

THE EARLY AGE STUDY OF CEMENT HYDRATION BY IN-SITU SYNCHROTRON X-RAYS DIFFRACTION

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Abstract

The x-ray diffraction technique is normally used to determine cement hydration products such as ettringite (AFt), monosulfate (AFm), and portlandite (CH). The hydrated samples have to be prepared in dry powder and the cement hydration reaction has to be stopped at a specific time. It is not practical to study the hydration products at a very early age. To overcome this limitation, the in-situ wide angle x-ray scattering technique (WAXS) was used to investigate cement hydration. Because of the high intensity of synchrotron x-rays, the measurement time was shortened. This enabled the study of cement hydration at a very early age by the WAXS technique which gave valuable information on the rate of formation and depletion of the cement hydration products at a very early age and an understanding of the cement's properties such as workability and early compressive strength.

Keywords: Wide angle X-ray scattering (WAXS), X-ray diffraction (XRD), cement hydration

Introduction

Cement is a building material which is widely used because it is the binder that acts as a strengthener to produce many cement applications, for example cement paste, mortar, and concrete. Cement generally is a dry powder which can set hard to get strength at the final stage due to the occurrence of the hydration reaction of cement with water. When cement is mixed with water, there is a state of suspension which enables it to flow for a while. The flowability of cement reflects its workability and also affects the mechanical property of a cement product in its

hardened state at a late age; the good flowability of cement in suspension leads to it being able to flow easily into a mold so that the hardened cement product tends to be a denser cement that has good compressive strength and good durability as well (Mechtcherine *et al.*, 2003; Banfill, 2006). The stages of cement, from its fresh state to its hardness state after mixing with water, comprise the dormant period, setting, and hardening stages, respectively. Consequently, the compressive strength is developed by the time for which cement is mixed with water due to the

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hydration reaction of the cement's compositions such as $3\text{CaO}\cdot\text{SiO}_2$ (C_3S), $2\text{CaO}\cdot\text{SiO}_2$ (C_2S), $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ (C_3A), $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ (C_4AF), gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), free lime (CaO), magnesium oxide (MgO), and alkali sulfate (as Na_2O or K_2O eq.). The hydration of the cement's composition leads to a lot of hydration products such as calcium silicate hydrate (C-S-H) gel, ettringite (AFt), calcium hydroxide (CH), monosulfate (AFm), sulphoaluminate, and sulphoferite. The hydration reaction of the C_3S and C_2S phases yields C-S-H gel as a major hydration product and CH. The hydration reaction of C_3A with gypsum leads to AFt and AFm (Figure 1) (The Siam Cement Group, 2005; Scrivener *et al.*, 2005; Stephana *et al.*, 2008; Bullard *et al.*, 2011).

A study of the hydration reaction of cement could normally use conventional x-ray diffraction (XRD) by using the powder form of cement specimens. However, the limitation of conventional XRD is that the study of the hydration phase development at a very early age after mixing with water is still not clear. Overcoming the limitation and understanding the cement's hydration at a very early age might result in knowledge of the cement's development, especially the improvement of the cement's workability for ready-mixed concrete. The limitation of conventional XRD is due to the low intensity of the x-ray radiation that is generated from a copper tube, so it needs a long x-ray exposure time of about 15-20 min to complete the hydration experiment and that leads to the occurrence of the time lag effect of the cement's hydration from a low to high 2θ in the range of 7° - 55° (Hesse *et al.*, 2011; Dittrich *et al.*, 2014). To overcome the limitation, the wide angle x-ray scattering technique (WAXS) from synchrotron radiation has the potential because of the very high intensity of the X-ray radiation that is generated from the synchrotron light source which can get all 2θ s at the same time at a very fast exposure time of a few seconds (Moritz-Caspar *et al.*, 2012).

Since the synchrotron light is generated from the emission of the energy of deflected electrons, it has a very high intensity, continuous energy emission, and wide wavelength from

infrared to X-ray radiation. Consequently, synchrotron radiation is widely used as a tool in research and applications in many science and technology fields such as the study of material elements, the size and shape of the molecules of nanoparticles, the surface characteristics of metals and semiconductors, the distance data of each atom in a molecule, the type of chemical bonding and elements of a material, and the building of the very small parts of devices using the lithography technique (The Synchrotron Light Research Institute, 2014).

Small angle X-ray scattering (SAXS) and WAXS are the techniques used to study a structure's characteristics from the nanosize to angstrom size of materials by measuring the X-ray scattering radiation at a small or wide angle. Analysis of a specimen by SAXS or WAXS can be done by imposing the X-ray beam onto the sample directly and then measuring the intensity of the scattering profile of the sample by the detector. The end results of the techniques were similar to the X-ray diffraction technique (Figure 2).

