JOURNAL OF MATERIALS SCIENCE **38** (2003) 4415–4421

Quantitative Rietveld analysis of the amorphous content in cements and clinkers[†]

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The potential presence of an amorphous content in OPC clinker and cements is usually overlooked when studying their phase composition. This is largely because of the difficulty in determining amorphous content experimentally. Despite this difficulty, the study of amorphous content and composition in these materials has merit due to the likely effects on the reactivity of the resulting cement.
This paper applied the Rietveld method using X-ray powder diffraction data to determine the amorphous content of a number of materials, including clinker, cements and single phases. The cementitious materials were found to contain widely varying, but significant, amorphous contents. The addition of amorphous slag to change the amorphous content by a known amount, gave results as expected from the calculated results for the pure cement and clinker amorphous contents. The results are discussed in relation to other studies published on the issue of amorphous content in cementitious materials. © *2003 Kluwer Academic Publishers*

1. Introduction

The cement industry uses a number of techniques to characterise their clinkers and final cement materials. These include solution-based techniques and X-ray fluorescence, results from which are then used in the Bogue calculation to generate the ratio of phases present. The Bogue calculation uses a number of assumptions and is known to be inaccurate when these are not met [1]. Optical microscopy can also be used, but is not a routine technique due to the time and skill required. Rietveld refinement of powder X-ray diffraction data is becoming increasingly popular to determine quantitatively the crystalline phases present [2] due to its speed and perceived simplicity. However, such an analysis ignores the possibility of significant amorphous content, which could have major effects on the cement's mineralogy and hydration properties. Given that modern cement clinker is quenched from high temperature by forced air cooling on removal from the kiln, it is not unlikely that the resultant material has a significant amorphous content.

In 1937, Lerch and Brownmiller used calorimetric techniques to determine the amorphous content in cement clinker [3]. In a series of experiments they found an amorphous content between 10 and 28% with an estimated error of ±5%. The variation appeared to be strongly linked to the Al:Fe ratio, as well as the cooling rate. Their most amorphous samples were quenched in mercury, so were cooled extremely rapidly. Their most crystalline samples were slow cooled to promote crystallization. These results seem to have been largely forgotten, but a few papers have recently appeared [4, 5] which use X-ray based techniques to determine the amorphous content in clinker, and various single phase cement-related materials. One conclusion that may be drawn from these results, is the amorphous contents of these materials are very sensitive to synthesis conditions and can vary significantly. One author quoted a value of 7% for a clinker [6], and 19% for a single phase monoclinic C_3S in another publication [7]. Another author studied a range of single-phase materials using a standardless X-ray technique (the Ruland method), and found wildly varying amorphous contents for the same compound [5]. Very recently a paper appeared citing values for amorphous contents from Rietveld analysis of between 6 and 15% for a number of cement clinkers [4]. The materials examined in their study, National Institute for Science and Technology (NIST) Standard Reference Materials (SRM) 8486-8488 clinkers and two Australian clinkers, are different from those in this work, but the values stated in their paper (from 6.1 to 15.9%) suggest that our results are reasonable. Unfortunately, these authors do not have access to the NIST SRM 8486-8488 clinkers and are unable to directly repeat or confirm the results of Suherman *et al.* [4].

Rietveld analysis was developed in the late 1960s for structural refinement of crystalline phases from

