Uncertainty in Bogue-Calculated Phase Composition of Hydraulic Cements

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Abstract

The Bogue calculations are used for cement manufacturing process control and acceptance limits for some cement classifications. While it is commonly understood that the Bogue calculations are estimates with potential intrinsic biases, the magnitudes of such biases are not generally known. The biases stem primarily from the compositional variation in phase solid solution, resulting in deviation of their bulk chemistry from that assumed in the calculations, and from bulk oxide measurement uncertainties. Uncertainties in Bogue estimates from these sources are quantified here through propagation-of-error analysis combining effects from bulk chemical analysis imprecision and estimates of variability in chemical compositions of the four principal clinker phases. Standard deviation (1σ) values of about 9.6 % for alite and belite, and 2.2 % and 1.4 % for aluminate and ferrite are calculated. This significant increase compared to uncertainty due to bulk oxide measurements is attributable to the imprecision of the Bogue constants.

Keywords: Bogue calculations, cement manufacture, characterization, uncertainty

1 Introduction

Cement manufacture and cement specifications routinely use estimates of phase composition obtained through the application of the Bogue calculation. These calculations use a set of constants based upon idealized phase chemistry and bulk oxide measurements to estimate phase abundance. L.A. Dahl [9] derived the corresponding formulae for clinker in 1939, which, with the addition of calcium sulfate, have remained essentially the same to this day. At the time the method was introduced, the extent and types of chemical variability in cement phases were not understood well enough to be incorporated. Variations in phase compositions were assumed to have only a minor effect on the calculated cement phase fractions [8]. Other neglected factors, such as insoluble residue and ignition loss were considered to exert only minor influences on the phase estimates.

The ability to estimate the phase fractions in a clinker or cement provides the means to relate composition to engineering performance attributes, especially durability-related ones such as sulfate resistance and properties for low heat cements. ASTM C150 was first issued in 1941 and included Bogue calculations and phase limits for different Types of cements [2, 27] as the primary means of classifying cements. Despite recurring concerns about phase estimate uncertainties, the magnitudes of such uncertainties are still not generally known.

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Nonetheless, the utility of the Bogue phase approach has been demonstrated by its use by industry for specifications over the past 70 years. The work of Bogue and Dahl [8, 9] implies that one can avoid direct phase determination using a chemical analysis based on a subset of the bulk oxides, which are generally easier to measure, and estimating the proportion of mineral phases from the oxides. Of the 13 analytes listed in ASTM C114 Table 1, only CaO, SiO_2, Al_2O_3, Fe_2O_3, and SO_3 are used in the Bogue calculations[1] because the calculations assume that each of the four mineral phases (alite, belite, aluminate, and ferrite) are chemically pure.

Actual uncertainties in phase estimates by Bogue calculation stem from a combination of sources: bulk oxide measurement uncertainties, differences between assumed phase and actual composition due to substitution, and compositional modifications during cooling reflecting absence of equilibrium. Taylor [25] suggested improvements to reduce estimate bias: unbiased bulk chemical analysis, corrections for components not present in the four major phases (free lime, insoluble residue) and, ideally, data on elements present in the phases other than the five utilized in the standard calculations. Unfortunately, this approach has never gained acceptance by the cement industry.

Any measurement is in reality only an estimate of the true value of the quantity being measured and should always be accompanied by an estimate of the measurement's uncertainty. Precision (Type A, random error) and bias (Type B, systematic error) are the two generic components of uncertainty. ASTM defines precision as "the closeness of agreement between independent test results obtained under stipulated conditions, which may be expressed as a standard deviation 1σ"[3]. Accuracy, or bias, is the closeness of agreement between a measurement and the corresponding true value, which is generally unknown. An estimate of the overall uncertainty requires consideration of the combined effects of Type A and Type B errors. There are multiple sources of uncertainty that are inherent in the Bogue calculations, which include the following:

- Matrix inversion numerical imprecisions due to numerical instabilities,

- Uncertainties in bulk oxide determinations,

- Covariances among oxide errors,

- Uncertainties in the Bogue constants, reflecting deviations of clinker phase chemistry from ideal assumptions,

- Lack of corrections for free lime and insoluble residue, and

- Method-of-measurement-specific biases (e.g., between reference methods and X-ray fluorescence by either fused glass or powder preparation.)

