

Phase Composition and Reaction Kinetics of OPC Hydration by *In Situ* Transmission XRD using a Focusing Elliptical Mirror

S.B. Feldman¹, P. Sandberg², D. Brown², F. Serafin²

¹PANalytical, Inc., Natick, MA USA;

²W.R. Grace & Co., Cambridge, MA USA

Abstract

We used an innovative focusing elliptical mirror in conjunction with a high-speed detector to study *in situ* depletion of unhydrated phases and the formation of crystalline and poorly crystalline phases in cement pastes using a laboratory diffractometer operating in transmission mode. Three cement pastes were prepared, including two mixtures with different concentrations of an accelerating chemical admixture. Samples were mounted between x-ray transparent foils to prevent loss of mixing water by evaporation and reaction of the paste with atmospheric CO₂, and analyzed spinning in transmission in order to curtail preferred orientation. Semi-quantitative phase analysis were performed using a full-pattern fitting Rietveld approach and data was compared to results from similar mixtures obtained at a synchrotron facility using standard glass capillaries. Results indicate that use of the focusing mirror makes it possible to perform quality *in situ* transmission XRD experiments in the laboratory without synchrotron x-rays.

1. Introduction

X-ray diffraction (XRD) analysis is one of the most suitable and accessible methods for studying phase composition and other mineralogical characteristics of cementitious materials. It is perhaps the best method for following *in situ* depletion of unhydrated crystalline phases and new crystal growth as a function of time in a hydrating cement paste.

In order to make accurate XRD measurements of wet pastes, several experimental parameters must be considered. At a minimum, it is necessary to present the sample in a sealed chamber in order to restrict dehydration and/or carbonation reactions that would severely bias the results. This can be done by covering the sample with x-ray transparent (e.g., Kapton™) film, but cement pastes tend to exhibit some degree of bleeding and segregation near the film resulting in different composition at the surface than the bulk paste, especially if the paste is prepared using a dispersing admixture. Many hydrates such as ettringite and portlandite, for example, tend to grow preferentially at nucleation sites associated with liquid-solid or liquid-gas interfaces present at the surface. Using the typical reflection geometry available on most conventional laboratory diffractometers (employing either focusing or parallel beams), these

phases may be overestimated because the penetration depth of an x-ray beam can be quite low ($<25\mu$) at low scan angles where major peaks for these phases are located¹.

A widely used approach for dealing with pastes has been to employ capillary transmission measurements [1] which, in addition to mitigating phase segregation effects, also provides the benefit of improving particle statistics and minimizing preferred orientation that may be problematic with respect to some phases (e.g., portlandite ($hk1$) and ettringite ($1kl$) reflections).

Glass capillaries yield considerably lower intensities than conventional reflection samples, however, and they tend to suffer from very poor angular resolution and high background, even if a very thin diameter capillary is used. Moreover, it can be difficult and time-consuming to prepare and align samples in the beam. The solution to these problems is typically either to scan for extremely long count times, or to visit a synchrotron facility. Of course, long count times limits the ability to obtain time-resolved data, and even synchrotron data may suffer from high background problems resulting from the amorphous glass signal.

We evaluated the use of a novel focusing elliptical mirror and a high-speed detector available on a commercially-available laboratory diffractometer for conducting *in situ* transmission XRD measurements of hydrated cement pastes. In this preliminary study, we prepared and analyzed pastes continuously, beginning immediately after initial wetting, both with and without chemical admixture, and we compared our results to data obtained on similar preparations at a synchrotron facility [2].

2. Experimental

2.1 Chemical admixtures

Calcium nitrite, a set and early strength accelerator, was selected for this study since it is known to accelerate ettringite formation as well as the general rate of cement hydration [2]. In order to compare results for the novel transmission method against transmission results using a synchrotron source, the same portland cement sample as used in [2] was used, conforming to ASTM Type I and II (designated cement “133”) at the same w/c ratio 0.50. This cement was tested without admixture and with 0.5 % s/s Calcium nitrite. Since this cement sample “133” had been stored in an air tight container for more than 4 years since it was used in the synchrotron study [2], another sample of fresh portland cement conforming to ASTM Type I and II (designated as “078”) was prepared with 2.0% s/s Ca-nitrite dose.

¹ Penetration depth calculated for a scan angles of $10^\circ 2\theta$ assuming ‘typical’ cement composition and mass absorption coefficients for $\text{CuK}\alpha$ radiation.

