National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2686a

Portland Cement Clinker

This Standard Reference Material (SRM) is intended for use in evaluating methods of phase abundance analysis of major phases in cement clinkers: the percentages of alite (C_3S)[(1)], belite (C_2S), aluminate (C_3A), ferrite (C_4AF), periclase (M), and alkali sulfates (aphthitalite and arcanite). A unit of SRM 2686a consists of four hermetically-sealed containers of approximately 7 g each of crushed portland cement clinker.

Certified Mass Fraction Values: The certified mass fractions for phase abundance are given in Table l. A NIST certified value is a value for which NIST has the highest confidence in its accuracy, in that all known or suspected sources of bias have been investigated or taken into account [1]. Further detail regarding the preparation, analysis, and phases of the SRM are described in references 2 and 3. The certified values listed are unweighted averages, the results of analyses performed at NIST using quantitative X-ray powder diffraction (QXRD) and from image analysis of scanning electron microscope backscattered electron and X-ray images. The QXRD used Reitveld refinement of powder diffraction data [4–6].

Reference Mass Fraction Values: Reference values for SRM 2686a, expressed as mass fractions are provided in Table 2 [3]. Reference values are noncertified values that are the best available estimates of the true values; however, the values, which are based on determinations done by reliable methods, do not meet the NIST criteria for certification [1].

Information Value: The bulk oxide mass fractions of the clinker analyzed by X-ray fluorescence (XRF) and atomic absorption are provided in Table 3. The loss on ignition (LOI) value is included in Table 3, as well. An information value is considered to be a value that will be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value [1].

Expiration of Certification: The certification of **SRM 2686a** is valid, within the measurement uncertainty specified, until **01 January 2018**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see "Instructions for Handling, Storage, and Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Overall direction and coordination of the analytical measurements leading to certification were performed by P.E. Stutzman and G. Lespinasse of the NIST Materials and Structural Systems Division.

Analytical measurements leading to certification were performed by P.E. Stutzman and G. Lespinasse of the NIST Materials and Structural Systems Division. Bulk chemistry analyses were performed by S. Lane, K. Stark, L. Smolinski, and G. Barger of the Ash Grove Cement Company, Overland Park, KS.

Statistical consultation for this SRM was provided by S.D. Leigh of the NIST Statistical Engineering Division.

Support aspects involved with the issuance of this SRM were coordinated through the NIST Measurement Services Division.

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Certificate Revision History on Last Page

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[(1)] Cement chemist's notation: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, M = MgO.

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Storage over desiccant is recommended to minimize the effects of exposure to humidity as the cement clinker is hygroscopic. Changes in the appearance of the etched surface of polished sections, particularly the appearance of free lime, which hydrates to epezite (calcium hydroxide), indicate change due to moisture exposure. Epezite exhibits a popcorn-like texture and high topographic relief. For XRD analysis, the presence of calcium hydroxide or calcium carbonate may be taken as an indication that moisture has altered the free lime. For XRD powders, heat-treating to 450 °C converts calcium hydroxide back to free lime without other alteration.

Sample Preparation and Analysis[(2)]: A representative sampling of each clinker was obtained through use of a random-stratified sampling scheme and totaled sixteen samples for XRD analysis and ten for microscopy. The splits for XRD were ground individually to a fineness less than about 250 μm using a mortar and pestle and were subjected to a final grinding by a micronizing mill to reduce to a mean particle size of about 7 μm using 200-proof ethanol (about 5 mL) as a grinding lubricant. The ground clinker was vacuum filtered to remove the ethanol, dried at 60 °C, and then placed in a sealed vial over desiccant in desiccators. Whole-clinker fragments were potted in a low-viscosity epoxy, which was cured at 60 °C for 24 h, cut to expose the embedded fragments, and polished using diamond pastes of 6, 3, 1, and 0.25 μm particle size. The polished sections were carbon-coated to eliminate charge buildup in the scanning electron microscope.

Qualitative phase identification by XRD was performed on three sub-samples: a potassium hydroxide-sucrose extraction residue (composed essentially of the silicates and periclase), a salicylic acid-methanol extraction residue (comprised of the interstitial phases periclase and alkali sulfates), and a bulk (untreated) clinker. Details on the extraction procedures may be found in reference 3. Each replicate was analyzed three times by XRD. At least six fields were analyzed for each replicate by microscopy and image analysis.

Homogeneity Assessment: Sampling for the X-ray study allowed assessment of within-vial and between-vial homogeneity and found the materials to be homogeneous.

