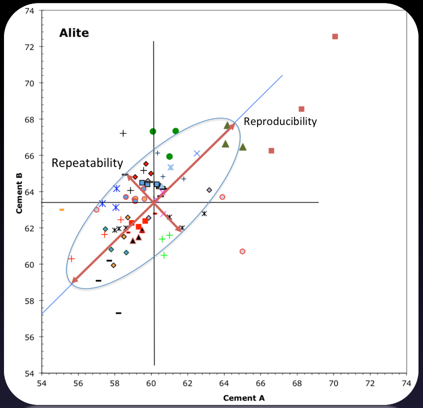
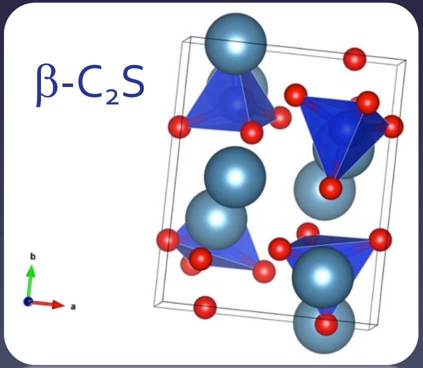
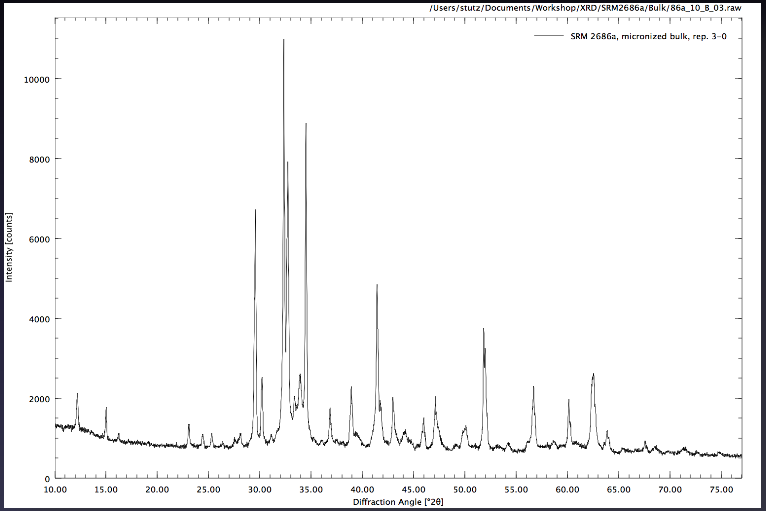
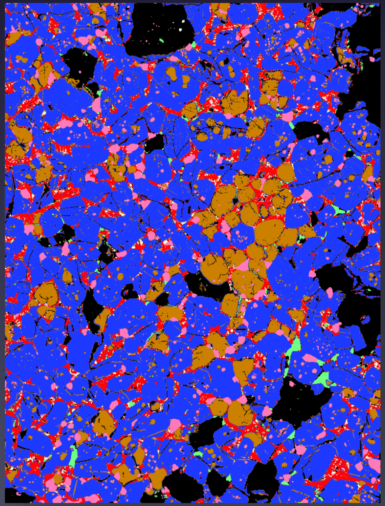
Cements Materials Characterization Workshop







Paul Stutzman
Jeffrey Bullard
Steve Feldman
Alexander Brand
Don Broton



October 30, 2018

Workshop Configuration

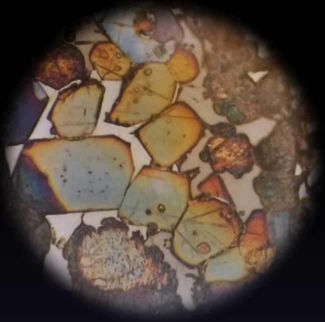
- We will focus on a number of materials characterization applications: X-ray powder diffraction (XRD), scanning electron microscopy (SEM) with X-ray imaging (XR), image processing and image analysis (IA) , X-Ray fluorescence (XRF), and Digital holographic microscopy (DHM).
- The XRD and SEM portions have an introductory presentation followed by a live demonstration and a lab practical
- The exercises have real lab data for the NIST SRM clinkers and portland cement
- The SRM certificates are provided for the clinkers for comparison of your estimates, and for the XRD exercise, the ASTM C1365 qualification criteria are provided

Early Work: Clinker Manufacture

It had been recognized that some limes were hydraulic and some were not but the reasons remained a mystery. John Smeaton found that the best limes were impure, containing a substantial amount of clay (25%), and additionally used a pozzolanic tuff. (1756)

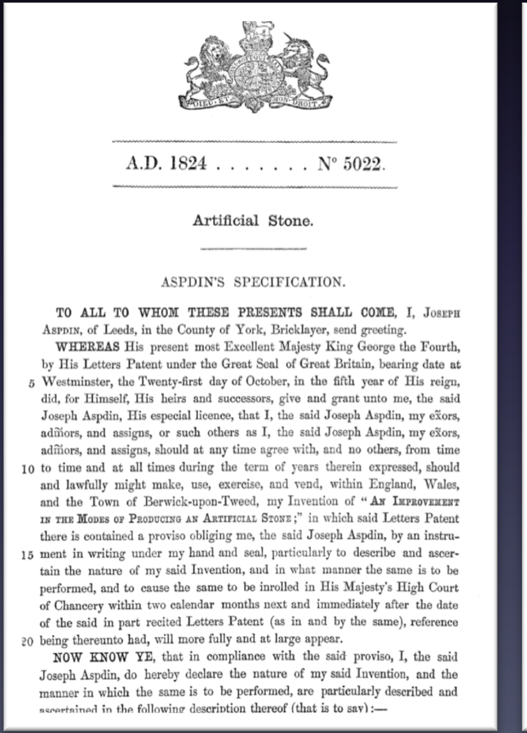
Similar findings appear to have been made independently in other countries

The reasons the materials were hydraulic remained a mystery



D. Campbell, CTL

Aspden Patent 1824



A.D. 1824 . . . . N° 5022.

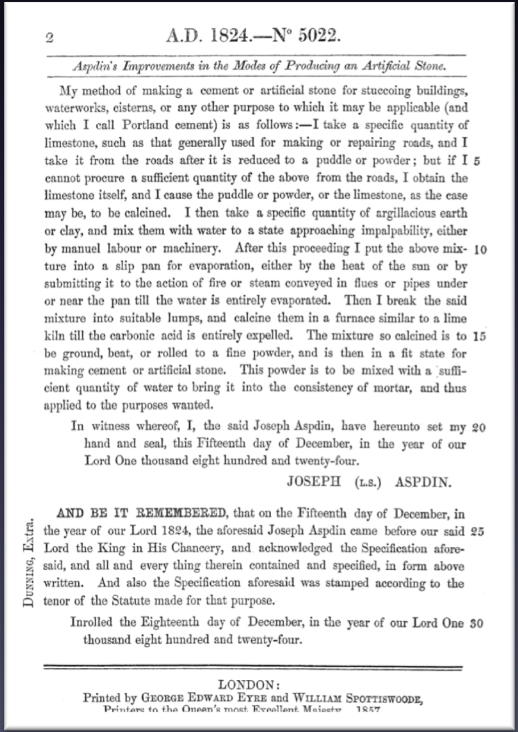
Artificial Stone.

ASPDIN'S SPECIFICATION.

TO ALL TO WHOM THESE PRESENTS SHALL COME, I, Joseph Aspdin, of Leeds, in the County of York, Bricklayer, send greeting.

WHEREAS His present most Excellent Majesty King George the Fourth, by His Letters Patent under the Great Seal of Great Britain, bearing date at Westminster, the Twenty-first day of October, in the fifth year of His reign, did, for Himself, His heirs and successors, give and grant unto me, the said Joseph Aspdin, His especial licence, that I, the said Joseph Aspdin, my ex̃ors, adm̃ors, and assigns, or such others as I, the said Joseph Aspdin, my ex̃ors, adm̃ors, and assigns, should at any time agree with, and no others, from time to time and at all times during the term of years therein expressed, should and lawfully might make, use, exercise, and vend, within England, Wales, and the Town of Berwick-upon-Tweed, my Invention of "An Improvement in the Modes of Producing an Artificial Stone;" in which said Letters Patent there is contained a proviso obliging me, the said Joseph Aspdin, by an instrument in writing under my hand and seal, particularly to describe and ascertain the nature of my said Invention, and in what manner the same is to be performed, and to cause the same to be inrolled in His Majesty's High Court of Chancery within two calendar months next and immediately after the date of the said in part recited Letters Patent (as in and by the same), reference being thereunto had, will more fully and at large appear.

NOW KNOW YE, that in compliance with the said proviso, I, the said Joseph Aspdin, do hereby declare the nature of my said Invention, and the manner in which the same is to be performed, are particularly described and ascertained in the following description thereof (that is to say):—



2 A.D. 1824.—N° 5022.

Aspdin's Improvements in the Modes of Producing an Artificial Stone.

My method of making a cement or artificial stone for stuccoing buildings, waterworks, cisterns, or any other purpose to which it may be applicable (and which I call Portland cement) is as follows:—I take a specific quantity of limestone, such as that generally used for making or repairing roads, and I take it from the roads after it is reduced to a puddle or powder; but if I cannot procure a sufficient quantity of the above from the roads, I obtain the limestone itself, and I cause the puddle or powder, or the limestone, as the case may be, to be calcined. I then take a specific quantity of argillacious earth or clay, and mix them with water to a state approaching impalpability, either by manuel labour or machinery. After this proceeding I put the above mixture into a slip pan for evaporation, either by the heat of the sun or by submitting it to the action of fire or steam conveyed in flues or pipes under or near the pan till the water is entirely evaporated. Then I break the said mixture into suitable lumps, and calcine them in a furnace similar to a lime kiln till the carbonic acid is entirely expelled. The mixture so calcined is to be ground, beat, or rolled to a fine powder, and is then in a fit state for making cement or artificial stone. This powder is to be mixed with a sufficient quantity of water to bring it into the consistency of mortar, and thus applied to the purposes wanted.

