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Publisher's version / Version de l'éditeur:

<https://doi.org/10.11541/1.2204056>

Powder Diffraction, 21, 2, pp. 111-113, 2006-06

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Quantitative Rietveld analysis of hydrated cementitious systems

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(Received 3 September 2005; accepted 1 April 2006)

A study examining the feasibility, and possible necessity, of using transmission data from capillary mounted samples for quantitative analysis of hydrated cement systems was conducted. In order to obtain true quantitative results, the amorphous contents were determined by the addition of an internal standard. The amorphous content of the starting tricalcium silicate was found to be approximately 21–22 wt %, in close agreement with previously published results. The study revealed that the spherical harmonics preferential orientation correction may not be reliable with unmiconized hydrated cement materials in reflection geometry, as chemically unreasonable progressions in Portlandite content with time were observed. The data obtained from capillary measurements, however, exhibited little or no preferential orientation, and appeared to produce the progression of phase contents expected from the reaction. The use of capillaries would appear to be justified in some circumstances to obtain reliable quantitative results from hydrated cementitious materials. In this particular system, a significant fraction of calcium carbonate was present as aragonite, as well as the more usual calcite. © 2006 International Centre for Diffraction Data. [DOI: 10.1154/1.2204056]

INTRODUCTION

The use of Rietveld refinement for quantitative phase analysis was first described in detail in 1987 (Rietveld, 1967; Hill and Howard, 1987). Its routine application to the quantification of complex mixtures, such as ordinary Portland cement, is a much more recent development, largely due to the introduction of innovations, such as convolution-based peak synthesis and fundamental parameters into Rietveld software (Cheary and Coelho, 1992). The reduction in the number of parameters required to describe the peaks of each phase makes such an analysis fairly routine with rapid acceptance within the commercial cement community for quality control (Scarlett *et al.*, 2001).

Rietveld analysis also affords the opportunity to quantify the presence of amorphous materials, both within unhydrated and hydrated cements (Suhrman *et al.*, 2002; Whitfield and Mitchell, 2003). This is achieved by the addition of a known amount of a crystalline internal standard material. The difference between the known and refined phase content gives the amount of “invisible” or amorphous material.

Reflection measurements can easily suffer from nonrandom particle statistics. The problems associated with nonrandom particle statistics in hydrated cementitious samples are accentuated by Portlandite [$\text{Ca}(\text{OH})_2$], one of the major crystalline cement hydration phases, which often exhibits large platelike crystal habits leading to preferential orientation. The conventional approach to dealing with these problems would be to micronize the sample, reducing the particle size and the anisotropy of the particle shape. Micronizing the sample may not always be appropriate, due to high shear levels, solvents, and high drying temperatures. Any one of these treatments may change the nature of the original sample leading to an erroneous result.

The classical approach for dealing with platelike materials, e.g. clays, has been to use capillary transmission measurements. The use of capillaries in laboratory instruments was once routine. However, capillary stages have become rather unusual accessories for the purchase of a modern instrument, and are often not available to the user. Capillaries yield lower intensities than conventional reflection samples, so either a high-speed position-sensitive detector (PSD) must be used or the experiment time increased significantly. Given the potential difficulties in obtaining high-quality capillary data, this study aimed to answer whether it is desirable, or even necessary, to do so.

EXPERIMENTAL

A single-phase triclinic $\text{Ca}_3\text{SiO}_5(\text{C}_3\text{S})$ was used rather than a Portland cement to simplify the study. Higher levels of

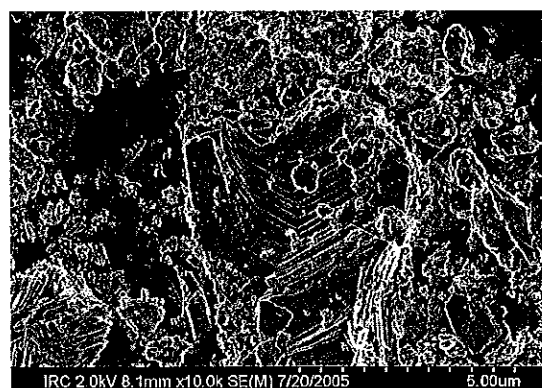


Figure 1. Scanning electron micrograph of Portlandite found in the 180 day old samples of hydrated C_3S .

