Designation: C 1365 – 06

Standard Test Method for Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-Ray Powder Diffraction Analysis[1]

1. Scope*

1.1 This test method covers direct determination of the proportion by mass of individual phases in portland cement or portland-cement clinker using quantitative X-ray (QXRD) analysis. The following phases are covered by this standard: alite (tricalcium silicate), belite (dicalcium silicate), aluminate (tricalcium aluminate), ferrite (tetracalcium aluminoferrite), periclase (magnesium oxide), gypsum (calcium sulfate dihydrate), bassanite (calcium sulfate hemihydrate), anhydrite (calcium sulfate), and calcite (calcium carbonate).

1.2 This test method specifies certain general aspects of the analytical procedure, but does not specify detailed aspects. Recommended procedures are described, but not specified. Regardless of the procedure selected, the user shall demonstrate by analysis of certified reference materials (CRM's) that the particular analytical procedure selected for this purpose qualifies (that is, provides acceptable precision and bias) (see Note 1). The recommended procedures are ones used in the round-robin analyses to determine the precision levels of this test method.

NOTE 1—A similar approach was used in the performance requirements for alternative methods for chemical analysis in Test Methods C 114.

1.3 The values stated in SI units shall be regarded as the standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazards, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

C 114 Test Methods for Chemical Analysis of Hydraulic Cement

C 150 Specification for Portland Cement

C 183 Practice for Sampling and the Amount of Testing of Hydraulic Cement

C 219 Terminology Relating to Hydraulic Cement

C 670 Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions are in accordance with Terminology C 219.*

3.2 *Phases* (**1**):[3]

3.2.1 *alite*, *n*—tricalcium silicate (C_3S)[4] modified in composition and crystal structure by incorporation of foreign ions; occurs typically between 30 to 70 % (by mass) of the portland-cement clinker; and is normally either the M_1 or M_3 crystal polymorph, each of which is monoclinic.

3.2.2 *alkali sulfates*, *n*—arcanite (K_2SO_4) may accommodate Na^+, Ca2$^+$, and CO_3 in solid solution, aphthitalite ($(K_{4-x},Na_x)SO_4$ with x usually 1 but up to 3), calcium langbeinite ($K_2Ca_2[SO_4]_3$) may occur in clinkers high in K_2O, and thenardite (Na_2SO_4) in clinkers with high Na/K ratios (**1**).

3.2.3 *aluminate*, *n*—tricalcium aluminate (C_3A) modified in composition and sometimes in crystal structure by incorporation of a substantial proportion of foreign ions; occurs as 2 to 15 % (by mass) of the portland-cement clinker; is normally cubic when relatively pure and orthorhombic or monoclinic when in solid solution with significant amounts of sodium (**2**).

3.2.4 *anhydrite*, *n*—calcium sulfate ($C\overline{S}$) and is orthorhombic (see Note 2).

NOTE 2—Calcium sulfate is added to the clinker during grinding to control setting time, strength development, and volume stability. Several phases may form as a result of dehydration of gypsum. The first 1.5

***A Summary of Changes section appears at the end of this standard.**

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[1] This test method is under the jurisdiction of ASTM Committee C01 on Cement and is the direct responsibility of Subcommittee C01.23 on Compositional Analysis.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[4] When expressing chemical formulae, C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, M = MgO, $\overline{S}$ = SO_3, and H = H_2O.

molecules of water are lost between 0 and 65 °C with minor changes in structure; and, above 95 °C, the remaining 0.5 molecules of water are lost transforming the structure to the metastable γ polymorph of anhydrite (sometimes referred to as 'soluble anhydrite') and subsequently the orthorhombic form (**3**).

3.2.5 *bassanite*, *n*—calcium sulfate hemihydrate ($C\overline{S}H_{1/2}$) and is monoclinic.

3.2.6 *belite*, *n*—dicalcium silicate (C_2S) modified in composition and crystal structure by incorporation of foreign ions; occurs typically as 15 to 45 % (by mass) of the portland-cement clinker as normally the β polymorph, which is monoclinic. In lesser amounts, other polymorphs can be present.

3.2.7 *calcite*, *n*—calcium carbonate is trigonal and may be present in a cement as an addition or from carbonation of free lime.

3.2.8 *ferrite*, *n*—tetracalcium aluminoferrite solid solution of approximate composition $C_2(A,F)$ modified in composition by variation in the Al/Fe ratio and by substantial incorporation of foreign ions as $C_4A_XF_{2-X}$ where $0 < x < 1.4$; constituting 5 to 15 % (by mass) of a portland-cement clinker; and is orthorhombic.

3.2.9 *free lime*, *n*—free calcium oxide (C); cubic (see Note 3).

NOTE 3—Free lime (CaO) may be present in clinker and cement but readily hydrates to form portlandite ($Ca(OH)_2$). Portlandite may carbonate to form calcium carbonate, generally as calcite. Heat-treating a freshly-ground sample to 600 °C is useful to convert any portlandite back to free lime but will also dehydrate the hydrous calcium sulfate phases (gypsum and bassanite) to anhydrite.

3.2.10 *gypsum*, *n*—calcium sulfate dihydrate ($C\overline{S}H_2$) and is monoclinic .

3.2.11 *periclase*, *n*—free magnesium oxide (M); cubic.

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *Certified Reference Material (CRM)*, *n*—a material whose properties (in this case phase abundance, XRD peak position or intensity, or both) are known and certified (see Note 4).

