NISTIR 4785

X-Ray Powder Diffraction Analysis of Three Portland Cement Reference Material Clinkers

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NIST

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April 1992

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ABSTRACT

Three portland cement clinker Reference Materials (RMs) are now available from the National Institute of Standards and Technology (NIST). They are intended for use in testing and developing methods for quantitative phase abundance analysis and have been selected as representative of the range of compositions and textures of North American clinkers.

Quantitative X-ray powder diffraction analysis was used to determine the phase abundance composition and compositional variability of eight randomly selected samples from each RM. In addition, each sample was split for duplicate analyses for evaluation of intra-sample phase abundance variability. The Reference Intensity Ratio method was used for powder diffraction calibrations and quantitative analysis. Both pure-phase standards and subsamples of the RM clinkers, which were point counted using the scanning electron microscope, were used for calibrations. Phase abundance values generally agree with those reported in earlier studies and the inter-sample standard deviation values were generally less than or equal to the intra-sample standard deviation values.

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1.0 INTRODUCTION

Advances in cement and concrete technology are based in the increased knowledge of their materials science. Reliable, practical techniques are needed for the characterization of concrete materials as necessary for understanding and predicting their performance. Portland cement is composed of an interground mixture of clinker and gypsum. Clinker is produced by firing a ground mixture of limestone and shale to about 1500°C where, after partial fusion, calcium silicates, calcium aluminates, and calcium aluminoferrites are formed. Phase abundance and texture of the clinker reflects the preparation, proportioning and firing of the raw materials and influences the performance and durability of the final product, the cement. This paper addresses the quantitative phase abundance analysis of cement clinker by X-ray powder diffraction.

Phase abundance composition can be estimated from chemical analysis data by using the Bogue equation. But, errors occur with the Bogue calculation because the chemical compositions of clinker phases can vary somewhat from the compositions assumed in the equations [1]. Methods for characterization of clinker microstructure and phase abundance include optical microscopy, X-ray powder diffraction, and scanning electron microscopy (SEM). Until recently, no reference material (RM) for phase abundance analysis of cement clinkers had been available.

Three RM clinkers have been produced in a joint effort by the Standard Reference Materials Program at the National Institute of Standards and Technology (NIST) and Construction Technology Laboratories (CTL) [2,3]. These clinkers represent the range of North American clinker production with respect to phase abundance, crystal size, and distribution and are intended for the testing and development of methods of quantitative phase abundance analysis of cement clinker.

To certify the phase abundance values in these clinkers, it was necessary to assess the intra- and inter-sample variability, and the purpose of this study was to determine these variabilities. Data already obtained using optical microscopy (Table 1) were not suitable for certifying phase abundance or for assessing sample variability because optical microscopy is not a bulk analytical technique. Quantitative X-ray powder diffraction analysis (QXRD), on the other hand, is a bulk analytical technique. Therefore this study examined the phase abundance composition of a set of randomly selected samples from each RM clinker using QXRD. Analysis of the data provided by this study may result in the certification of the clinker RMs and their reclassification as Standard Reference Materials.

Table 1. Phase abundances as determined by reflected white-light microscopy, expressed as mass percentages [2,3].

PHASE	RM 8486	RM 8487	RM 8488
Alite, C_3S	58.47	73.39	64.97
Belite, C_2S	23.18	7.75	18.51
Aluminate, C_3A	1.15	12.09	4.34
Ferrite, C_4AF	13.68	3.27	12.12
Free Lime, CaO	0.18	2.45	0.00
Periclase, MgO	3.21	0.09	0.05
Alkali Sulfate	0.14	0.98	0.03

Abbreviated notations for cement clinker phases commonly used in cement and concrete literature are used here, with C for CaO, A for Al_2O_3, F for Fe_2O_3, and S for SiO_2. Therefore alite is designated C_3S, belite is C_2S, aluminate is C_3A, and ferrite is C_4AF. Formulas for periclase (MgO) and free lime (CaO) are not abbreviated.

2.0 EXPERIMENTAL

2.1 Sampling and Sample Preparation

Samples were drawn from the packaged NIST clinker RMs. Each RM set is stored in three boxes, three flats deep. The packaged clinker RMs for analysis were selected using a random, stratified sampling scheme by specifying the flat, row, and column locations by computer-generated random numbers. About 50 g of each clinker was also sampled from bulk storage containers of reserve material.

Careful sample preparation and handling is important for quantitative X-ray diffraction analysis. Since cement clinker phases such as free lime (CaO) can be altered by exposure to air, the powdered samples must be stored in a vacuum desiccator. Each clinker sample (about 10 grams) was split providing duplicates, which were ground to moderate fineness (about −150 μm) with a mortar and pestle, and then wet ground for 18 minutes in a micronizing mill[1,2] using 10 ml of absolute ethanol as a grinding

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[1]McCrone Micronizing mill, McCrone Research, Westmont, IL

[2]Mention of brand names is made to provide complete details of the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are the best available for the purpose.