In witness whereof, I, the said Joseph Aspdin, have hereunto set my hand and seal, this Fifteenth day of December, in the year of our Lord One thousand eight hundred and twenty-four.

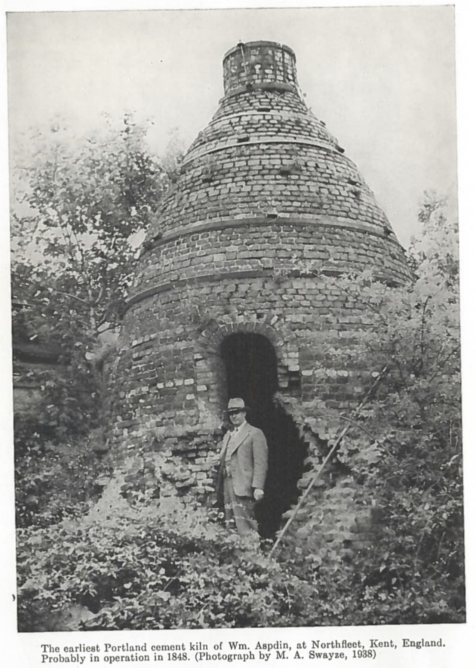
JOSEPH (L.S.) ASPDIN.

AND BE IT REMEMBERED, that on the Fifteenth day of December, in the year of our Lord 1824, the aforesaid Joseph Aspdin came before our said Lord the King in His Chancery, and acknowledged the Specification aforesaid, and all and every thing therein contained and specified, in form above written. And also the Specification aforesaid was stamped according to the tenor of the Statute made for that purpose.

Inrolled the Eighteenth day of December, in the year of our Lord One thousand eight hundred and twenty-four.

Dunning, Extra.

LONDON:
Printed by George Edward Eyre and William Spottiswoode,
Printers to the Queen's most Excellent Majesty. 1857.



The earliest Portland cement kiln of Wm. Aspdin, at Northfleet, Kent, England. Probably in operation in 1848. (Photograph by M. A. Swayze, 1938)

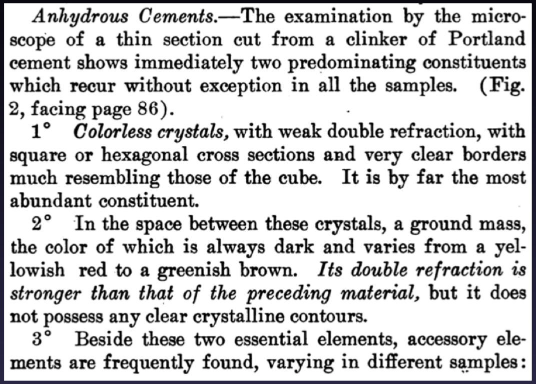
from The Chemistry of Portland Cement, RH Bogue, 1954

Bottle kilns at Lehigh PA

Le Châtelier and Tornebohm – the first look

Microscopy of thin sections, 1883

- description of the clinker phases
- postulate compositions
- observed decomposition of $SiO_2.2CaO$
- relating excess free lime to durability problems

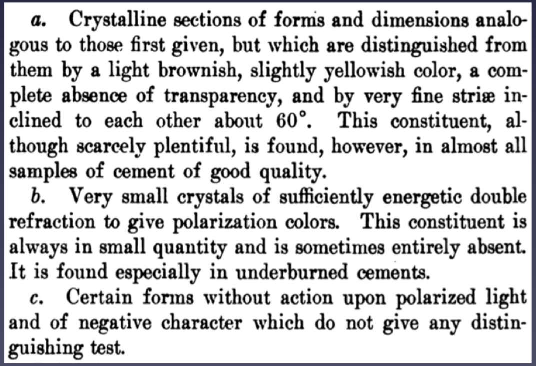


Anhydrous Cements.—The examination by the microscope of a thin section cut from a clinker of Portland cement shows immediately two predominating constituents which recur without exception in all the samples. (Fig. 2, facing page 86).

1° *Colorless crystals,* with weak double refraction, with square or hexagonal cross sections and very clear borders much resembling those of the cube. It is by far the most abundant constituent.

2° In the space between these crystals, a ground mass, the color of which is always dark and varies from a yellowish red to a greenish brown. *Its double refraction is stronger than that of the preceding material,* but it does not possess any clear crystalline contours.

3° Beside these two essential elements, accessory elements are frequently found, varying in different samples:

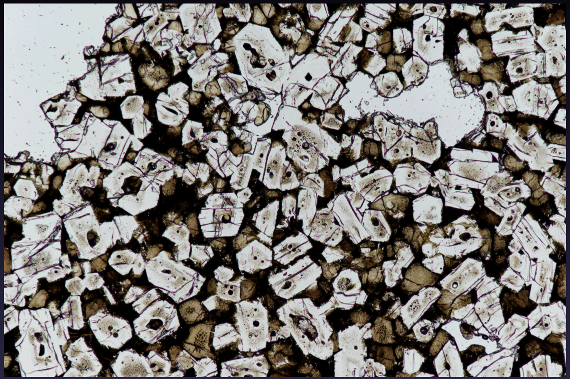


a. Crystalline sections of forms and dimensions analogous to those first given, but which are distinguished from them by a light brownish, slightly yellowish color, a complete absence of transparency, and by very fine striæ inclined to each other about 60°. This constituent, although scarcely plentiful, is found, however, in almost all samples of cement of good quality.

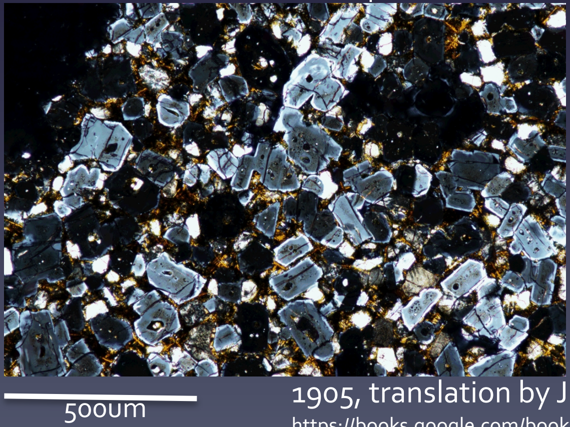
b. Very small crystals of sufficiently energetic double refraction to give polarization colors. This constituent is always in small quantity and is sometimes entirely absent. It is found especially in underburned cements.

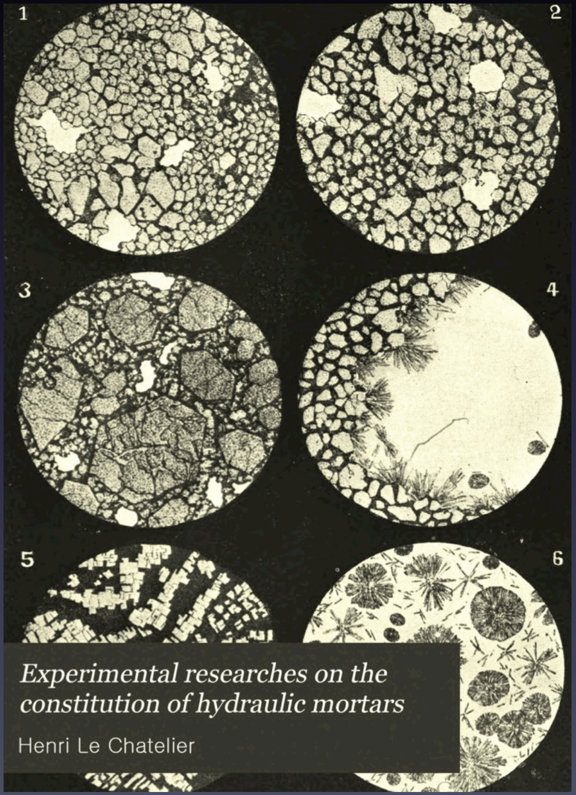
c. Certain forms without action upon polarized light and of negative character which do not give any distinguishing test.

Plane-Polarized light: SRM2688



crossed polars SRM2688





1905, translation by J.L. Mack

https://books.google.com/books/about/Experimental_Researches_on_the_Constitut.html?id=PVFDAAAAIAAJ

Geophysical Laboratory, Early 1900's

Light microscopy was limited by the equipment of the day, the subtle differences in optical properties, and the fineness of the constituent phases but remained useful for examination of laboratory-prepared mixtures

Three general theories prevailed on cement:

- a sold solution of various silicates and calcium aluminates
- a definite lime, silica and alumina compound
- composed of separate silicates and aluminates, some or all of which are hydraulic

Work at the Geophysical Laboratory on binary systems CaO-Al2O3, CaO-SiO2, and Al2O3-SiO2 and the ternary system CaO-SiO2-Al2O3 using *many* compounded samples and optical microscopy concluded that cement is composed of separate silicates and aluminates

A.L. Day, E.S. Shephard, F.E. Wright "The Lime Silica Series of Minerals", Am. Jour. Sci. (4) xxii, 265 1906

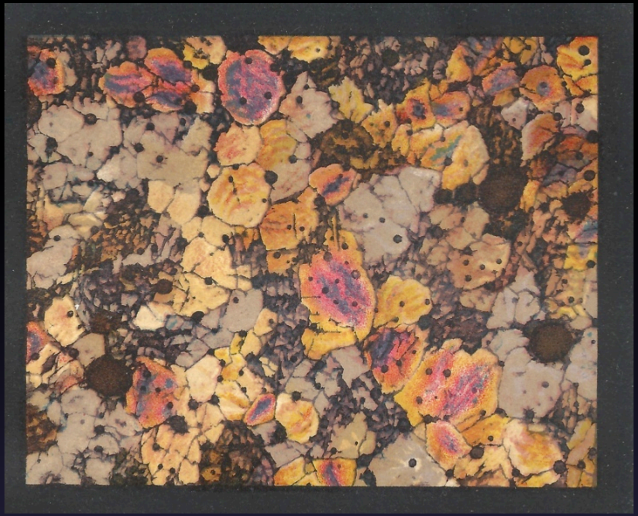
E.S. Shepherd, G.A. Rankin, F.E. Wright, The Binary Systems of Alumina, with Silica, Lime, and Magnesia, Am. Jour. Sci. (4) xxviii, 293, 1909