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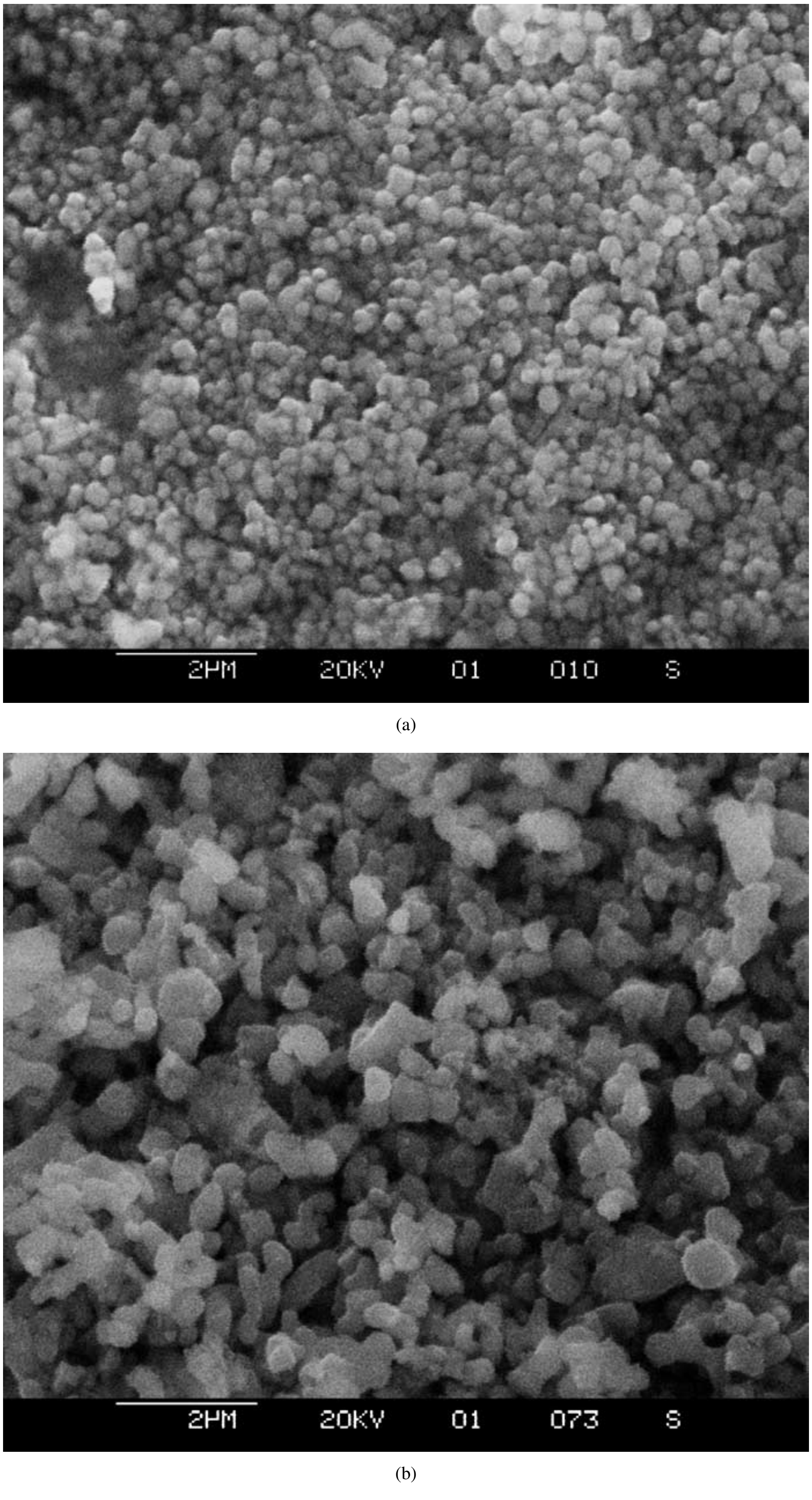
powder neutron diffraction data [8]. The Rietveld analysis technique has developed in scope and rigor, to the stage where accurate quantitative analysis of complex mixtures of crystalline phases using laboratory X-ray diffractometers may be attempted [9]. One common application of this technique is on-line quantitative analysis of cements for quality control purposes. Recently, through the use of selective and well-characterised internal standards, the application of Rietveld analysis to determine amorphous content of complex mixtures has been described [10]. The amorphous content is calculated from the difference in the



(a)

(b)

Figure 1 SEM micrographs of (a) Ti-Pure ®R900 rutile and (b) SRM676 alumina.

TABLE I Table of the linear absorption coefficients for Cu K_α radiation for diferent materials of interest

Phase	$\mu_{1.5418\,\text{Å}}$ (cm^{-1})	Phase	$\mu_{1.5418\,\text{Å}}$ (cm^{-1})
TiO_2	528	C_3A	274
Al_2O_3	127	C_4AF	509
$CaCO_3$	201	Anhydrite	232
SiO_2	95	Bassanite	201
C_3S	323	Gypsum	146
C_2S	311		

known wt% content of the spike and the wt% calculated from the refinement.

Determination of amorphous content from such analyses is more challenging experimentally than obtaining the ratio of crystalline phases. Issues such as microabsorption complicate matters considerably [11], and in extreme cases can make the analysis impossible. A judicious choice of an internal standard can make for much improved results using the Brindley microabsorption correction [12]. A standard for this task should have a well defined and narrow particle size distribution, as well as having an absorption coefficient similar to the mixture's components. It has been demonstrated in the literature, that inappropriate use of the Brindley correction can be worse than using no such correction [13].

