Pergamon

Cement and Concrete Research, Vol. 25, No. 3, pp. 639-646, 1995

0008-8846/95 $9.50+.00

0008-8846(95)00052-6

A COMPARISON OF LABORATORY, SYNCHROTRON AND NEUTRON DIFFRACTION FOR THE REAL TIME STUDY OF CEMENT HYDRATION

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(Refereed)
(Received June 2; in final form November 14, 1994)

ABSTRACT The use of real time powder diffraction for the study of cement hydration is presented. Three techniques are described: laboratory X-ray diffraction with a linear position sensitive detector, neutron diffraction with a curved position sensitive detector and energy-dispersive powder diffraction with a synchrotron source of X-rays. Data collected during the hydration of a triclinic form of tricalcium silicate are used to illustrate the methods of data capture and analysis for each of the three techniques. The rate of tricalcium silicate depletion is presented for each case and an attempt at a quantitative comparison of the three techniques is made.

Introduction

Powder diffraction is a well established laboratory tool used principally for phase identification and quantitative analysis (1). Recent developments in laboratory based powder diffraction systems and the advent of high flux neutron and X-ray synchrotron sources now allow powder diffraction patterns to be collected in real time. The well established techniques used for phase identification and quantitative analysis can now be applied to the real time study of chemical reactions. This development is of particular importance for the study of multi-component systems, such as cement hydration, because the rate of formation or depletion of each component can be determined, allowing the development and testing of different models of cement hydration. An additional advantage of this technique is that the data are collected *in-situ* removing any ambiguities due to quenching and subsequent processing of hydration products.

For time resolved studies it is important to collect the whole of the diffraction pattern simultaneously so that all diffraction peaks are measured at the same point along the reaction coordinate. There are two possible diffraction modes: using monochromatic radiation (either neutrons or X-rays) with a position sensitive detector (PSD) or using polychromatic radiation with a solid state detector (either energy-dispersive powder diffraction (EDPD) with X-rays or

time of flight powder diffraction with neutrons). Available PSDs for X-ray diffraction are well matched to laboratory X-ray sources but have too low an angular resolution and count rate for the full exploitation of a synchrotron source. For neutron diffraction the time of flight technique offers excellent resolution, but the time required to collect a powder spectrum from an hydrating cement sample (15 minutes to 2 hours) is too long for most kinetic studies. So the preferred techniques are: EDPD at a synchrotron, using a PSD in the laboratory and using a PSD with a monochromatic source of neutrons.

Time resolved powder diffraction patterns were collected using all three of these techniques from hydrating samples of tricalcium silicate (C_3S). The degree of depletion of C_3S was determined in each case from these data and values for the rate of depletion were calculated by fitting these depletion curves to the dispersion model developed by Knudsen (2,3). A careful error analysis was undertaken, the results of which allow some comparison of these three techniques. Although it is possible to obtain "better" results with each of these techniques, the data presented here represent the quality of results that one can expect to obtain from hydrating cement mixtures and as such form a reasonable set for comparison.

Sample Characterisation and paste preparation

The samples of tricalcium silicate used in these studies were from one batch prepared by Blue Circle Cement Ltd. and donated for this project. High resolution powder diffraction (4) showed that the C_3S was of single phase and of type T_3 with unit cell parameters: **a**=11.6292 Å, **b**=14.1456 Å, **c**=13.6412 Å, α=105.5°, β=94.702° and γ=90.0°; similar to those determined by Golovastikov (5).

Great care was taken when preparing hydrating mixtures to avoid contamination from the air. Preweighed samples of C_3S and distilled, deionised water were mixed for five minutes inside a nitrogen filled glove bag before the paste was poured into the appropriate sample holder. The sample holders were carefully sealed to allow no contact with air during the diffraction measurements. All data were collected at room temperature with a water to cement ratio of 0.5.

Laboratory measurements

A Siemens D500 powder diffractometer equipped with a Braun position sensitive detector (PSD) was used for these measurements. The diffractometer uses a special slewing procedure which involves scanning the PSD around the two-theta circle of an otherwise normal Bragg-Brentano diffractometer. The PSD collects six degrees of data simultaneously. These data are accumulated using software inside the diffractometer to give a total pattern. Although this procedure does not give a true time resolved measurement, because the whole of the spectrum is not collected simultaneously, the time of data collection (twenty minutes) is short compared to the duration of the experiment (16 hours) and so forms a basis for comparison.

