National Institute of Standards & Technology

Report of Investigation

Reference Materials 8486, 8487, 8488

Portland Cement Clinker

These Reference Materials (RM's) are intended primarily for use in the determination of the abundance of major phases in cement clinkers, i.e., the percentages of alite (C_3S)*, belite (C_2S), aluminate (C_3A), and ferrite $C_2(A,F)$. These RM's provide samples so investigators in different laboratories can be assured that they are investigating the same materials. Each RM consists of three hermetically-sealed, glass vials containing approximately 10 grams of crushed portland cement clinker. The materials selected for these three RM's differ widely in phase abundance, crystal sizes, and distribution of crystals.

Background

Portland cements produced in the United States are assessed by their conformance to ASTM C 150 "Standard Specification for Portland Cement," comprising chemical composition requirements, fineness specifications, and performance in physical tests. The ASTM C 150 compositional requirements are defined entirely by the computed cement compound composition, based on the "Bogue" formula which gives the theoretical phase abundance of the cement in terms of the ideal pure compounds: C_3S, C_2S, C_3A, C_4AF, and C_2F. A large part of portland cement performance can be attributed to the abundance of phases found in clinker. It is well known, however, that actual phase abundance in clinker is influenced by many factors, including minor elements such as magnesium, sulfur, potassium, and sodium, as well as the raw feed, particle size, kiln atmosphere, and thermal history.

Currently, no standard test methods exist for determining clinker phase abundance, although analytical techniques do exist that are capable of determining phase abundance. The problem appears to lie in the complexity of clinker phases, and in the difficulty and expense of conducting quantitative phase analysis by either of the two applicable techniques, quantitative X-ray diffraction (QXRD) or microscopic point counting (MPC). Task groups under ASTM and RILEM are actively pursuing specifications of standard methods for the quantitative phase analysis of cements and clinkers by both QXRD and MPC methods. The availability of the RM's should make the work of these groups much easier. Furthermore, industry representatives have expressed a need for such reference materials. These RM's can be used by cement plant operators to aid in developing techniques to assess the quality of portland cement as it is being produced.

Several studies [1,2,3,4,5] have compared the results of QXRD and MPC methods with the predictions of chemical analysis and the Bogue calculations. The studies indicate that for the silicate phases, MPC is more precise than QXRD (i.e., the interlaboratory errors are smaller), because there is relatively little disagreement between laboratories regarding microscopic identification of alite and belite. On the other hand, QXRD methods can distinguish some phases that cannot be accurately measured by microscopy. QXRD and MPC are therefore complementary techniques.

*Cement chemist's notation: $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$

Disclaimer - Certain commercial equipment, instruments, and materials are identified in this report to adequately specify the procedures used for the preparation of these RM's. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the equipment, instruments, and materials are necessarily the best available for the purpose.

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Stanley D. Rasberry, Chief
Office of Standard Reference Materials

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The microscopical method is restricted to the analysis of coarsely crushed clinker because cement is too finely ground to produce useful polished sections or thin sections, therefore, the RM's are crushed clinker rather than finely ground cement. As pointed out by Aldridge[1], the restriction to crushed material as opposed to finely ground entails the risk of sampling error when attempting to analyze a batch of normal production clinker at a cement plant. However, for these materials we believe that the crushed clinker is suitable since they have been restricted to a narrow size range and were carefully selected to minimize variability between samples.

Source and Processing

Approximately 454 kg of each clinker was obtained from three selected cement plants and analyzed for particle size distribution by sieving to determine the modal particle size. The purpose of this process was to reduce the variability in the RM's by eliminating clinker nodules in which the phase abundance and crystal characteristics might be significantly different from the modal size, due to differences in thermal history.