NOTE 4—NIST Standard Reference Material (SRM®) Clinkers 2686, 2687, and 2688 are suitable CRMs for qualification.[5]

3.3.2 *diffractometer*, *n*—the instrument, an X-ray powder diffractometer, for determining the X-ray diffraction pattern of a crystalline powder.

3.3.3 *phase*, *n*—a homogeneous, physically distinct, and mechanically separable portion of a material, identifiable by its chemical composition and crystal structure.

3.3.3.1 *Discussion*—Phases in portland-cement clinker and cements that are included in this test method are four major phases (alite, belite, aluminate, and ferrite) and one minor phase (periclase).

3.3.3.2 *Discussion*—Precision values are provided for additional phases (gypsum, bassanite, anhydrite, arcanite, and calcite). Values for these constituents may be provided using this method but are considered informational until suitable certified reference materials for qualification are available.

3.3.4 *qualification*, *n*—process by which a QXRD procedure is shown to be valid.

3.3.5 *Rietveld analysis*, *n*—process of refining crystallographic and instrument variables to minimize differences between observed and calculated X-ray powder diffraction patterns for one or more phases, estimating their relative abundance.

3.3.6 *standardization*, *n*—process of determining the relationship between XRD intensity and phase proportion for one or more phases (see Note 5).

NOTE 5—In the literature of X-ray powder diffraction analysis, the standardization process has been commonly referred to as calibration; however, we have determined that standardization is a more accurate term.

3.3.6.1 *Discussion*—Rietveld analysis uses crystal structure models to calculate powder diffraction patterns of phases that serve as the reference patterns. The pattern-fitting step seeks the best-fit combination of selected pattern intensities to the raw data. The relative pattern intensities along with the crystallographic attributes of each phase are used to calculate relative abundance. The standardization approach uses powdered samples of pure phases to assess the relationship between diffraction intensity ratios and mass fraction ratios of two or more constituents; and is referred to here as the traditional method.

3.3.7 *X-ray diffraction (XRD)*, *n*—the process by which X-rays are coherently scattered by electrons in a crystalline material.

4. Background

4.1 This test method assumes general knowledge concerning the composition of cement and portland-cement clinker. Necessary background information may be obtained from a number of references (**1, 4**).

4.2 This test method also assumes general expertise in XRD and QXRD analysis. Important background information may be obtained from a number of references (**5-10**).

5. Summary

5.1 This test method covers direct determination of the proportion by mass of individual phases in cement or portland-cement clinker using quantitative X-ray powder diffraction analysis. The following phases are covered by this standard: alite (tricalcium silicate, C_3S), belite (dicalcium silicate C_2S), aluminate (tricalcium aluminate, C_3A), ferrite (tetracalcium aluminoferrite, C_4AF), periclase (magnesium oxide, M), arcanite (potassium sulfate, ($K\overline{S}$)), gypsum (calcium sulfate dihydrate, ($C\overline{S}H_2$)), bassanite (calcium sulfate hemihydrate, ($C\overline{S}H_{1/2}$)), anhydrite (calcium sulfate ($C\overline{S}$)), and calcite (calcium carbonate, $CaCO_3$.

A QXRD test procedure includes some or all of the following: *(a)* specimen preparation; *(b)* data collection and phase identification; *(c)* standardization (for the standardization approach); *(d)* collecting a set of crystal structure models for refinement (for the Rietveld approach); *(e)* use of an internal or external standard (to correct for various effects on intensity besides phase proportion); *(f)* analysis of the sample (in which the powder diffraction pattern is measured and/or the intensity

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[5] Portland cement clinker SRM's® from the Standard Reference Material Program, National Institute of Standards and Technology.

of selected XRD peaks or patterns are measured); and *(g)* calculation of the proportion of each phase.

5.2 This test method does not specify details of the QXRD test procedure. The user must demonstrate by analysis of certified reference materials that the particular analytical procedure selected for this purpose provides acceptable levels of precision and bias. Two recommended procedures (the Rietveld approach and the traditional approach used to determine the acceptable levels of precision and bias) are given in Appendix X1 and Appendix X2.

6. Significance and Use

6.1 This test method allows direct determination of the proportion of some individual phases in cement or portland-cement clinker. Thus it provides an alternative to the indirect estimation of phase proportion using the equations in Specification C 150 (Annex A1).

6.2 This test method assumes that the operator is qualified to operate an X-ray diffractometer and to interpret X-ray diffraction spectra.

6.3 This test method may be used as part of a quality control program in cement manufacturing.

6.4 This test method may be used in predicting properties and performance of hydrated cement and concrete that are a function of phase composition.

6.5 QXRD provides a bulk analysis (that is, the weighted average composition of several grams of material). Therefore, results may not agree precisely with results of microscopical methods.

7. Apparatus

7.1 *X-Ray Diffractometer*—The X-ray diffractometer allows measurement of the X-ray diffraction pattern from which the crystalline phases within the sample may be qualitatively identified and the proportion of each phase may be quantitatively determined. X-ray diffractometers are manufactured commercially and a number of instruments are available. The suitability of the diffractometer for this test method shall be established using the qualification procedure outlined in this test method.

8. Materials

8.1 *Standardization Phases*—The use of standardization phases is recommended for establishing the intensity ratio/mass ratio relationships when using the traditional quantitative method. These phases must usually be synthesized (**12, 13**).

8.2 *CRM Clinker*—The use of three CRM clinkers is required to qualify the QXRD procedure.

8.3 *Internal Standard*—The use of an internal standard is recommended for the standardization approach. Suitable materials include chemical reagents (see 8.4) or CRM's (see Appendix X1).