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aid. Wet grinding is preferable to dry grinding because it reduces the possibility of sample damage during the grinding operation [4].

Finely powdered samples (1 μm to 10 μm) minimize QXRD problems such as sample homogeneity, preferred orientation, extinction, and microabsorption [5]. Particle size distribution data (Figure 1) indicate that the grinding procedure used here produces powders in which 99 percent of the particles are finer than 7 μm and only 8 percent of the particles are finer than 0.5 μm (Figure 1a). In comparison, grinding these clinkers in a ring-and-puck mill (both wet and dry grinding) produced powders with a maximum of only 73 percent of the material finer than 10 μm and the finest particles being approximately 0.5 μm (Figure 1b).

Wet grinding for longer than 20 minutes resulted in sample degradation, as evidenced by less intense, broader diffraction peaks. This phenomenon has been observed by Klug and Alexander [5] and was attributed to layers of amorphous material on the particle surfaces as a result of excessive grinding. While the peak areas may not change with this broadening, the overlapping peaks will be more difficult to resolve and weak intensity peaks may be more difficult to separate from the background.

2.2 Scanning Electron Microscopy (SEM) of Polished Sections

Samples (25 g) from the homogenized, reserve material for each RM clinker were split providing a subsample for SEM analysis and X-ray powder diffraction analysis. Two polished sections were examined by backscattered electron imaging and point counted to determine phase abundance composition. The X-ray diffraction (XRD) subsample was prepared using procedures provided later in this paper.

2.3 Salicylic Acid and Methanol Extraction (SAM)

The matrix phases in clinker can be concentrated by SAM extraction, where C_3S and C_2S and CaO are dissolved. The remaining material is comprised of C_4AF, C_3A, MgO, and alkali sulfates [2,3]. The concentration of these phases facilitates their identification by XRD and, when done quantitatively, can be used as another method for determination of total silicate and CaO abundance. The SAM extraction procedure involves the following steps from [2,3]:

(1)   preparation of the SAM solution at 1.0 g of salicylic acid per 5 ml of methanol.

(2)   5-10 g of powdered clinker sample is added to 300 ml of SAM solution in a 500 ml Erlenmeyer flask, methanol is then added to increase the volume to 500 ml and the flask is capped.

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PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION 405030 - NIST/SRD - Rm 8488   DATE 9-24-91

Density 8.15 g/cc   LIQUID 962   Density 0.807 g/cc   Viscosity 4.01 cp   BY ES

Preparation   TEMPERATURE 88 C

RATE 495 START DIA 100 μ

CUMULATIVE MASS PERCENT

EQUIVALENT SPHERICAL DIAMETER μm

(a)

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION   DATE

Density   g/cc   LIQUID   Density   g/cc   Viscosity   cp   BY

Preparation   TEMPERATURE   C

RATE   START DIA   "