Twenty-four inch, square sieves were used for this purpose with their mesh openings checked for size in accordance with ASTM D-11, "Standard Specification for Wire Cloth Sieves." The sieve analyses are given below:

Weight Percent Retained on U.S. Standard Sieves

Sieve Openings	RM 8486	RM 8487	RM8488
19mm	16.3	17.2	18.6
12.5mm	16.7	22.4	15.0
4.75mm	30.6	35.0	26.0
2.36mm	12.1	10.7	9.2
Pan	24.1	14.7	31.2

Based on these sieve analyses, the following size fractions were selected for further processing:

RM 8486: 2.4 - 12.5mm
RM 8487: 4.8 - 12.5mm
RM 8488: 2.4 - 12.5mm

Clinker from two 55-gal barrels of each source was sieved to produce the narrow size fraction noted above. (Information on the sources of the clinkers, raw feed data, kiln data, and clinker cooler data are given in the attached "source record" for each clinker.) The material was then passed through a Denver roller crusher (10-in rolls) and the product sieved on the No. 8 (2.36 mm) and No. 16 (1.18 mm) sieves. Material in this size range was retained as the final product ready for blending. Oversize clinker was repeatedly passed through the roller crusher and sieved until all the clinker was processed and material passing the No. 16 sieve was discarded. This processing produced the following masses of RM's which were sealed in stainless steel barrels ready for blending: RM 8486-85 Kg; RM 8487-68 Kg; RM 8488-90 Kg.

The clinkers were homogeneized using a Littleford Bros. Model FM-130D blender. This type of blender with air seals and plow-shape blades was chosen for its rapid mixing with minimal grinding action. The blender was operated for five minutes to homogenize each clinker which was then loaded into plastic-lined steel drums. The blending and transferring operations were performed in a room maintained at 23 ± 2 °C and 50 ± 5 % relative humidity.

Packaging

The clinkers were sealed in inner shell vials using Lumelite low-density polyethylene snap caps. The filling operation was performed in a glove box continuously purged with argon, using spinning rifflers to evenly distribute the clinkers with minimal segregation. The inner vials were then loaded into "outer" shell vials, cap end downward, a fiberglass pad was inserted, and the outer vial was flame sealed using the NIST flame sealing machine. Approximately 2500 vials of each clinker were produced and the remaining clinker was stored in sealed steel barrels for future sealing in individual glass vials.

Homogeneity Testing

No rapid, precise method exists for determining phase abundance in clinker. Therefore, homogeneity of the clinkers was assessed by X-ray fluorescence spectrometric analysis for four chemical elements, using methods developed to assess the homogeneity of the NIST cement SRM's. Calcium, silicon, aluminum, and iron are the four most abundant elements in clinker and the principal constituents of the four major clinker phases. Counts were collected for each of these elements using a Rigaku Model 3064 XRF spectrometer with the following instrument settings:

Analyte	X-Ray Line	Crystal	Detector	Angle (°2Θ)	Count Time (sec)
Ca	K_β	LiF (200)	FPC	100.22	20
Si	K_α	EDDT	FPC	108.19	80
Al	K_α	EDDT	FPC	142.84	80
Fe	K_α	LiF(200)	SC	57.49	80

Two specimens were prepared from each of 6 randomly selected glass vials by the following method. Approximately 0.700 g of clinker was ground by hand using a high-density alumina mortar and pestle. (This sample mass contained approximately 150 clinker particles, roughly the number of particles viewed in a microscopical point count specimen.) Next, 0.5000 ± 0.0005 g ground clinker was added to 6.5000 ± 0.0005 g lithium tetraborate (EM Reagents Spectromelt A10), stirred to mix well in a 30 mL Pt/5% Au Claisse-form crucible, fused at approximately 1025 °C for ten minutes using a Leco FX-200 fluxer, and cast in a 31 mm diameter Pt/5% Au Claisse-form mold. The cooled fused disc was ground flat using diamond impregnated, metal bonded abrasive wheels of 70 μm and the 30 μm grits. The ground discs were then analyzed in an X-ray spectrometer in randomized order.

Data from the homogeneity tests were analyzed using Construction Technology Laboratory's (CTL's) version of the NIST program HOMOTS, written by Pella, Paule, and Tao. No significant differences were observed for the four analytes in the selected specimen. The within-vial variability of these RM's is considerably larger than that usually observed for the NIST cement SRM's. These clinkers show relative standard deviations (RSD's) ranging roughly between one and eight percent. The higher RSD values are likely caused by the clinker being coarsely crushed rather than finely ground. The clinker particle size was chosen after thorough evaluation of the compromise required to produce millimeter-size particles for microscopical use at the expense of high homogeneity obtainable with finer material. Chemical analyses by X-ray spectrometry is given in Table 1.