8.4 *Reagent Chemicals*—Reagent grade chemicals, if used either as an internal standard or during chemical extraction of certain phases, shall meet the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the chemical is sufficiently pure to permit its use without lessening the accuracy of the determination.

9. Hazards

9.1 The importance of careful and safe operation of an X-ray diffractometer cannot be overemphasized. X-rays are particularly hazardous. An X-ray diffractometer must be operated safely to avoid serious injury or death. The X-rays are generated by high voltages, perhaps as high as 55 kV peak, requiring care to avoid serious electric shock. Klug and Alexander (**6**) (pp. 58–60) state, "*The responsibility for safe operation rests directly on the individual operator*" (italics are theirs).

10. Sampling and Sample Preparation

10.1 Take samples of cement in accordance with the applicable provisions of Practice C 183. Take samples of portland-cement clinker so as to be representative of the material being tested.

10.2 Prepare samples as required for the specific analytical procedure (see Appendix X2).

11. Qualification and Assessment

11.1 *Qualification of Test Procedure*:

11.1.1 When analytical data obtained in accordance with this test method are required, any QXRD test procedure that meets the requirements described in this section may be used.

11.1.2 Prior to use for analysis of cement or portland-cement clinker, qualify the QXRD test procedure for the analysis. Maintain records that include a description of the QXRD procedure and the qualification data (or, if applicable, re-qualification data). Make these records available to the purchaser if requested in the contract or order.

11.1.3 If more than one X-ray diffractometer is used in a specific laboratory for the same analysis, even if the instruments are substantially identical, qualify each separately.

11.1.4 If more than one procedure is used to mount specimens for QXRD, the use of each procedure shall constitute a separate test procedure and each procedure shall be qualified separately.

11.1.5 Qualification shall consist of replicate determinations of the three SRM® clinkers, re-mounting the specimen for each analysis, (see Note 6) for the proportions of C_3S, C_2S, C_3A (cubic and orthorhombic), C_4AF, and M using the desired QXRD procedure (see Note 7).

NOTE 6—Prior to qualification, it may be convenient to carry out a preliminary assessment in which one or more mixtures of synthetic phases are analyzed. Such a preliminary assessment should produce no more than the permissible variation described in 11.2.

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[6] *Reagent Chemicals, American Chemical Society Specifications* , American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

NOTE 7—It is recommended that at least two replicate analyses be carried out, but three determinations may be used for assessing permissible variation.

11.2 *Permissible Variation*:

11.2.1 The values of permissible variation were computed from the within-laboratory standard deviation values obtained in round robin analyses of mixtures of SRM® clinkers and synthetic phases (see 14.2).

11.2.1.1 *Discussion*—Qualification limits in Table 2 are prediction intervals (95 %) for a future mean and are designed to bracket values of a mean of k (=2,3,4) future measurements of the relevant phases. The intervals are based upon the performance of the 11 round robin participants.

11.2.2 Replicate analyses shall differ from each other by no more than the within-lab repeatability value shown in Table 1.

11.2.3 The mean result shall differ from the known value by no more than the value shown in Table 2 for the particular number of replicates.

11.2.4 *Known Values*—The known values of each phase in the SRM® clinkers provided by NIST was determined using quantitative X-ray powder diffraction and optical microscopy (**11**).

11.3 *Partial Results*:

11.3.1 QXRD procedures that provide acceptable results for some phases but not for others shall be used only for those phases for which acceptable results are obtained. However, it is not expected that a QXRD procedure would provide acceptable results for some phases and not for others, and such a result may indicate that the procedure is not, in fact, valid.

11.4 *Assessing the Diffractometer*:

11.4.1 The procedures described in the Annex shall be used to assess the diffractometer. Note that assessment is different from qualification or re-qualification.

11.4.2 The diffractometer shall be assessed each month that this test method is used.

11.4.3 The diffractometer shall be assessed after any substantial modification in the instrument (see Note 8).

NOTE 8—Substantial modification of the diffractometer includes changing the X-ray tube, changing a detector, adding or removing a monochromator, and realignment.

11.4.4 QXRD procedure shall be assessed upon receipt of evidence that the test procedure is not providing data in accordance with the permissible variation.

TABLE 1 Permissible Maximum Difference Between Replicate Values (percent of clinker or cement)^A

	Repeatability Within-Lab		Reproducibility Between-Lab	
	s-within	d2s-within	s-between	d2s-between
alite	0.74	2.04	2.27	6.30
belite	0.64	1.77	1.40	3.87
aluminate	0.47	1.31	0.79	2.19
ferrite	0.49	1.36	0.89	2.47
periclase	0.23	0.63	0.50	1.39
arcanite	0.22	0.60	0.34	0.94
gypsum	0.21	0.59	0.59	1.65
bassanite	0.39	1.08	0.58	1.60
anhydrite	0.27	0.74	0.64	1.77
calcite	0.99	2.73	0.50	1.50

^{A}As described in Practice C 670.

TABLE 2 Permissible Maximum Difference Between Mean Value and Known Value (Mass percent) Expressed at a 95 % Confidence Level for the Mean of a Selected Number of Replicates (k) = 2, 3, 4^A

Phase	2 replicates	3 replicates	4 replicates
alite	5.93	4.91	4.31
belite	3.70	3.06	2.69
aluminate	2.14	1.77	1.55
ferrite	2.46	2.04	1.79
periclase	0.77	0.64	0.56
arcanite	0.85	0.70	0.61
gypsum	1.55	1.28	1.12
bassanite	1.52	1.26	1.11
anhydrite	1.67	1.38	1.21
calcite	0.68	0.56	0.49

^{A}Computed from within-laboratory standard deviation using 95 % confidence interval and 30 df.