CUMULATIVE MASS PERCENT

EQUIVALENT SPHERICAL DIAMETER
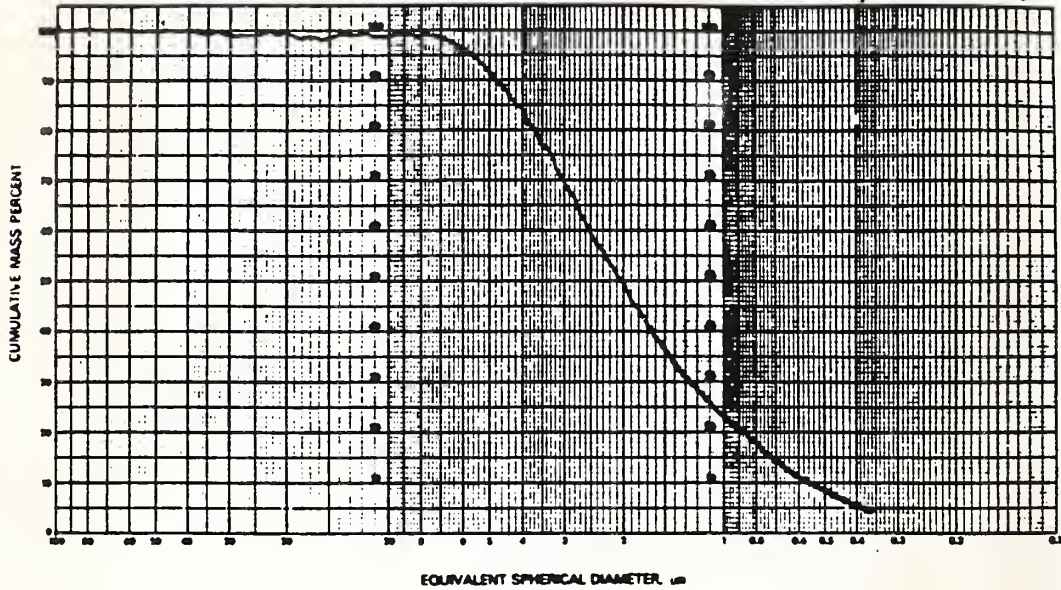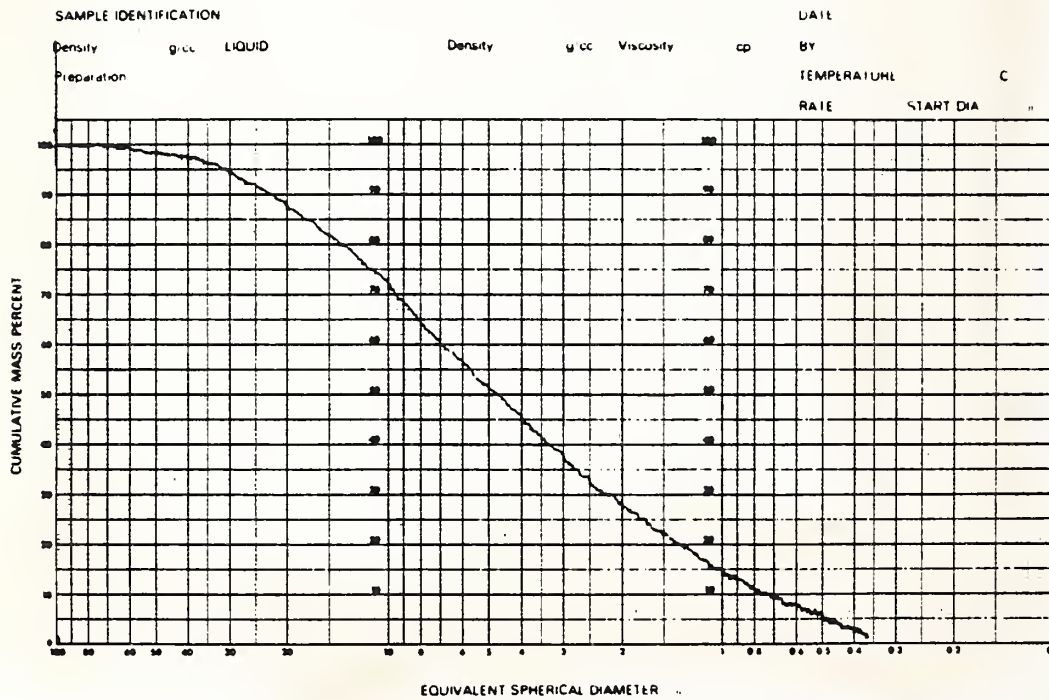
(b)

Figure 1. Particle size distribution data of powders ground in
a micronizing mill (a) and a ring-and-puck mill (b).

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(3) stir the solution for one hour using a magnetic stirring bar, then allow to settle for 15 minutes.

(4) the supernatant is vacuum filtered through a pre-weighed 11 mm diameter Whatman No. 50 filter using a ceramic Buchner funnel and a filter flask. The remaining solids and liquid are poured onto the filter paper, washed with about 250 ml of methanol, and vacuumed dry.

(5) the residue and paper are weighed, the insoluble residue percentage is calculated, and the sample is placed in a sealed glass vial for storage.

2.4 X-Ray Powder Diffraction

An automated Philips X-ray powder diffractometer with sample changer was used for data collection. The system operates at 45 kV and 35 mA using copper Kα radiation, a variable divergence slit, 0.02° receiving slit, diffracted beam monochromater, and a scintillation detector. The diffraction data are processed by personal computer for phase identification, peak profile fitting, and quantitative analysis. Examples of a portion of the powder diffraction patterns of the RM clinkers (Figure 2) show differences in peak intensities reflecting the differences in phase abundances.

Identification of polymorphs of the individual phases in a bulk clinker sample can be difficult because of the large number of overlapping peaks and similarity of the patterns [1]. Monoclinic C_3S is the predominant polymorph in each of the clinkers, although RMs 8486 and 8487 appear to also contain triclinic C_3S.

SEM examination of RMs 8486 and 8488 revealed the presence of cubic and some orthorhombic C_3A. The cubic variety is identified by its fine-grained, equant crystals, and the orthorhombic variety by its lath-shaped crystals [1]. However, the matrix of RM 8487 was too fine-grained for the observation of individual C_3A crystals. Diffraction data of SAM residues did not clearly indicate the presence of orthorhombic C_3A in RM 8487. Because the cubic polymorph is predominant in the other SAM residues cubic RIRs were used for analysis of C_3A.

Inherent problems of QXRD include sample preparation, particle size of the powder, sample heterogeneity, sample absorption effects, preferred orientation, accurate calibrations, and consistent analysis of the diffraction data.