E.S. Shepherd, G.A. Rankin, F.E. Wright, "Preliminary Report on the Ternary System CaO-Al2)3-SiO2. A Study on the Constitution of Portland Cement Clinker", J. Ind. Eng. Chem., iii, 211-227, 1911

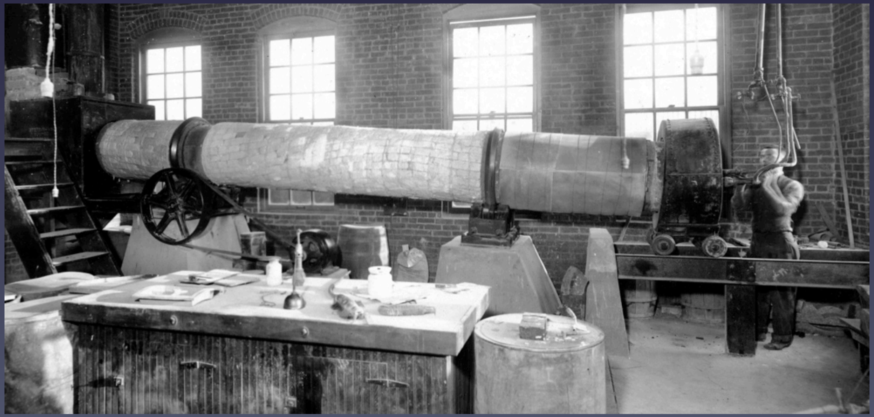
P.H. Bates and A.A. Klein, Properties of the Calcium Silicates and Calcium Aluminate Occurring in Normal Portland Cement, Technologic Papers of the Bureau of Standards, No. 78, 1917

1. "At early periods the constituents of Portland cement of normal composition and manufacture, in the order of their strength-conferring properties, are: tricalcium silicate, tricalcium aluminate, and dicalcium silicate,
2. At periods beyond 28 days the dicalcium silicate gains sufficient strength to place it almost on equality with the tricalcium silicate,
3. Tricalcium aluminate containing 10 percent plaster gains practically no strength after the first period at which it was tested; that is, 24 hours,
4. Tricalcium silicate of the purity used in this investigation (90 per cent $3\,CaO.SiO_2$ in one case and 95 per cent in the other) has all the important properties of Portland Cement, especially those of the "rate of setting" and strength developed,
5. dicalcium silicate, such as used in this investigation, sets too slowly and attains strength too slowly to be of any commercial value when used alone,
6. Tricalcium aluminate alone, as used in this investigation, sets too rapidly and attains too little strength to be of any commercial value as a hydraulic cementing material
1. Plaster of Paris, when added to any of the compounds or mixtures of those studied, generally increased their strength. This effect is more marked at the early periods."

Thin section of dicalcium silicate, crossed Nichols, 90x



Tricalcium silicate (gray), along with dicalcium silicate crossed Nichols, 190x



Cement Chemist Nomenclature

Cement chemists use a variety of methods for expressing chemical formulae; 1) standard, 2) a sum of oxides and, 3) an abbreviated oxide nomenclature that stems from the Geophysical Laboratory work of Rankin and Wright (1915).

For example, tricalcium silicate (Ca_3SiO_5) may also be expressed as $3CaO \cdot SiO_2$ and as C_3S

Simple oxide phases such as free lime (CaO) or periclase (MgO) generally are expressed without abbreviation

$C = CaO$
$M = MgO$
$T = TiO_2$

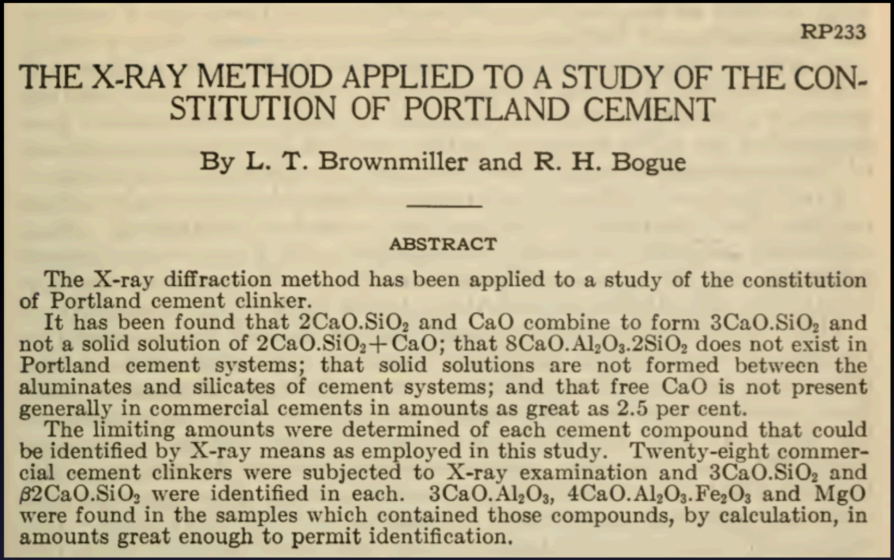
$S=SiO_2$
$K = K_2O$
$P = P_2O_5$

$A = Al_2O_3$
$S=\overline{S}O_3$
$H = H_2O$

$F = Fe_2O_3$
$N = Na_2O$
$C = \overline{C}O_2$

To ensure things remain confusing, C_3S or tricalcium silicate usually refers to the pure phase (i.e., no chemical substitution) while alite refers to the impure industrial products. *This convention is often not followed and the names are used inter-changably*

1930 X-Ray Powder Diffraction Camera work by the Portland Cement Association Fellowship at the National Bureau of Standards



RP233

THE X-RAY METHOD APPLIED TO A STUDY OF THE CONSTITUTION OF PORTLAND CEMENT

By L. T. Brownmiller and R. H. Bogue

ABSTRACT

The X-ray diffraction method has been applied to a study of the constitution of Portland cement clinker.

It has been found that $2CaO.SiO_2$ and CaO combine to form $3CaO.SiO_2$ and not a solid solution of $2CaO.SiO_2+CaO$; that $8CaO.Al_2O_3.2SiO_2$ does not exist in Portland cement systems; that solid solutions are not formed between the aluminates and silicates of cement systems; and that free CaO is not present generally in commercial cements in amounts as great as 2.5 per cent.

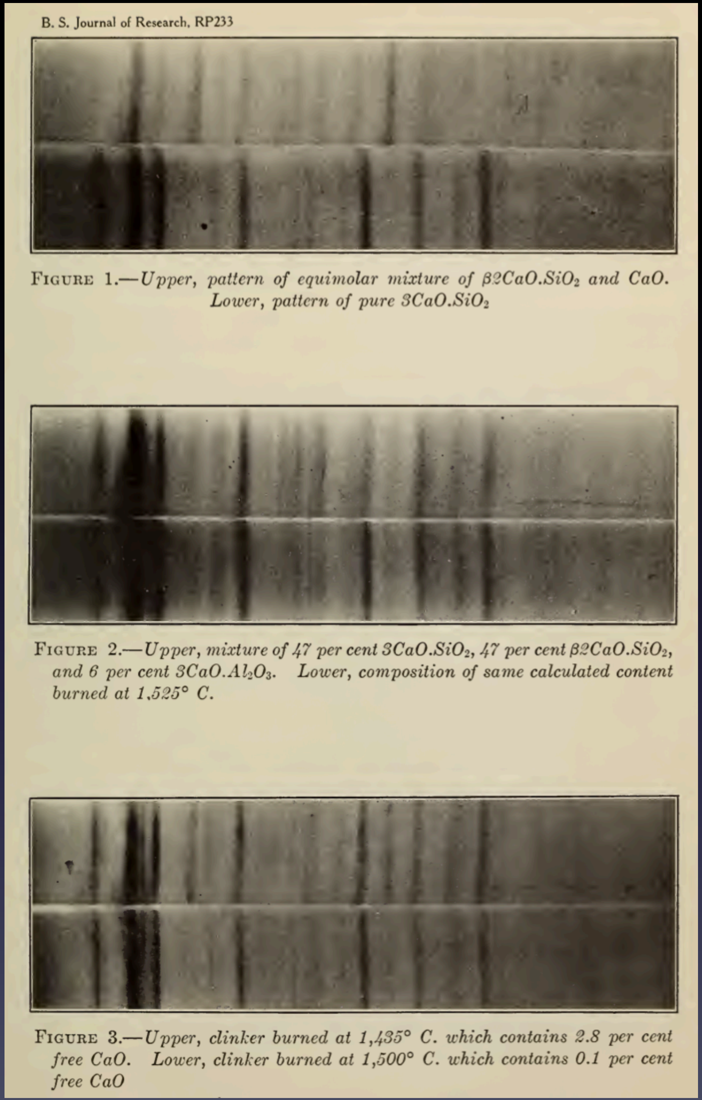
The limiting amounts were determined of each cement compound that could be identified by X-ray means as employed in this study. Twenty-eight commercial cement clinkers were subjected to X-ray examination and $3CaO.SiO_2$ and $\beta 2CaO.SiO_2$ were identified in each. $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$ and MgO were found in the samples which contained those compounds, by calculation, in amounts great enough to permit identification.