Cement paste samples for transmission XRD were prepared using a conventional planetary mixer for 60 seconds. After mixing, a small drop of slurry was spread between two layers of Kapton film to form a thin layer with a thickness of 100-150 μ . Based on linear absorption coefficients for a typical cement paste composition, we calculate <30% beam attenuation for this thickness, suggesting that XRD information is being provided from the full depth of the sample.

In the previous study at the Brookhaven National Synchrotron Light Source [2], cement pastes were transferred into 0.7 mm diameter glass capillaries immediately after mixing before being sealed using high vacuum grease. Paste sample preparation and mounting of sample prevented any XRD data collection during the initial 10 minutes hydration.

Table 1. Characteristics of portland cement “133” and “078”

	Cement «133 » [2]	Cement « 078 »
Analyte	Weight %	Weight %
SiO ₂	20.86	19.49
Al ₂ O ₃	4.00	4.93
Fe ₂ O ₃	3.33	3.74
CaO	64.61	64.25
MgO	1.09	1.04
SO ₃	2.88	3.18
Na ₂ O	0.18	0.19
K ₂ O	0.64	0.36
TiO ₂	0.17	0.25
P ₂ O ₅	0.05	0.16
Mn ₂ O ₃	0.04	0.05
SrO	0.04	0.07
Cr ₂ O ₃	<.01	<.01
ZnO	<.01	<.01
L.O.I. (950°C)	1.80	2.34
Total	99.7	100
Alkalies as Na ₂ O	0.60	0.42
<i>Water-soluble Alkali</i>		
Na ₂ O	0.06	0.06
K ₂ O	0.40	0.24
Calculated Compounds per ASTM C 150-00		
C ₃ S	65	66
C ₂ S	11	6
C ₃ A	5	7
C ₄ AF	10	11
Blaine Surface Area (m ² /kg)	360	450

2.2 Data collection and analysis

X-ray diffraction data was collected using a PANalytical X'Pert Pro MPD diffractometer equipped with a focusing elliptical mirror, transmission spinner stage, and high speed X'Celerator detector for fast data collection. Scans were collected using $\text{CuK}\alpha$ radiation (45kV and 40mA) from 5° - $65^\circ 2\theta$ with stepping parameters of 0.017° and 43 s step^{-1} for a total data collection time of 20 minutes per scan. Initial data collection began within 5 minutes of paste preparation and continued for at least 16 hours.

Semi-quantitative phase analysis and lattice parameter refinements were performed using a full-pattern fitting Rietveld approach and compared to results from similar mixtures obtained in [2] using a synchrotron source.

2.3 Transmission XRD using a conventional laboratory diffractometer

Parabolic mirrors that provide a parallel beam for commercial diffractometers have been available for years, but only recently has a focusing (elliptical) mirror been introduced into the marketplace. Some of the principal advantages of a focusing mirror are that they provide both a high intensity signal and high resolution required for transmission work, Fig. 1. In parallel beam applications, the size of the beam and the sample – especially capillary diameter - dramatically influences resolution. However, with focusing geometry, resolution is virtually independent of sample size indicating that larger capillaries can be used with no penalty on resolution, Fig. 2. Additionally, with focusing geometry, the full beam can be used at low 2θ angles without the need for small divergence slits to avoid beam overflow. Transmission through the entire sample also results in better particle statistics with no segregation effects that are inherent in other diffraction methods.

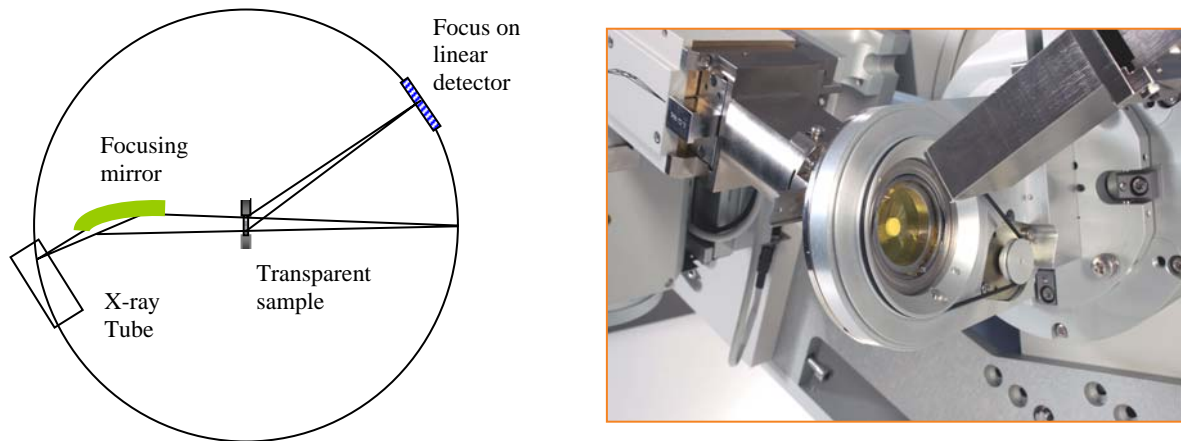


Fig. 1. Beam path schematic of the focusing elliptical x-ray mirror (left) and sample spinner showing cement paste between Kapton foils (right).

