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# Quantitative study of Portland cement hydration by X-ray diffraction/Rietveld analysis and independent methods

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## Abstract

X-ray diffraction (XRD) is a powerful technique for the study of crystalline materials. The technique of Rietveld refinement now enables the amounts of different phases in anhydrous cementitious materials to be determined to a good degree of precision. This paper describes the extension of this technique to a pilot study of the hydration of a typical Portland cement. To validate this XRD–Rietveld analysis technique, its results were compared with independent measures of the same materials by the analysis of backscattered electron images (BSE/IA) and thermogravimetric analysis (TGA). In addition, the internal consistency of the measurements was studied by comparing the XRD estimates of the amounts of hydrates formed with the amounts expected to form from the XRD estimates of the amounts of anhydrous materials reacted.

*Keywords:* X-ray diffraction; Hydration; Cement paste; Hydration products; Rietveld analysis

## 1. Introduction

The microstructure of a material, i.e., the types, amounts and distribution of its constituent phases, is the fundamental link between the processes that form the material and its properties. However, the complexity, heterogeneity and large range of relevant length scales in cementitious materials has meant that microstructural studies have not, as yet, fully realised their potential in helping to understand the process–microstructure–property relationships for these materials. A major obstacle is the lack of rapid, reliable, and accurate techniques to quantify the amounts of the different phases present. For example, whereas the overall pattern of microstructural development during the hydration of cement paste is established [1–3], methods are not generally available that are capable of quantifying differences between broadly similar materials, due to use of admixtures, cement composition, or thermal history, for example.

Rietveld analysis of X-ray diffraction patterns (XRD/Rietveld) is a technique that has the potential to change this situation. Nevertheless, the control files essential to successful Rietveld refinement can only be developed through extensive calibration with model mixtures and with materials for which the actual phase composition is known by independent methods. Work over several years [4–6] has led to the development of files that permit accurate analysis of anhydrous cementitious materials, including analysis of mineral additions with a high amorphous content. Table 1 gives the maximum errors for the determination of the major and minor phases in anhydrous cementitious materials by Rietveld analysis [5].

This paper describes the development of a XRD/Rietveld analysis technique for the quantitative determination of the principal phases in hydrated cement paste. Traditional X-ray diffractometers require about 1 h to acquire a suitable pattern through the angular range 8–55° $2\theta$. This time period is relatively insignificant compared to the rate of hydration after about 1 day, but at younger ages the hydration must be stopped (e.g., by grinding in a solvent) before analysis and a separate sample prepared for each hydration time. New X-ray detectors (e.g., X'celerator detector, Panalytical) enable the acquisition time to be reduced to less than 10 min. Furthermore, a climatic chamber (temperature-controlled humidity chamber, Anton Paar) in which temperature and humidity can be controlled may be installed in the X-ray diffractometer so that the hydration of a sample of cement paste can be studied in situ without stopping hydration.

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Table 1
Typical values and accuracies for the determination of phases present in anhydrous cement

| Phase | Typical value with accuracy (%) | Phase | Typical value with accuracy (%) |
|---|---|---|---|
| Alite | $60 \pm 2.0$ | Gypsum | $2 \pm 0.3$ |
| Belite | $15 \pm 1.5$ | Hemihydrate | $2 \pm 0.3$ |
| Ferrite | $4 \pm 0.6$ | Anhydrite | $2 \pm 0.3$ |
| Aluminate | $4 \pm 0.6$ | Portlandite | $1 \pm 0.3$ |
| Free lime | $1 \pm 0.3$ | Calcite | $1 \pm 0.3$ |
| Periclase | $1 \pm 0.3$ | Quartz | $1 \pm 0.3$ |

Here we present the first study of cement hydration by these techniques and compare the quantitative results with those from the same samples obtained by independent techniques—analysis of backscattered electron images (BSE/IA) and thermogravimetric analysis (TGA).