Table 1. Chemical Analysis by X-ray Fluorescence Spectrometry (wt.%)

	RM 8486	RM 8487	RM 8488
Analyte			
SiO_2	22.48	21.43	22.68
Al_2O_3	4.70	5.53	4.90
Fe_2O_3	3.60	1.98	4.07
CaO	63.36	67.20	66.50
MgO	4.73	1.48	0.98
SO_3	0.27	0.83	0.31
Na_2O	0.10	0.14	0.11
K_2O	0.42	0.72	0.35
TiO_2	0.25	0.27	0.24
P_2O_5	0.06	0.29	0.08
Mn_2O_3	0.10	0.04	0.03
SrO	0.05	0.11	0.13
L.O.I.	0.16	0.17	0.21
Total	100.28	100.20	100.60
Calculated compounds (per ASTM C 150-86)			
C_3S	48	65	57
C_2S	28	12	22
C_3A	7	13	7
C_4AF	11	6	12

Microscopical Point Counting

Manual point counting using a reflected light microscope was chosen as the primary method for determining the abundance of phases in the three clinkers. In typical clinkers, the major and minor phases are clearly visible after appropriate specimen preparation such as grinding, polishing, and etching. However, expertise is needed to identify phases and to distinguish artifacts (voids, epoxy, polishing grit, etc.) from clinker phases. The task of collecting 3100 points per specimen on four specimens of each clinker (over 37,000 points in all) was performed by Dr. Donald H. Campbell, Principal Research Petrographer of the Construction Technology Laboratories, using the following procedures:

Crushed clinker particles from each of the randomly selected vials were encapsulated/impregnated with epoxy resin (Epo-Tek 301, n = 1.56) in labelled, 25.4-mm diameter polyethylene cups. Each encapsulation was cut with a slow-speed diamond-rimmed saw (Buehler Isomet). The sawcut surface was ground on horizontal, rotating, metal-bonded diamond grinding wheels and polished with 0.3 μm alumina on Buehler Texmet. Propylene glycol was used as the cutting and grinding vehicle and isopropyl alcohol was used as the cleaning fluid between grinding and polishing steps. After polishing, the prepared surface was ultrasonically cleaned for five minutes in isopropyl alcohol.

To facilitate phase identification during the point count, the polished surface was etched with distilled water at approximately 40 °C for 8-10 sec, dried with forced warm air, etched with nital (99 mL isopropyl alcohol plus 1 mL nitric acid) for 6-8 sec, and dried again.

The point counting was performed using a Leitz Ortholux microscope with achromat objective lenses selected to provide magnifications such that successive points did not fall on the same crystal (except for a very few large crystals of alite). A 25-point square grid eyepiece reticle was used to define the points. For each encapsulation, the phase under each point was identified and counted electronically (Swift Model F 415C) along successive lines of traverse until approximately 3100 total points had been counted. The lines of each traverse across the polished section were positioned manually at an arbitrary interval of 1 mm. Each polished section required approximately 150 fields of view to establish a sufficient number of points. Approximately 150 clinker particles were traversed in each polished section.

The point count data were converted to weight percentages as given in Tables 2, 3, and 4. Weight percentages were calculated from the point count volume percentages by the following formula:

$$W_A = \frac{V_A \cdot P_A \times 100\%}{\Sigma_x [V_x . P_x]}$$

W_A = wt. % phase A
V_A = volume % phase A
P_A = density phase A
$\Sigma_x(V_x.P_x)$ = sum of products for all phases

Example (RM 8486)

Phase	P_A density	V_A observed volume%	$V_A \cdot P_A$	W_A calculated weight %
alite	3.15	60.51	190.6	58.47
belite	3.28	23.04	75.57	23.18
aluminate	3.03	1.24	3.76	1.15
ferrite	3.73	11.95	44.57	13.67
free CaO	3.34	0.18	0.60	0.18
periclase	3.58	2.92	10.45	3.21
alkali sulfate	2.66	0.17	0.45	0.14
			$\Sigma (v_A.P_A) = 326.0$	

Crystal form and etch characteristics clearly distinguish the silicate phases. The typical lamellar structure of belite and its normally round to subround form render an easy identification, separating it from the subhedral to euhedral, pseudohexagonal form of alite.

