DEVELOPMENT OF AN ASTM STANDARD TEST METHOD ON X-RAY POWDER DIFFRACTION ANALYSIS OF HYDRAULIC CEMENTS

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ABSTRACT

X-ray powder diffraction provides a direct analysis of phase abundance of portland cement clinkers and cements. The ASTM C01 (Cement) Committee formed a task group to investigate quantitative X-ray powder diffraction analysis that resulted in the ASTM C 1365 standard test for X-ray powder diffraction of portland cement clinker and portland cement. Estimates of test precision and bias are required in ASTM test methods with round robin testing used to generate these data. Seven laboratories participated in a clinker round robin using the NIST Standard Reference Material (SRM) clinkers and Rietveld analysis. The results were used to estimate inter- and intra-laboratory precision and bias. The application of the Rietveld method for analysis of complex powder diffraction patterns of clinker and cements provides an improved means to measure individual phase pattern intensities by accommodating the intrinsic variability of parameters affected by chemical substitution. Results indicate an improvement over round robins conducted prior to use of Rietveld method in cements analysis. The standard test method is being modified to include this approach.

INTRODUCTION

Hydraulic cement composition and fineness, along with other concrete constituents, influences fresh concrete properties such as rheology, heat evolution, setting, rates of strength development, ultimate strength, and color. For hardened concretes, the hydration products (and on occasion, residual cement phases) affect concrete durability. Phase composition and texture of clinker result from complex interactions of raw feed particle size, feed homogenization, and the plant heating and cooling regime. Mill grinding affects the cement microstructure through fracturing of the calcium silicates and interstitial phase crystals and, depending upon conditions, it may alter the form of calcium sulfate added at this stage to control cement setting. These features in turn influence the cement’s hydration characteristics, the process of conversion of the anhydrous cement and water to hardened hydration products that ultimately affect the development of strength and durability of a structure.

Recognizing these variables, classification of cements in ASTM C 150 is made on the basis of bulk chemistry, fineness, and, for some cements, limits on phase abundance [1]. Estimates of phase abundance are derived from the bulk chemistry using formulas referred to as the Bogue calculation. Errors in these estimates derive, in part, from the variability of clinker phase chemistry relative to the assumed compositions, and not accounting for minor constituents [2,3]. An alternative approach for quantitative phase analysis is X-ray powder diffraction (XRD).
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BACKGROUND

The application of XRD to quantitative phase abundance analysis dates back to the mid-1920s with the Portland Association Fellowship at the National Bureau of Standards (now National Institute of Standards and Technology, NIST) [4]. The late 1950s through the 1980s saw increased use of XRD in the analysis of cements and the first international round robins on quantitative powder diffraction analysis [5,6,7]. The results of these round robins were pessimistic on the suitability for XRD in the laboratory or cement plant due to the poor reproducibility and repeatability.

In 1980, ASTM Committee C01.23 on Compositional Analysis established a task group to explore XRD methods for phase analysis of portland cements. Initial work on measurement of the interstitial phases of clinker - periclase, aluminates and ferrite [7], resulted in adoption of a standard test method for XRD analysis of portland cement and clinker [8].

A qualification approach was adopted from ASTM C 114 on chemical analysis where the analyst may choose any method for analysis as long as he is able to demonstrate, or qualify, his approach through analysis of SRM materials. For the XRD method, the NIST SRM clinkers are used because they have certified phase composition [9] and the qualification limits are developed through round robin testing.

The round robin testing was initially based on a standardization using pure clinker phases and either peak area or whole-pattern measurement techniques. The difficulty in standardization and measurement limited the number of laboratories willing to participate. It was then decided to analyze clinker data by the Rietveld method. This also allowed inclusion of some data sets in the literature that included NIST SRM clinker data. Round robin participants were selected that have experience in XRD analysis of portland cement clinker. Three additional data sets were taken from published studies that included the NIST clinkers [10,11,12]. Some guidance was provided on specimen preparation, and scan conditions (except for data sets from literature). Participants were requested to grind the clinker to -10 μm median particle size and collect duplicate data sets (with sample re-packing) from a two-theta range of at least 20° – 65° (Cu Kα). Results with a single estimate are shown here but were not included in the statistical analyses.