### 1.1. Rietveld analysis, principles and limitations

The XRD pattern of each crystalline material is unique. The positions of the peaks are determined by the spacing of the crystallographic planes according to Bragg's law:

$$n\lambda = 2d\sin\theta$$

where n is an integer, $\lambda$ is the wavelength of the radiation used, $d$ the spacing of the crystal planes, and $\theta$ the angle of the diffraction peak.

The intensity of the peaks is determined by the types and positions of the atoms in the crystal lattice according to the structure factor:

$$F(hkl) = \sum_{I}^{N} f_n \exp 2\pi i(hx_n + ky_n + lz_n)$$

where $hkl$ are the Miller indices of the reflecting planes, $f_n$ the atomic structure factor, and $x_n$, $y_n$, and $z_n$, the coordinates of the $n$th atom in the unit cell containing $N$ atoms.

In addition, the parameters of the equipment will affect the peak shape.

The principle of Rietveld analysis [7] is to iteratively compare the experimental pattern with a pattern simulated based on the presumed amounts, crystal parameters, and equipment parameters of a mixture of known phases. All these parameters may be adjusted between iterations to minimise the difference between experimental and simulated patterns by least squares fitting. Although the principle of the technique is straightforward, Rietveld analysis encounters several practical difficulties.

- The large amount of data to be manipulated leads to a requirement for fast computation. This is no longer a problem today with modern computers, but it explains the long delay between the first publication of the method by Rietveld in 1969 and its widespread adoption.
- The mathematical fitting algorithm must be robust to avoid convergence to false minima or failure to find a solution. Again, this problem has largely been solved through the latest software available (e.g., Topas available from Bruker AXS, or Xpert HighScore Plus from PANalytical).
- The large number of parameters available means that a good "fit" may apparently be obtained for unrealistic values of the crystalline parameters and therefore wrong values of the phase amounts.

This last point means that to obtain good accuracy the control files must be developed through extensive comparison with model mixtures of synthetic phases, extractions from real materials by selective dissolution, and test materials for which the actual values are known by independent methods (e.g., for clinker, by point counting of polished sections by optical microscopy). Once control files have been developed, analysis of unknown samples is very rapid. It is now possible to refine the pattern from a typical Portland cement in 1–2 min on a personal computer. This determination of the phases present in the anhydrous cement provides the starting point for this work.

Rietveld analysis always gives the sum of the phases present normalised to 100%. Therefore, all the phases present must be entered into the analysis and their crystal structures known. If amorphous or unknown phases are present, the amounts of the crystalline phases estimated by the analysis will be higher than the true amounts present. This problem may be overcome by adding a known amount of a reference standard. The analysis may then be corrected by dividing the values by the ratio of the measured to true amount of standard. The difference between the total of the corrected phase quantities and 100% gives the amount of amorphous (or unknown) phases. This method has been used to develop control files that enable the amorphous content of fly ashes, slags, and CEM II and CEM III cements containing these additions, to be evaluated to an accuracy of 2% [6].

The work described here concerns the development of control files for the analysis of hydrated cement pastes. For this work, independent methods were needed to verify the results from Rietveld analysis. Backscattered electron image analysis (BSE/IA) of polished section in the SEM was chosen for the measurement of anhydrous phases, and TGA for the measurement of calcium hydroxide. The BSE/IA method has already been shown to give good results for the measurement of the amount of remaining anhydrous material compared to loss on ignition measurements [8,9]. TGA is widely accepted as a good method to measure calcium hydroxide. To verify the internal consistency of the Rietveld analysis, the amounts of hydrate phases (CSH, CH, ettringite, and AFm) were calculated from the amounts of anhydrous phases reacted by stoichiometry as described below.