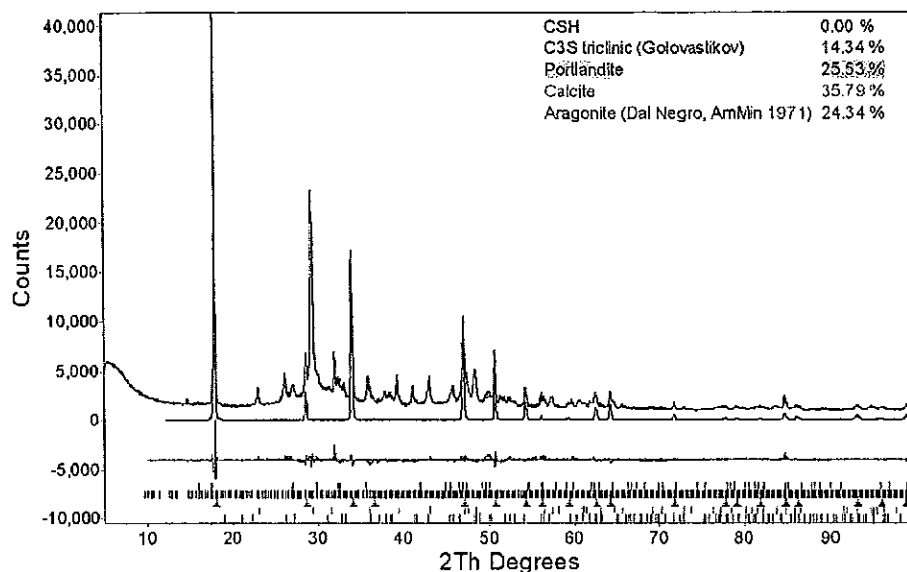


Figure 2. Reflection data from the 180 day hydrated material highlighting the pronounced preferred orientation of the Portlandite.

Portlandite were expected in the hydrated samples. The samples (water to cement ratio of 0.5) were cast in 15 mm molds and kept in a desiccator at 100% relative humidity. They were removed at the appropriate conditioning interval. Upon removal, the hydration reaction was halted using a freeze-drying technique. Materials were ground with a mortar and pestle then stored in sealed vials until the measurements were carried out.

X-ray diffraction data were obtained using a Bruker D8 system equipped with a primary Göbel mirror and a Vantec-1 PSD detector. Using this configuration, both reflection and transmission data could be obtained using the same optics. The Vantec-1 detector was equipped with radial Soller slits, and an air-scatter sink was used to reduce parasitic scattering toward lower angles. After an internal standard (25 wt %) was added, samples were lightly ground using a mortar and pestle, and either top loaded onto a silicon zero-background holder, or loaded into a 0.5 mm glass/quartz capillary.

The capillary measurements were taken using a 3° detector window, while the reflection data were taken with a 6° detector window. A 0.8 mm exit slit was used in the primary mirror for both sets of experiments.

The internal standard material chosen for the study was a commercial rutile produced by DuPont known as R900. This material has a small ($\sim 0.4 \mu\text{m}$) and uniform particle size, and possesses a linear absorption coefficient closer to C_3S than Al_2O_3 . R900 is known to have an amorphous content of its own, so was standardized versus the NIST SRM676 corundum standard. Previously, the amorphous content of SRM676 was thought to be 2%, but recently this has been revised to approximately 8%. This has a significant effect on the calculated amorphous content of the R900®, and consequently the sample under study. The effect on the calculated amorphous content of R900® is to increase it substantially from $\sim 5.6\%$ to approximately 14%. Previous publications where the old amorphous content of SRM676 was used (Whitfield and Mitchell, 2003; Winburn *et al.*, 2000) conse-

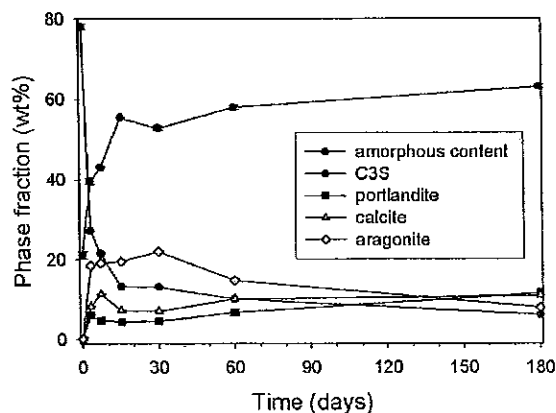


Figure 3. Phase fractions (wt %) against time for the data collected in reflection.

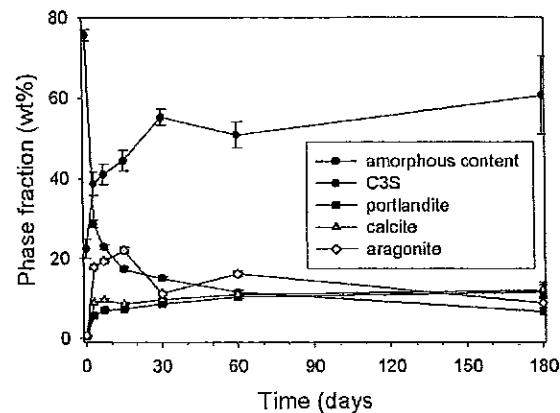


Figure 4. Phase fractions (wt %) against time for data collected in transmission.