The hydrating mixture was held in a spinning flat plate sample holder inside an environmental chamber which contained an atmosphere of dry nitrogen. Multiple scans were made from 16° to 65° 2θ using Cu Kα radiation. Each scan took twenty minutes and data were collected over a sixteen hour period. Some of these patterns are shown in Figure 1. The

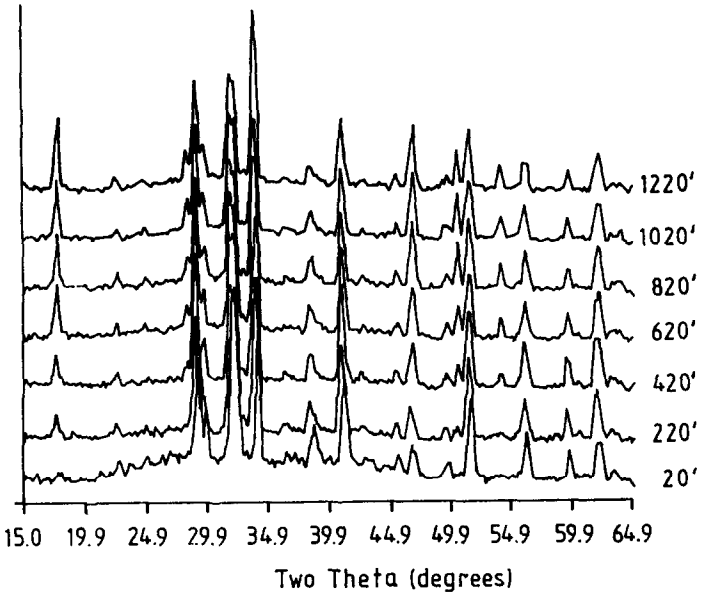

FIG. 1
Real time laboratory X-ray diffraction patterns from hydrating C_3S.

intensities of the (06-6) and (08-2) reflections of C_3S were used to estimate the degree of depletion (Figure 2). The results of fitting this data to Knudsen's linear model are contained in Table 1.

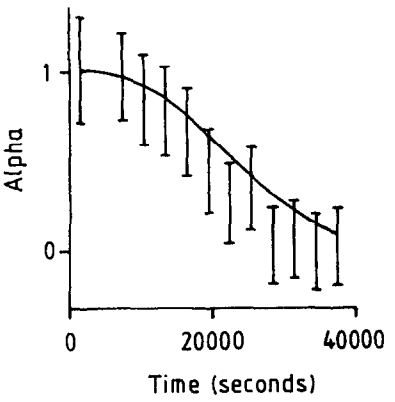

FIG. 2
The amount of C_3S, scaled from 0 to 1, as a function of time fitted to a linear Knudsen model.

Neutron Diffraction

An alternative to using X-ray diffraction is to use neutron diffraction. Intense sources of neutrons, such as the high flux reactor at the Institute Laue Langevin (ILL) in Grenoble, combined with a large position sensitive detector, such as the banana detector on instrument D1b at the ILL, can realise a time resolution of five to ten minutes at about 10^6 counts per minute. The high penetration of neutrons allows studies to takes place on large volumes of sample getting away from the relatively small samples used for laboratory studies and getting closer to the real life situation.

Data were collected using instrument D1b at the ILL. Thermal neutrons are conducted along a curved guide tube from the reactor to the instrument. A monochromatic beam of

Table 1. Fit parameters for C_3S depletion using a first order Knudsen equation.