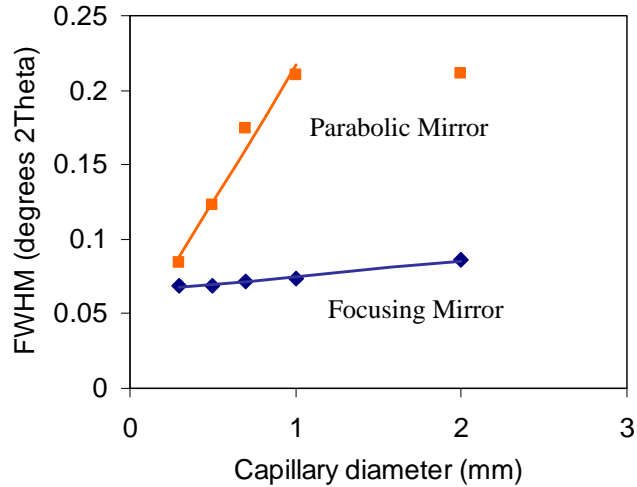


Fig. 2. Full width at half-maximum (FWHM) of identical peaks from tetracycline hydrochloride powder measured in glass capillaries of varying diameter using both a parabolic (parallel beam) mirror and the focusing mirror.

3. Results

Twenty-minute scans collected in the lab using the focusing mirror had intensities comparable with 40-minute synchrotron scans with no difference in resolution as indicated by a FWHM of $\sim 0.09^\circ 2\theta$ for equivalent C_3S peaks, Fig 3. The laboratory scans also had a relatively flat background in contrast to the noticeable amorphous glass ‘hump’ from the 0.7mm capillaries used in the synchrotron study.

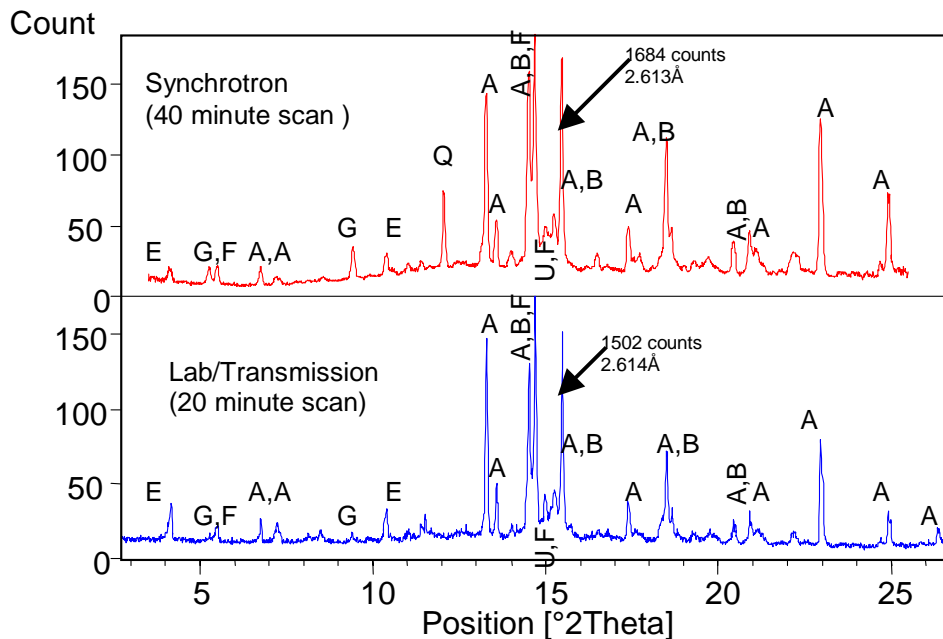


Fig. 3. Twenty-minute scan obtained using the focusing elliptical mirror/transmission XRD configuration on the 2% Ca-nitrite treated sample compared to similar data obtained at the synchrotron. Both scans were collected within the first 15 minutes of hydration. Note: i) the laboratory data (bottom trace) was scaled to the synchrotron 2θ axis, and ii) the synchrotron data shows the presence of a quartz internal standard that was not used in the laboratory study.