Promising standard materials for such a study would be rutile and corundum. Corundum has a linear absorption lower than most of the cement phases, and rutile higher (see Table I). The US National Institute of Standards and Technology (NIST) supply a quantitative X-ray corundum standard known as SRM676. SRM676 has a known amorphous content of 1.77% ± 0.68 [14], and acts as the primary standard in this study. This SRM is too expensive to use routinely, so a rutile material was chosen as a standard material. The rutile used in this study was Dupont's Ti-Pure® R900. This material is claimed to have a narrow particle size distribution around approximately 0.4 μm, which would reduce microabsorption, and makes possible the use of the Brindley microabsorption correction if it becomes a problem.

2. Experimental

The equipment used in the study was a Bruker D8 with parallel beam, double Göbel mirror optics, using $Cu_{K\alpha}$ radiation with a scintillation detector. Errors in the value of amorphous content of the R900 rutile add significantly to the final errors in amorphous content of the samples. Therefore, to standardise the R900, an extended scan, with a 20 s count time, and range from 20–100° 2θ was used to reduce signal:noise, and subsequent errors in the refinement of the SRM676-rutile mixture. The cements and clinker were examined using both short and long scan times. Long scans were undertaken on the complex samples between 10–100° 2θ using a 20 s count time and 0.03° step, yielding data with a very good signal:noise ratio. To gauge the effect on the results and errors of a shorter, more routine data collection, scans with a 3 s count time and 0.03° step size were chosen to collect data between 10–80° 2θ. Data were collected for the single-phase samples using only the shorter scan conditions.

The particle sizes of the rutile, SRM676 and polishing corundum were examined by the use of a Cambridge Stereoscan 250 Scanning Electron Microscope (SEM) using carbon adhesive pads on aluminium stubs.

R900 is not 100% crystalline rutile, and was standardised using the SRM676. Using a carefully prepared 50:50 mixture of the SRM676 and R900, the amorphous content of R900 was determined using Rietveld technique.

Samples and standards were mixed in either a 50:50 or 75:25 ratio. The significantly different rutile content might be expected to have a large effect on calculated amorphous contents if absorption contrast is a problem in a sample. Data were obtained from a type 10 clinker, its corresponding cement product, and a second type 10 cement from another manufacturer.

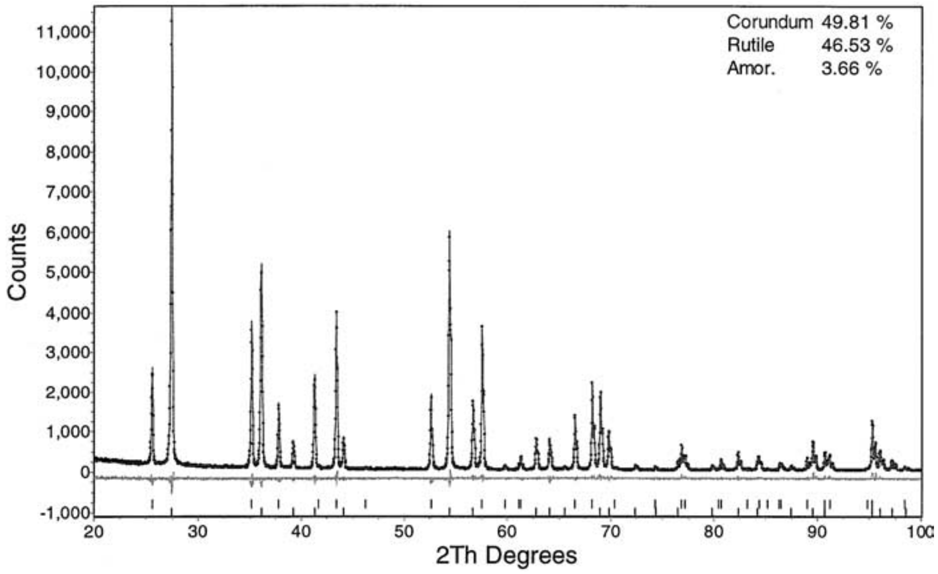


Figure 2 Rietveld difference plot for the standardisation refinement of R900 rutile and SRM676 alumina. The tickmarks represent the calculated peak positions of each phase and the phase composition is displayed in the plot. The amorphous content indicated in the plot is not corrected for the rutile content.