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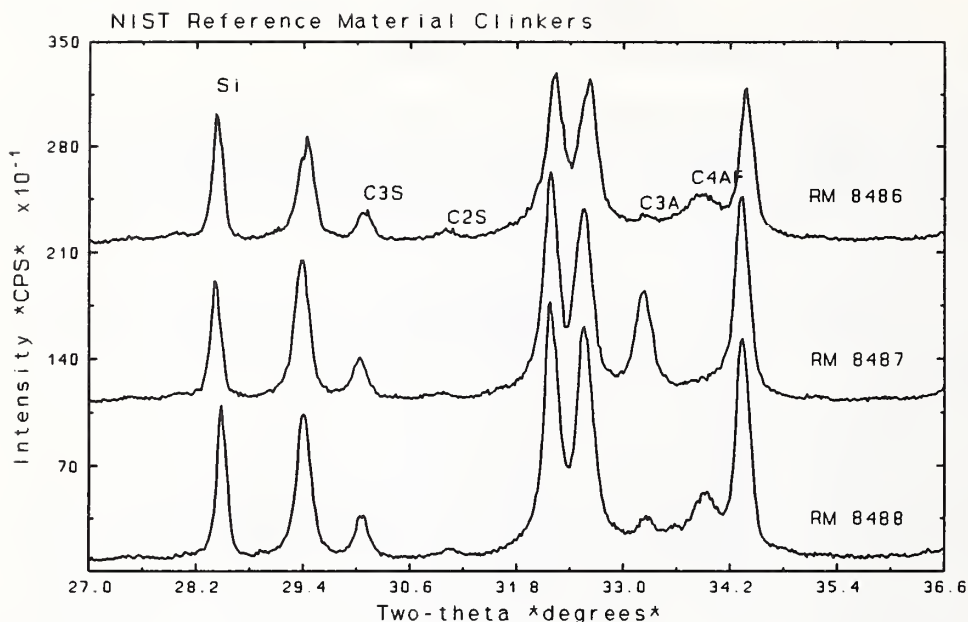
Figure 2. X-ray powder diffraction patterns from RMs 8486, 8487, and 8488.

The program SHADOW[3] was used for profile fitting, and the pseudo-Voight profile shape function provided the best fit to the clinker diffraction peaks. Profile fitting (Figure 3) fits a profile to the raw diffraction data, estimates a background, and separates overlapping peaks. It determines the area under the profile after minimizing the differences between the raw data and calculated profiles, thereby producing a background-subtracted peak area using the calculated profiles. The ability to run SHADOW in batch mode facilitated rapid and reproducible peak area measurements.

Figure 3 also illustrates some potential errors in the use of profile fitting for peak area determination. Cement clinker diffraction patterns are complex, exhibiting many partial to complete peak overlaps. Profile fitting is helpful in resolving partially overlapped peaks or peak groups as seen in Figure 3, but peaks such as the 32.2° and 32.5° fit as single peaks are actually multiple peaks from both C_3S and C_2S. These peaks were not used in this study.

Sample homogeneity problems can be identified by low precision in peak intensities from replicate scans from repacked sample mounts. Based on mass absorption coefficients (about 90 for C_3S and C_2S, 100 to 180 for C_4AF depending on composition, 85 for C_3A, and 28 for MgO), the diffracted beam emanates from approximately the top 35 μm of the packed clinker powder. An extremely fine particle size is desirable since a greater number of particles, ideally of different phases, are then present in the volume of powder.

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[3]Materials Data, Inc., Livermore, CA.
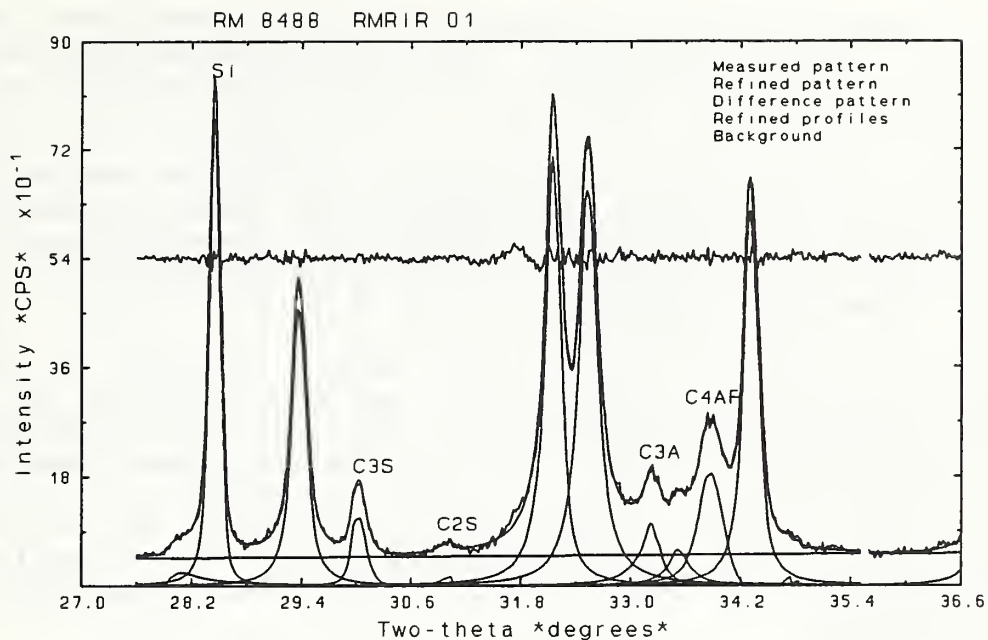
Figure 3. Profile fitting for the determination of background-
subtracted peak areas for labeled peaks of the silicon
internal standard, C_3S, C_2S, C_3A, and C_4AF.