Samples used in the lab study were weighed periodically throughout the data collection period and showed no more than 0.07% weight loss suggesting that dehydration and carbonation reactions were negligible. In contrast to the sealed samples used for the transmission experiments, we also collected sub-samples of the surface and bottom 'skin' layers and the interior bulk paste after set. The surface skin was enriched with ~12 %calcite and depleted in both ettringite and portlandite relative to the bulk interior zone that was unaffected by atmospheric conditions. No evidence of calcite was found in any sample used for transmission work.

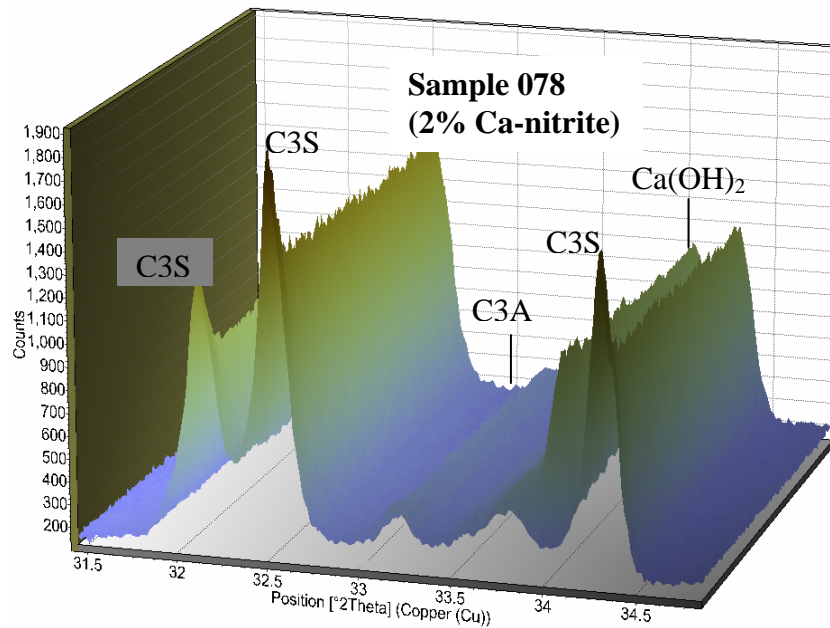
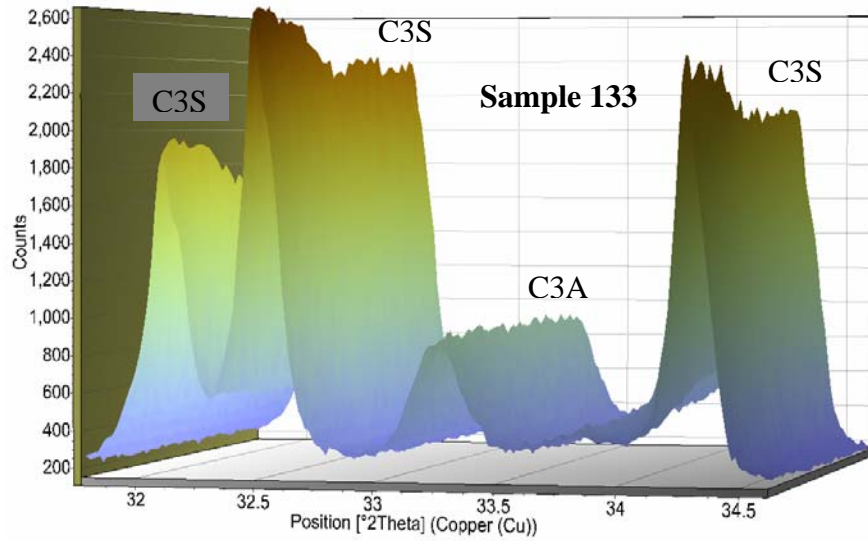


Fig. 4. Selected 2-theta region of the scans collected on untreated Sample #133 and Sample #078 with 2% Ca-nitrite. The first scan at ~5 minutes is in the front, the last scan shown obtained at 6 hours.

The untreated sample (#133) showed depletion of C3S beginning almost immediately, ranging from a maximum of ~70% to a minimum of ~63% after 6 hours, Fig 4. This C3S depletion corresponded to the onset of ettringite formation, which also reached a maximum at ~6 hours, Fig. 5.

Gypsum depletion also began almost immediately, with full depletion by 4.5 hours. Portlandite formation began at 2.5 hours and reached a maximum at 5.5 hours, preceding the ettringite maximum slightly. C_3A (orthorhombic and cubic) alteration was surprisingly negligible in this study.