The cements and clinker were of the same age, and had been stored in water and air-tight containers for a period of two years. In addition, data were collected from synthetic triclinic C_3S, β-C_2S, C_3A and C_4AF (Construction Technologies Laboratories, Inc). Besides forming a study of pure cement phases, they acted as a cross-check for possible problems with absorption from the iron-containing phases in copper radiation. Sample mixtures of the cementitious phases were prepared immediately before data collection. Additional data were collected from materials that had an additional spike of approximately 10 wt% of amorphous blast furnace slag. In the event that the refinements give results close to those expected after perturbing the amorphous content, additional confidence in the accuracy of the technique would be gained.

Highly crystalline materials in the form of a 0.3 μm polishing corundum, and reagent grade $CaCo_3$, were also examined to ensure the technique gave consistent results across a range of crystallinities.

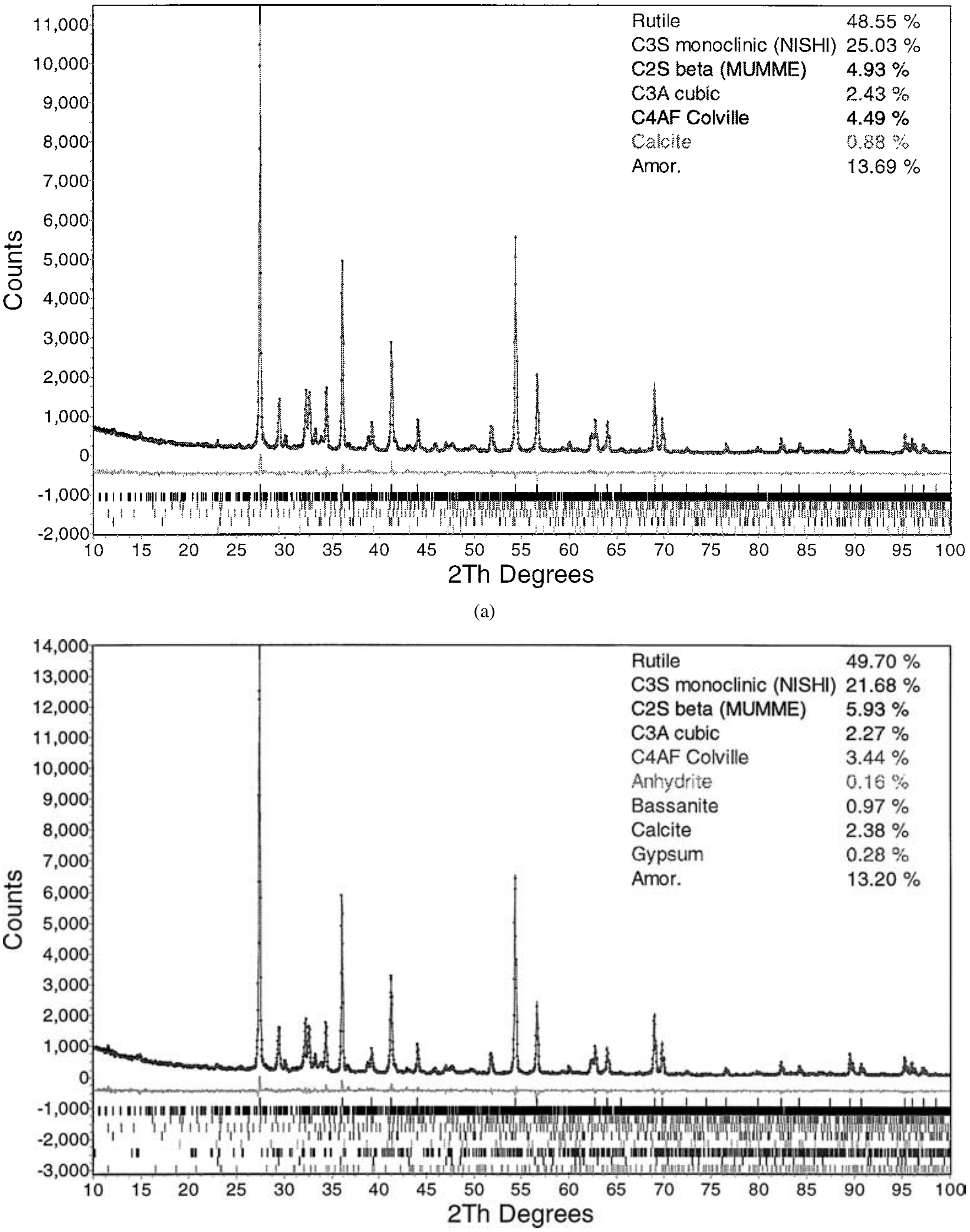
Data were analysed using a beta version of Bruker's Topas V2.1 software [15]. The fundamental parameters approach was used to generate the instrument broadening contribution to line broadening [16]. The parameters used were generated after refining models to fit the NIST LaB_6 660a standard. This approach is useful in reducing the number of variables during the refinement, as well as yielding information about crystallite size. The Lorentz polarisation factor used for the twin mirrors was 0°. Structures refined for the clinker were alite, belite, C_3A, and C_4AF, together with the internal standard and calcite to account for carbonation of the samples. For the cement samples, gypsum, bassanite (hemihydrate) and anhydrite were refined in addition to those phases previously mentioned. A number of other possible phases were considered but did not appear in these samples. No evidence of $Ca(OH)_2$ was found, suggesting that the sample container seals remained intact. The C_3S structure used was the monoclinic structure described by Nishi [17], and the β-C_2S that described by Mumme [18]. Refined parameters for each phase were lattice parameters and crystallite size. The structures included values for site occupancies and thermal parameters, but these were fixed during the refinements. Despite the implications alluded to in the introduction, no attempt was made to determine the Al:Fe ratio of the C_4AF, as peak overlap and broadening made refining site compositions impossible. Preferential orientation was refined for C_3S, $CaCO_3$ Al_2O_3 and TiO_2 using the March-Dollase correction [19]. The spherical harmonics usually gives better results in quantitative analysis [11], but the severe peak overlap of monoclinic C_3S and $CaCO_3$ tended to make the refinement unstable due to the correlations. The single-phase triclinic C_3S was fitted using a structure described by Golovastikov [20].