Forrester et al.[11] estimated uncertainty in Bogue calculations due to bulk oxide measurements made by two operators using traditional wet chemical analyses.

These traditional chemical methods are referred to as the Reference and the Alternate Methods in ASTM C114[1]. Eardley et al.[10] examined the effects of rounding on estimates through compilation of studies with replicate determinations. Aldridge[5] and Aldridge and Eardley[7] in the 1970's evaluated measurement uncertainty of the then relatively new X-ray fluorescence (XRF) analysis by a collaborative study with 23 laboratories and 6 cements. Aldridge[6] compared precision and bias of cement phase estimates by Bogue, XRD, and microscopy, and stated that while the Bogue method was the most suitable, each method suffered from bias and sampling error imprecision.

Stutzman and Lane[24] calculated enhanced Bogue phase estimate uncertainties by taking onto account oxide imprecisions for measurements by common bulk chemical analysis methods: the reference methods, X-ray fluorescence analyses by either wavelength-dispersive or energy-dispersive, and powder and glass preparations from CCRL proficiency test data. Oxide precision was slightly lower for the powder preparations, but the differences between wavelength and energy-dispersive instruments were small. While inter-method biases were found for some analytes, the Bogue-calculated values were roughly in agreement. In contrast to earlier findings of Aldridge[6], precisions for the Bogue-calculated silicates and aluminate phases were similar to those by X-ray powder diffraction, although for the ferrite phase the Bogue values appeared to be more precise.

Table 1: Published Bogue calculation uncertainties (1σ) expressed as mass fraction percent, based upon oxide measurement uncertainties.

Reference	Alite	Belite	Aluminate	Ferrite
Forrester et al.[11]	±2	±2	±0.7	±0.08
Aldridge and Eardley[7]	±(0.6 to 4.0)	±(0.6 to 4.0)	±(0.1 to 1.1)	±(0.06 to 0.4)
Aldridge[5]	±2.2	±2.0	±0.4	±0.2
Stutzman and Lane[24]				
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

Modified Bogue calculations determined upon chemical analyses of the four principal clinker phases have met with limited success, probably because the intrinsic variability in the phase bulk chemistry is not taken into account. Midgley[17] used electron microprobe analyses to determine the oxide compositions on the principal phases to calculate revised Bogue constants and compared such results to those from the traditional Bogue, quantitative X-ray powder diffraction and point-counting using light microscopy. He concluded that the modified Bogue procedure was only slightly better than the standard alternatives. Expanding upon his earlier work, Midgley[18] utilized 9 components, with the addition of MgO, K_2O, Na_2O, P_2O_5, and TiO_2, finding that improvement in phase estimates was realized only for sulfate-resisting cements with less than 3.5 % aluminate. Yamaguchi and Takagi[28] had inconclusive results from chemical analyses for the four major phases from eight clinkers, comparing microscopy, XRD, Bogue and their modified Bogue. Taylor[25] averaged bulk chemistry measurements for the primary phases to create a modified Bogue calculation, and concluded that the compositions were consistent enough to use averaged values. This yielded an improvement for all but the ferrite phase when compared to XRD values of the same clinkers.

2 Input Data for Expanded Calculations of Uncertainties

Propagating error around the classic ASTM C150 Bogue calculations should include incorporating uncertainties due to (1) oxide measurements and (2) the Bogue coefficients. Data for (1) come from interlaboratory test and proficiency programs, while data for (2) reflect the chemical variability of the principal clinker phases and come from measurements of Bogue matrices from multiple researchers. It might be objected that introducing variation in the Bogue matrix coefficients from a range of cements necessarily inflates the coefficient contributions to the phase estimate uncertainties. However, the C150 calculations are applied across the spectrum of cement Types, justifying the use of this set of coefficients.