11.5 *Re-qualification of QXRD Procedure*:

11.5.1 If assessment shows that the X-ray diffractometer is not properly aligned (as discussed in Annex A1), it shall be realigned following the manufacturer's instructions. When subsequent assessment shows that the X-ray diffractometer is properly aligned (or was not properly aligned when the QXRD procedure was previously qualified), qualification of the QXRD procedure shall be repeated.

12. Recommended Procedure

12.1 For required analytical data see Section 11 and the recommended QXRD procedures described in Appendix X1.

13. Report

13.1 Report the following information:

13.1.1 The phase and its proportion, and which method (Rietveld or standardization) was used. Round figures to the number of significant places required in the report only after calculations are completed, in order to keep the final results substantially free of calculation errors. Follow the rounding procedure outlined in Practice E 29.

14. Precision and Bias

14.1 *Analysis*—A round-robin analysis by Rietveld refinement of the SRM® clinkers with calcium sulfate and calcium carbonate additions has been carried out following experimental procedures described in Appendix X1. An earlier cooperative standardization of mixtures of synthetic phases and a round-robin analysis[7] of the RM clinkers have been carried out (**12, 13**) following the experimental procedures described in Appendix X2 (see Note 9). Results were analyzed statistically according to Practices E 691 and C 670 to determine precision levels.

NOTE 9—Analysis of clinker is likely to include variance in addition to that found in analysis of mixtures of synthetic phases.

14.1.1 The precision values are all expressed as percentage points by mass relative to the total clinker or cement.

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[7] SRM's from the Standard Reference Material Program, National Institute of Standards and Technology are Certified Reference Materials.

14.2 *Precision*—The within-laboratory standard deviation and the between-laboratory standard deviation for all phases are given in Table 1, representing pooled results from the four test mixtures. The within-laboratory standard deviation for each phase is reported as 's-within.' Results of two properly conducted tests by the same operator should not vary more than d2s-within in 95 % of comparisons, where d2s-within = $1.96 \cdot \sqrt{2} \cdot_{\text{swithin}}$. The multi-laboratory standard deviation for each phase is reported as 's-between.' Results of two properly conducted tests on the same clinker or cement by two different laboratories should not differ from each other by more than d2s-between in 95 % of comparisons, where d2s-between $=1.96 \cdot \sqrt{2} \cdot_{\text{sbetween}}$.

14.3 *Bias*—The difference between the estimate of true mean phase concentration and the accepted reference values.

14.4 *Discussion*—Eleven laboratories participated in a co-operative round-robin analysis of mixtures of four separate reference materials. Reference values were that of the SRM® clinkers adjusted for the known amounts of added calcium sulfates and calcite. Taylor (**1**) concluded that the four major phases in portland-cement clinker may be determined using QXRD with an absolute accuracy of 2 to 5 percentage points (by mass) for alite and belite and 1 to 2 percentage points (by mass) for aluminate and ferrite. The SRM® clinkers do not contain gypsum, bassanite, anhydrite or calcite so these data are provided for informational purposes. The qualification requires assessment of certified phases in the clinker SRMs® only. As new SRMs® become available, additional phase qualifications will be added to the test method. There is insufficient data to estimate method bias at this time.

15. Keywords

15.1 alite; alkali sulfate; aluminate; belite; cement; clinker; diffractometer; ferrite; periclase; phase analysis; quantitative X-ray powder diffraction analysis; QXRD; Rietveld analysis; X-ray powder diffraction; XRD

ANNEX

(Mandatory Information)

A1. ASSESSING THE X-RAY DIFFRACTOMETER

A1.1 *Introduction*—This Annex provides a procedure for assessing the diffractometer to assure the validity of the QXRD procedure over a long period of time (several years or longer). A QXRD analysis of portland cement and portland-cement clinker is made particularly difficult by the fact that individual clinker phases used for standardization are not stable over long periods of time, because they hydrate easily, and are not easily synthesized. Thus it is difficult to assess standardizations directly by reanalysis of one or more standardization specimens. In addition, it is not desirable to repeat the standardization unless absolutely necessary. A more reasonable strategy is to use an external standard to assess the diffractometer and to decide when it is necessary to re-qualify a particular procedure. This Annex provides a procedure for assessing the diffractometer to assure the validity of the QXRD procedure over a long period of time (several years or longer).

A1.2 *Overview*:

A1.2.1 As long as certain aspects of the procedure are not changed, the relationship between peak intensity ratio and mass ratio is assumed to be universal (that is, valid over an indefinite period of time, even after changes in the diffractometer such as realignment and replacement of the X-ray tube, and transferable from one diffractometer to another).

A1.2.2 The requirements for the QXRD standardization to be universal are: *(1)* specimens are free from preferred orientation, primary extinction, and microabsorption, *(2)* the irradiated volume of the specimen is constant and independent of scattering angle, *(3)* monochromator polarization effects are corrected, *(4)* integrated peak intensity is used, *(5)* when using an internal standard, standardization and analyses are carried out with an internal standard from the same lot because differences in the particle size distribution between lots of the same material can cause significant difference in peak intensity, and *(6)* standardization and analyses are carried out with the diffractometer in proper geometric alignment.

A1.2.3 If analyses are carried out using only the instrument on which the standardization was carried out, then it is necessary only that preferred orientation, extinction, microabsorption, irradiated volume, and integrated peak intensity are reproducible. In that case, the standardization is valid (though not universal, in that it cannot be transferred from one diffractometer to another) as long as methods of specimen preparation, specimen mounting, and data collection are suitable and are not changed. For example, thus the use of a variable divergence slit for traditional standardization-based analyses is acceptable, because it provides reproducible irradiated volume (see Note A1.1).