## 2. Experimental

### 2.1. Sample preparation

The composition of the cement and the Rietveld analysis of the anhydrous phases are given in Table 2. This is a typical standard Portland cement (CEM I in European nomenclature; Type 1 in ASTM nomenclature). The cement paste was mixed by hand for 2 min at a water-to-cement ratio of 0.4. Ten percent corundum ($Al_2O_3$), relative to the weight of cement, was blended with the cement powder before mixing to serve as an internal standard. This material was chosen because it does not react with water and has no influence on the hydration reaction. The cement paste was then either placed in the sample tray of the climatic chamber of the X-ray diffractometer described below or cast into a cylinder 30 mm in diameter and 50 mm in length. After setting, the cylinder mould was topped up with water and the sample kept saturated. At the ages of 1, 2, 3, 7, 14, and 28 days, slices about 4 mm thick were sawn from the cylinder and immediately washed with isopropanol to dry the surface. The slices were then immediately placed in the diffractometer ( ~ 5 min after cutting) and an XRD pattern acquired. The same slices were then dried by placing them in isopropanol for 7 days and then kept in a desiccator over silica gel. Part of the slice was reserved for TGA; the rest of the slice was impregnated with resin and polished to 0.25 μm for examination by BSE-SEM.

To study the phase evolution up to 1 day, a climatic chamber specially designed for the X-ray diffractometer was used. This chamber, shown in Fig. 1, allows the temperature and relative humidity to be closely controlled. For temperatures from 20–50 °C it is possible to maintain the relative humidity (RH) at 95 ± 2%. At this RH, the drying of the cement paste during the first 1 or 2 days is negligible and the rate of hydration is not affected. The cement paste is placed in a small tray 1 mm deep. Once the chamber is installed and the temperature and RH stabilised, the sample can be placed in the chamber and equilibrium re-established within 2–3 min of mixing the cement. With the X-ray equipment used, diffraction patterns of sufficient resolution for Rietveld analysis can be obtained in 8 min (step size 0.017° 2$\theta$, 20 s per step). Thus, the first measurement covers the period $x$ to $x+8$ min. Subsequent measurements were taken at 10-min intervals.

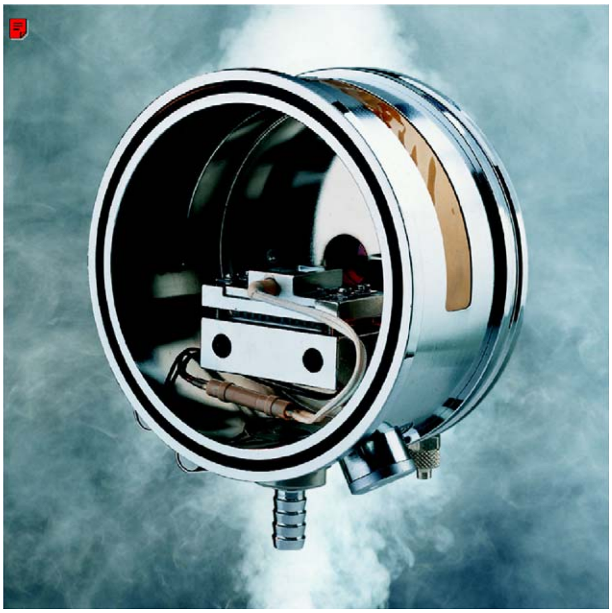

Fig. 1. Temperature-controlled humidity chamber.

Table 2
Phase composition by Rietveld for cement studied

| | XRD (wt.%) | | Wt.% |
|---|---|---|---|
| Alite | 69.9 | $SiO_2$ | 19.76 |
| Belite | 8.3 | $Al_2O_3$ | 4.86 |
| Ferrite | 6.3 | $Fe_2O_3$ | 2.69 |
| Aluminate | 7.5 | CaO | 63.54 |
| Lime | 0.2 | MgO | 1.45 |
| Periclase | 0.4 | $K_2O$ | 0.88 |
| Gypsum | 2.9 | $Na_2O$ | 0.07 |
| Hemihydrate | 1.5 | $SO_3$ | 3.75 |
| Anhydrite | 0.3 | $TiO_2$ | 0.29 |
| Calcite | 1.1 | $Mn_2O_3$ | 0.03 |
| Portlandite | 0.9 | $P_2O_3$ | 0.48 |
| Quartz | 0.9 | $Cr_2O_3$ | < 0.01 |
| | | $ZrO_2$ | < 0.01 |
| | | SrO | 0.06 |
| | | P.F. | 2.47 |