For the uncertainty calculations in this paper, chemical oxide data for the four principal clinker phases from industrial clinkers were taken from Yamaguchi and Takagi[28], Kristmann[15], Ghose and Barnes[13], Harrison et al.[14] and data from the NIST SRM clinkers 2686, 2687, and 2688, and pure phase chemistries used in the current C150 calculations, providing fourteen 5 x 5 Bogue matrices in all. Calcium sulfate, as anhydrite, was added as the fifth phase to complete each matrix. The matrices are listed in Appendix A.

Bulk oxide means (Table 2) and uncertainties (Table 3) for the Reference Methods were calculated using data from the CCRL proficiency test program results for portland cements 163 (A) and 164 (B) using the paired sample analysis described in[4]. Uncertainties for bulk oxide analyses were taken from the ASTM C1.23 inter-laboratory studies by X-ray fluorescence, identified by specimen type as fused glass or pressed powder preparation[23, 22].

Table 2: Bulk oxide estimates for cements A and B expressed as mass percent by reference methods, wavelength-dispersive XRF by glass (WL-G) and powder (WL-P).

Cement A	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3
Reference	63.94	20.59	4.93	2.75	2.88
WL-G	63.875	20.533	5.008	2.737	2.851
WL-P	64.106	20.674	4.824	2.744	2.907
Cement B					
Reference	63.64	20.20	5.13	4.24	3.58
WL-G	63.509	20.236	5.132	4.240	3.568
WL-P	63.709	20.119	5.131	4.248	3.551

Table 3: Repeatability and reproducibility values expressed as 1σ and 95 % limits (ASTM d2s, 2.77*1σ) for XRF glass and powder methods and the reference chemical methods [23, 22].

Repeatability	XRF Glass		XRF Powder		Reference	
	1σ	95 % Limits	1σ	95 % Limits	1σ	95 % Limits
SiO_2	0.054	0.150	0.105	0.291	0.10	0.27
Al_2O_3	0.023	0.064	0.026	0.071	0.11	0.30
Fe_2O_3	0.013	0.035	0.017	0.048	0.05	0.13
CaO	0.111	0.307	0.131	0.362	0.15	0.40
SO_3	0.042	0.115	0.028	0.078	0.02	0.06
Reproducibility	XRF Glass		XRF Powder		Reference	
	1σ	95 % Limits	1σ	95 % Limits	1σ	95 % Limits
SiO_2	0.130	0.361	0.202	0.561	0.15	0.42
Al_2O_3	0.064	0.176	0.096	0.266	0.15	0.42
Fe_2O_3	0.035	0.097	0.045	0.126	0.06	0.18
CaO	0.360	0.999	0.319	0.885	0.23	0.64
SO_3	0.078	0.217	0.115	0.319	0.04	0.12

3 First-Order Propagation-of-Error Applied to the Bogue Calculations

The ASTM C150 Bogue matrix is based on the chemical compositions of "pure" phases since the types and amounts of solid solution were not known at the time of original publication. Expressed in matrix vector notation, oxides =B(phases), phases = B^{-1}(oxides) where B and B^{-1} are 5 (row) x 5 (column) matrices. Oxides and phases are both represented as 5 x 1 vectors.

$$\begin{bmatrix} CaO \\ SiO_2 \\ Al_2O_3 \\ Fe_2O_3 \\ SO_3 \end{bmatrix} = \begin{bmatrix} 0.7368 & 0.6512 & 0.6226 & 0.4610 & 0.4119 \\ 0.2632 & 0.3488 & 0.0000 & 0.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.3774 & 0.2100 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.3290 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.5881 \end{bmatrix} \left(\begin{bmatrix} C_3S \\ C_2S \\ C_3A \\ C_4AF \\ C\overline{S} \end{bmatrix} \right)$$

Inversion of the ASTM C150 Bogue matrix provides a set of equations, commonly called the Bogue calculations, for alite, belite, aluminate, and ferrite, respectively[2]:

$C_3S = (4.071 \cdot \%CaO) - (7.600 \cdot \%SiO_2) - (6.718 \cdot \%Al_2O_3) - (1.430 \cdot \%Fe_2O_3) - (2.852 \cdot \%SO_3)$

$C_2S = (2.867 \cdot SiO_2) - (0.7544 \cdot C_3S)$

$\quad = (-3.075 \cdot CaO) + (8.608 \cdot SiO_2) + (5.703 \cdot Al_2O_3) + (1.071 \cdot Fe_2O_3) + (2.154 \cdot SO_3)$

$C_3A = (2.65 \cdot Al_2O_3) - (1.692 \cdot Fe_2O_3)$

$C_4AF = (3.043 \cdot Fe_2O_3)$

In what follows, B represents the C150 Bogue matrix, B$_t$ (t=1...14) represents the 14 Bogue matrices selected from the literature used to impute uncertainties on the B matrix coefficients (Appendix A). Expressed in matrix vector notation, oxides = B(phases) and oxide$_t$ = B$_t$(phase$_t$). From the chemical analyses we have oxides and wish to estimate phases. A Bogue analysis with error considered to reside only in the oxides represents a simplest kind of uncertainty model. If δ is the vector of uncertainties in the oxides represented as a 5 x 1 vector, then:

$oxide \pm \delta = B(phase)$ and $phase = B^{-1}(oxide \pm \delta)$

$oxide \pm \delta = B_t(phase)$ and $phase = B_t^{-1}(oxide \pm \delta)$

Previous studies have employed simple linear propagation-of-error on the Bogue estimates using only the bulk oxide uncertainties. However, the coefficients of B are also uncertain, so that a more comprehensive error model is represented by:

$oxide \pm \delta = (B + \epsilon)(phase)$ and $(phase) = (B + \epsilon)^{-1}(oxide \pm \delta)$

$oxide \pm \delta = (B_t + \epsilon)(phase)$ and $(phase) = (B_t + \epsilon)^{-1}(oxide \pm \delta)$

ε is the 5 x 5 matrix of errors in the entries of B, which can be estimated from variabilities among Bogue data matrix coefficients taken from the literature (Appendix A). The primary rules for first-order propagation-of-error used in the calculations written out in the explicit formulas that follow make use of the following conventions for all calculations: Work at the 1σ (population standard deviation) level computed as s (sample standard deviation) or $s/\sqrt{n}$ (standard deviation of the mean), where n = relevant sample size. If desired, multiply by a coverage factor k = 2, 3 to obtain nominal 95 %, 99 % confidence only at the end. Means are used for oxides for each method. Type A (precision) components of uncertainty are expressed as $s/\sqrt{n}$ or their squares (variances) computed from "within" components of variance. Type B (bias) components of uncertainty are expressed as s or their squares computed from "between" components of variance.

After matrix inversion, phase calculations involve only addition and multiplication. If covariances are first ignored, the basic arithmetic is reduced to the repeated use of two rules [[16], Table 1]. Absolute uncertainties in sums propagate as root sums of squares of absolute uncertainties.

$$s_{\overline{x+y}} = \sqrt{s_{\overline{x}}^2 + s_{\overline{y}}^2}$$

Relative uncertainties in products propagate as root sums of squares of relative uncertainties.

$$\frac{s_{\overline{xy}}}{\overline{xy}} = \sqrt{\left(\frac{s_{\overline{x}}}{\overline{x}}\right)^2 + \left(\frac{s_{\overline{y}}}{\overline{y}}\right)^2}$$

Use of these formulas would appear to treat the propagation-of-error as a pure Type A problem. However, biases (Type B uncertainties), due to incorrect measurement of the oxides and B coefficients, enter through the inter-method biases inherent in the use of 14 sources of data (literature plus C150) as well.