At that time there were three prevailing theories on phase composition of portland cement clinker:

- a complex compound containing lime, alumina, and silica
- lime and silicates form a loosely bound solid solution
- lime and silica form two separate silicates

Comparison of synthesized phases to commercial clinkers demonstrated the presence of tricalcium silicate as the primary phase, as postulated by LeChatelier previously (1882, 1905), observed by Tornebohm (1887) independently, and the work of Rankin and Wright (1915) on the system $CaO\text{-}Al_2O_3\text{-}SiO_2$

Other phases identified included what are now called belite, aluminate, ferrite and periclase.



B. S. Journal of Research, RP233

FIGURE 1.—*Upper, pattern of equimolar mixture of* $\beta 2CaO.SiO_2$ *and CaO. Lower, pattern of pure* $3CaO.SiO_2$

FIGURE 2.—*Upper, mixture of 47 per cent* $3CaO.SiO_2$*, 47 per cent* $\beta 2CaO.SiO_2$*, and 6 per cent* $3CaO.Al_2O_3$*. Lower, composition of same calculated content burned at 1,525° C.*

FIGURE 3.—*Upper, clinker burned at 1,435° C. which contains 2.8 per cent free CaO. Lower, clinker burned at 1,500° C. which contains 0.1 per cent free CaO*

X-ray diffraction powder camera patterns required 50 h exposure times!

1930 Powder Camera work by the Portland Cement Association Fellowship at the National Bureau of Standards

The wide-angle goniometer introduced in the late 1940's provided improved resolution, more stable and intense X-ray sources and an output to a strip chart that facilitates position and intensity measurement

Debye-Scherrer Camera

Museum of Optical Instruments

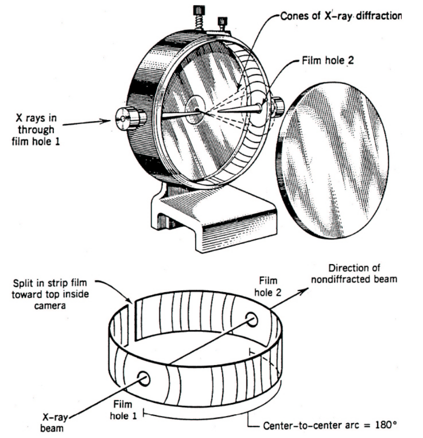
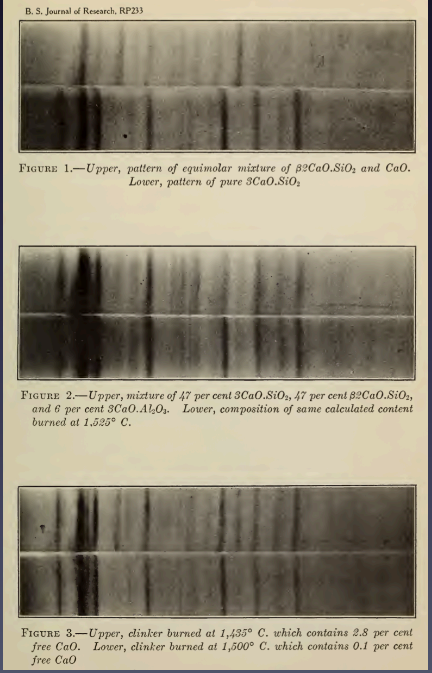


Fig. 2. The "Norelco" Geiger counter diffractometer consists of three independent parts: a basic diffraction unit (X-ray tube with high voltage generator and controls, at left), the high angle precision Geiger counter goniometer placed on top of it, and an electronic circuit rack with automatic 10″ strip chart recorder (at right).

Philips Technical Review, Vol. 16, No. 4, 1954



B. S. Journal of Research, RP233

FIGURE 1.—*Upper, pattern of equimolar mixture of $\beta 2CaO.SiO_2$ and CaO. Lower, pattern of pure $3CaO.SiO_2$*

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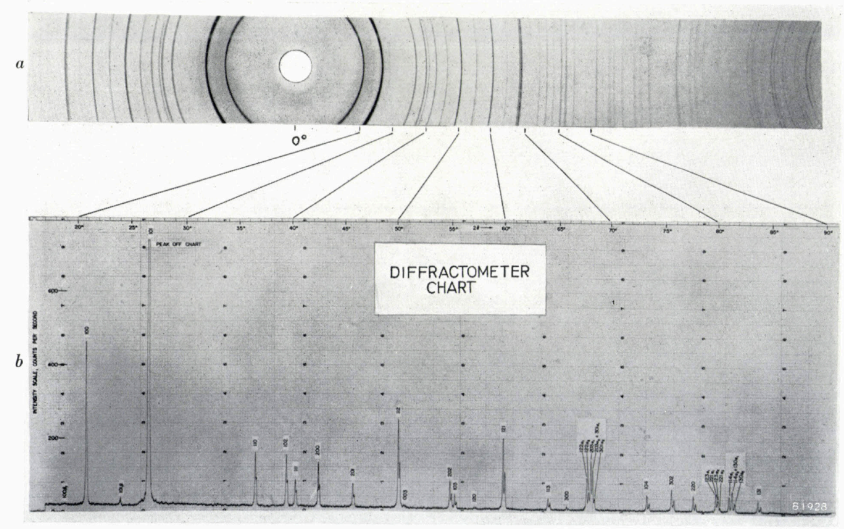
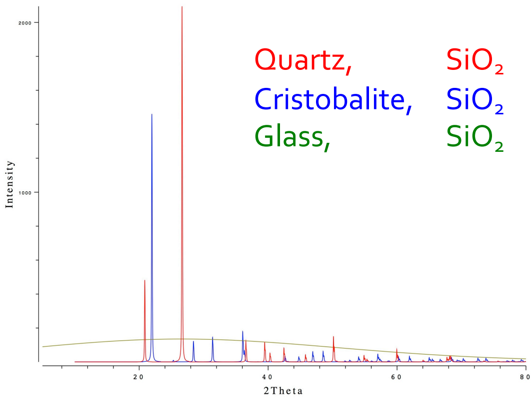


Fig. 6. *a*) X-ray diffraction pattern of quartz powder photographed with a 114.6 mm diameter Debye-Scherrer camera. Filtered CuKα radiation, 40 kV$_p$, 20 mA, exposure time 2 hours. *b*) Automatically recorded chart obtained with the new Norelco X-ray diffractometer using the same X-ray tube conditions. Recording time 4.8 hours.

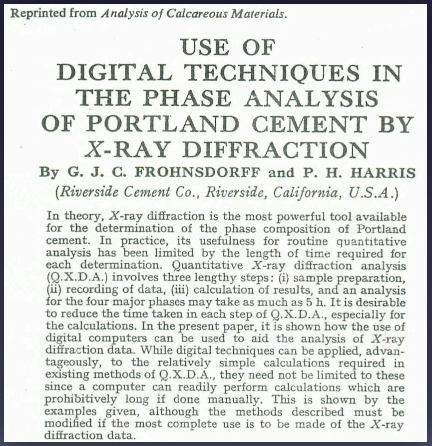


Quartz, SiO_2
Cristobalite, SiO_2
Glass, SiO_2

Cements-Related Developments in XRD

- PCA Fellowship: Bogue, Brownmiller, Harrington, Ordway
- L.E. Copeland and R.H. Bragg: Quantitative analysis procedures with or without calibration curves, including a means to deal with overlapping lines (1958)
- PCA controlled atmosphere (RH, N_2) experiments on cement hydration
- G. Frohnsdorff, R. Berger, P. Harris, P. Johnson: automated powder diffractometer (1964), sample changer and least-squares decomposition of diffraction patterns
- PK Mehta, M.J. Shah: Standards-based XRD analysis of clinker for closed-loop kiln control
- Studies on precision by AE Moore (1964), L. Aldridge (1982)

- 1978: XRD Task Group started in ASTM C01.23, Compositional Analysis
    - initial data using sets of pure phases and calibration curves
    - development of the NIST Reference Clinkers to develop and test the methods
    - development of the first ASTM standard C1365 for XRD analysis of cements
    - amending the standard XRD test to include Rietveld analysis



Reprinted from *Analysis of Calcareous Materials.*

USE OF
DIGITAL TECHNIQUES IN
THE PHASE ANALYSIS
OF PORTLAND CEMENT BY
X-RAY DIFFRACTION

By G. J. C. FROHNSDORFF and P. H. HARRIS

(*Riverside Cement Co., Riverside, California, U.S.A.*)

In theory, *X*-ray diffraction is the most powerful tool available for the determination of the phase composition of Portland cement. In practice, its usefulness for routine quantitative analysis has been limited by the length of time required for each determination. Quantitative *X*-ray diffraction analysis (Q.X.D.A.) involves three lengthy steps: (i) sample preparation, (ii) recording of data, (iii) calculation of results, and an analysis for the four major phases may take as much as 5 h. It is desirable to reduce the time taken in each step of Q.X.D.A., especially for the calculations. In the present paper, it is shown how the use of digital computers can be used to aid the analysis of *X*-ray diffraction data. While digital techniques can be applied, advantageously, to the relatively simple calculations required in existing methods of Q.X.D.A., they need not be limited to these since a computer can readily perform calculations which are prohibitively long if done manually. This is shown by the examples given, although the methods described must be modified if the most complete use is to be made of the *X*-ray diffraction data.