Method	χ^2	k (sec^{-1})	t_o(sec)	t_1(sec)
Lab.	13.8	-0.0008(3)	0.0024	1250
Neutron	97	-0.0000119(7)	0.00003	84034
EDPD	14.3	-0.00073(1)	0.00788	1370

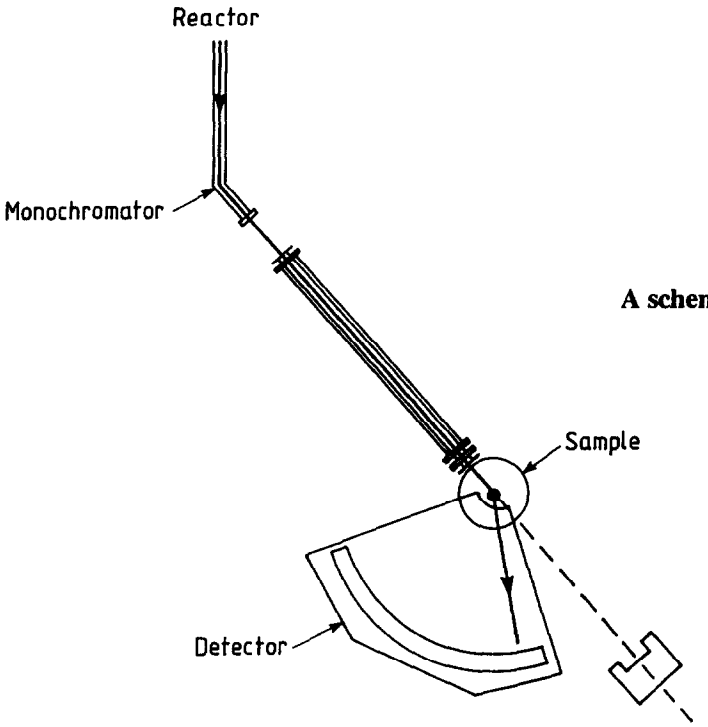

FIG. 3
A schematic diagram of instrument D1b at the ILL.

neutrons is produced by a curved pyrolytic graphite monochromator. The monochromator selects neutrons with a wavelength of 2.52Å. Scattered neutrons are detected by a curved multidetector filled with $^3He/Xe$ with 400 active elements covering a two-theta range of 80° (Figure 3). Samples were held in sealed vanadium cylinders which were 1 cm in diameter and 5 cm high. D_2O was used instead of H_2O to hydrate the C_3S in order to avoid the large background noise expected from incoherent scattering from hydrogen. A series of patterns were collected from an hydrating mixture of C_3S and D_2O. Each pattern was collected for five minutes and data were collected for a total of 16 hours. The resulting powder patterns are quite complex (Figure 4): they consist of sharp powder peaks from CD and C_3S and smooth background contributions from D_2O and CSD. Also, the powder pattern of C_3S contains 974 peaks in the region up to 100° at this wavelength. Deconvoluting the wealth of information contained in these patterns is difficult especially because the resolution of D1b is relatively poor. However, the strong rhombohedral pseudo-symmetry of C_3S results in most peaks having a very low intensity, below 5% of the strongest peak, and peaks of considerable intensity are grouped closely together into fifteen regions. Here the poor resolution can be used in our favour: the strong peaks in each region can be treated as a single composite peak which can be fitted using a single gaussian profile.

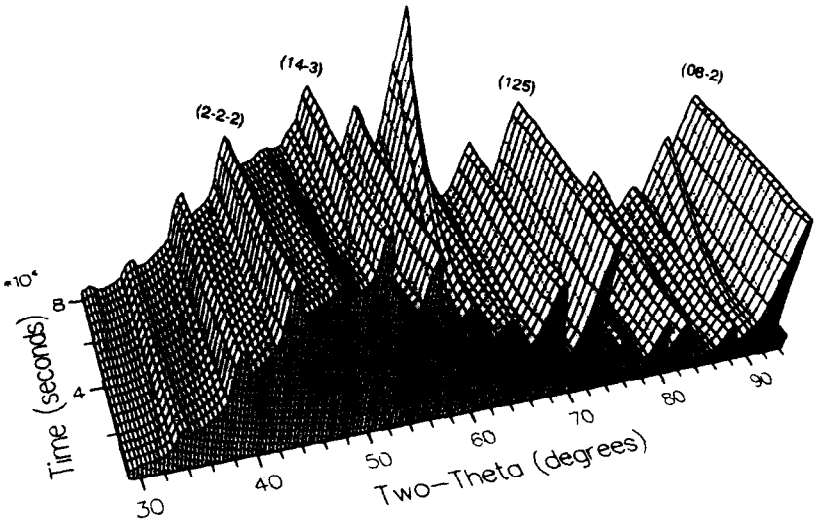

FIG. 4
3-d plot of a series of neutron diffraction spectra taken in real time from an hydrating mixture of C_3S and D_2O.