The 2% Ca-nitrite-treated sample displayed similar trends as the untreated sample with the exception of the magnitude and kinetics of these reactions. C_3S levels decreased sharply after initial wetting, with a near 20% loss before reaching a steady-state after ~7 hours, Fig. 5. C_3A also showed no major change in this sample. Rates of ettringite, portlandite, and C_3S alteration all increased as expected.

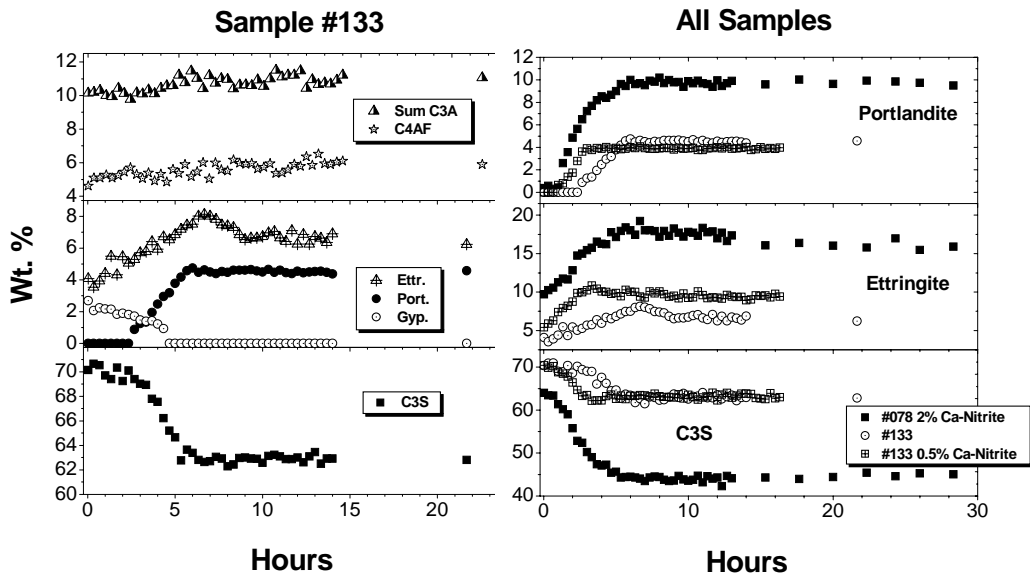


Fig. 5. Selected results of Rietveld refinement for all scans collected on the untreated Sample #133 (left), and portlandite, ettringite, and C_3S trends for each sample studied (right).

4. Discussion

The purpose of this work was to explore if a laboratory diffractometer in transmission mode could generate good quality in situ XRD information on the early cement hydration kinetics. While the focusing elliptical mirror seems to make this possible, several issues such as the following needs further work:

- 1) In all tests with the laboratory diffractometer in transmission mode the cement hydration appeared to cease after about 6 hours, Fig. 5. The reason for this is unclear and could not be explained by drying

since the weight loss was insignificant and no evidence of carbonation was seen.

- 2) Further work is needed to better understand the limitations of this new XRD method. However, this method appears to be useful for in-situ studies of the early hydration up to approximately 6 hrs without the limitations of most reflection methods.

5. Conclusions

Our initial work indicates that *in situ* transmission experiments using a new focusing elliptical mirror provided high quality data using a conventional diffractometer. With samples of $\sim 100\mu$ thickness (or less), absorption effects are minimal and the progress of cement hydration can be followed in the laboratory with equal or better accuracy than when using capillaries at a synchrotron source. Some advantages of the focusing geometry over that of parallel beam optics are that:

- A high intensity beam is generated where resolution is independent of the sample (e.g., capillary diameter) or beam size,
- Information is provided from the full depth of the sample, with no surface segregation effects,
- Sample preparation is easy and samples can be analyzed either continuously, or at different times while maintaining the same particle statistics and orientation in the beam,

References

- [1] L.D. Mitchell, J.C. Margeson, and P.S. Whitfield. 2006. Quantitative Rietveld analysis of hydrated cementitious systems.
- [2] P. Sandberg, C. Porteneuve, F. Serafin, J. Boomer, N. LoConte, V. Gupta, B. Dragovic, F. Doncaster, L. Alioto, T. Vogt. 2007. Effect of Admixture on Cement Hydration Kinetics by *in situ* Synchrotron XRD and Isothermal Calorimetry, Proceedings of the 12th International Congress on the Chemistry of Cement, Montréal, Canada.