Compositional Analysis of NIST Reference Material Clinker 8486

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Reprinted from Accuracy in Powder Diffraction III, Proceedings. National Institute of Standards and Technology. April 22-25, 2001, Gaithersburg, MD, Poster #2, 2001.

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

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Portland cement concrete is one of the most widely used construction materials with consumption, at about 5.5 billion tons per year, second only to water in per-capita demand. Improvements in the production and use of portland cements, a primary component of concrete requires the application of material science which, in turn, requires the ability to determine and describe micro- and macrostructures. Current industry practice utilizes an estimate of potential cement phase composition based upon a bulk chemical analysis, which has long been recognised as inaccurate. Rietveld refinements to model the complex, overlapping X-ray powder diffraction (XRD) patterns of cementitious materials will provide improved phase abundance information that will provide an improved basis from which to investigate relationships between cement chemistry and performance properties.

RM 8486 is one of three NIST reference clinkers used for developing and testing methods of quantitative phase analysis [1]. Clinker is ground with gypsum to produce portland cement. These clinkers were selected as representative of the range of North American clinker production with respect to phase abundance, crystal size, and crystal distribution. Reference values are currently based upon an optical microscope examination of polished sections.

The XRD study provides an additional independent estimate which to examine inter- and intra- sample heterogeneity. For this study, nine randomly selected samples were split into replicates and analysed in duplicate. The optical data sets include one set of of four samples and three sets of one sample all analysed in duplicate. The combined data sets establish the certified values. RM 8486 will be discussed in this report.

Measurements from different sources, laboratories, instruments, and from different methods can exhibit significant between-method variability, as well as distinct within-method variances. The data were treated using a weighted scheme, based upon work by Mandel-Paule-Vangel-Rukhin, to establish best-consensus values and to provide meaningful uncertainties [2]. This approach is favored as it produces a weighted mean that does not necessarily skew the consensus value in the direction of the larger number of XRD values, and that takes between- as well as within-method variation into account.

Clinker 8486 (Fig. 1) is intermediate in crystal size and exhibits heterogeneous phase distribution relative to the other clinkers. Alite occurs as subhedral to anhedral crystals approximately 25 μm in size. Belite occurs in large clusters with an approximate crystal size of 15μm.

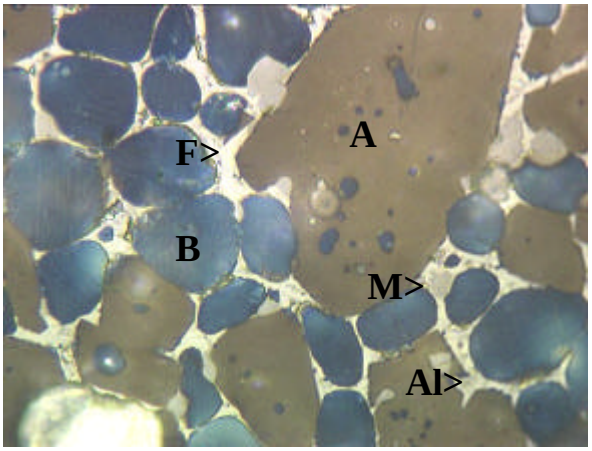

Fig. 1. *Reflected light micrograph of RM 8486 showing alite (A), belite (B), ferrite (F), aluminate (Al), and periclase (M). Field Width: 250 mm*

Equant periclase crystals up to 15 μm are common throughout the microstructure. A medium- to fine-grained lath-like ferrite, with aluminate filling the inter-lath voids, forms the interstitial constituents.

Reitveld refinement [3] of the powder diffraction data allowed calculation of a set of best-fit reference patterns and their scale factors. Because of significant contrast in the linear attenuation coefficients of the calcium aluminoferrite and periclase, relative to the estimated mean matrix linear attenuation coefficient, a Brindley correction was applied to the scale factors. The mean particle size was obtained using an X-ray settling method from a single specimen.

Selective chemical extractions of the silicates and interstitial phases facilitated refinement of a set of experiment files using structure models from the literature. Separate analysis of the phase groups (silicates, aluminates, ferrite) simplified subsequent analyses by allowing refinement of each structure model and the peak shape parameters with less interference from the other clinker constituents. Initial data sets showed an anticorrelation in phase abundance between belite and ferrite. Examination of re-calculated patterns revealed a significant peak overlap and that the calculated ferrite peak profile shape would broaden and suppress the belite scale factor. These intermediate models and peak shapes were used for the analyses of the bulk clinker patterns.

Variables refined for each phase include scale, specimen displacement, background, lattice parameters, atomic coordinates (subject initially to bond length constraints for the silicates), aluminum and iron fractions in ferrite

tetrahedral and octahedral sites, peak shapes, and for alite, preferred orientation. Fixing these variables, especially the profile shape parameters, in the subsequent analyses eliminated problematic correlations. Finally, a Brindley absorption correction was applied to the scale factors. QXRD results are given in Table I.