Materials and Methods

Materials

The materials that were used were ordinary portland cement type I (OPC), clinker, gypsum,

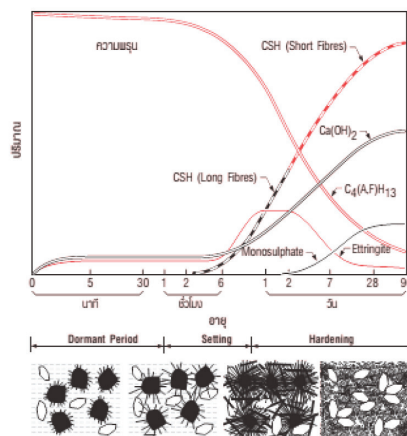


Figure 1. The hydration product development of cement hydration by time (The Siam Cement Group, 2014)

hemihydrate, anhydrite, type D cement admixture, deionized water, and Kapton® film as a window for the WAXS sample container cell.

Method

Cement Powder Preparation

Cement preparation was by grinding together each material such as clinker with gypsum, hemihydrate, or anhydrite.

The Study of the Cement Hydration by XRD

Each cement paste was prepared by mixing water with 10g of each type of sulfate cement at a water to cement ratio of about 0.485;

then, the cement paste was poured into the sample container of the conventional XRD (Bruker D4 Endeavor X-ray diffraction solution, Bruker Corporation, Billerica, MA, USA). The specification of the device is as follows: the Cu tube is Anode, and the energy is 35kV and 40mA. The 2theta angles were analyzed from 5 to 40 by using a step size of 0.02 degree at a scanning rate of about 28 sec.

The Study of the Cement Hydration by WAXS

A 2g amount of cement was mixed with water at a water to cement ratio of about 0.485 and then the cement paste was patched onto the thin Kapton® film of the WAXS sample

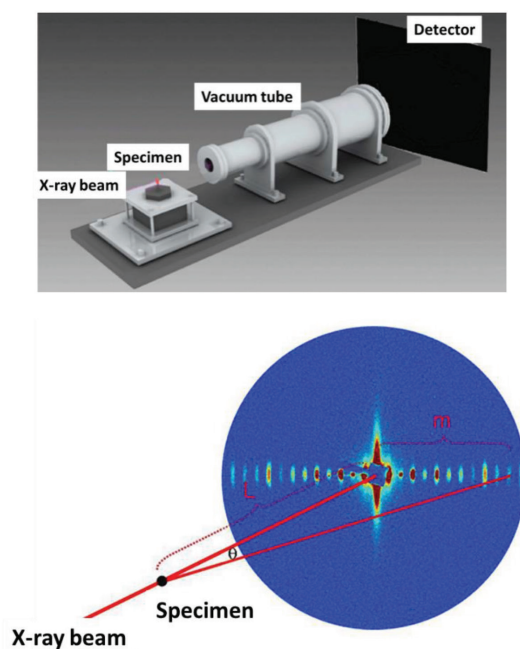


Figure 2. The SAXS and WAXS using synchrotron light as the X-ray radiation source (The Synchrotron Light Research Institute, 2014)



Figure 3. Sample container of cement paste for WAXS analysis

container (Figure 3). The X-ray energy was 8 keV and used a charge-coupled device as a detector to keep the X-ray scattering profile. The result of the X-ray scattering profile was interpreted by the SAXSITS program (Rugmai and Soontaranon, 2014).

Results and Discussion

To study the cement hydration by conventional XRD, the appropriate sample was prepared in a dry powder form which can be done by various techniques such as the solvent replacement method, freeze drying, oven drying, and vacuum drying. However, the sample preparation method might have an effect on some hydration products and the porosity of the specimens Collier *et al.*, 2008. The XRD results of the dry powder from the drying process might be slightly erroneous because it was not measured from real fresh cement paste. The measurement of fresh cement by XRD at different times from a very early age at 2.50

to 32 min showed a very low signal of the Aft peak ($2\theta \approx 9^\circ$) at the beginning of the test and also the quantity error of the gypsum depletion rate due to heat accumulation from the XRD scanning process (Figure 4).

Conversely, the results from the study of fresh cement paste by the WAXS technique yielded a very clear Aft peak and also the quantity of the gypsum depletion by time at a very fast X-ray exposure time in a few seconds due to the high intensity of the X-ray radiation source from the synchrotron light.

The good point of the very high intensity of X-ray radiation is that the fresh cement paste was illuminated by the X-ray very quickly. The shortening of the time could have prevented the sample's heat accumulation and yielded the good quality of the spectra due to the increase of the signal to noise ratio (Figure 5).