For the BSE/IA, 50 images were taken at a nominal magnification of × 800. The anhydrous material was segmented by setting a threshold at the minimum grey level between the peaks corresponding to anhydrous material and calcium hydroxide. Calcium hydroxide was segmented between this minimum and the point between the peaks for other hydrates and calcium hydroxides, followed by removal of the rims around the anhydrous grains as described in Ref. [8].

TGA for the calcium hydroxide was conducted at a heating rate of 10 °C/min under a nitrogen atmosphere.

The amount of C-S-H formed was estimated from the amounts of anhydrous silicate phases consumed according to the stoichiometric equations:

$$C_3S + 5.3H \rightarrow C_{1.7}SH_4 + 1.3CH$$

$$C_2S + 4.3H \rightarrow C_{1.7}SH_4 + 0.3CH.$$

## 3. Results and discussion

### 3.1. Pastes 1 day and older

For the Rietveld analysis, the phases alite, belite, aluminate, ferrite, periclase, gypsum, bassanite (hemihydrate), anhydrite, and calcite as well as the hydrated phases portlandite, ettringite, calcium monosulfoaluminate, and calcium monocarboaluminate were considered. The "amorphous" content was calculated from the apparent content of the internal standard. No AFm phases (calcium monosulfoaluminate, calcium monocarboaluminate) were detected in any of the samples. These phases are often poorly crystalline, in which case they would contribute to the amorphous phases measured. Otherwise, the amorphous content is considered to be predominantly C-S-H.

### 3.1.1. Degree of reaction

Because XRD measures mass fraction, whereas microscopy measures volume fraction, the most straightforward comparison between the two techniques is the degree of reaction. To calculate the degree of reaction for the BSE/IA technique, the volume originally occupied by the anhydrous cement was calculated from the water-to-cement ratio.

The results for the two techniques are compared in Fig. 2. The apparent decrease in degree of hydration from 2 to 3 days clearly indicates some problem of sampling or of stopping the hydration. Nevertheless, there is good general agreement between the two techniques. (Note: The results from the 3-day sample are not included in the subsequent graphs due to the doubts about the preparation of the sample.)

The largest difference between the two measures is at 1 day, where the degree of hydration measured by BSE/IA is significantly higher than that by XRD. This can best be explained by the assumption that small anhydrous grains (< ~ 0.5 μm) are often not detected by BSE/IA. Omission of small grains will lead to overestimation of the degree of reaction. At ages later than 1 day, small grains are completely reacted and so this source of error is less important.

The density of the samples was measured in order to convert the BSE/IA measurements to weight percent. When this is compared to the weight percent measured by XRD (Fig. 3), good agreement between the two techniques is confirmed.

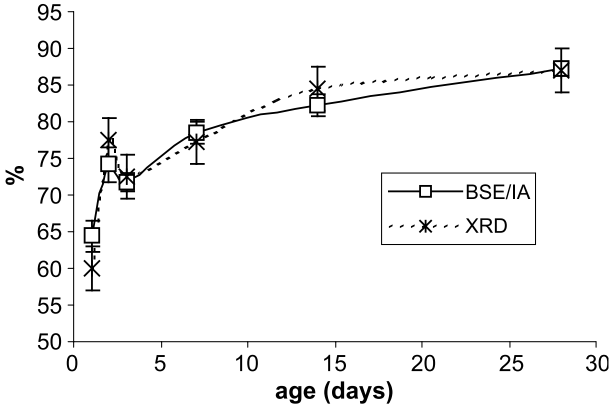

Fig. 2. Comparison of degree of hydration measured by XRD/Rietveld and BSE/IA. (The error for the XRD/Rietveld measurement corresponds to that found in previous work [4–6]; the error for the BSE/IA corresponds to the standard error of the set of field measured.)