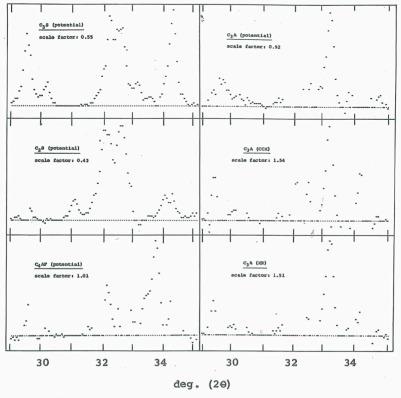
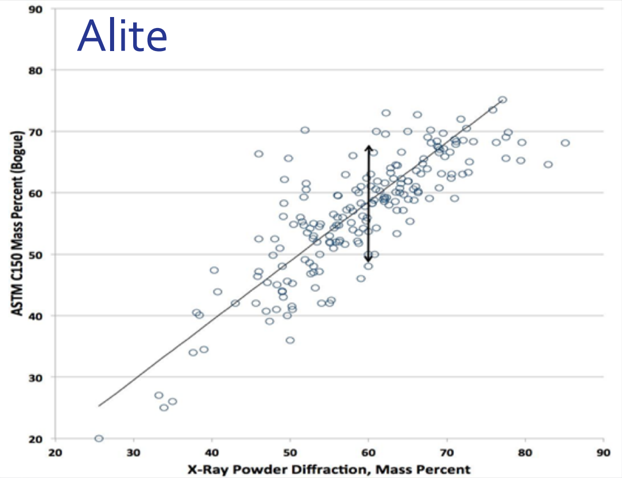


Figure 3. Standard vectors for the four major cement compounds derived from potential compound compositions; additional standard vectors for C_3A shown for comparison were derived from the PCA's CCX and XR compound compositions.

Uncertainty in Bogue-Calculated Phase Content of Portland Cement

The traditional means of estimating potential cement composition using the Bogue calculations (1929) has limits recognized since inception.



$C_3S=(4.070 \times \%CaO)-(7.610 \times \%SiO_2)-(6.720 \times \%Al_2O_3)-(1.420 \times \%Fe_2O_3)-(2.850 \times \%SO_3)$

$C_2S=(2.867 \times \%SiO_2)-(0.7544 \times \%C_3S)$

$C_3A=(2.650 \times \%Al_2O_3)-(1.692 \times \%Fe_2O_3)$

$C_4AF=(3.040 \times \%Fe_2O_3)$

Bogue Calculations

- Uncertainties in bulk oxide determinations,
- Uncertainties in the Bogue constants, reflecting deviations of clinker phase chemistry from ideal assumptions,
- Not accounting for all phases, and
- Covariances among oxide errors,

oxide uncertainty
±1-σ mass percent

oxide <u>and</u> constants uncertainty
±1-σ mass percent[2]

Reference	Alite	Belite	Aluminate	Ferrite
Forrester et al.	± 2	± 2	± 0.7	± 0.08
Aldridge, Eardley	± 0.6 to 4.0	± 0.6 to 4.0	± 0.1 to 1.1	± 0.06 to 0.4
Aldridge	± 2.2	± 2.0	± 0.4	± 0.2
Stutzman, Lane				
Reference Methods	± 2.2	± 2.0	± 0.5	± 0.3
XRF-glass	± 2.0	± 1.8	± 0.2	± 0.1
XRF powder	± 2.5	± 2.5	± 0.3	± 0.2
Oxides and Constants				
Reference	± 9.5	± 9.5	± 2.3	± 1.1
XRF-Glass	± 9.6	± 9.5	± 2.1	± 1
XRF-Powder	± 9.7	± 9.5	± 2.1	± 1

[1] P.E. Stutzman, and D.S. Lane, "Effects of Analytical Precision on Bogue Calculations of Potential Portland Cement Composition," Journal of ASTM International, Vol. 7, No. 6

[2] P. Stutzman, A. Heckert, A. Tebbe, and S. Leigh, "Uncertainty in Bogue-Calculated Phase Compositions of Hydraulic Cements", Cement and Concrete Research, 61 (2014) 40 – 48

ASTM C01 Cement Committee

Develops specifications, methods of test, recommended practices,

and terminology for hydraulic cements

- C01.23 Subcommittee on Compositional Analysis
  - To develop and maintain test methods and practices for determination of chemical and mineralogical composition of hydraulic cements
  - XRD Task Group established in 1978

- C114 Standard Test Methods for Chemical Analysis of Hydraulic Cement
- C1356 Standard Test Method for Quantitative Determination of Phases in Portland Cement Clinker by Microscopical Point-Count Procedure
- C1365 Standard Test Method for Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-Ray Powder Diffraction Analysis

ASTM C 150 Limits

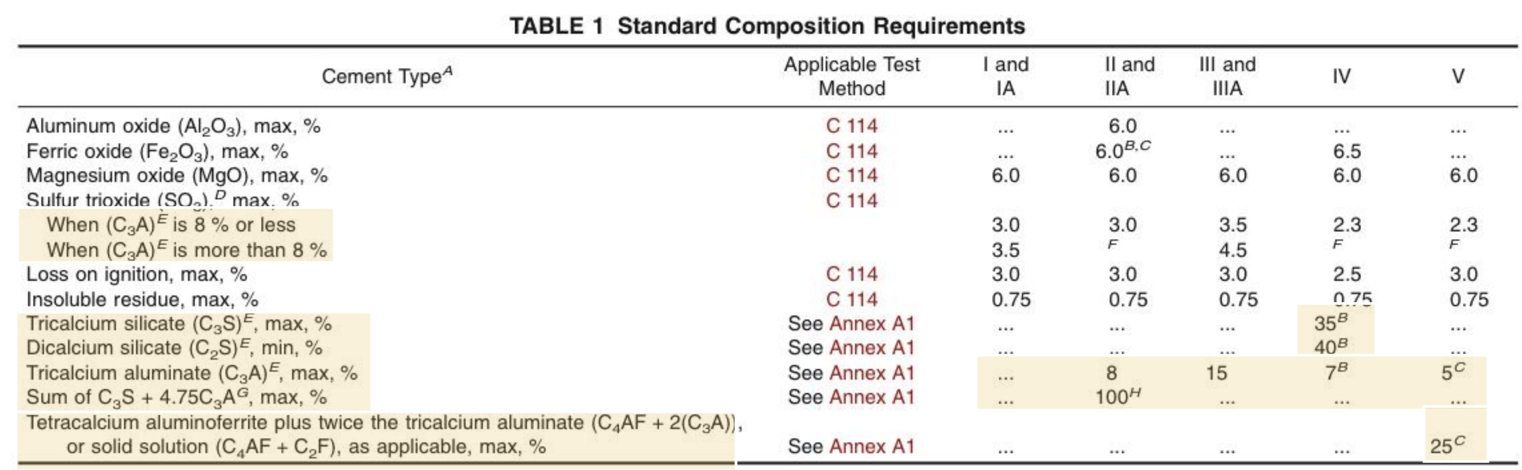


TABLE 1 Standard Composition Requirements

Cement Type^A	Applicable Test Method	I and IA	II and IIA	III and IIIA	IV	V
Aluminum oxide (Al_2O_3), max, %	C 114	...	6.0	...	...	...
Ferric oxide (Fe_2O_3), max, %	C 114	...	$6.0^{B,C}$	...	6.5	...
Magnesium oxide (MgO), max, %	C 114	6.0	6.0	6.0	6.0	6.0
Sulfur trioxide (SO_3),^{D} max, %	C 114					
When $(C_3A)^E$ is 8 % or less		3.0	3.0	3.5	2.3	2.3
When $(C_3A)^E$ is more than 8 %		3.5	^{F}	4.5	^{F}	^{F}
Loss on ignition, max, %	C 114	3.0	3.0	3.0	2.5	3.0
Insoluble residue, max, %	C 114	0.75	0.75	0.75	0.75	0.75
Tricalcium silicate $(C_3S)^E$, max, %	See Annex A1	...	...	...	35^B	...
Dicalcium silicate $(C_2S)^E$, min, %	See Annex A1	...	...	...	40^B	...
Tricalcium aluminate $(C_3A)^E$, max, %	See Annex A1	...	8	15	7^B	5^C
Sum of $C_3S + 4.75C_3A^G$, max, %	See Annex A1	...	100^H	...	...	...
Tetracalcium aluminoferrite plus twice the tricalcium aluminate ($C_4AF + 2(C_3A)$), or solid solution ($C_4AF + C_2F$), as applicable, max, %	See Annex A1	...	...	...	...	25^C

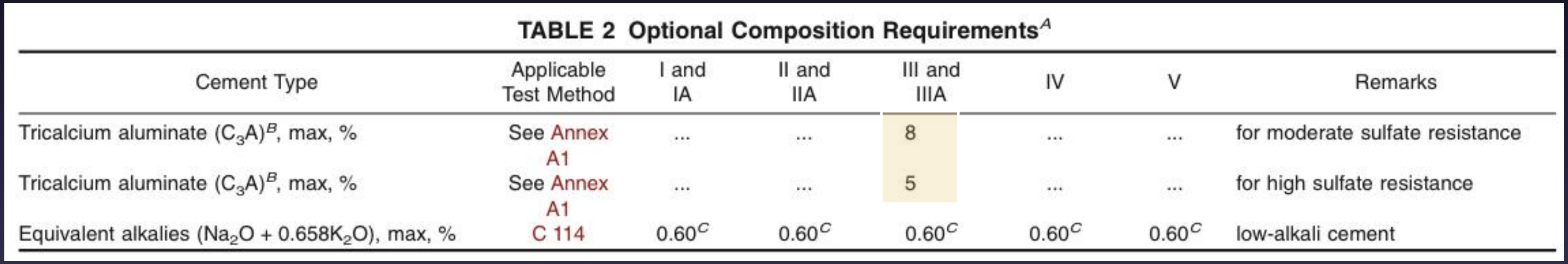
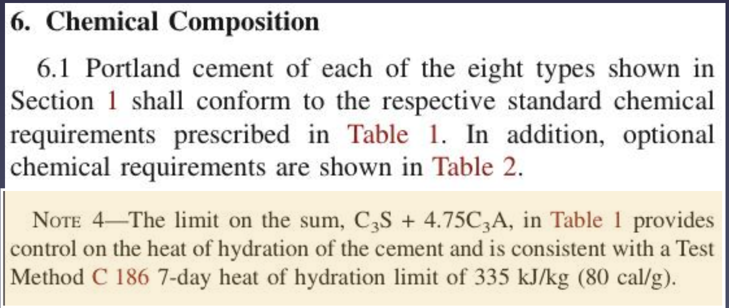