Using the WAXS technique for studying the in-situ hydration rate of fresh cement that had a different form of calcium sulfate, such as gypsum, hemihydrate, and anhydrite, produced

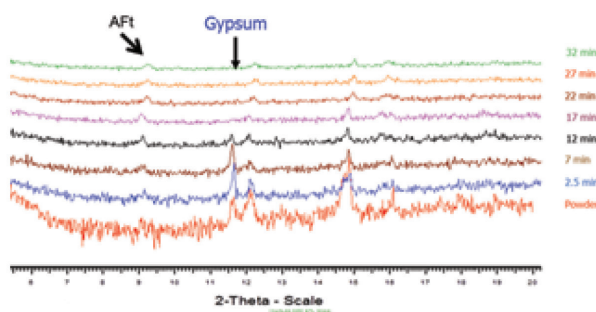


Figure 4. XRD spectra of fresh cement hydration by conventional XRD

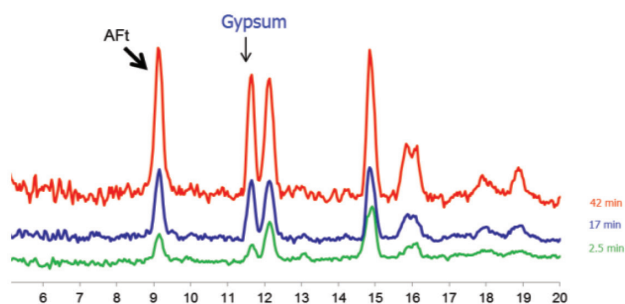


Figure 5. Spectra of fresh cement hydration from WAXS

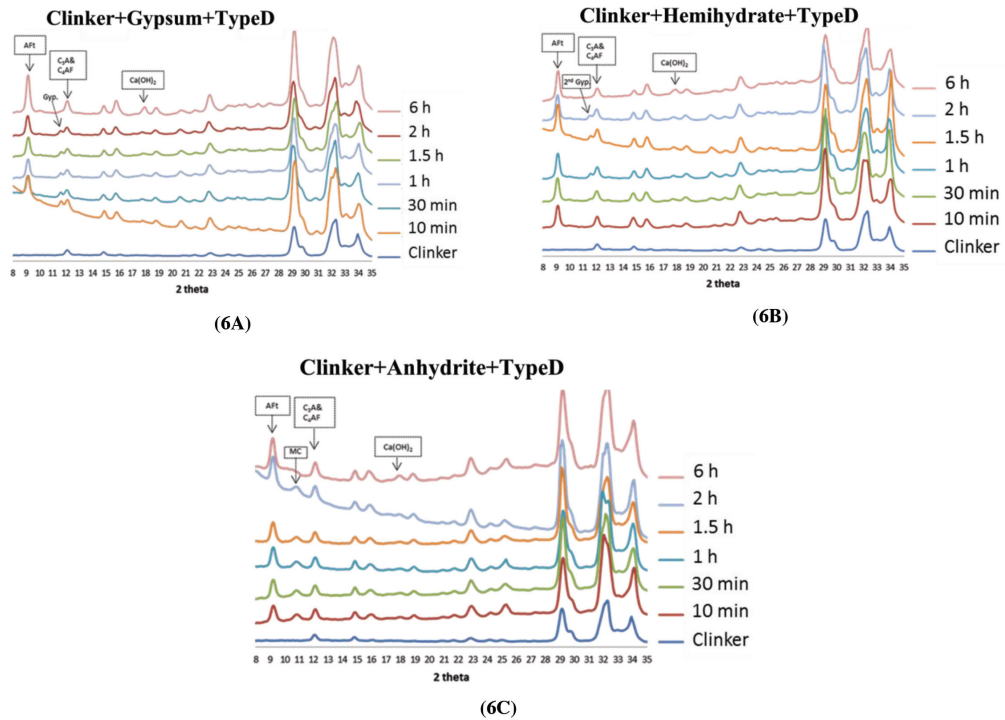


Figure 6. WAXS spectra of fresh cement paste with gypsum (6A), hemihydrate (6B), and anhydrite (6C)