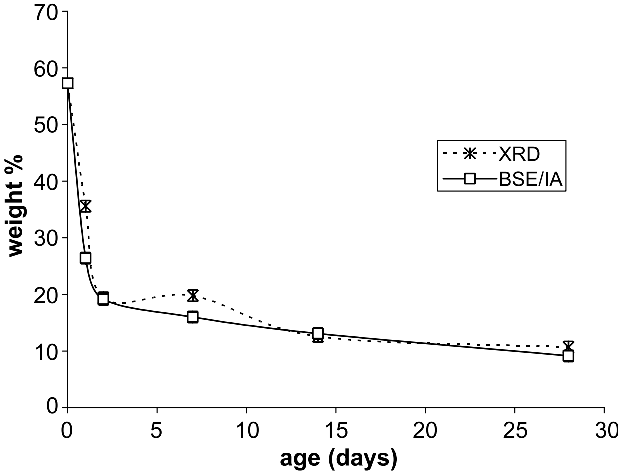

Fig. 3. Comparison of amount of unreacted cement by XRD/Rietveld and BSE/IA.

A major advantage of the XRD technique is the speed and ease of measurement (10 min compared to a minimum of 5 h to polish and analyse by SEM). But, perhaps more importantly, the different anhydrous phases can be

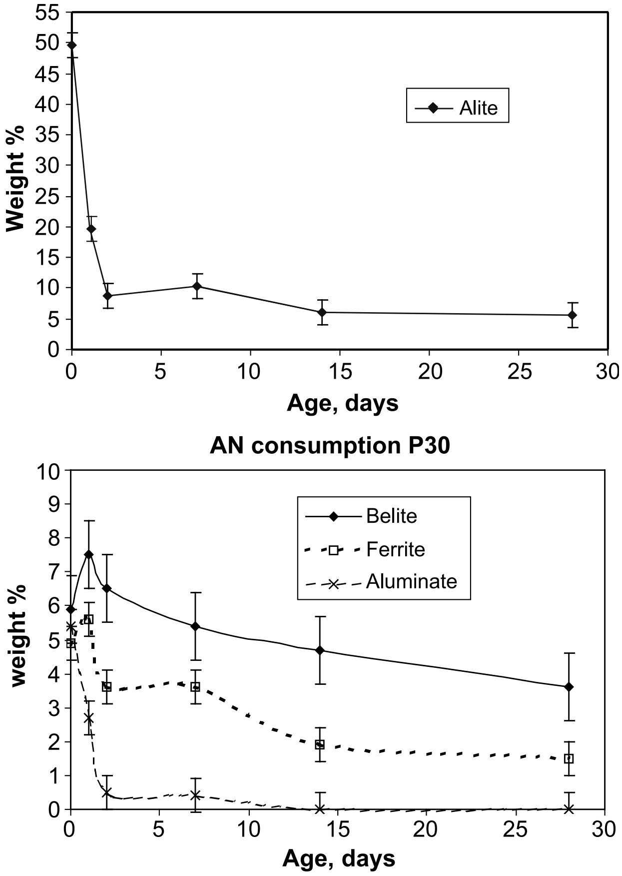

Fig. 4. Amounts of the different anhydrous cement phases remaining by XRD/Rietveld.