Preferred orientation can be recognized through variation in
relative peak intensities of peaks produced by one phase from
replicate scans. Finely powdered samples and careful use of either
the back-loaded mounting method (used in this study) or side-
drifted mounting method minimize preferred orientation [5,6].

Microabsorption and extinction problems result in incorrect peak
intensities. The apparent concentration of C_4AF, with a relatively
high mass absorption coefficient, will be greater in coarse-
grained powders (greater than 10 μm) due to microabsorption
effects. Particle sizes of less than 10 μm minimize problems due
to microabsorption. Extinction effects arise from destructive
interference of the primary beam with the diffracted beam [4].
Since most of the diffraction peaks used in these analyses are
weak, problems from extinction should be minimal [4].

2.4.1   The Internal Standard or Reference Intensity Ratio
Method for QXRD

The RM cement clinkers are composite samples of more than four
phases, each with a different chemical composition and therefore a
different level of X-ray absorption. While the peak intensities
are roughly proportional to the abundance of a phase in a mixture,

the peak intensity-concentration relationship is not linear because of phase and sample absorption. Klug and Alexander [5] show that an absorption correction can be made by use of an internal standard and calibration curves.

The internal standard is a phase not present in the sample that is added to the mixture in a known proportion. With the addition of a known amount of internal standard, the concentration of the unknown phase can be related to the peak intensity ratio of the unknown and internal standard.

The Reference Intensity Ratio (RIR) method utilizes an internal standard for QXRD and the RIR is a constant relating the X-ray scattering power of a phase to that of the internal standard [7,8]. The RIR is defined as the ratio of the strongest peak of the unknown phase to that of an internal standard in a one-to-one mixture [7,8]. Because of the severe overlapping of the stronger peaks of clinker phases, RIRs for this study were determined for the strongest non-overlapped peaks or peaks that were resolved by profile fitting.

2.4.2 Selection of an Internal Standard

The ideal internal standard should not produce diffraction peaks interfering with peaks from phases in the sample, and should be an easily obtainable, stable, pure material with a fine (1 μm-10 μm) particle size, and low susceptibility to orientation [5]. Some previous QXRD studies of cement clinker and cement have used silicon [3,9,10], rutile [11,12,13], potassium bromide [14], cerium oxide [15] and corundum [1] as an internal standard. Silicon, rutile, and α-alumina X-ray diffraction standards are available from the Standard Reference Materials Program at NIST. This study used NIST SRM 640, silicon powder, as the internal standard.

2.4.3 Clinker Calibration Standards

Selection of standards representative of the unknown samples is important for obtaining correct calibrations. Gutteridge [12] illustrated the variability of diffraction peak positions and intensities for a number of C_3S polymorphs. Significant RIR differences due to compositional variations in other, natural minerals have been reported by Bish and Chipera [6]. Means of obtaining standards include purchase of commercially available pure compounds, selective extraction of phases from the unknown samples, laboratory synthesis of polymorphs and use of separate calibration curves, and calibration from a bulk sample of known phase abundance composition.

Calibration mixtures are not restricted to equally proportioned binary mixtures but, as demonstrated by Chung [7], can be multi-phase mixtures of known phase abundance composition. Bish and Snyder [16] found that multiple calibration mixtures using different phase-to-standard ratios provided more accurate RIRs,

while the use of multiple peaks for each phase minimized effects of preferred orientation.

Therefore for the RIRs used in this study, pure phase calibration mixtures were blended at 50:50 and 80:20 phase-to-standard proportions using phases synthesized at Construction Technology Laboratories. Information on synthesis of pure phases can be found in [17]. Additional calibrations (C_3S, C_2S, and C_4AF) were made using well-characterized subsamples of the RM clinker reserve material. About 25 g of each clinker was split providing samples for QXRD and two polished samples for SEM point count analysis (Table 2).

For the point count analysis, the half width of an approximately 95 percent confidence interval were calculated from eqn. 1:

$$E_{95.4} = 2\sqrt{\frac{P(100-P)}{N}} \qquad (1)$$

where: E = the half width in percent,
           N = the total number of points or grains counted, and
           P = the percentage of the phase:

Phase abundance values from the point count (Table 2) were converted to mass percent values using the density using eqn. 2:

$$W_A = \frac{V_A * P_A \times 100\%}{\Sigma\,[V_X * P_X]} \qquad (2)$$

where: W_A = Mass percent of phase A
           V_A = Volume percent of phase A
           P_A = Density of phase A
     $\Sigma(V_X * P_X)$ = Sum of products for all phases

The QXRD split was blended with internal standard with clinker-to-standard proportions of 80:20 and 91:9. The composite sample was wetted with ethanol to make a slurry and blended with the assistance of a high-power ultrasonic probe. A second homogenization of the dried powder by mortar and pestle improved peak intensity reproducibility.

