of time on a narrow angular domain to illustrate the evolution of the main crystalline phases involved in hydration. On top the 3D assembly of patterns and on the bottom the projection as 2D contour map.

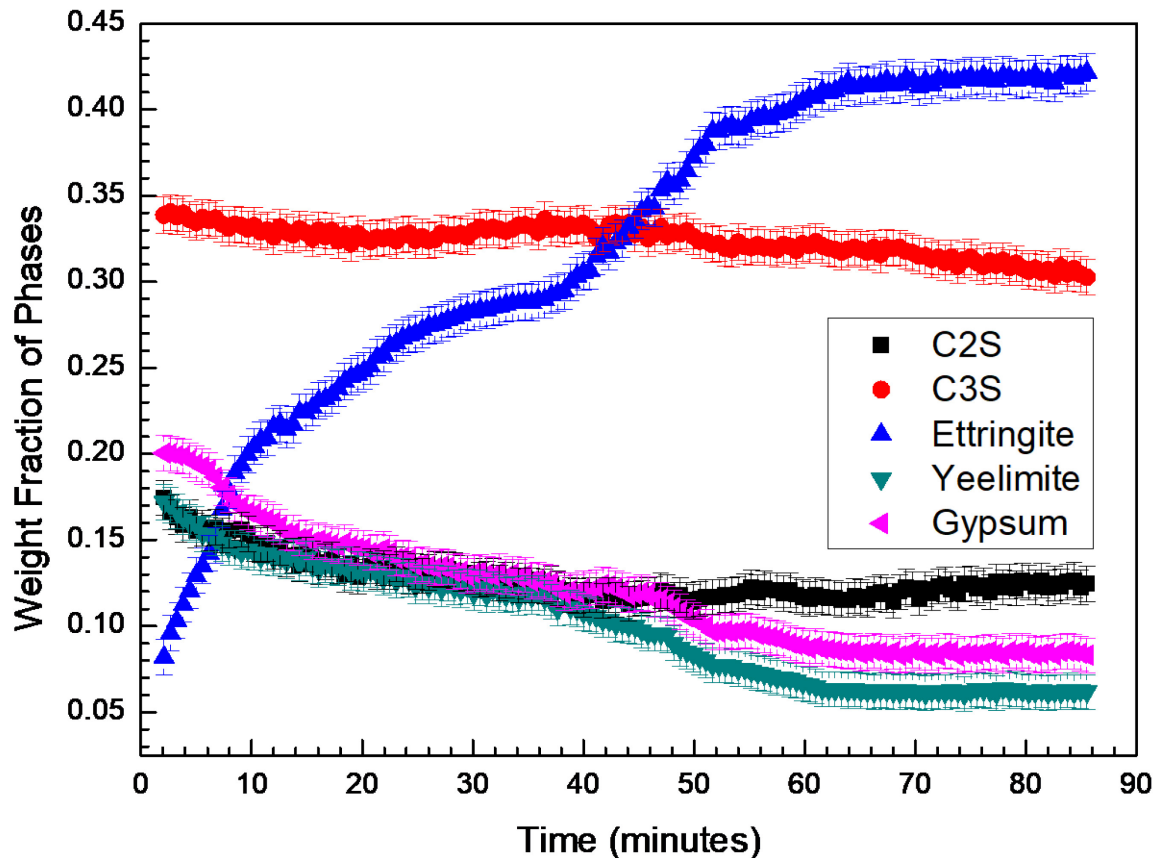
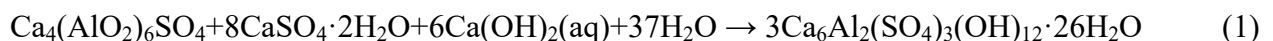


Fig. 2. The hydration, as a function of time, of an admixture of ye'elemite, gypsum and Portland clinker. The weight fractions of the crystalline phases are plotted as determined by quantitative Rietveld analysis with GSAS. Some other non-crystalline products such as gibbsite and CSH gel are not taken in consideration.

The hydration of the silicates yields in first place CSH gel and calcium cations counterbalanced with OH^- groups that eventually could precipitate as portlandite ($\text{Ca}(\text{OH})_2$). In this particular case the Ca^{2+} and OH^- groups most likely react with ye'elemite and gypsum to produce ettringite according to the equation:



The absence of portlandite, that is very conspicuous when it is present even in small quantities, seems to support this hypothetical chemical route. Another fact observed is that the hydration was not completed since the amount water placed in the capillary was not enough to complete the reaction.

Conclusion

These preliminary results show that the uncompleted hydration of a mixture of calcium sulphoaluminate cement and Portland clinker seems to take place in two stages with the apport of calcium released first by calcium disilicate and later on by calcium trisilicate. The final major product as expected is ettringite. The XRD1 beamline of LNLS is very adequate to study the hydration of cementitious mixtures. The statistics of the diffraction patterns acquired in 35 s allows quantification of crystalline phases by Rietveld analysis. In this particular example, at 40 °C, the hydration happens in less than two hours. Further experiments are planned to determine the kinetics of the chemical reactions by monitoring the crystalline phases concentrations as a function of time at higher temperatures.

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