Certified Mass Fraction Values: Each certified value is a weighted average of replicated values for multiple samples, measured by XRD and microscopy, and it was obtained by fitting a Gaussian random effects model to the data [1,6]. The measurement uncertainty associated with each value is an expanded uncertainty, $U = ku_c$, consistently with the ISO Guide [7], and the coverage factor was $k = 2$ for approximate 95 % coverage probability.

Table 1. Certified Mass Fraction Values for Phase Abundance of SRM 2686a.

Phase	Mass Fraction (%)
Alite	63.35 ± 1.29
Belite	18.68 ± 1.42
Aluminate	2.46 ± 0.67
Ferrite	10.76 ± 1.44
Periclase	3.40 ± 0.40
Alkali Sulfates	0.87 ± 0.27

[(2)] Certain commercial equipment, instruments, or materials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Reference Mass Fraction Values: The reference values are expressed with an expanded uncertainty, U, at the 95 % level of confidence, which is calculated according to the method described in the ISO Guide [7]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the measurement error. The coverage factor used for the expanded uncertainties listed in Table 2, $k = 2$, corresponds to an approximate 95 % level of confidence. The standard deviations for aphthitalite and arcanite are 0.22 and 0.19, respectively. The number of measurments is 98 and the number of samples is 33.

Table 2. Reference Mass Fraction Values for Alkali Sulfate Phases by XRD.

Phase	Mass Fraction (%)
Aphthitalite	0.74 ± 0.08
Arcanite	0.27 ± 0.07

Information Values: Each bulk oxide mass fraction value is the mean result samples analyzed for bulk oxide content by wavelength–dispersive X-ray fluorescence (XRF) on lithium borate fused beads with the exception of sodium and potassium. The mass fractions for sodium and potassium are the unweighted means of the XRF analysis and the mean results from samples analyzed by atomic absorption performed lithium borate fusions that had been dissolved in dilute nitric acid for sodium and potassium oxide. Table 3 includes the LOI mass fraction mean result.

Table 3. Information Values for Bulk Oxides and LOI.

Constituents[(a)]	Mass Fractions (%)
SiO_2	21.71
Al_2O_3	3.70
Fe_2O_3	3.65
CaO	64.09
MgO	4.81
SO_3	0.56
Na_2O	0.20
K_2O	0.49
TiO_2	0.22
P_2O_5	0.07
Mn_2O_3	0.13
SrO	0.04
LOI	0.51

[(a)] The constituents listed in this Certificate of Analysis are expressed as the oxide forms and in the order given in ASTM C 114-10, Section 3, Table 1 [8].

REFERENCES

[1] May, W.; Parris, R.; Beck, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements;* NIST Special Publication 260–136; U.S. Government Printing Office: Washington, DC (2000); available at http://www.nist.gov/srm/publications.cfm (accessed Nov 2012).

[2] SRM 2686, *Portland Cement Clinker*; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (2002); available at https://www-s.nist.gov/srmors/certificates/archive/2686.pdf.

[3] Stutzman, P.; Lespinnasse, G.; Leigh, S.; *Compositional Analysis and Certification of NIST Reference Material Clinker 2686a*; NIST Technical Note 1602; U.S. Government Printing Office: Washington, DC (2008).[(3)]

[4] ASTM C 1356M, S*tandard Test Method for Quantitative Determination of Phases in Portland Cement Clinker by Microscopical Point-Count Procedure*; Annu. Book of ASTM Stand., Vol. 4.01 (2006).

[5] Young, R.A.; *The Rietveld Method*; IUCr Monographs on Crystallography, Oxford Science Publications, Oxford University, Vol. 5 (1995).

[6] Rukhin, A.L.; Vangel, M.G.; *Estimation of a Common Mean and Weighted Means Statistics*; J. Am. Stat. Assoc., Vol. 93, No. 441, pp. 303–308 (1998).

[7] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (ISO GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (JCGM) (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Nov 2012); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at http://physics.nist.gov/Pubs/ (accessed Nov 2012).

[8] ASTM C 114–09, *Standard Test Method for Chemical Analysis of Hydraulic Cement*; Annu. Book of ASTM Stand., Vol. 4.01 (2010).

Certificate Revision History: 05 November 2012 (Revised certified values for alite, belite ferrite, alkali sulfates, revised uncertainty for all certified values; uncertainty for reference values added; removed standard deviation from reference values; revised sulfur trioxide value and uncertainty from informational values; updated number of samples for reference values; editorial changes); 04 August 2009 (Original certificate date).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.

[(3)] This Technical Note uses a deprecated method for the combination of measurement results from two different methods. For this reason, the assigned values and associated expanded uncertainties listed in this certificate differ from those in Table 4 of the Technical Note. The assigned values are very close to those in the Technical Note, but the uncertainties listed here are substantially larger than those reported in the Technical Note.