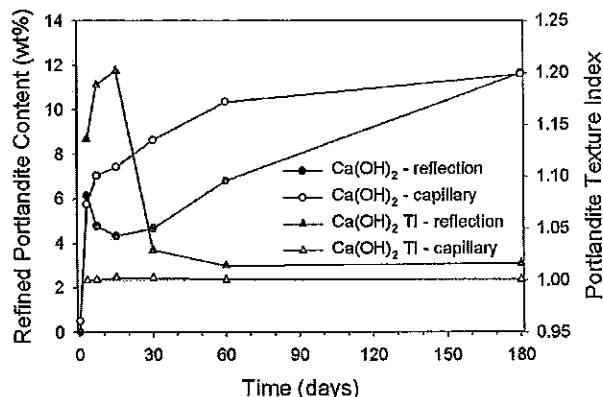


Figure 5. Portlandite phase fractions (wt %) against time for data collected in both transmission and reflection. The corresponding textural index values are also shown on a second Y axis.

quently underestimate the amorphous content. Samples were loaded into 0.5 mm glass/quartz capillaries and sealed using a flame. Glass/quartz capillaries exhibit high backgrounds so data were also collected for a blank capillary. This was used to simplify the background by subtraction. Sample effects such as surface roughness and capillary absorption were accounted for within the software (Topas 3 beta).

The effects of the largely amorphous calcium silicate hydrate (C–S–H) particles on the background were corrected for by a Pawley fit on an approximate cell derived from synthetic C–S–H. The synthetic C–S–H was made by reacting stoichiometrically blended CaO and amorphous SiO₂ together in excess water for 360 days.

The Ca(OH)₂ was refined with a fourth-order spherical harmonic (SH) correction in both reflection and capillary datasets. The SH coefficients from Topas were input into a General Structure Analysis System to calculate a texture index. This index was subsequently used to gauge the randomness of the powder.

The index limits are:

- 1 = random powder (no orientation); and
- ∞ = single crystal (total orientation).

RESULTS AND DISCUSSION

A large layered Portlandite crystal can be seen in Figure 1. Also visible in the bottom left of the micrograph are acicular crystals of aragonite. The large and platy Portlandite crystals are quite numerous, and can be seen in the samples at all ages. The severe texture, exhibited by these crystals, is responsible for the observed preferential orientation in the X-ray data (see Figure 2).

Figure 2 shows the potentially high levels of preferential orientation; the first highlighted peak at 18.0° 2θ is Portlandite's 72% peak (PDF No. 14-1481); with the 100% peak positioned at 34.1° 2θ. It is easily observed that Portlandite's 74% peak at 18.05° 2θ is the most intense peak in the pattern, easily overwhelming the true 100% peak at 34.1° 2θ. Without a correction, the intensity mismatch caused by orientation will increase the error in the concentration.

The weight fractions that were calculated from the reflection and transmission data are shown in Figures 3 and 4, respectively. The Portlandite results are more clearly shown in Figure 5, along with the results from the textural index. It is apparent that the higher levels of orientation (found by the textural index) in the 7, 15, and 30 day reflection results, correspond to the inconsistent quantified values. Chemically the levels of Ca(OH)₂ should not reduce with time.

The textural index for the capillary results show little orientation. This, in addition to a much more acceptable quantified value implies that the use of capillaries can give the X-ray spectroscopist a distinct advantage.

Some work has been published previously in the literature (Sitepu *et al.*, 2005) comparing the effectiveness of the March-Dollase (Dollase, 1986) and spherical harmonics (Von Dreele, 1997) preferential orientation correction on quantitative Rietveld analysis. It was concluded on the basis of using synthetic mixtures that the spherical harmonics correction was superior in terms of a figure-of-merit for the quantitative results (Sitepu *et al.*, 2005). The results of this study however, indicate that caution is required when naturally occurring mixtures are studied.

CONCLUSIONS

As expected, data from the capillary measurements eliminated preferential orientation from the observed pattern of Portlandite. The spherical harmonics correction successfully corrected the Portlandite misfits in the Rietveld difference plots of the reflection data. The quantitative results of the capillary and reflection data are however, not equivalent. It has been demonstrated that the presence of texture in the Portlandite can lead to chemically unreasonable trends in the Portlandite phase fractions.

The problems with the reflection data suggest the presence of significant microabsorption. This is consistent with large, orientating Portlandite particles in the reflection 3 samples.

The refined amorphous content of the unhydrated triclinc C₃S was found to be 21–22 wt % for both reflection and transmission geometry, which is in remarkable agreement with the result of 19 wt % for monoclinic C₃S reported by De La Torre *et al.* (2001).

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