Multiple phase vectors are estimated by multiple inversions and averaging of B_t^{-1} compounding the errors in the coefficients of the final resulting B^{-1}. Applying B^{-1} to an oxide vector, which also contains errors, further magnifies the errors in B^{-1} coefficients and oxides, propagating through to overall errors in phases.

B_t^{-1} inversions could result in conditioning error. Successful numerical inversion of a matrix requires that the matrix be "well-conditioned" for the inverse to be accurate and meaningful. If B_t is ill-conditioned, phase estimates derived from phase $= B^{-1}$ (oxide), with oxide values reported to 3 decimal places can be very different from phase estimates obtained applying the same formula with the same B_t^{-1} matrix with oxide values rounded to only 1 decimal place. Condition numbers, κ, are computed from real entry matrices to pre-assess the reliability of the inversion and upper bound the ratio of the relative error in the input to the relative error in the output [26]. Modest condition numbers, on the order of 1 to 100, imply clean invertibility of the matrix, while large condition numbers, on the order of $>10^5$, imply numerical instability. Matrix inverses were calculated for each of the 14 Bogue matrices employed here using Dataplot[2], which employs Linpack[3] routines SGECO and SGEDI for matrix inversion based upon Gaussian elimination[4]. The condition numbers for the 14 Bogue matrices used here range from 12 to 18 (Appendix A). Consequently, the numerically calculated inverse coefficients employed in the propagation-of-error calculations here are reliable, and uncertainty due to inversion may be safely ignored for the level of precision being reported here.

The C150 Bogue formulae coefficients are used for the propagation-of-error, with the expanded formula for belite to avoid correlation problems between C_3S and SiO_2 as discussed by Forrester et al.[11]. These cements do not contain limestone, so CO_2 was not determined, nor were any related adjustments made. The oxide uncertainties, ε_{oxide}, are expressed as 1σ, taken to be the square root of the sum of the squares of the repeatabilities and reproducibilities for each of the calcium, silicon, aluminum, iron, and sulfur oxide determinations separately. The Bogue constants uncertainties, for example $\varepsilon_{4.071}$, are expressed as standard uncertainties of means, $s/\sqrt{14}$, based on the 14 individual literature determinations.

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[2]Dataplot is a public-domain, multi-platform software system for scientific visualization, statistical analysis, and non-linear modeling available from: http://www.itl.nist.gov/div898/software/dataplot/

[3]"LINPACK User's Guide," Dongarra, Bunch, Moler, and Stewart, Siam, 1979.

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

The first order propagation-of-error formula's for alite, belite, aluminate and ferrite then become[16]:

$$\sigma alite = \sqrt{(4.071 \cdot CaO)^2 \left[\frac{\varepsilon_{4.071}^2}{4.071^2} + \frac{\varepsilon_{CaO}^2}{CaO^2} \right] + (7.600 \cdot SiO_2)^2 \left[\frac{\varepsilon_{7.600}^2}{7.600^2} + \frac{\varepsilon_{SiO_2}^2}{SiO_2^2} \right] + (6.718 \cdot Al_2O_3)^2 \left[\frac{\varepsilon_{6.718}^2}{6.718^2} + \frac{\varepsilon_{Al_eO_3}^2}{Al_2O_3^2} \right]}$$

$$\overline{+ (1.430 \cdot Fe_2O_3)^2 \left[\frac{\varepsilon_{1.430}^2}{1.430^2} + \frac{\varepsilon_{Fe_2O_3}^2}{Fe_2O_3^2} \right] + (2.852 \cdot SO_3)^2 \left[\frac{\varepsilon_{2.852}^2}{2.852^2} + \frac{\varepsilon_{SO_3}^2}{SO_3^2} \right]}$$

$$\sigma\, belite = \sqrt{(3.075 \cdot CaO)^2 \left[\frac{\varepsilon_{3.075}^2}{3.075^2} + \frac{\varepsilon_{CaO}^2}{CaO^2} \right] + (8.608 \cdot SiO_2)^2 \left[\frac{\varepsilon_{8.608}^2}{8.608^2} + \frac{\varepsilon_{SiO_2}^2}{SiO_2^2} \right] + (5.073 \cdot Al_2O_3)^2 \left[\frac{\varepsilon_{5.073}^2}{5.073^2} + \frac{\varepsilon_{Al_eO_3}^2}{Al_2O_3^2} \right]}$$