TABLE 2 Optional Composition Requirements^A

Cement Type	Applicable Test Method	I and IA	II and IIA	III and IIIA	IV	V	Remarks
Tricalcium aluminate $(C_3A)^B$, max, %	See Annex A1	...	...	8	...	...	for moderate sulfate resistance
Tricalcium aluminate $(C_3A)^B$, max, %	See Annex A1	...	...	5	...	...	for high sulfate resistance
Equivalent alkalies ($Na_2O + 0.658K_2O$), max, %	C 114	0.60^C	0.60^C	0.60^C	0.60^C	0.60^C	low-alkali cement



6. Chemical Composition

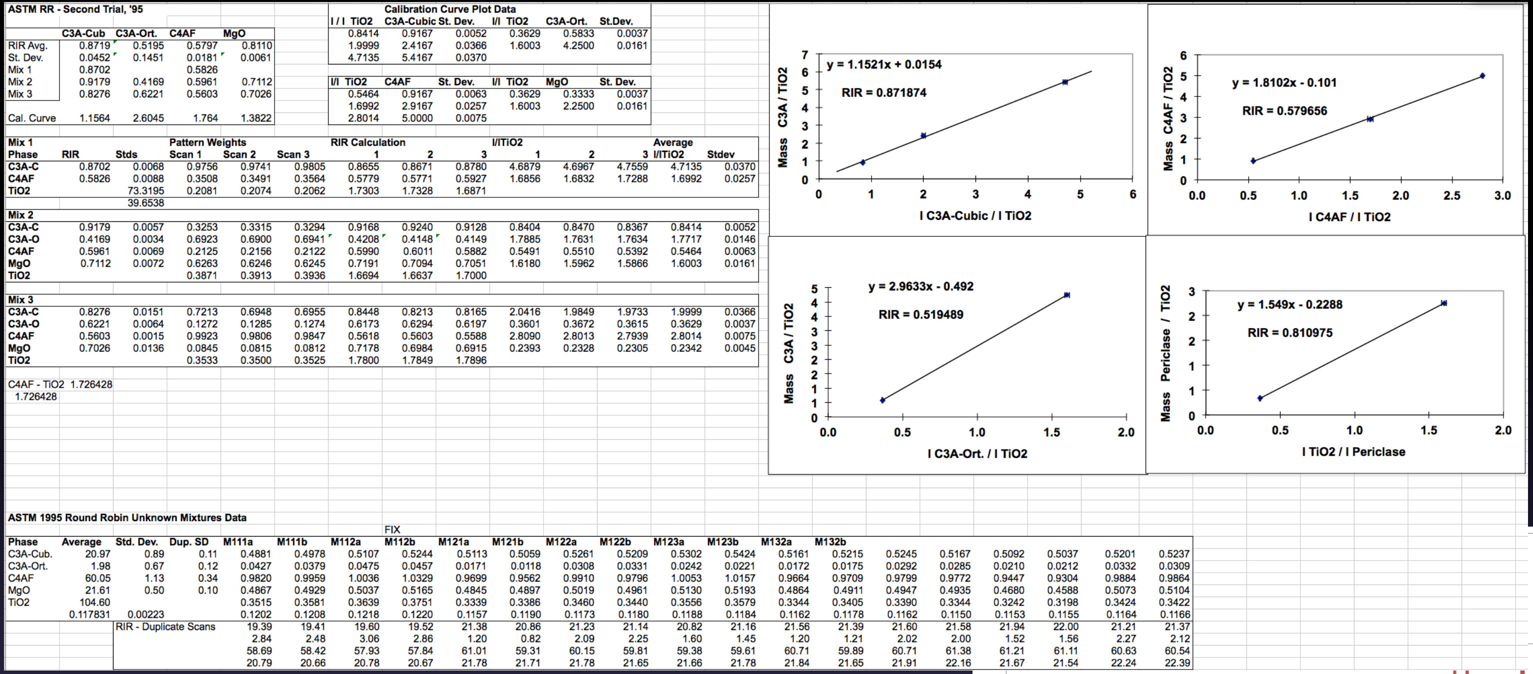
6.1 Portland cement of each of the eight types shown in Section 1 shall conform to the respective standard chemical requirements prescribed in Table 1. In addition, optional chemical requirements are shown in Table 2.

NOTE 4—The limit on the sum, $C_3S + 4.75C_3A$, in Table 1 provides control on the heat of hydration of the cement and is consistent with a Test Method C 186 7-day heat of hydration limit of 335 kJ/kg (80 cal/g).

Currently, these phase mass fractions are estimated using the Bogue calculations of potential composition from a bulk chemical analysis.

We can relate the existing specification criteria to XRD-derived phase measurements via calibration

ASTM C01.23 Interstitial Phase Calibration



ASTM RR - Second Trial, '95

	C3A-Cub	C3A-Ort.	C4AF	MgO
RIR Avg.	0.8719	0.5195	0.5797	0.8110
St. Dev.	0.0452	0.1451	0.0181	0.0061
Mix 1	0.8702		0.5826	
Mix 2	0.9179	0.4169	0.5961	0.7112
Mix 3	0.8276	0.6221	0.5603	0.7026
Cal. Curve	1.1564	2.6045	1.764	1.3822

Calibration Curve Plot Data

I / I TiO2	C3A-Cubic	St. Dev.	I/I TiO2	C3A-Ort.	St.Dev.
0.8414	0.9167	0.0052	0.3629	0.5833	0.0037
1.9999	2.4167	0.0366	1.6003	4.2500	0.0161
4.7135	5.4167	0.0370			

I/I TiO2	C4AF	St. Dev.	I/I TiO2	MgO	St. Dev.
0.5464	0.9167	0.0063	0.3629	0.3333	0.0037
1.6992	2.9167	0.0257	1.6003	2.2500	0.0161
2.8014	5.0000	0.0075			

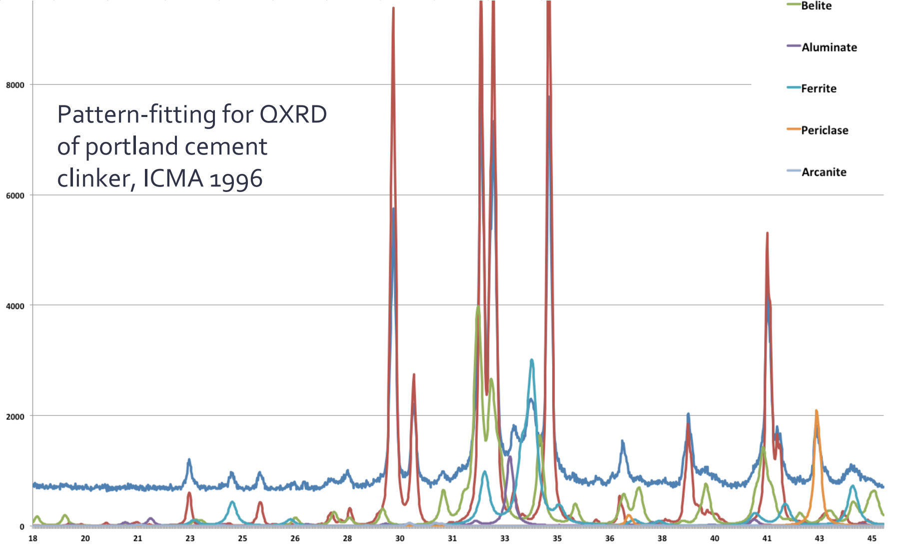
Mix 1			Pattern Weights			RIR Calculation			I/ITiO2			Average	
Phase	RIR	Stds	Scan 1	Scan 2	Scan 3	1	2	3	1	2	3	I/ITiO2	Stdev
C3A-C	0.8702	0.0068	0.9756	0.9741	0.9805	0.8655	0.8671	0.8780	4.6879	4.6967	4.7559	4.7135	0.0370
C4AF	0.5826	0.0088	0.3508	0.3491	0.3564	0.5779	0.5771	0.5927	1.6856	1.6832	1.7288	1.6992	0.0257
TiO2		73.3195	0.2081	0.2074	0.2062	1.7303	1.7328	1.6871					
		39.6538											
Mix 2													
C3A-C	0.9179	0.0057	0.3253	0.3315	0.3294	0.9168	0.9240	0.9128	0.8404	0.8470	0.8367	0.8414	0.0052
C3A-O	0.4169	0.0034	0.6923	0.6900	0.6941	0.4208	0.4148	0.4149	1.7885	1.7631	1.7634	1.7717	0.0146
C4AF	0.5961	0.0069	0.2125	0.2156	0.2122	0.5990	0.6011	0.5882	0.5491	0.5510	0.5392	0.5464	0.0063
MgO	0.7112	0.0072	0.6263	0.6246	0.6245	0.7191	0.7094	0.7051	1.6180	1.5962	1.5866	1.6003	0.0161
TiO2			0.3871	0.3913	0.3936	1.6694	1.6637	1.7000					
Mix 3													
C3A-C	0.8276	0.0151	0.7213	0.6948	0.6955	0.8448	0.8213	0.8165	2.0416	1.9849	1.9733	1.9999	0.0366
C3A-O	0.6221	0.0064	0.1272	0.1285	0.1274	0.6173	0.6294	0.6197	0.3601	0.3672	0.3615	0.3629	0.0037
C4AF	0.5603	0.0015	0.9923	0.9806	0.9847	0.5618	0.5603	0.5588	2.8090	2.8013	2.7939	2.8014	0.0075
MgO	0.7026	0.0136	0.0845	0.0815	0.0812	0.7178	0.6984	0.6915	0.2393	0.2328	0.2305	0.2342	0.0045
TiO2			0.3533	0.3500	0.3525	1.7800	1.7849	1.7896					