NOTE A1.1—Variable divergence slits maintain a fixed irradiated area on the specimen surface. For lower angle regions, they keep the beam from spreading beyond the specimen, while at higher angles they provide a larger irradiated area (and so, volume) than do fixed slit systems. However, Rietveld analysis requires the constant volume provided by a fixed divergence slit. Therefore, data collected with a variable slit needs to be transformed to fixed slit by multiplying by $\sin\Theta$ (**7**).

A1.3 *Terminology*:

A1.3.1 *extinction*—a decrease in intensity during diffraction due to interference by successive crystal planes.

A1.3.1.1 *Discussion*—Extinction is affected by the crystallite size and is negligible for specimens ground to a particle diameter of 5 or 10 µm.

A1.3.2 *irradiated volume*—the volume of specimen that produces XRD signal.

A1.3.2.1 *Discussion*—Irradiated volume is constant from specimen to specimen as long as the proper geometric alignment is maintained and the specimen is sufficiently thick.

A1.3.3 *microabsorption*—an increase or decrease in intensity produced by a combination of phases that differ in absorption coefficient.

A1.3.3.1 *Discussion*—Microabsorption is affected by the extent to which the absorption coefficients differ and by the crystallite size. For phases whose mass absorption coefficients differ by less than 100, microabsorption is not significant for specimens ground to a particle diameter of <10 µm.

A1.3.4 *pattern intensity measurements*—the scale factor for a diffraction pattern of an individual phase determined by a least-squares procedure on a point-by-point basis.

A1.3.5 *peak intensity measurements*—the integrated intensity of the particular diffraction peak.

A1.3.6 *preferred orientation*—the nonrandom orientation of grains relative to the specimen surface.

A1.3.6.1 *Discussion*—Preferred orientation causes major changes in intensity of certain XRD lines, and therefore may be a source of error in QXRD analysis. Preferred orientation is not thought to be a major problem with portland cement clinker phases because they do not typically cleave along crystallographic directions. Preferred orientation is reduced (but not prevented) by prolonged grinding. The mounting procedure must be one that reduces preferred orientation, such as the procedure as described by Klug and Alexander (**6**, pp. 372–374) or Bish and Post (**7**)

A1.4 *Alignment*:

A1.4.1 Loss of proper alignment causes systematic variations in peak intensity with 2θ angle, thus rendering the QXRD procedure invalid.

A1.4.2 In order to assess alignment, an external standard shall be analyzed each month that this test method is used. Measurements shall include peak position, intensity, and resolution (that is, peak width or the ratio of the peak to valley intensity of partially overlapping peaks) of two or more peaks at widely separated 2θ angles. Suitable external standards include SRM® 1976 or polished specimens of novaculite quartz or silicon (**7**).

A1.4.3 Proper alignment is indicated by all of the following: *(1)* correct peak position, *(2)* suitable peak intensity, *(3)* suitable ratio of peak intensity of one or more peaks, and *(4)* suitable peak resolution. These must all be determined for suitably intense peaks. The correct peak position is within 0.01°2θ (Cu Kα) of its nominal value; for the (101) line of novaculite quartz, this value is 26.64°2θ (Cu Kα). Suitable peak intensity depends on many aspects besides alignment and therefore must be determined for a particular diffractometer based on experience; 1000 counts per second per mA is a reasonable expected value for the (101) line of novaculite quartz. Suitable peak intensity ratio is within 5 % of the nominal value. Suitable peak resolution must likewise be determined for a particular diffractometer based on experience. A reasonable indication is provided by clear separation of the five quartz peaks [(122) α_1, (122) α_2, (203) α_1, (203) α_2 plus (301) α_1, and (301) α_2] that appear at about 68°2θ (Cu Kα) (**5**, p. 392–394). Another indication is provided by resolution of the (110) Kα1–2 doublet of tungsten that appears at about 40.4°2θ (Cu Kα); the valley between these peaks must be no greater than 0.5 times the intensity of the α_2 peak (**6**).

A1.4.4 NIST SRM® 1976 may be used for instrument sensitivity assessment (**16**). Certified relative intensities of diffraction peaks, by both peak height or peak area, may be used to assess and correct for instrument bias. Plotting the ratios of the observed to certificate relative intensities will allow assessment of instrument performance relative to a diffractometer deemed to be "in control." If the plot of intensity ratios is pattern-less and falls within the control limits, the diffractometer may be considered "in control."

A1.4.5 When a diffractometer is found to not be properly aligned, then it must be realigned according to the manufacturer's instructions.

APPENDIXES

(Nonmandatory Information)

X1. RIETVELD ANALYSIS OF X-RAY POWDER DIFFRACTION PATTERNS FROM CEMENTS

X1.1 *Introduction*—The Rietveld method employs a least-squares refinement to minimize the difference between a calculated and measured X-ray powder diffraction pattern based upon refinement of crystal structure, specimen, and instrument effects (**9**). The resulting refined crystal structure data for each phase include pattern intensity information used to calculate relative phase abundance. Chemical (solid solution) and structural properties (lattice parameters) of each phase may also be obtained. Crystal structure data describe the structure and chemical composition of crystalline phases that may occur in cements.