$$\overline{+ (1.071 \cdot Fe_2O_3)^2 \left[\frac{\varepsilon_{1.071}^2}{1.071^2} + \frac{\varepsilon_{Fe_2O_3}^2}{Fe_2O_3^2} \right] + (2.154 \cdot SO_3)^2 \left[\frac{\varepsilon_{2.154}^2}{2.154^2} + \frac{\varepsilon_{SO_3}^2}{SO_3^2} \right]}$$

$$\sigma\, aluminate = \sqrt{(2.650 \cdot Al_2O_3)^2 \left[\frac{\varepsilon_{2.650}^2}{2.650^2} + \frac{\varepsilon_{Al_eO_3}^2}{Al_2O_3^2} \right] + (1.692 \cdot Fe_2O_3)^2 \left[\frac{\varepsilon_{1.692}^2}{1.692^2} + \frac{\varepsilon_{Fe_2O_3}^2}{Fe_2O_3^2} \right]}$$

$$\sigma\, ferrite = \sqrt{(3.043 \cdot Fe_2O_3)^2 \left[\frac{\varepsilon_{3.043}^2}{3.043^2} + \frac{\varepsilon_{Fe_2O_3}^2}{Fe_2O_3^2} \right]}$$

The expression for $\sigma_{ferrite}$ comes from the direct application of the (relativized) uncertainty of a product rule [[16], Table 1] to the single product term of the Bogue formula for C$_4$AF. The oxide uncertainty comes from Table 3. The Bogue constant "3.043" uncertainty comes from a standard deviation of the 14 Fe$_2$O$_3$ Bogue coefficients from each of the 14 ferrite rows in the matrices of Appendix A (right-hand panel), divided by $\sqrt{14}$. So, explicitly, $s/\sqrt{14}$ for the ferrite Fe$_2$O$_3$ constant is computed from the vector of entries (3.04, 5.62, 10.54, 5.90, 5.67, 6.26, 5.82, 4.04, 5.24, 6.34, 6.05, 5.10, 8.82, 4.72). The C150 value of 3.043 is used as the Bogue multiplying and dividing constant in the formula to be consistent with the calculations as used in ASTM C150.

The expression for σaluminate comes from application of the same technique just described to each of the two product terms of the aluminate formula, then adding the two component uncertainties in variance (squared) form.

The expressions for the σ_{alite} and σ_{belite} are similarly computed, except that there are now five product terms, each of whose uncertainties must be computed via their relativized forms, and the five uncertainties added together.

Table 4: Multiplicative Covariances

	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$
Alite	-0.00258	-0.00068	-0.00056	-0.00621	0.00004
Belite	-0.00195	-0.00819	0.00067	0.00314	-0.00019
Aluminate	-0.00087	-0.00016	-0.02717	-0.03833	0.00000
Ferrite	0.00006	-0.00061	-0.00845	-0.05368	-0.00001

4 Second-Order Additions to the Propagation-of-Error

Second-order terms must also be calculated because, if large enough, these covariance terms could significantly increase or decrease the first order estimates. The correction terms here take two generic forms.

4.1 Covariance Corrections to the (Bogue - Oxide) Product Uncertainties

First, (Bogue - Oxide) mean product relativized covariances, which modify the individual product uncertainty terms, must be calculated. Such product correction terms take the form [[16], Table 1]:

$$\frac{2 \cdot COV(x,y)}{\overline{x} \cdot \overline{y}} = \left[\frac{2 \cdot COV(Bogue, oxide)}{Bogue \cdot oxide} \right]$$