The data sets generally show reasonable agreement in the estimates of the individual phase abundance (Fig. 3.). The data do not agree as well in the estimate of aluminate content, with the optical data being significantly lower. This may be the result of the fine size of the aluminate crystals and the resulting difficulty in their microscope identification. The XRD data exhibit greater precision than that of the microscopy point counts.

The boxplot is a schematic graphical device for comparing the empirical distributions represented by batches of numbers. This plot can be considered a visual one-way anova or t-test with the location of the distributions, their spread, and extremes embedded in the graphical display. The combined data are in Table II.

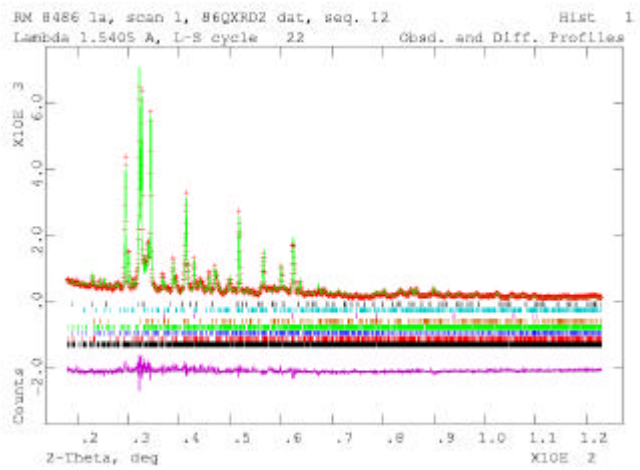

Fig. 2. *Raw data, calculated and difference curves for RM 8486 specimen 1, duplicate 1, scan 1.*

Table I. *XRD phase abundance and 95 % confidence limits for the mean compared to ASTM method C-150.*

	Lower	Mean	Upper	C-150
Alite	56.5	56.7	57.0	48
Belite	20.9	21.0	21.2	28
Aluminate	3.4	3 5	3.5	7
Ferrite	14.4	14.6	14.8	11
Periclase	4.1	4.1	4.2	not estimated

Table II. *Combined optical and XRD estimates showing the mean and 95 % uncertainty interval*

	Alite	Belite	Ferrite	Aluminate	Periclase
Mass %	58.6	23.3	14.1	2.3	3.3
2-σ	4.0	2.8	1.4	2.1	1.9

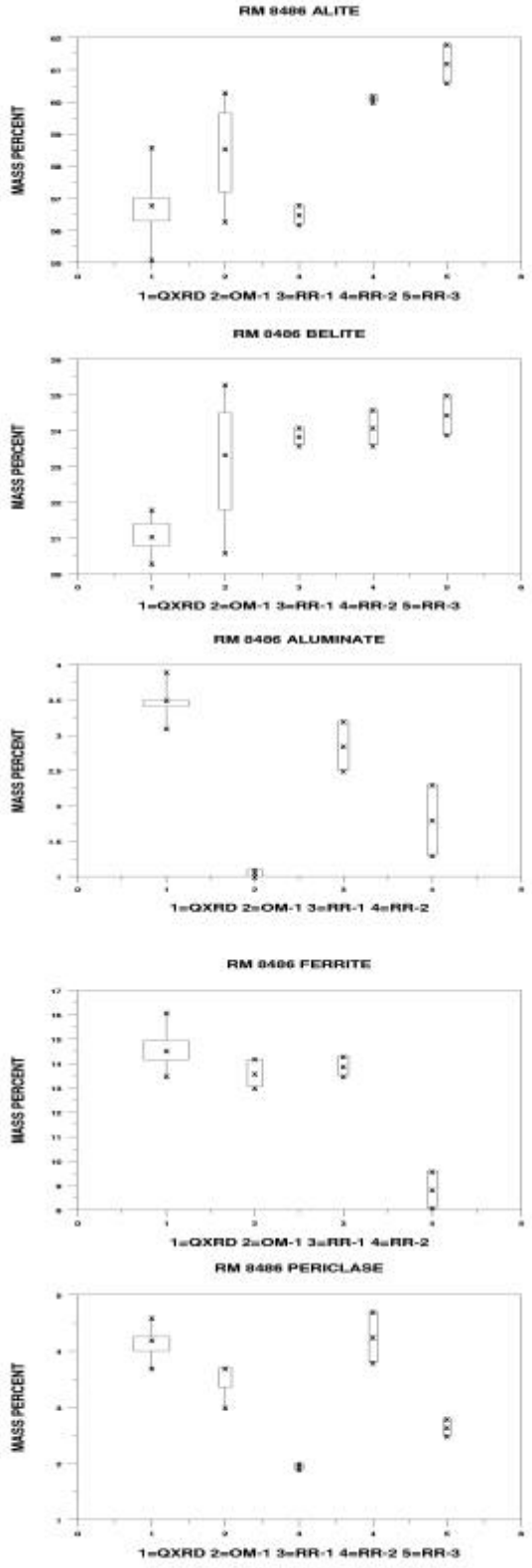

Fig. 3. *Boxplot comparisons of XRD and OM data*

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