3. Results and discussion

The particle size of the R900 rutile was found to be approximately 0.3 μm by SEM (Fig. 1a). No anatase was visible in the diffraction pattern, and the particles' alumina coating was invisible to the X-rays. The SRM676 alumina was found by SEM to have particle sizes of approximately 0.5 μm (Fig. 1b), although it did contain a fraction of particles of up to 1 μm in size. A good fit was obtained from the Rietveld analysis of the 50:50 mixture of R900 rutile and SRM676 alumina (see Fig. 2). Residuals from the refinement were calculated to be 8.23% for R_{wp}, and 6.15% for R_{exp}. The amorphous content of the R900 was calculated to be 5.60% ± 1.15, taking into account the error in SRM676, refinement errors and a Brindley correction for 0.3 μm rutile and 0.5 μm alumina. A previous study using the same methodology found their batch of R900 material

TABLE II Percentage amorphous contents of the materials studied. Quoted errors were calculated using 2σ (~90% confidence limits) from the Rietveld esd's, and absolute errors include uncertainty in the amorphous content of the standard

Sample	% Absolute amorphous content (using 50 wt% TiO_2)	% Comparative error (using 50 wt% TiO_2)	% Absolute amorphous content (using 25 wt% TiO_2)	% Comparative error (using 25 wt% TiO_2)
Type 10 Clinker A (short scan)	21.1 ± 3.7	2.7	–	–
Type 10 Clinker A (long scan)	21.3 ± 2.8	1.7	25.1 ± 1.9	1.6
Type 10 Clinker A with 9.3 wt% slag (long scan)	–	–	31.2 ± 1.8 (expected = 31.2% using 25.1% amorphous value for clinker)	1.4
Type 10 Cement A (short scan)	21.2 ± 4.5	3.4	–	–
Type 10 Cement A (long scan)	20.7 ± 3.0	1.9	21.0 ± 2.1	1.7
Type 10 Cement A with 11.2 wt% slag (long scan)	–	–	28.7 ± 2.0 (expected = 29.9% using 21.0% amorphous value for cement)	1.7
β-C_2S (short scan)	31.2 ± 3.8	2.7	30.2 ± 2.5	2.2
Triclinic C_3S (short scan)	5.8 ± 2.9	1.7	8.2 ± 2.4	2.1
C_4AF (short scan)	38.4 ± 2.7	1.7	43.3 ± 2.1	1.7
C_3A (short scan)	28.9 ± 2.4	1.3	34.4 ± 1.6	1.2
Type 10 Cement B (short scan)	18.2 ± 4.2	3.1	–	–
Type 10 Cement B (long scan)	18.4 ± 3.0	1.9	17.8 ± 2.2	1.8
Type 10 Cement B with 12.7 wt% slag (long scan)	–	–	25.8 ± 2.1 (expected = 28.2% using 17.8% amorphous value for cement)	1.7
0.3 μm polishing Al_2O_3 (short scan)	0.4 ± 3.1		2.3 ± 2.3	
$CaCO_3$ (short scan)	2.3 ± 3.3	–	−4.2 ± 2.7	