RIR calibration samples were backloaded against a frosted glass plate in a standard 16 mm by 20 mm cavity mount. Data scans encompassed a 2θ range to include all peaks of interest at a scan rate of 2 seconds per 0.02° (2θ) step. Peak intensity ratios from four replicate scans, with the sample repacked for each scan, were averaged to establish the calibration.

Table 2. Mass percent phase abundance and probable error of SEM point counts for RIR calibrations.

	C_3S	C_2S	C_3A	C_4AF	MgO	CaO
Density g/ml	3.15	3.73	3.58	3.73	3.58	3.34
RM 8488 1600 points	60.8 ±2.4	17.7 ±1.9	4.9 ±1.1	15.9 ±1.7	0.7 ±0.4	3.2
RM 8487 1000 points	66.7 ±3.9	7.3 ±2.3	18.2 ±3.4	4.7 ±1.7	0.0	3.2
RM 8486 540 points	52.7 ±3.1	21.0 ±2.6	2.8 ±1.1	17.0 ±2.1	6.5 ±1.4	0.0

2.4.4   Determination of RIR Values

RIR values (Table 3) were calculated using eqn. 3:

$$K_{i\alpha} = \frac{I_{i\alpha}}{I_{jSi}} \times \frac{X_{Si}}{X_\alpha} \qquad (3)$$

where: $K_{i\alpha}$ = RIR for peak i of phase alpha,
  $I_{i\alpha}$ = Peak intensity (area) of peak i of phase alpha,
  I_{jSi} = Peak intensity (area) of peak j of the internal standard, silicon,
  X_{Si} = Concentration of internal standard in the composite sample and,
  X_α = Concentration of phase alpha in the composite sample

Table 3. Reference Intensity Ratios (I/I_{Si}) as calculated from the RM clinkers and pure phases. Some peaks used only pure phase RIRs (P); blanks indicate peaks not measured for analysis.

PEAK 2θ	PHASE	RM 8486	RM 8487	RM 8488	Pure Phase
12.16	C_4AF	0.0339	0.0339	0.0367	0.0536
21.05	C_3A-Cubic	---	P	---	0.0171
21.84	C_3A-Cubic	P	P	P	0.0344
22.95	C_3S	0.0108	0.0090	0.0111	0.0121
24.36	C_4AF	P	P	P	0.0281
25.14	C_3S	0.0054	0.0066	0.0052	0.0068
30.01	C_3S	0.0249	0.0455	0.0340	0.0344
31.02	$C_2S-\beta$	0.0212	0.0371	0.0316	0.0281
33.2	C_3A	P	P	P	0.5420
35.26	$C_2S-\beta$	0.0082	---	0.0188	0.0182
36.77	$C_2S-\beta$	0.0750	0.1671	0.0550	0.0370
37.33	$C_2S-\beta$	0.0381	P	0.0350	0.0398
42.9	MgO	P	P	P	0.9779
56.1	C_3S	0.1688	0.1733	0.1842	0.1771

2.4.5 QXRD of the RM Clinkers

With the calibration RIRs available, analysis of the unknowns involved the following sequence of steps:

(1) powdering the clinker to -10 μm,

(2) addition and homogenization of a known amount of internal standard forming a composite sample,

(3) collect replicate diffraction patterns, repacking the powder for each scan,

(4) measure the peak areas of the internal standard and clinker phases,

(5) calculate phase abundances by averaging the results from the replicate diffraction patterns.

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Addition of six percent by weight silicon powder to the powdered clinker resulted in a composite sample (clinker plus internal standard) with 5.66 percent silicon. The sample was homogenized using the ultrasonic probe and mortar and pestle as described earlier.

Diffraction scans of the RM clinkers were made from 10 to 54° (2θ) with a two second count time per 0.02° (2θ) step. The concentration of phase alpha in the composite sample is given by eqn. 4:

$$X_\alpha = \frac{I_{i\alpha}}{I_{jSi}} \times \frac{X_{Si}}{RIR_{i,\alpha}} \qquad (4)$$

The concentration of the phase in the original sample is given by eqn. 5:

$$X_\alpha = X_\alpha / (1-X_{Si}) \qquad (5)$$

3.0 RESULTS

Peak intensity variations due to heterogeneity of the composite sample, preferred orientation, and the difficulty in accurate measurement of very weak peaks contribute to the imprecision of the QXRD data. Examination of the QXRD data from replicate scans (Table 4) provides estimates of the precision of this QXRD method and illustrates the necessity of averaging values from multiple scans. The sample standard deviation (STDS) is a measure of how close the values lie to the mean of the distribution. Data in Table 4a is from replicate scans of the same sample mount, without repacking the powder for each scan. The reported weight percentages reflect the variations in peak intensities in the replicate scans resulting from data collection and measurement of the peak areas. Variations in weight percentages in replicate scans of samples repacked for each scan (Table 4b) are greater for most phases. These replicates additionally include the effects of sample heterogeneity and variations in particle orientation.