Quantitative phase determinations of cements and portland cement clinkers have been difficult to obtain from powder diffraction patterns because of the large number of phases and the large extent of diffraction peak overlap. Traditional peak area measurement approaches are relatively imprecise because of the difficulty in decomposing the highly-overlapped patterns. The advantages of the Rietveld method over these traditional standardization-based methods is the whole-pattern decomposition of simultaneous refinement of crystal structure data from X-ray powder diffraction patterns of multiple phases. This approach provides improved reproducibility in intensity measurement, accommodation of specimen displacement shifts in the pattern, adjustments in crystal lattice parameters affecting peak positions, and relative peak intensities affected by chemical substitution.

The resulting set of relative phase scale factors, phase densities, and cell volumes are used to calculate relative phase abundance according to Eq X1.1:

$$W_p = \frac{S_p\,(ZMV)_p}{\sum_p [S_p\,(ZMV)_p]} \qquad \text{(X1.1)}$$

where:

W_p = the mass fraction of phase p,
S_p = the Rietveld scale factor,
Z = the number of formula units per unit cell,
M = the mass of the formula unit, and
V = the unit cell volume.

X1.2 The minimum requirements for a successful analysis are *(1)* collection of accurate powder diffraction data by step scanning, *(2)* having crystal structure data that are close to the actual structures found in the specimens, and *(3)* a model that accurately reflects systematic errors in the pattern and peak shapes (**7**).

X1.3 Qualitative phase identification may be performed through the principal diagnostic peaks listed in Table X1.1, which lists peaks that are generally resolvable (not too highly overlapped) and unique. This approach is useful since the number of phases and the high degree peak overlap preclude traditional means for phase identification. Confirmation of each phase should be accomplished using the patterns from the ICDD reference database or some other reference patterns of pure phases.

X1.4 The following variables should be refined: *(1)* background, *(2)* specimen displacement, *(3)* individual phase scale (intensity), *(4)* individual phase lattice parameters, *(5)* alite preferred orientation (if necessary), and *(6)* individual phase peak shapes. Examination of the correlation matrix can generally identify variables with high correlation that may create difficulties in refining to the proper values.

X1.4.1 Suitable results can be achieved by refining only the variables listed in X1.4. Refinement of atom site occupancy (Fe–Al ratios) for the ferrite phase is possible but not necessary as the effect on phase fraction is generally small. In addition, the scale and site occupancy factors can be strongly-correlated. Refining preferred orientation for phases other than alite (lower-concentration phases) can create correlation problems that lead to incorrect refinements.

TABLE X1.1 Diagnostic Peaks and ICDD Entry Number for Common Cement Phases (15)

d-spacing (nm)	Two-Theta (CuKα)	Phase (rel. I)	ICDD No.
0.7627	11.593	gypsum (100)	33-311
0.7249	12.200	ferrite (45)	30-226
0.5997	14.759	bassanite (80)	41-224
0.4284	20.717	gypsum (100)	
0.4235	20.959	aluminate, cubic (6)	38-1429
0.4175	21.264	arcanite (28)	5-613
0.4158	21.352	arcanite (23)	
0.4079	21.770	aluminate, cubic (12)	
0.3799	23.397	gypsum (17)	
0.3670	24.231	aphthitalite (20)	20-928
0.3653	24.346	ferrite (16)	
0.3497	25.450	anhydrite (100)	37-1496
0.3468	25.666	bassanite (40)	
0.3313	26.889	langbeinite (95)	19-975
0.3271	27.241	langbeinite (80)	
0.3263	27.309	langbeinite (80)	
0.3225	27.637	langbeinite (100)	
0.3065	29.111	gypsum (75)	
0.3040	29.355	alite, triclinic (55)	31-301
0.3036	29.395	alite, monoclinic (40)	42-551
0.3025	29.504	alite, triclinic (65)	
0.3025	29.504	alite, monoclinic (75)	
0.3002	29.736	bassanite (80)	
0.3000	29.756	arcanite (77)	
0.2985	29.909	alite, triclinic (25)	
0.2974	30.022	alite, triclinic (18)	
0.2965	30.115	alite, triclinic (20)	
0.2961	30.157	alite, monoclinic (25)	
0.2940	30.378	aphthitalite (75)	
0.2902	30.785	arcanite (100)	
0.2880	30.960	arcanite (53)	
0.2886	31.026	langbeinite (18)	
0.2876	31.070	belite, β-form (21)	33-302
0.2838	31.497	aphthitalite (100)	
0.2784	32.124	ferrite (25)	
0.2714	32.976	aluminate, orthorhombic (65)	
0.2710	33.026	belite α-form (100)	23-1042
0.2698	33.178	aluminate, cubic (100)	
0.2692	33.254	aluminate, orthorhombic (100)	26-957
0.2644	33.875	ferrite (100)	
0.2610	34.330	belite, β-form (42)	
0.2405	37.360	free lime (100)	37-1497
0.2220	40.605	belite, α-form (40)	
0.2110	42.920	periclase (100)	4-829
0.1940	46.788	belite, α-form (60)	
0.1764	51.783	alite, monoclinic (55)	
0.1757	52.004	alite, monoclinic (30)	

X1.5 Examination of the difference profile plot is considered the best means of assessing the progress of the refinement. Numerical measures of the degree of fit include the reliability factor (R values), representing some measure of the degree of agreement between the observed and calculated data. This value is dependent upon the quality of the experimental data and so, the plots are ultimately the best means to assess the quality of the fit. Additional discussion may be found in Bish and Post (**7**), Young (**9**), and McCusker (**10**).

X2. STANDARDIZATION-BASED QXRD PROCEDURES USED TO DETERMINE ACCEPTABLE LEVELS OF PRECISION AND BIAS

X2.1 *Introduction*—During development of the traditional procedure, a round-robin analysis of the RM clinkers was carried out to determine acceptable levels of precision and bias (**12, 13**). Details of the QXRD procedure were specified during this analysis. Although this test method does not include detailed QXRD procedures, the procedures used in the cooperative standardization and round robins described in Appendix X1 or Appendix X2 are recommended.