STATISTICAL ANALYSIS

Precision is an assessment of the variability one may expect when the test method is used by one or more reasonably competent laboratories; the ASTM definition being “the closeness of agreement among test results obtained under prescribed conditions” [13]. Estimates of within-laboratory variability or repeatability (sr) and between-laboratory precision or reproducibility (sR), represent standard deviations of replicate analyses. From the sr and sR, limits on the difference between two test results may be calculated, which are designated 95 % repeatability (r) and reproducibility (R). This is accomplished by multiplying the appropriate standard deviation by the factor $1.96*\sqrt{2}$. Methods for estimating r and R and the standard deviations upon which they are based are given in ASTM E177 – 86 [14]. The estimates from each clinker were pooled using the standard formula for pooling variances and standard deviations [15].
RESULTS

Figure 1 shows replicate values from each participant for SRMs 2686, with the certificate values and 2σ limit indicated by a solid line and dashed line, respectively. Most participants’ data fell within the 2σ ranges for each of the clinkers, indicating that there was no significant bias among test results. Microabsorption corrections improve estimates of ferrite and periclase, and the lack of a correction resulted in a bias for four participants in the estimation of ferrite. The use of these corrections needs further investigation.

Based upon these data and calculations, a provisional precision and bias statement for ASTM may be developed using the individual phase values pooled across the three clinkers (Table 1). Precision and bias levels are all expressed as percentage points by mass relative to the total clinker. These results will be balloted in the Compositional Analysis Subcommittee (C01.23) and a summary of the findings will be incorporated in an appendix of the test method describing the Rietveld approach for clinker analysis. Comparison with results from earlier round robins [5,6] indicates an improvement in both within- and between-laboratory repeatability and reproducibility (Fig. 2). This is most likely the result of improved intensity estimates from the method’s whole-pattern approach, through the ability to refine lattice parameters and peak shapes. The earlier round robin data were mostly based upon peak area measurements on duplicate scan data. A cement round robin is currently underway to assess the precision and bias for a cement analysis and the influence of microabsorption corrections. Results will be incorporated in a revised XRD standard test.

Figure 1. SRM 2686 results. The solid line indicates certificate value and the dashed lines (or arrows), the 95% uncertainty bounds.
<table>
<thead>
<tr>
<th></th>
<th>Alite</th>
<th>Belite</th>
<th>Aluminate</th>
<th>Ferrite</th>
<th>Periclase</th>
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<tbody>
<tr>
<td><strong>Within-laboratory</strong></td>
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<td>1.1</td>
<td>0.7</td>
<td>0.6</td>
<td>0.4</td>
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<tr>
<td><strong>Standard Deviation (sr)</strong></td>
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<tr>
<td><strong>95% coverage factor</strong></td>
<td>2.9</td>
<td>3.1</td>
<td>2.1</td>
<td>1.7</td>
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<td>same clinker by the</td>
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<td>same lab (r)</td>
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<tr>
<td><strong>Multi-Laboratory</strong></td>
<td>1.2</td>
<td>1.4</td>
<td>1.7</td>
<td>1.4</td>
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<tr>
<td><strong>95% coverage factor</strong></td>
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<td>3.8</td>
<td>4.8</td>
<td>4.0</td>
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<td>laboratories (R)</td>
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</table>

Table 1. Within- and multi-laboratory repeatability and reproducibility estimates.

Figure 2. Multi-laboratory standard deviations (sR) for alite, belite, aluminate, and ferrite from this round robin (ASTM '03), from Moore [5], and Aldridge [6] shows improvement with the application of Rietveld pattern fitting approach.
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