C4AF - TiO2 1.726428
1.726428

ASTM 1995 Round Robin Unknown Mixtures Data

							FIX														
Phase	**Average**	**Std. Dev.**	**Dup. SD**	**M111a**	**M111b**	**M112a**	**M112b**	**M121a**	**M121b**	**M122a**	**M122b**	**M123a**	**M123b**	**M132a**	**M132b**						
C3A-Cub.	20.97	0.89	0.11	0.4881	0.4978	0.5107	0.5244	0.5113	0.5059	0.5261	0.5209	0.5302	0.5424	0.5161	0.5215	0.5245	0.5167	0.5092	0.5037	0.5201	0.5237
C3A-Ort.	1.98	0.67	0.12	0.0427	0.0379	0.0475	0.0457	0.0171	0.0118	0.0308	0.0331	0.0242	0.0221	0.0172	0.0175	0.0292	0.0285	0.0210	0.0212	0.0332	0.0309
C4AF	60.05	1.13	0.34	0.9820	0.9959	1.0036	1.0329	0.9699	0.9562	0.9910	0.9796	1.0053	1.0157	0.9664	0.9709	0.9799	0.9772	0.9447	0.9304	0.9884	0.9864
MgO	21.61	0.50	0.10	0.4867	0.4929	0.5037	0.5165	0.4845	0.4897	0.5019	0.4961	0.5130	0.5193	0.4864	0.4911	0.4947	0.4935	0.4680	0.4588	0.5073	0.5104
TiO2	104.60			0.3515	0.3581	0.3639	0.3751	0.3339	0.3386	0.3460	0.3440	0.3556	0.3579	0.3344	0.3405	0.3390	0.3344	0.3242	0.3198	0.3424	0.3422
	0.117831	0.00223		0.1202	0.1208	0.1218	0.1220	0.1157	0.1190	0.1173	0.1180	0.1188	0.1184	0.1162	0.1178	0.1162	0.1150	0.1153	0.1155	0.1164	0.1166
		RIR - Duplicate Scans		19.39	19.41	19.60	19.52	21.38	20.86	21.23	21.14	20.82	21.16	21.56	21.39	21.60	21.58	21.94	22.00	21.21	21.37
				2.84	2.48	3.06	2.86	1.20	0.82	2.09	2.25	1.60	1.45	1.20	1.21	2.02	2.00	1.52	1.56	2.27	2.12
				58.69	58.42	57.93	57.84	61.01	59.31	60.15	59.81	59.38	59.61	60.71	59.89	60.71	61.38	61.21	61.11	60.63	60.54
				20.79	20.66	20.78	20.67	21.78	21.71	21.78	21.65	21.66	21.78	21.84	21.65	21.91	22.16	21.67	21.54	22.24	22.39

Compensating
Polar Planimeter

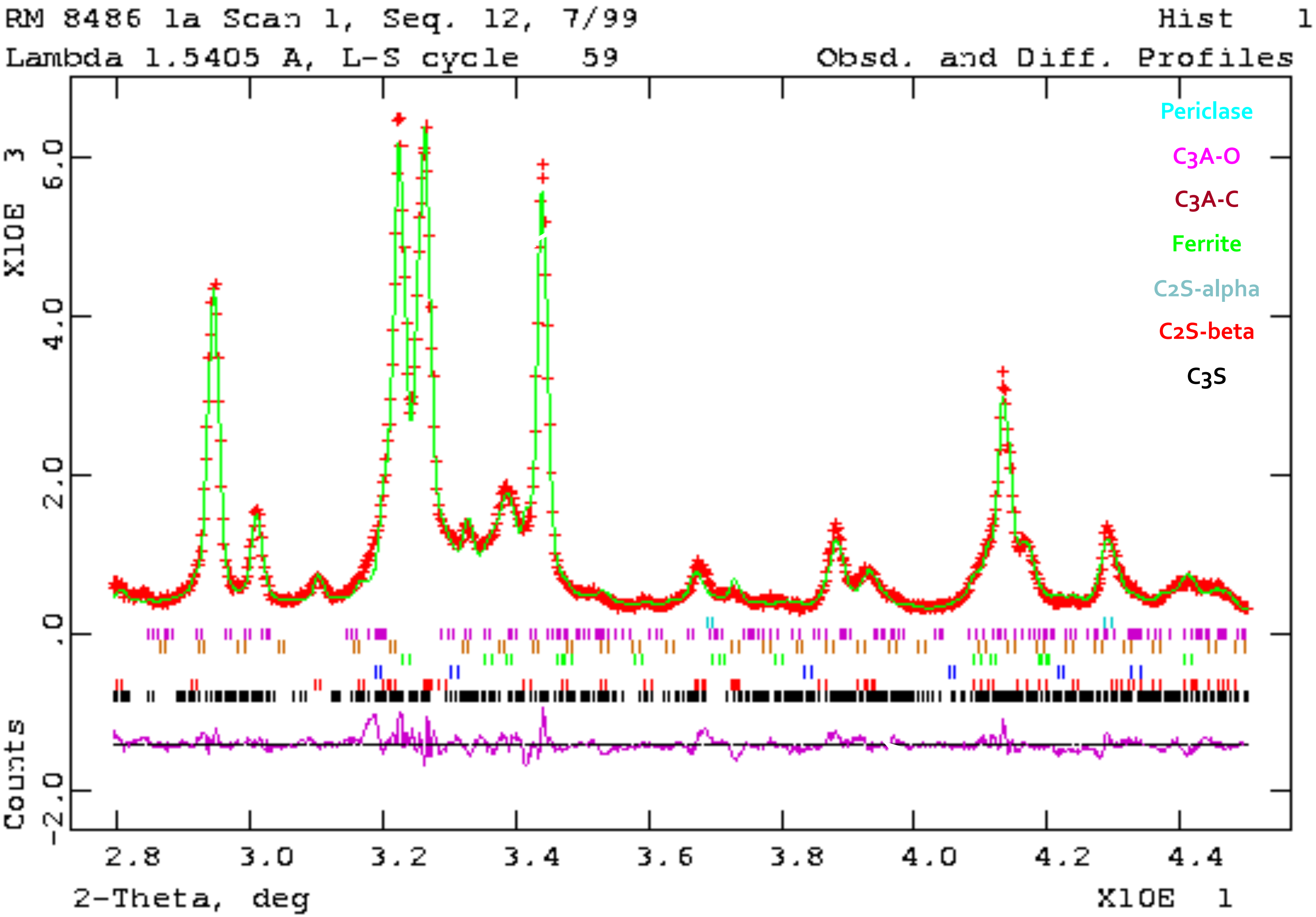


Pattern-fitting for QXRD of portland cement clinker, ICMA 1996

Early efforts used individual peak area measurement and calibration curves plotted as mass ratios vs. intensity ratios

Pattern-fitting improved the precision of the estimates of the calibration curves and for the unknown specimens

The first version of ASTM C1365 covered the interstitial phases based upon calibration curves developed using mixtures of pure phases


RM 8486 la Scan 1, Seq. 12, 7/99
Hist 1
Lambda 1.5405 A, L-S cycle 59
Obsd. and Diff. Profiles
X10E 3
6.0
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.0
-2.0
Counts
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
2-Theta, deg
X10E 1
Periclase
C_3A-O
C_3A-C
Ferrite
C_2S-alpha
C_2S-beta
C_3S

Phase Abundance Analysis

Simultaneous refinement of X-ray diffraction patterns of multiple phases allows quantitative analysis:

$$W_p = (S_p\,(ZMV)_p) \,/\, (\Sigma_i[S_i\,(ZMV)_i])$$

where

W_p - the mass fraction of phase p

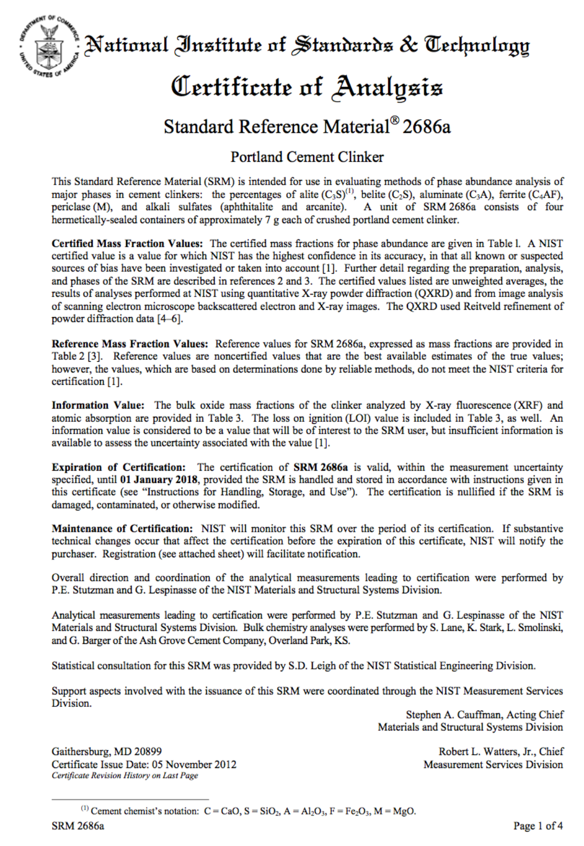
S - the Rietveld scale factor

Z - the number of formula units per unit cell

M - the mass of the formula unit

V - the unit cell volume

SRM Clinker Certificate



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.