Because of the very fine crystalline nature of some interstitial phases, it was necessary to produce polished sections of the highest possible quality. Even so, recognition was particularly difficult for some of the tiny C_3A grains that occurred between ferrite crystals in RM 8486. Therefore, the reflected light microscopy (RLM) values for aluminate and ferrite in RM 8486 are close in total to the aluminate plus ferrite values obtained by XRD (not reported herein, and is the subject of ongoing work at NIST) but the XRD values are likely to be more accurate for the individual phase percentages.

At present, RLM does not permit discrimination among alkali sulfate phases. Thus, they were counted as a single group.

Recommended Phase Abundance

The abundance of phases, in weight percent, in the three clinkers are given in Tables 2, 3, and 4. The phases were determined by point counting using reflected light microscopy. The recommended values are the averages of 4 measurements from a single laboratory and the uncertainty is reported as the observed standard deviation of a single measurement. The uncertainty is not given as a statement of accuracy but rather as an indication of the expected precision when performing point counting using reflected light microscopy.

NIST will continue to characterize these RM's in an attempt to upgrade them to SRM status. Also work in ASTM task groups CO1.23.01 and CO1.23.02 is expected to provide additional data for updating these RM's and extend their utility.

Much more information about the preparation and analysis of these RM's will be given in a planned NIST Special Publication "Production and Characterization of Portland Cement Clinker Phase Abundance Reference Materials".

Table 2

RM 8486

Weight Percentages

	----------Sample No.----------					
Phase	1	2	3	4	Mean	Observed Std. Dev.
Alite	59.05	56.37	60.30	58.15	58.47	1.65
Belite	23.01	25.34	20.66	23.70	23.18	1.94
Aluminate	1.17	1.14	1.02	1.26	1.15	0.10
Ferrite	13.09	13.17	14.27	14.18	13.68	0.63
Free CaO	0.27	0.10	0.03	0.33	0.18	0.14
Periclase	3.09	3.79	3.72	2.23	3.21	0.72
Alkali sulfate	0.32	0.08	0.00	0.16	0.14	0.14
Totals	100.00	99.99	100.00	100.01	100.01	

Table 3

RM 8487

Weight Percentages

Phase	----------Sample No.---------- 1	2	3	4	Mean	Observed Std. Dev.
Alite	73.19	71.64	73.25	75.46	73.39	1.57
Belite	7.29	9.59	7.14	6.98	7.75	1.23
Aluminate	12.43	12.29	12.82	10.82	12.09	0.88
Ferrite	4.00	3.72	2.78	2.56	3.27	0.70
Free CaO	2.25	1.91	3.01	2.63	2.45	0.48
Periclase	0.03	0.21	0.03	0.07	0.09	0.09
Alkali sulfate	0.82	0.62	0.98	1.49	0.98	0.37
Totals	100.01	99.98	100.01	100.01	100.02	

Table 4

RM 8488

Weight Percentages

Phase	----------Sample No.---------- 1	2	3	4	Mean	Observed Std. Dev.
Alite	65.14	64.98	64.20	65.54	64.97	0.56
Belite	18.30	19.31	18.48	17.94	18.51	.58
Aluminate	3.08	4.15	3.87	6.24	4.34	1.35
Ferrite	13.46	11.56	13.20	10.25	12.12	1.50
Free CaO	0.00	0.00	0.00	0.00	0.00	0.00
Periclase	0.00	0.00	0.18	0.03	0.05	0.09
Alkali sulfate	0.02	0.00	0.08	0.00	0.03	0.04
Totals	100.00	100.00	100.00	100.00	100.02	

These RM's were prepared and characterized by the Construction Technology Laboratories, Inc., Skokie, Illinois 60077-1030, on contract to the National Institute of Standards and Technology.

The overall direction and coordination of the technical measurements were performed by H. Kanare of the Construction Technology Laboratories.

The technical and support aspects involved in the preparation and development of these RM's were coordinated through the Office of Standard Reference Materials by T.E. Gills.

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