A profile fitting procedure was developed (4) that allowed a mathematical function, that described the C_3S and CD diffraction peaks and the D_2O and CSD amorphous peaks, to be fitted to each powder pattern from the time series collected during the hydration of C_3S (figure 5). One type of parameter determined from this fitting procedure is the diffraction peak areas from

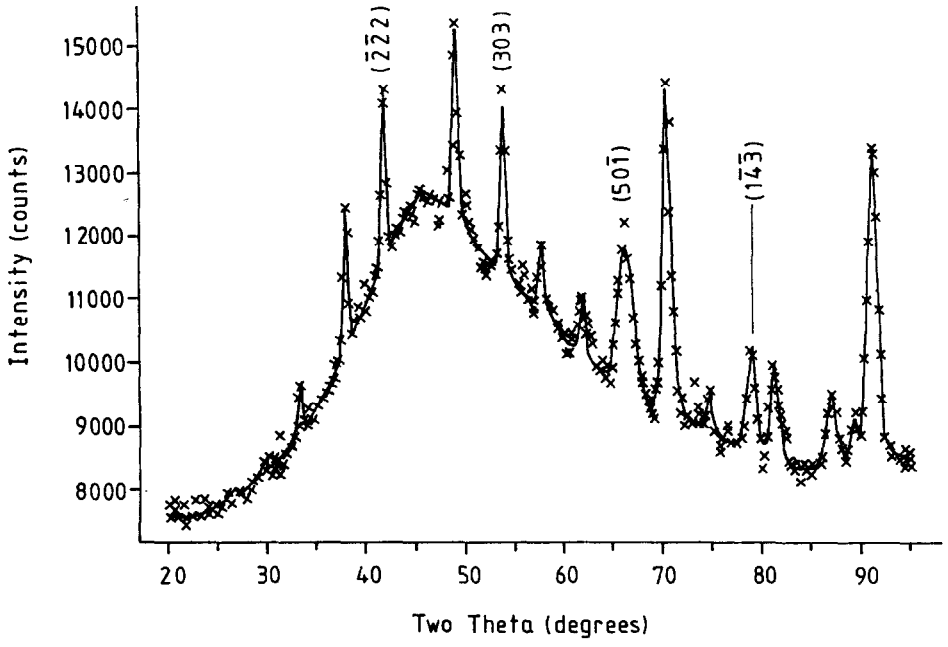

FIG. 5 Profile fit to a neutron diffraction spectrum.

which the amount of C_3S as a function of time was determined. The parameters determined by fitting a linear Knudsen model to this data are contained in Table 1.

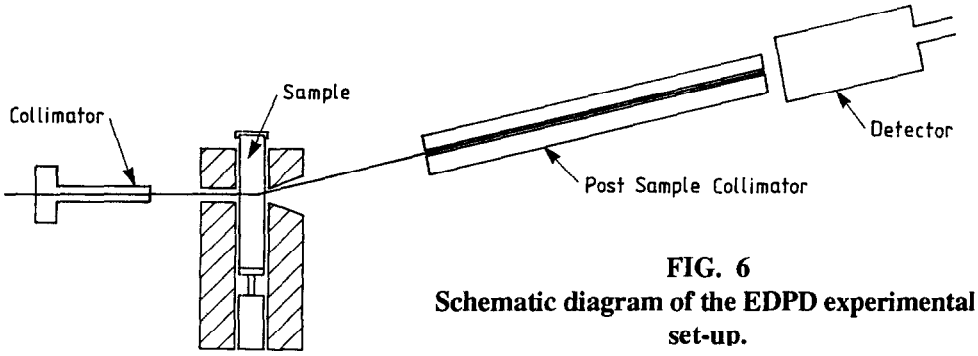

FIG. 6
Schematic diagram of the EDPD experimental set-up.