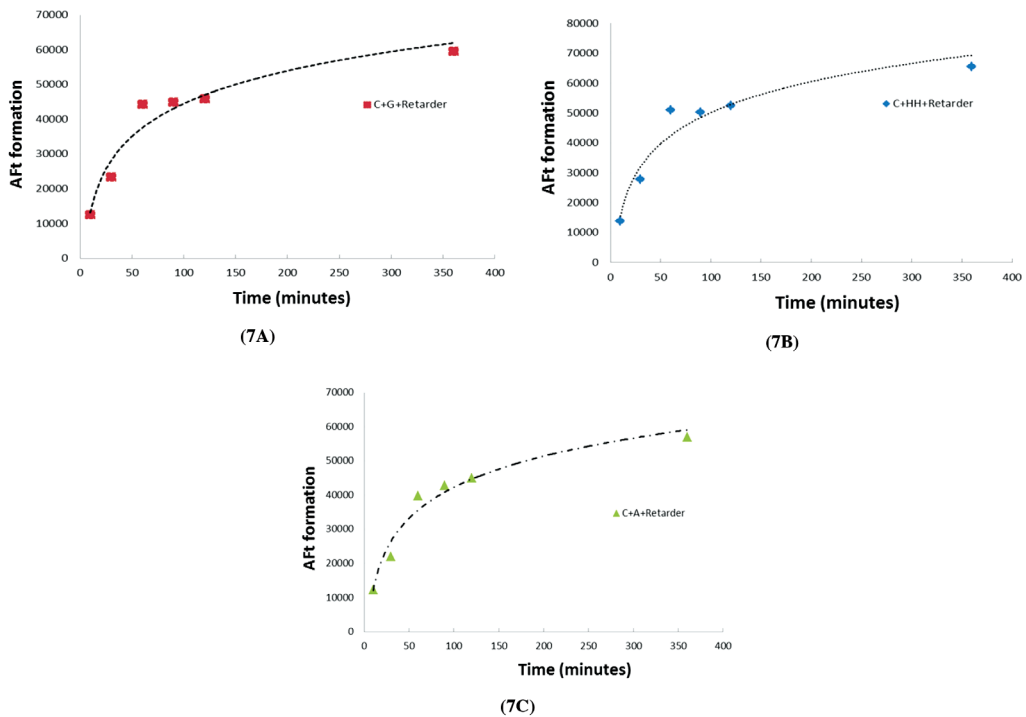


Figure 7. The rate of AFt formation of fresh cement paste with gypsum (7A), hemihydrate (7B), and anhydrite (7C)

results that showed that all of the calcium sulfate forms tended to both increase the AFt quantity ($2\theta \approx 9.2$) and the CH ($2\theta \approx 18$) but that the calcium sulfate content ($2\theta \approx 12$) decreased with time due to the reaction with C3A for the formation of AFt (Figure 6(a)).

In the case of hemihydrate, its solubility was very high compared with the other calcium sulfates. It was able to dissolve very fast and then generated secondary gypsum crystal ($2\theta \approx 12$) (Figure 6(b)). Because anhydrite has a very low solubility, monocarboaluminate that was the byproduct of hydration could be found ($2\theta \approx 10.7$). The results of in-situ spectra of various

calcium sulfate forms showed the different hydration products that could be studied with WAXS and showed that the rate of fresh cement hydration from 10 min to 6 h yielded an increase of the AFt for all the calcium sulfate forms (Figure 7(a)-7(c)).

Moreover, different kinds of calcium sulfate forms also affected the rate of the AFt formation (Figure 8). The anhydrite had the lowest effect rate on the formation of AFt due to its low solubility; meanwhile, the hemihydrate had the highest effect rate on the formation of AFt because of its high solubility (Figure 9).

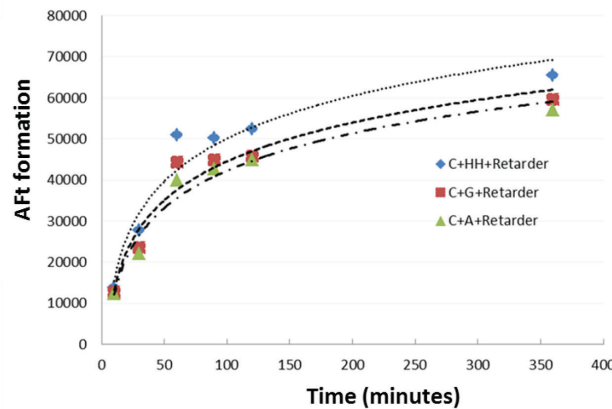


Figure 8. Rate of AFt formations with various types of calcium sulfate

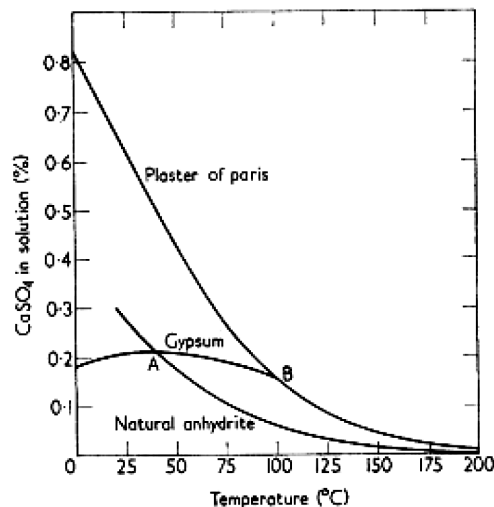


Figure 9. Solubility value of gypsum, hemihydrate, and anhydrite (Power *et al.*, 1964)

Conclusions

In this study, WAXS could be applied for use in the study on hydration product formation at a very early age. This technique is a viable alternative to conventional XRD to evaluate the Aft formation in various types of calcium sulfate forms.

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