(a)

(b)

Figure 3 Rietveld difference plots for a 50:50 mixture of R900 rutile and Type 10 materials from manufacturer A—clinker (a), and corresponding cement product (b). The tickmarks represent the calculated peak positions of each phase and the phase composition is displayed in the plot. The amorphous content indicated in the plot is not corrected for the rutile content.

to have an amorphous content of 5.6% [10]. This would seem to be a remarkable agreement, but their study used a value of 1.6% (as opposed to 1.77%) for the amorphous content of SRM676. An amorphous content of 1.6% for SRM676 would lead to a value of 5.77% in our calculations.

The calculated amorphous contents are shown in Table II. The amorphous content of the clinker (around 21%) seemed high compared to convention [1], although the same source states that there can be approximately 27% liquid phase in a typical clinker composition at 1400°C [1]. The results were not disimilar to those found by Lerch and Brownmiller [3] using a completely different technique. The fits obtained in the mixtures of R900 rutile and the cementitious materials were quite good as seen in Fig. 3a and b. Results obtained after the addition of a known quantity of amorphous slag were as expected within error, with good fits to the data (Fig. 4). This confirmed that the technique does detect the presence of amorphous material in a quantitative manner.

It can be seen in Table II that the use of different data collection strategies had a negligible effect on the result but reduced the inherent errors. Reducing the rutile addition from 50 to 25% also reduced the absolute errors for most materials but increased the comparative error for others. In a single-phase system with only a 25% addition of rutile, structural inadequacies become more apparent and contribute an increasingly large proportion of the error. In a complex mixture this effect is

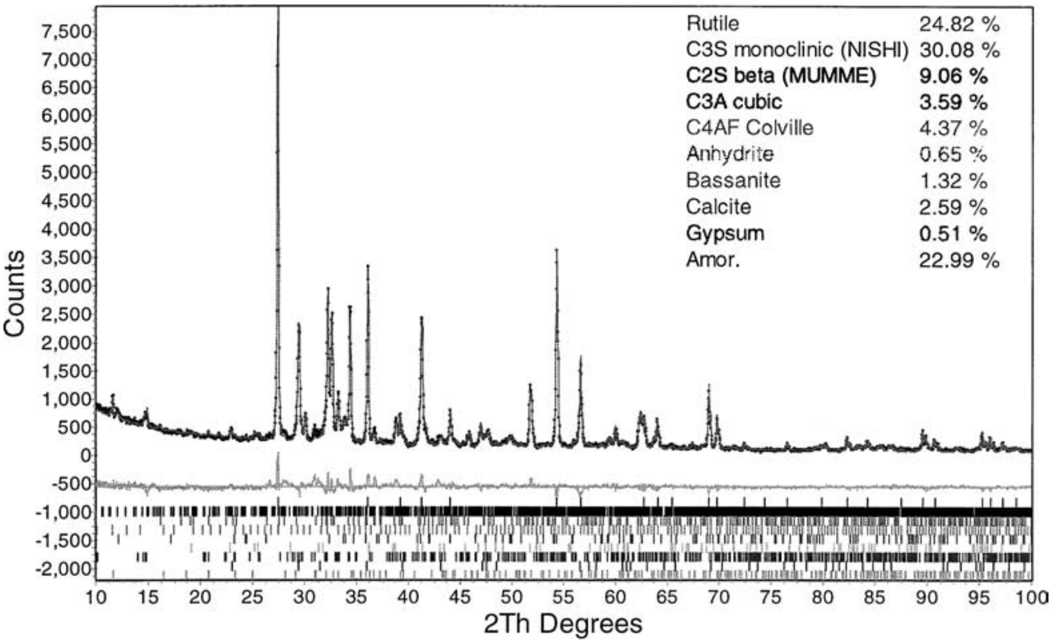


Figure 4 Rietveld difference plot of a cement/slag mixture. The mixture contained 11.2 wt% slag and the cement was from manufacturer A. The rutile spike was approximately 25 wt%. The amorphous content indicated in the plot is not corrected for the rutile content.