X2.2 *Overview*—This QXRD procedure has a number of critical features: standardization using mixtures of synthetic phases, use of an internal standard, intensity measurement of a specified peak for each phase, measurement of peak area to determine intensity, grinding samples until at least 90 % (by mass) is smaller than 10 µm in diameter, and the use of chemical extractions in the analytical scheme (see Note X2.1).

NOTE X2.1—Alternative QXRD procedures may provide satisfactory precision and bias and thus be acceptable under this test method. An external standard may be used rather than an internal standard. Intensity of each phase may be measured using many peaks or even the entire pattern. Chemical extractions need not be used in the analytical scheme. The particular procedure described in this appendix simply constitutes a recommendation.

X2.3 *Standardization Mixtures*:

X2.3.1 Three standardization mixtures were prepared using cubic C_3A, orthorhombic C_3A, C_4AF, and M. These individual phases were obtained from the Construction Technology Laboratories, and procedures used to prepare these individual phases and standardization mixtures were described by Struble and Kanare (**12**).

X2.3.2 The proportions in each mixture are listed in Table X2.1. The phases in this standardization are the principal phases in a clinker that has been chemically extracted using maleic acid or salicylic acid (see X2.3.3).

X2.3.3 Standardization phases were ground such that at least 95 % (by mass) was finer than 10 µm and not more than 5 % were finer than 1 µm in diameter. This particle size was selected to minimize microabsorption preferred orientation and to avoid loss of X-ray intensity due to grinding to particle sizes <1 µm.

X2.4 *Internal Standard*:

X2.4.1 Participants were required to use an internal standard—a pure, stable material, 95 % of which is finer than 10 µm. One recommended material was SRM® 640c (silicon).[8] However, it should be noted that silicon intensity may be affected by particle size distribution. Also recommended were any one of the materials in SRM® 674.[8] Another suitable material is SRM® 676.[8]

X2.4.2 Standardization mixtures were mixed with the internal standard material in recommended proportions of 0.1200 g internal standard per 1.0000 g standardization or unknown mixture, corresponding to 0.0200 g internal standard per 1.0000 g clinker. These proportions assume that the standardization mixture and unknown mixtures represent 17 % (by mass) of a clinker.

TABLE X2.1 Proportion of Phases in Standardization Mixtures

Phase	Percent of Mixture			Percent of Clinker		
	A	B	C	A	B	C
Orthorhombic C_3A	0	51	7	0.00	8.67	1.19
Cubic C_3A	65	11	29	11.05	1.87	4.93
C_4AF	35	11	60	5.95	1.87	10.20
M	0	27	4	0.00	4.59	0.68

X2.5 *Blending*—Components must be blended to provide homogeneous specimens. The recommended procedure was to blend each standardization mixture for approximately 10 min using a vibratory-type mill with approximately 5 mL of a nonaqueous solvent (see Note X2.2) for each gram of powder and with appropriate grinding media.

NOTE X2.2—Suitable solvents include cyclohexane or alcohol (ethanol, methanol, or 2-propanol). Alcohol often contains sufficient water to cause hydration, so this water must be removed (**17**).

X2.6 *Diffraction Procedures*—Participants were instructed to use their normal procedures for preparing specimens and for collecting diffraction patterns. Specimen preparation procedures should minimize preferred orientation. Procedures to collect diffraction patterns should provide reproducible peak intensity measurements (for example, slow scanning speeds and moderately large receiving-slit widths).

X2.7 *Peak Selection*—Participants were required to measure intensity of the peaks specified in Table X2.2 plus one or more peaks for the internal standard, though they were encouraged to measure additional peaks, as many as possible for each phase. Analysis using a manual diffractometer is probably limited to the few peaks in Table X2.2, whereas analysis using a computer-controlled diffractometer can utilize many peaks for each phase.

TABLE X2.2 Peaks Recommended for QXRD Analysis

Phase	hkl	*d*-spacing (nm)	Position (°2θ) using Cu Kα
Orthorhombic C_3A^A	(113)	0.4210	21.1
Cubic C_3A	(023)	0.4236	21.0
	(213)	0.4083	21.8
C_4AF	(130)	0.3654	24.3
M	(200)	0.2106	42.9

[A] Note that the intensity of the (113) peak of orthorhombic C_3A must be corrected for any contribution from the (023) peak of cubic C_3A. The intensity of the (023) peak is calculated by multiplying the (213) peak by a correction factor. The correction factor is determined by measuring the intensity ration of the (023) peak to the (213) peak in a sample containing cubic C_3A and no orthorhombic C_3A.

X2.8 *C_3A Correction*—The intensity of the (113) peak of orthorhombic C_3A must be corrected for any contribution from the (023) peak of cubic C_3A. This (023) intensity contribution is calculated by multiplying the (213) peak by a correction factor, which is the intensity ratio of the (023) peak to the (213) peak for cubic C_3A using Sample A (which contains no orthorhombic C_3A).

X2.9 *Intensity Measurement*—Integrated intensity above the background must be measured for each peak. There are a number of procedures for measuring integrated intensity, and no specific procedure is required for this standardization.