Results of the QXRD analyses of the RM clinkers with sample set averages and sample standard deviations are given in Tables 5, 6, and 7, duplicate splits of each sample are designated A and B. Data from earlier studies [2,18,19] is provided for comparison. In general, the values are in agreement with those of previous studies. The inter-sample standard deviation values are generally equal to or less than standard deviations of replicate scans indicating that the precision of the analysis was high.

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Table 4. QXRD Data from replicate scans of sample 1, split A from RM 8486, without repacking the powder (a) and replicate scans after repacking the powder for each scan (b). Weight percent values in (a) reflect peak intensity variations due to data collection and processing while (b) additionally includes variations due to sample heterogeneity and particle orientation.

(A)

Phase	Scan 1	Scan 2	Scan 3	Scan 4	Average	STDS*
C_3S	61.26	56.70	55.53	56.78	57.28	1.98
C_2S	22.98	18.37	20.16	17.69	18.79	1.04
C_4AF	8.51	9.47	12.42	11.48	11.08	1.23
C_3A	1.43	1.09	3.69	2.65	2.22	1.19
MgO	3.91	5.45	7.26	5.98	5.65	1.70

(B)

Phase	Scan 1	Scan 2	Scan 3	Scan 4	Average	STDS	RM-STDS**
C_3S	61.26	60.34	66.57	65.47	63.41	3.07	7.55
C_2S	22.98	23.67	24.27	25.01	23.98	0.86	5.16
C_4AF	8.51	8.45	10.84	10.21	9.50	1.21	2.29
C_3A	1.43	2.15	1.85	1.38	1.70	0.37	1.15
MgO	3.91	3.88	4.26	3.97	4.01	0.17	0.69

* - Sample standard deviation (STDS) is a measure of the spread of values about the mean.
** - Sample standard deviation for all 64 replicates of RM set 3.

Table 5. QXRD data for Reference Material Clinker 8486 with
optical microscopy point count data (OM) and QXRD
data from [2,3], QXRD data from [18], and an SEM point
count of one sample [19]. Sample designation 31A
indicates RM set **3**, sample **1**, and duplicate **A**.

Sample	C_3S	C_2S	C_4AF	C_3A	MgO	SUM
31A	63.4	24.0	9.5	1.7	3.5	102.6
31B	57.5	22.6	9.7	1.7	3.5	95.0
32A	58.3	26.4	7.6	1.8	3.5	97.6
32B	64.0	18.7	7.7	1.6	3.5	95.5
33A	59.1	15.9	13.3	2.6	4.1	95.0
33B	61.8	16.5	13.3	3.0	4.9	99.5
34A	55.2	17.4	10.6	2.6	4.0	89.8
34B	59.2	15.1	12.3	4.0	4.5	95.1
35A	58.9	13.3	12.5	3.6	4.6	92.9
35B	64.2	13.9	13.0	3.3	4.8	99.2
36A	57.9	11.6	12.9	2.8	4.4	89.6
36B	59.9	11.2	12.4	2.2	4.5	90.2
37A	64.4	12.2	13.1	3.8	5.1	98.6
37B	65.7	13.2	12.5	3.6	5.1	100.1
38A	61.2	17.5	12.8	2.7	4.6	98.8
38B	62.8	21.3	12.4	4.0	4.8	105.3
Avg.	60.8	16.9	11.6	2.8	4.4	96.5
STDS	3.0	4.6	1.9	0.8	0.5	
OM [2,3]	58.5	23.2	13.7	1.2	3.2	
QXRD [2,3]			11.1	4.7	3.4	
QXRD [18]			12.9	4.0	3.0	
SEM [19]	57.0	23.0	15.0	1.0	4.0	

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Table 6. QXRD data for Reference Material Clinker 8487, with optical microscopy point count (OM) and QXRD data from [2,3], QXRD data from [18], and SEM point count data of one sample from [19].

Sample	C_3S	C_2S	C_4AF	C_3A	MgO	SUM
21A	72.2	11.8	3.4	12.9	0.8	101.2
21B	62.2	10.7	3.5	10.9	0.8	88.0
22A	69.9	11.8	3.1	11.6	0.9	97.3
22B	69.3	11.8	2.1	10.5	0.9	94.6
23A	70.0	11.9	1.5	10.1	0.9	94.4
23B	67.7	10.0	2.5	11.5	0.9	92.6
27A	66.9	11.4	2.9	11.7	0.8	93.7
27B	64.3	9.3	2.3	11.2	0.7	87.8
25A	71.5	10.6	3.0	12.7	0.8	98.7
25B	72.3	12.5	2.7	12.4	0.8	100.9
26A	59.9	12.3	2.4	10.0	0.6	85.2
26B	67.7	12.7	2.3	11.4	0.8	94.9
27A	68.3	9.7	2.8	12.0	0.8	93.6
27B	66.2	9.2	2.4	10.8	0.8	89.4
27A	66.3	10.4	2.2	10.9	0.8	90.5
27B	65.5	10.8	3.2	11.0	0.7	91.2
Average	67.5	11.1	2.7	11.4	0.8	100.5
STDS	3.5	1.3	0.5	0.9	0.1	
OM [2,3]	73.4	7.8	3.3	12.1	0.1	
QXRD [2,3]			2.1	11.3	0.3	
QXRD [18]			2.5	13.0	0.3	
SEM [19]	70.0	3.0	3.3	21.0	0.0	

Table 7. QXRD data for Reference Material 8488, with optical microscopy point count (OM) and QXRD data from [2,3], QXRD data from [18], and SEM point count data of one sample from [19].