diluted considerably. This leads to the surprising result that the calculated amorphous content of the cements and clinker were actually more reproducible than the single phases when the spiking level was changed. The errors shown in Table II were calculated using a statistical level of 2σ with regard to the Rietveld estimated standard deviations (esd's) to give errors within ~90% confidence limits. When a comparative study is desired rather than absolute values for amorphous content, then the error in the amorphous content of the standard can be ignored, and this comparative error for the cementitious phases is also in Table II.

Potential additional errors could be introduced by the presence of other phases, and attempts were made using the long scans to identify other possible minor phases such as periclase, quartz, alternative calcium silicate polymorphs, etc. The particle sizes of the individual cementitious phases were unknown, therefore correct application of the Brindley microabsorption correction was not possible. However, the application of this correction to cement B at 50% dilution, assuming a size of 40 μm for all the cement phases, increased the final amorphous content by only 0.7%. The iron-containing phases do not seem to have an undue effect in these cases, possibly helped by significant dilution with the rutile.

The results for the amorphous content of the pure synthetic cement phases varied between 6% for t-C_3S and 43% for C_4AF (Table II). The results are repeatable, but high values of amorphous content for some of the materials could be related to their advanced age. Despite the good storage conditions for the cements and clinkers, the particle surfaces could have slowly carbonated and/or hydrated, forming a thin film that would be effectively invisible to X-rays. In addition, microabsorption could have had an effect on the results obtained for the pure calcium silicate and aluminate cement phases, due to the absorption contrast between them and rutile (Table I). However, the addition of a 40 μm Brindley correction to the C_2S refinement actually increases the amorphous content by 1.1% rather than decreasing it. The $Cu_{K\alpha}$ linear absorption for C_4AF is almost identical to that of rutile. The particularly high amorphous content of the C_4AF should not be too surprising given the relationship between the Al:Fe ratio and the glass contents found by Lerch and Brownmiller in their study [3]. Both Yang [5] and this study have found that many lab-prepared phases have significant amorphous contents. The samples chosen as crystalline did indeed yield low amorphous contents. The results for these crystalline materials show that there is no systematic error in the technique that would consistently give erroneously high amorphous contents.

4. Conclusions

A study of the amorphous content of cements, cement clinkers, and single phases using Rietveld analysis of X-ray powder diffraction has been undertaken. It was found that many of them contained significant quantities of amorphous material. Given the current forced-air cooling of clinker used in the cement industry, the range of values obtained for the cementitious materials (between 18–25%) seem reasonable compared to the range of values obtained by Lerch and Brownmiller [3]. They calculated values for amorphous content in clinkers as low as 10%, and up to 28% using calorimetry, with an estimated error of 5%. This study also defined an upper range of amorphous content, as their most amorphous clinkers were quenched in mercury—a very efficient if hazardous operation. Their results for the rapidly quenched samples agreed well with typical values (~27%) for the amount of liquid phase present in the cement kiln at 1400°C [1]. The Rietveld approach to amorphous content determination is able to cope with carbonated samples or those with sulphate additions, whereas the thermal analysis approach cannot. The addition of a known quantity of amorphous slag to the clinker and cements was successfully detected, which gave additional confidence that the technique measures amorphous content in a quantitative manner.

It was apparent that a significant portion of the error in the absolute values of amorphous content, were due to uncertainties in the rutile standard. The primary SRM676 alumina standard was responsible for much of that error, and the lack of a standard with a well-defined amorphous content is the main obstacle in this respect. Until a primary (e.g., NIST) standard with an extremely well defined amorphous content, with a small error, is produced, the errors inherent in determination of absolute amorphous contents will be significant. Rietveld analysis of a material 'spiked' with a well characterised, suitable standard, with sub-micron particles and a narrow size distribution, can yield consistent results for the amorphous contents of cementitious and other materials.