X2.10 *Standardization Curve*—Once the standardization mixtures have been analyzed, standardization curves relating the measured intensity of each peak, relative to the intensity of the internal standard peak, to the known proportion of the

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[8] In this test method, SRM clinkers refer specifically to SRM 2686, SRM 2687, and SRM 2688. These are available from the Standard Reference Material Program, National Institute of Standards and Technology.

phase must be developed. These curves may be prepared graphically or using accepted statistical procedures to determine the best-fitting curve. When an internal standard is used, it is assumed that the peak intensity is linearly related to the phase proportion. However under certain circumstances it may be found that the relationship is not linear, but is better described by some other mathematical function.

X2.11 *Analysis of Unknown Mixtures*—Two additional mixtures of the standardization phases were analyzed using the same QXRD procedures to provide a preliminary assessment of the standardization.

X2.12 *Analysis of Cement or Clinker*—The following procedures were followed during analysis of the SRM® clinkers and are recommended for analysis of any portland cement or portland-cement clinker.

X2.12.1 *Grinding*—The clinker samples were ground such that at least 95 % was finer than 10 µm and not more than 5 % was finer than 1 µm. The following procedure has been found to be suitable: grind using a tungsten carbide ring and puck mill, with approximately 5 drops ethylene glycol as a grinding aid, for 4 to 6 min. It is necessary to start with enough sample to provide sufficient powder for the specimen mount, considering that extraction of the calcium silicates will leave ca. 15 to 20 % (by mass) for XRD analysis.

X2.12.2 *Ignition*—In the case of analyzing portland cement for C_3A, C_4AF, and M, gypsum $(C\bar{S}H_2)$ and hemihydrate $(C\bar{S}H_{1/2})$ must be converted to anhydrite $(C\bar{S})$ before QXRD analysis to eliminate interfering XRD peaks. This conversion can be carried out by igniting the cement for 30 min at 500 °C.

X2.12.3 *Blending with Internal Standard*—The ground sample was blended with the internal standard using the same procedure as used during the standardization. The recommended proportion was 0.0200 g internal standard per gram of clinker to approximate the 12 % (by mass) recommended for the standardization mixtures.

X2.12.4 *Extraction*—The calcium silicates were extracted chemically using salicylic acid or maleic acid and methanol using procedures described by Struble (**17**). This extraction was not quantitative; because the internal standard was added relative to unextracted clinker, the phase contents were determined relative to the un-extracted clinker.

X2.12.5 *XRD Analysis*—The clinkers were analyzed using the same procedures (for example, collection of the diffraction pattern, measurement of peak intensities, and calculation of phase proportions) that were used in the standardization.

REFERENCES

(**1**) Taylor, H. F. W., *Cement Chemistry*, 2nd edition, Thomas Telford, New York, 1997.

(**2**) Takeuchi, Y., Nishi, F., and Maki, I., *Zeit Krist*., 152, 1980, p. 259.

(**3**) Klein, C., *Manual of Mineralogy*, after J. D. Dana, 22th Edition John Wiley and Sons, New York, 2002.

(**4**) Lea, F. M., *The Chemistry of Cement and Concrete*, 3rd ed., Arnold, London, 1970, p. 727.

(**5**) Cullity, B. D., and Stock, S. R., *Elements of X-Ray Diffraction*, Prentice Hall, 2001.

(**6**) Klug, H. P., and Alexander, L. E., *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, 2nd ed, John Wiley & Sons, New York, NY, 1974.

(**7**) Bish, D. L., and Post, J. E., eds., *Modern Powder Diffraction*, Reviews in Mineralogy, Vol 20, Mineralogical Society of America, Washington, DC, 1989.

(**8**) *Methods and Practices in X-Ray Powder Diffraction*, 3rd ed., International Centre for Diffraction Data, Newtown Square, PA, 1989.

(**9**) *The Rietveld Method*, Young, R. A., ed., Oxford University Press, 1993.

(**10**) McCusker, L. B., Von Dreele, R. B., Cox, D. E., Louer, D., and Scardi, P., "Rietveld Refinement Guidelines," *Jour. Appl. Cryst*. 32, 1999, pp. 36-50.

(**11**) Stutzman, P. E., and Leigh, S. L., "Phase Composition Analysis of the NIST Reference Clinkers by Optical Microscopy and X-Ray Powder Diffraction," *NIST Technical Note 1441*, 2002, p. 44.

(**12**) Struble, L., and Kanare, H., "Cooperative Calibration and Phases, Report 2," *Structural Research Series No. 556*, University of Illinois at Urbana-Champaign, 1990.

(**13**) Struble, L., "Quantitative Phase Analysis of Clinker Using X-Ray Diffraction," *Cement, Concrete and Aggregates*, Vol 13, No. 2, 1991, pp. 97–102.

(**14**) Stutzman, P. E., and Leigh, S. L., "Phase Analysis of Hydraulic Cements by X-Ray Powder Diffraction: Precision, Bias, and Qualification," NIST IR, in press, 2006.

(**15**) *The Powder Diffraction File*, International Centre for Diffraction Data, Newtown Square, PA.

(**16**) Certificate of Analysis, "Standard Reference Material 1976, Instrument Sensitivity Standard for X-ray Powder Diffraction," Standard Materials Reference Program, National Institute of Standards and Technology, Gaithersburg, MD.

(**17**) Struble, L., "The Effect of Water on Maleic Acid and Salicylic Acid Extractions," *Cement and Concrete Research*, Vol 15, 1985, pp. 631–636.

SUMMARY OF CHANGES

Committee C01 has identified the location of selected changes to this test method since the last issue, C 1365 – 05, that may impact the use of this test method. (Approved December 15, 2006)

(*1*) The standard was extensively revised to include new development in X-ray powder diffraction analysis as well as provide for a more complete analysis, and to include a precision statement.

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