Sample	C_3S	C_2S	C_4AF	C_3A	SUM
11A	69.8	16.9	13.8	4.4	104.9
11B	63.0	16.9	14.1	6.4	100.4
12A	61.3	16.6	14.9	4.8	97.6
12B	65.9	17.7	16.5	7.0	107.1
13A	61.5	17.4	15.7	5.8	100.4
13B	62.9	18.7	13.6	4.9	100.1
14A	68.0	17.7	15.8	6.8	107.6
14B	61.1	16.2	14.7	6.2	96.8
15A	61.3	17.5	13.8	6.0	98.6
15B	58.4	15.9	14.5	4.0	92.8
18A	65.1	16.9	16.9	6.8	106.8
18B	57.2	16.9	16.9	6.2	92.7
12A	69.3	16.7	15.5	5.8	106.8
12B	60.0	15.4	13.7	4.9	95.1
18A	63.5	17.9	15.2	5.1	101.7
18B	58.6	13.6	13.3	6.2	91.7
Average	62.9	16.7	14.8	5.8	100.1
STDS	3.8	1.4	1.1	0.9	
OM [2,3]	65.0	18.5	12.1	4.3	
QXRD [2,3]			11.6	4.4	
QXRD [18]			13.5	5.5	
SEM [19]	62.0	22.0	11.0	5.0	

Discrepancies between QXRD and optical data exist for matrix phases C_4AF, and C_3A. Because of their fine particle size these phases are probably the most difficult to quantify by optical microscopy [2,3]. Separate analysis of SAM residues where these phases are concentrated may help in their analysis. Differences in C_2S values for RM 8486 may reflect the heterogeneity of C_2S within the clinker.

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4.0 DISCUSSION

QXRD analysis of cement clinker is difficult because of the complex diffraction patterns and numerous peak overlaps. Selection of weak peaks for calibration is necessary because of these overlaps, making accurate measurement of peak intensities very important. Use of a two second step time in data collection reduced noise, though data collection times were about 1.3 hours. Profile fitting provided peak areas, consistency in background estimation, and resolved most overlapped peaks. Batch processing of the diffraction data made multiple-peak calibrations and analyses simpler. Use of multiple peaks is recommended to minimize orientation effects.

Use of a well characterized subsample from each of the RM clinkers for calibrations was used to address a common QXRD problem, that of matching the standards to the samples. As mentioned earlier, Gutteridge [12] illustrated the variability of peak positions and relative intensities of different polymorphs. Use of a single, laboratory-synthesized pure phase may not be representative of that phase in the unknowns resulting in an inaccurate calibration. Examination of the RIRs for different peaks shows that while some of the differences are very small, differences do exist for other peaks. These differences probably reflect structural and chemical differences between the pure-phase and the industrial clinker standards.

5.0 SUMMARY

Quantitative X-ray powder diffraction data was collected from randomly selected samples of the NIST Reference Material clinkers. Phase abundance values generally agreed with those reported in earlier studies and inter-sample standard deviation values were generally less than or equal to the intra-sample standard deviation values. The ability to accurately and rapidly determine the phase abundances in a cement clinker will aid in the correlation of clinker phase composition with performance and durability properties of cement and concrete. The NIST Reference Material clinkers can be used to test and develop methods of quantitative phase abundance analysis.

6.0 ACKNOWLEDGEMENTS

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TITLE AND SUBTITLE

X-Ray Powder Diffraction Analysis of Three Portland Cement Reference Material Clinkers

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ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

Three portland cement clinker Reference Materials (RMs) are now available from the National Institute of Standards and Technology (NIST). They are intended for use in testing and developing methods for quantitative phase abundance analysis and have been selected as representative of the range of compositions and textures of North American clinkers.

Quantitative X-ray powder diffraction analysis was used to determine the phase abundance composition and compositional variability of eight randomly selected samples from each RM. In addition, each sample was split for duplicate analyses for evaluation of intra-sample phase abundance variability. The Reference Intensity Ratio method was used for powder diffraction calibrations and quantitative analysis. Both pure-phase standards and subsamples of the RM clinkers, which were point counted using the scanning electron microscope, were used for calibrations. Phase abundance values generally agree with those reported in earlier studies and the inter-sample standard deviation values were generally less than or equal to the intra-sample standard deviation values.

KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

Cement clinker; composition; optical microscopy; quantitative analysis; reference materials; scanning electron microscopy; X-ray powder diffraction