The comparative errors were significantly lower, and reducing the spiking level from 50 to 25% improved the absolute error due to better statistics for the cement phases. Improved statistics from the cement phases, and a reduction in the absolute error associated with large additions of the standard contributed to this. Conversely, in some of the synthetic pure phases, the errors on reducing the spiking level from 50 to 25% actually increased. In these instances the improved statistics highlighted inadequacies in the structural models used.

The results obtained in this study warrant further work into the area of amorphous contents in cementitious materials. Neutron diffraction experiments would be useful to confirm these results given the greater bulk sampled by that technique and its insensitivity to effects such as microabsorption. Given a technique to reliably calculate amorphous contents, any effects on cement hydration and other properties could then be determined.

Acknowledgements

We would like to thank Arnt Kern of Bruker AXS GmbH for supplying the authors with updated beta versions of the Topas software.

Mr Jim Margeson is thanked for his efforts in obtaining the SEM images that appear in this paper.

Appendix—Cement Nomenclature

$C_3S = Ca_3SiO_5$
$C_2S = Ca_2SiO_4$
$C_4AF = Ca_2(Al_{1-x}Fe_x)_2O_5$
$C_3A = Ca_3Al_2O_6$
Gypsum = $CaSO_4{\cdot}2H_2O$
Bassanite = $CaSO_4{\cdot}1/2H_2O$
Anhydrite = $CaSO_4$

References

1. H. F. W. TAYLOR, "Cement Chemistry" (Academic Press Ltd., London, 1990).
2. J. C. TAYLOR, L. P. ALDRIDGE, C. E. MATULIS and I. HINCZAK, "Structure and Performance of Cements," edited by J. Bensted and P. Barnes (Spon Press, London, 2002) p. 420.
3. W. LERCH and L. T. BROWNMILLER, *J. Res. Nat. Bur. Stand.* **18** (1937) 609.
4. P. M. SUHERMAN, A. VAN RIESSEN, B. O'CONNOR, D. BOLTON and H. FAIRHURST, *Powder Diffraction* **17** (2002) 178.
5. R. YANG, *Cem. Concr. Res.* **26** (1996) 1451.
6. A. G. DELA TORRE, A. CABEZA, A. CALVENTE, S. BRUQUE and M. A. G. ARANDA, *Anal. Chem.* **73** (2001) 151.
7. A. G. DELA TORRE, S. BRUQUE and M. A. G. ARANDA, *J. Appl. Cryst.* **34** (2001) 196.
8. H. M. RIETVELD, *Acta Cryst.* **22** (1967) 151.
9. R. J. HILL and C. J. HOWARD, *J. Appl. Cryst.* **20** (1987) 467.
10. R. S. WINBURN, D. G. GRIER, G. J. MCCARTHY and R. B. PETERSON, *Powder Diffraction* **15** (2000) 163.
11. N. V. Y. SCARLETT, I. C. MADSEN, L. M. D. CRANSWICK, T. LWIN, E. GROLEAU, G. STEPHENSON, M. AYLMORE and N. AGRON-OLSHINA, *J. Appl. Cryst.* **35** (2002) 383.
12. G. W. BRINDLEY, *Philos. Mag.* **3** (1945) 347.
13. R. S. WINBURN, S. L. LERACH, B. R. JARABEK, M. A. WISDOM, D. G. GRIER and G. J. MCCARTHY, *Adv. X-Ray Anal.* **42** (2000) 387.
14. Certificate of Analysis: Standard Reference Material 656. Silicon Nitride Powders for Quantitative Analysis by Powder Diffraction, Gaithersburg, MD, USA (1995).
15. User Manual, TOPAS V2.0: General Profile and Structure Analysis Software for Powder Diffraction Data, Karlsruhe, Germany (2000).
16. R. W. CHEARY and A. A. COELHO, *J. Appl. Cryst.* **25** (1992) 109.
17. F. NISHI, Y. TAKEUCHI and I. MAKI, *Zeitschrift für Kristallographie* **172** (1985) 297.
18. W. G. MUMME, R. J. HILL, G. BUSHNELL-WYE and E. R. SEGNIT, *Neues Jahrbuch für Mineralogie Abhandlungen* **169** (1995) 35.
19. W. A. DOLLASE, *J. Appl. Cryst.* **19** (1986) 267.
20. N. I. GOLOVASTIKOV, R. G. MATVEEVA and N. V. BELOV, *Soviet Phys. Cryst.* **20** (1976) 441.

Received 10 December 2002
and accepted 7 July 2003