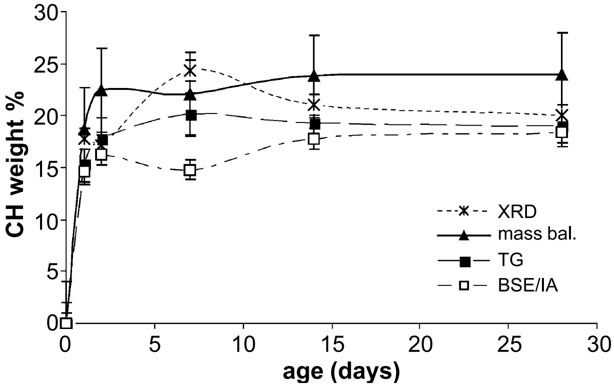

Fig. 5. Amount of calcium hydroxide determined by different measurement techniques.

distinguished. Although it is possible to identify the different phases on polished sections by BSE, these cannot be measured with any reasonable accuracy due to the difficulty of defining the boundaries between them.

The evolution of the four main clinker phases during hydration is shown in Fig. 4. The starting values for the anhydrous phases take account of the water added during mixing, which in the long term is combined in the hydrated solid phases and is part of the total weight of the sample. If water evaporates, rather than being incorporated into the solid phases, this will increase the proportions of the crystalline solid phases measured. This may explain the apparent increase in the amounts of belite and ferrite phases measured at 1 day. Nevertheless, these apparent increases are well within the acknowledged precision of the method. Further work is needed to improve measurement accuracy and precision and thus to eliminate such perverse effects.

### 3.1.2. Calcium hydroxide

Fig. 5 shows the amount of calcium hydroxide measured by four different methods: (1) XRD/Rietveld, (2) BSE/IA, (3) TGA, and (4) mass balance calculation, from the amounts of the anhydrous silicate phases reacted, measured by XRD/Rietveld.

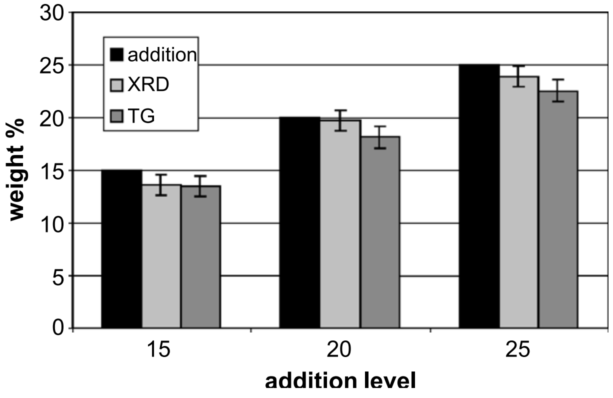

Fig. 6. Model mixtures of calcium hydroxide and anhydrous cement, quantification of calcium hydroxide by different methods.

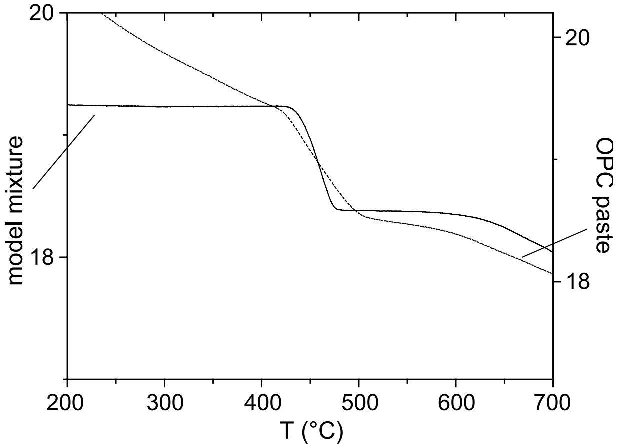

Fig. 7. Thermogravimetric analysis of calcium hydroxide, plots for model mixtures and cement pastes.

Here there is not such close agreement between the different measurement techniques. All the methods used have possible sources of error that are difficult to quantify. As the areas of CH are highly fragmented, BSE/IA is likely to miss small areas. The mass balance calculation assumes a calcium-to-silicon ratio of 1.7 in the C-S-H, whereas microanalysis measurements in the SEM indicate higher values at early ages.