Stephen A. Cauffman, Acting Chief
Materials and Structural Systems Division

Gaithersburg, MD 20899
Certificate Issue Date: 05 November 2012
Certificate Revision History on Last Page

Robert L. Watters, Jr., Chief
Measurement Services Division

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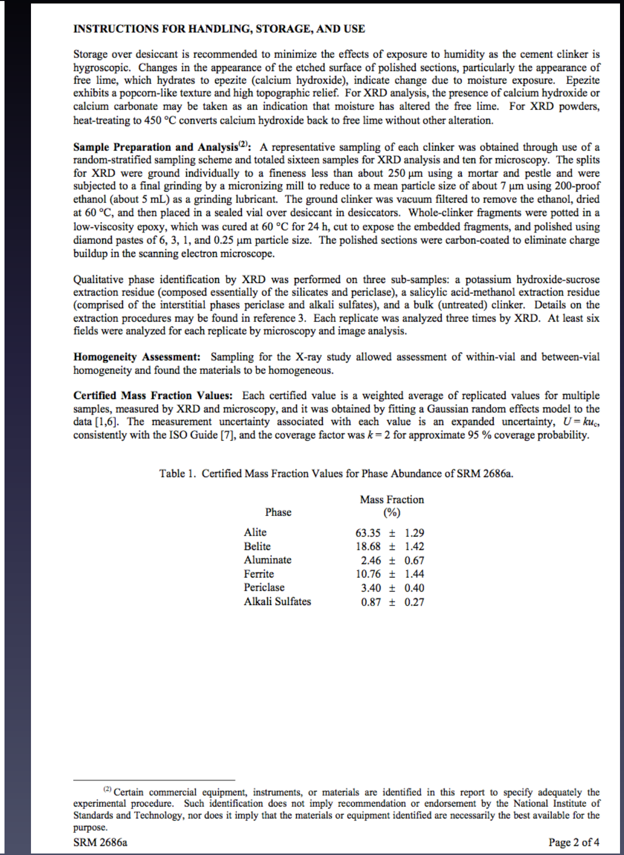
[1] Cement chemist's notation: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, M = MgO.



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

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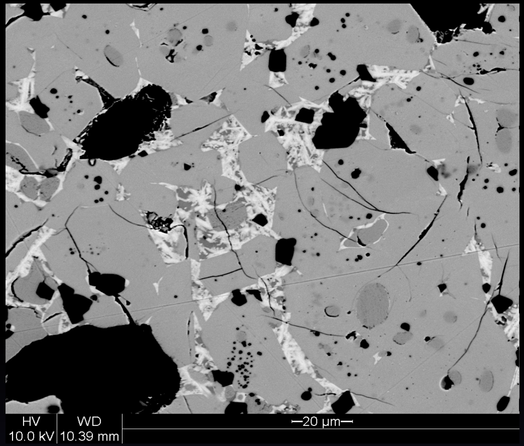
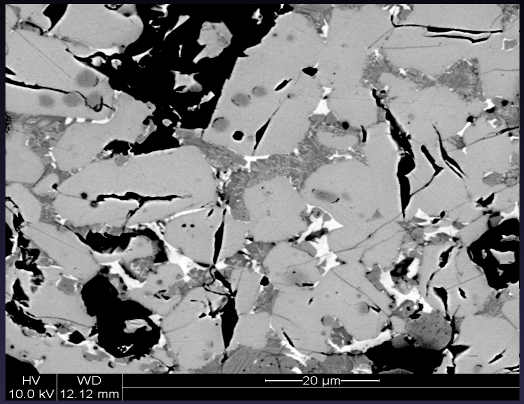
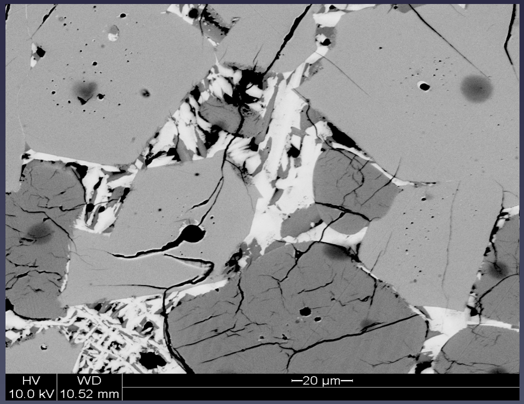
[2] Certain commercial equipment, instruments, or materials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment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



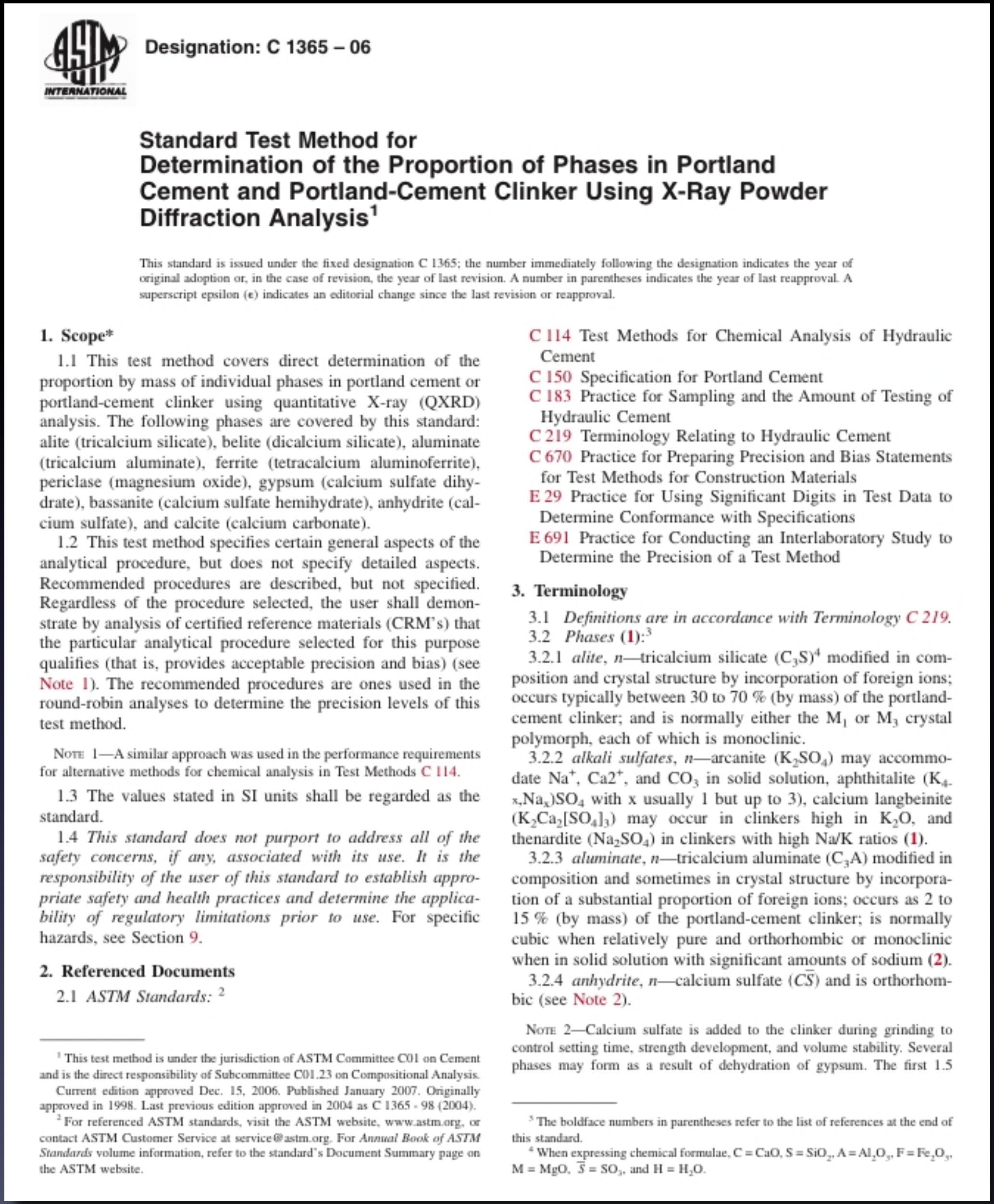




ASTM C1365

No detailed procedure; provides flexibility but increases potential for precision and bias

- Qualification approach based upon each user's analysis of SRM clinkers
- Precision and accuracy criteria based upon an inter-laboratory study
- Four cements compounded using SRM clinkers and lab-prepared calcium sulfates
- Rietveld and traditional methods are acceptable
- Some guidance provided for phase identification and analytical procedures



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]

This standard is issued under the fixed designation C 1365; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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

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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.

Current edition approved Dec. 15, 2006. Published January 2007. Originally approved in 1998. Last previous edition approved in 2004 as C 1365 - 98 (2004).

[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 $H = H_2O$.

Qualification

11.1.2 Prior to use for analysis each QXRD test procedure must be qualified. The laboratory shall maintain records that include a description of the procedure and the qualification data. These records shall be made available to the purchaser.

11.1.5 Qualification shall consist of analyzing the three SRM clinkers for the proportions of C_3S, C_2S, C_3A (cubic and orthorhombic), C_4AF, and M.

11.2.2 If replicate analyses are carried out, results should differ from each other by no more than the value shown in Table 1.

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

The inter-laboratory study included the calcium sulfates and calcite in anticipation of the analysis of cement, but those phases are not specified in the C150 specification

The numbers are pooled across four cements and are expressed in 1-s terms.

To convert sr and sR to ASTM r and R multiply by 1.96*√2

	Repeatability Within-lab		Reproducibility Between-lab	
	s within	r	s between	R
Alite	0.74	2.04	2.23	6.18
Belite	0.64	1.77	1.41	3.91
Aluminate	0.47	1.31	0.74	2.05
Ferrite	0.49	1.36	0.95	2.63
Periclase	0.23	0.63	0.32	0.89
Arcanite	0.22	0.60	0.41	1.13
Gypsum	0.21	0.59	0.58	1.62
Bassanite	0.39	1.08	0.81	2.24
Anhydrite	0.27	0.74	0.63	1.75
Calcite	0.99	2.73	0.50	1.50

The within-laboratory standard deviation for each phase is reported as 's-within'. Therefore, results of two properly conducted tests by the same operator should not vary more than 'r'.

The multi-laboratory standard deviations are 's-between'. Therefore, 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 'R'.

Table 2: Prediction Intervals

Accuracy:
"the closeness of agreement between a test result and a accepted reference value",
- *includes both random and systematic error*

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

The prediction intervals (95%) are designed to bracket values of a mean of k (=2,3,4) future measurements of the relevant phases

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***