Energy-dispersive powder diffraction

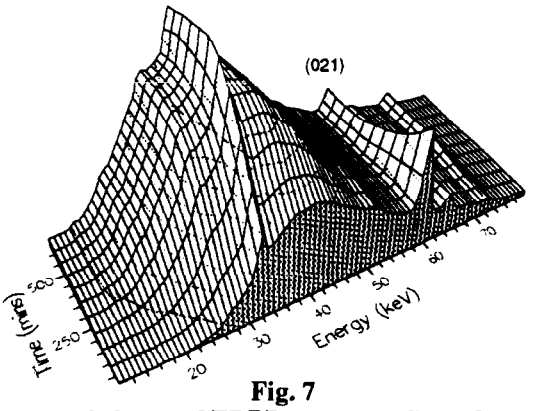

Fig. 7
3-d plot of EDPD spectra collected from a hydrating mixture of C_3S and H_20.

In the conventional powder diffraction method a monochromatic beam of X-rays is used and the diffraction angle is varied in order to sample a range of lattice planes. In the energy-dispersive method the diffraction angle is kept fixed and a polychromatic beam of X-rays is used. Each set of lattice planes diffracts X-rays of different energy which are detected by a semiconductor detector which produces a current pulse of amplitude proportional to the X-ray photon energy. The main advantages of EDPD are that: the fixed detector angle makes it possible to use sample environments with restricted entrance and exit windows and the whole pattern is collected simultaneously and rapidly thus allowing the study of continuously changing phenomena. The main disadvantages are that: the momentum resolution is an order of magnitude worse than the conventional powder method and the maximum count rate is limited by the detector electronics to about $5x10^4$ counts per second.

Data were collected at the EDPD facility of the Daresbury Laboratory Synchrotron Radiation Source (SRS) (7,8). The SRS is a low emittance storage ring which is operated at 2 GeV with typical stored beam currents in excess of 200mA. The EDPD facility benefits from radiation emitted from two poles of a superconducting wiggler magnet of peak field 5 Tesla. The facility receives useful X-ray flux in the range from 5keV to 80keV with a peak flux of about 7 x 10^{11} photons/second/mm^2 in a 0.1% bandwidth at 10keV. The energy at which a diffraction peak occurs depends upon the diffraction angle at which the detector is held. Appropriate choice of diffraction angle allows one to select which range of diffraction peaks occur inside the window of available energies as defined by the range of useful X-ray flux. In this case we chose a diffraction angle of two degrees which selects a number of low index C_3S peaks and one CH peak (Figure 7). The experimental set-up is shown in Figure 6.

Patterns were collected, from a hydrating mixture contained in a large volume spinning sample holder (9), for ten minutes each over a twenty four hour period. (Figure 7). The pattern fitting procedure described above was also used to obtain the amount of C_3S as a function of time from these data. The parameters obtained by fitting a linear Knudsen model to the C_3S depletion curve are contained in Table 1. Large changes in the shape of the base line of the powder diffraction patterns can be seen during hydration (Figure 7). These changes can be correlated with changes in composition and density of the paste (4).

Discussion

All of the C_3S depletion curves gave a good fit to a linear Knudsen model. Reasonable agreement was found between the rate constants determined from laboratory and EDPD data and those of Knudsen (4); although Knudsen's data are from systems that are not strictly comparable with our measurements. The rate constant determined from the neutron diffraction data is much lower than those determined from the other measurements which suggests that the reaction between C_3S and D_2O proceeds at a slower rate than the reaction between C_3S and H_2O.

Table 2 Comparison of the precision of laboratory, neutron and EDPD methods.

Method	2000 secs	20000secs
Laboratory	8.8%	9.3%
Neutron	8.5%	7.4%
EDPD	1.8%	5.4%

The recent increase in the use of time resolved powder diffraction for the study of cement hydration (4,9,10,11,12) makes a quantitative comparison of these three methods timely. In order to attempt such a comparison we have calculated the percentage error in the amount of C_3S, determined at 2000 and 20000 seconds of hydration, using each method (Table 2). The neutron and laboratory measurements gave a similar precision but the EDPD measurement gave a more precise result. The data collection time is shortest with EDPD and longest in the laboratory.

Acknowledgements

This work was carried out by SMC as part of a PhD thesis under the direction of PB in the Crystallography Department of Birkbeck College, University of London. SMC would like to thank him and all of the staff in the Crystallography Department for their help with this work but in particular SMC would like to thank Dr. S.E. Tarling for help with collecting the laboratory data presented here. We would like to thank Blue Circle Cement for supplying the C_3S used in this work and for providing SMC with some financial support.

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