To further study the quantification of calcium hydroxide, model mixtures were made in which 15%, 20%, or 25% of pure calcium hydroxide powder was intermixed with unhydrated cement. Results of the analyses of these mixtures by XRD and TG are shown in Fig. 6. It can be seen that there is excellent agreement between the two techniques, which both measure amounts very close to the actual composition of the mixture. Further examination of the TG curves showed that the CH “step” for the model mixtures was much better defined than in the pastes (Fig. 7). These results indicate that Rietveld–XRD is at least as good as TGA for quantifying the amount of calcium hydroxide and has the

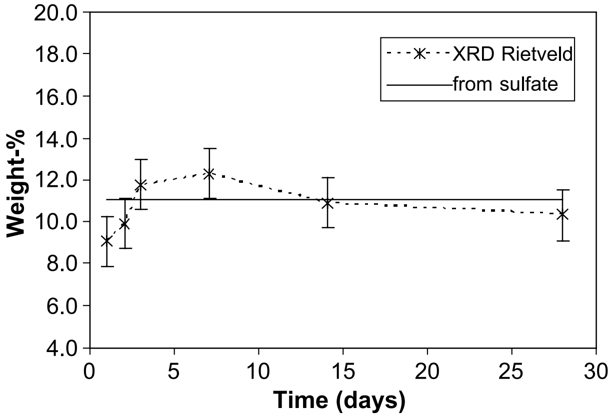

Fig. 8. Quantification of ettringite by XRD/Rietveld compared to the quantity of ettringite that would form from incorporation of all calcium sulfate in this phase.

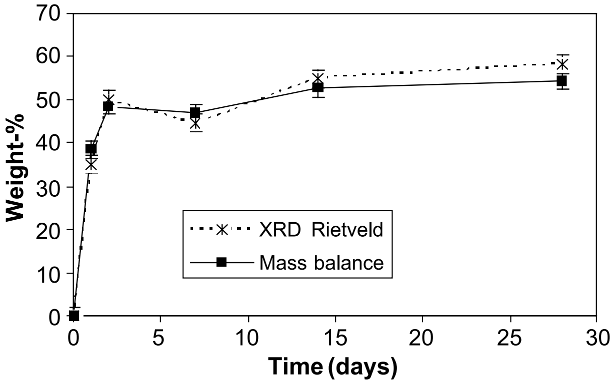

Fig. 9. Quantification of amorphous phases by XRD/Rietveld and mass balance.

considerable advantage of providing information on the other phases at the same time.

### 3.1.3. Ettringite

There is no good independent method for quantifying ettringite. Although differential thermal analysis has been proposed, there is considerable overlap of the ettringite and C-S-H peaks, which makes the measure unreliable.

Fig. 8 shows the amount of ettringite measured by Rietveld and the maximum amount of ettringite that could be formed, assuming all the original calcium sulphate phases are combined in ettringite. This indicates that the ettringite measurements by XRD/Rietveld are reasonable, but further work is needed to verify their accuracy. It is difficult to make good mass balance calculations for this phase, as it is known that a significant amount of aluminate (and perhaps sulphate) can enter the C-S-H phase.

### 3.1.4. Amorphous phases

The amounts of amorphous phases measured by XRD compared with the amounts expected by mass balance calculation from the amount of reaction of the silicate phases are shown in Fig. 9. There is good general agreement between the two measures. Nevertheless, caution is needed, as there are several indications that the

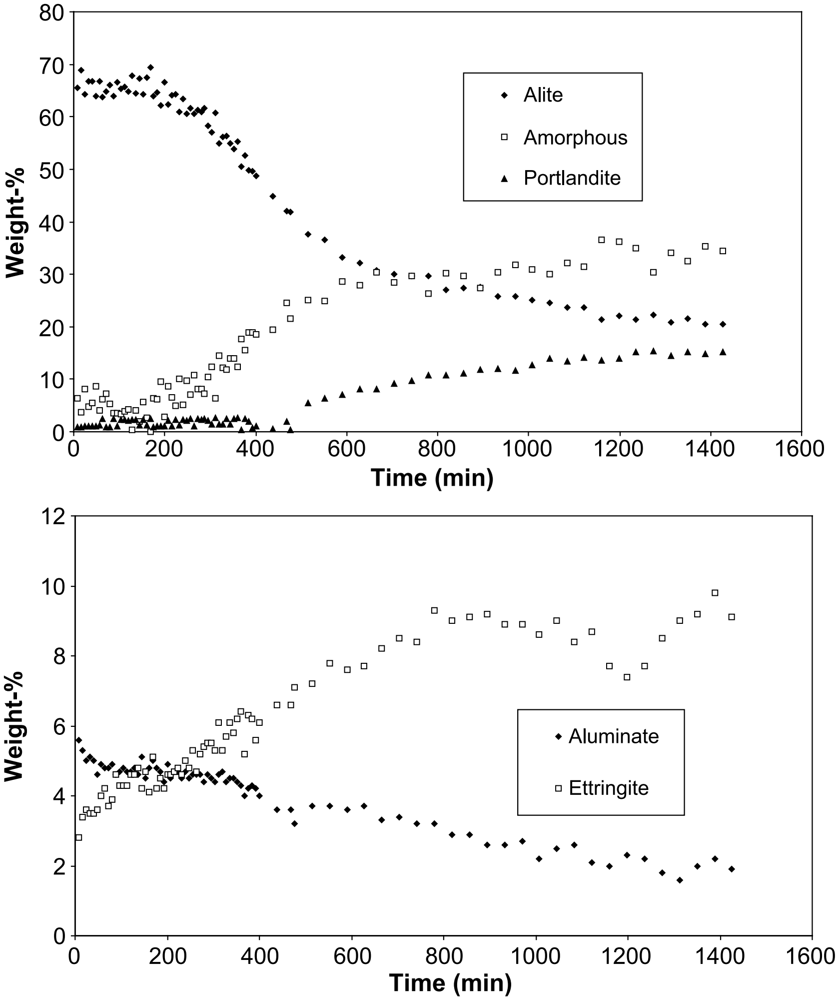

Fig. 10. Continuous measurement of phases by XRD/Rietveld.

Table 3
Phases in hydrated pastes at 24 h from sliced specimens and continuous measurement

| | Slice | Continuous |
|---|---|---|
| Alite | 19.8 | 20.4 |
| Belite | 7.5 | 7.0 |
| Ferrite | 5.6 | 4.8 |
| Aluminate | 2.7 | 1.9 |
| Portlandite | 17.8 | 15.1 |
| Ettringite | 7.0 | 9.1 |
| Amorphous | 35.0 | 34.9 |

mass balance calculation used here underestimates the amount of C-S-H formed, due to a combination of: the possibility of a higher C/S ratio for the C-S-H, incorporation of aluminate ions, and the inclusion of the AFm phases in the ‘‘amorphous’’ measurement.

### 3.2. Continuous measurements up to 24 h

Because of the different configuration of the diffractometer (size of area irradiated, absence of solar slits to increase intensity, etc.), different Rietveld control files had to be developed to analyse the data from the continuous hydration experiment. Furthermore, when the amount of amorphous material is low, the error in this value is high, due to the form of the equation used to calculate this amount from the measurement of the internal standard. This explains the high noise seen in the graphs shown in Fig. 10. Nevertheless, the consumption of alite corresponds well to formation of amorphous material (C-S-H) and the consumption of aluminate corresponds well to ettringite formation. Furthermore, the quantities of the phases measured at 24 h agree well with those measured in the experiments described previously (Table 3).

## 4. Concluding remarks

This pilot study indicates that XRD/Rietveld analysis is a very promising method for quantitative study of the phases in cement paste during hydration. Work is in progress to validate the technique over a range of cements.

## Acknowledgements

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