The covariance is the scalar ("dot") product of the Bogue and oxide vectors, each vector normalized by subtracting its mean, divided by the number of entries common to the vectors minus 1. For example, the ferrite uncertainty calculation now becomes:

$$\sigma_{ferrite} = \sqrt{(3.043 \cdot Fe_2O_3)^2 \left[\frac{\epsilon_{3.043}^2}{3.043^2} + \frac{\epsilon_{Fe_2O_3}^2}{(Fe_2O_3)^2} + \frac{2 \cdot COV\left[3.043, Fe_2O_3\right]}{3.043 \cdot Fe_2O_3} \right]}$$

The ferrite Fe$_2$O$_3$ Bogue coefficient vector from the right-hand panel of Appendix A written out explicitly above, and the vector of matching Fe$_2$O$_3$ mass percent values from the left-hand panel of Appendix A: [(3.04, 32.90), (5.62, 21.40), (10.54, 20.00), (5.90, 22.20), (5.67, 22.10), (6.26, 22.10), (5.82, 20.80), (4.04, 26.70), (5.24, 25.00), (6.34, 19.60), (6.05, 20.50), (5.10, 21.60), (8.82, 17.10), (4.72, 24.80)].

For the multi-term Bogue formulas, such relativized covariances are computed for each of the product terms, then added or subtracted according to the sign of the covariance. The results (1σ) are shown in Table 4.

4.2 Covariance Corrections to the Sums of (Bogue - Oxide) Uncertainties

Additive Corrections

Second, for each of the Bogue formulas containing more than one parenthesized term from among CaO, SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, SO$_3$ twice the covariance between the various added terms must also be incorporated. So, for example, in the aluminate calculation 2 COV[2.650 Al$_2$O$_3$, -1.692 Fe$_2$O$_3$] must be added 2 COV[x,y] = 2 COV [(Bogue.Oxide)$_1$, (Bogue.Oxide)$_2$] [[16], Table 1]. Again, "2.650" and "1.692" stand for the vectors of varying aluminate Al$_2$O$_3$ and Fe$_2$O$_3$ coefficients, respectively, across the 14 literature-based and ideal Bogue matrices, [(2.65, 37.74; -1.692, 0.00), (3.67, 31.30; -3.95, 5.10) ... (3.29, 34.90; -2.96, 5.80)]. The results (1σ) are shown in Table 5. While individual covariances are uniformly small, there is nonetheless a modest cumulative effect on several of the overall uncertainties tabulated in Table 6.

Table 5: Additive Covariances by Method

	Glass		Powder		Reference	
	A	B	A	B	A	B
CaO/SiO_2	0.033	0.031	0.024	0.031	0.036	0.027
CaO/Al_2O_3	0.006	0.007	0.000	-0.013	-0.038	-0.016
CaO/Fe_2O_3	0.000	0.002	0.006	0.006	-0.004	-0.011
CaO/SO_3	0.000	-0.004	-0.002	-0.001	0.014	0.014
SiO_2/Al_2O_3	0.008	0.005	0.003	0.005	0.004	0.003
SiO_2/Fe_2O_3	0.001	0.000	0.000	0.002	-0.004	-0.007
SiO_2/SO_3	0.002	0.002	0.002	0.005	0.004	0.007
Al_2O_3/Fe_2O_3	0.000	-0.001	0.002	0.006	0.003	0.002
Al_2O_3/SO_3	0.000	0.001	0.002	0.018	-0.004	-0.003
Fe_2O_3/SO_3	0.000	0.001	0.000	0.002	0.000	-0.002

5   Results and Discussion

The addition of consideration of the uncertainties in the Bogue constants results in an increase in phase estimate uncertainty by a factor of about five to six over that obtained from just using the oxide uncertainties by themselves (Table 6 vs. Table 1). The practical significance of such differences can be illustrated with multiple examples.

For example, nominal specification limits are often placed on the aluminate phase used as an indicator of sulfate resistance in ASTM C150 cements. The distinction between a Type II aluminate limit of 8 % versus 5 % for a high sulfate-resistant Type V cement becomes essentially negligible if these newer estimates of phase uncertainty are taken into account. Similarly, the nominal limits for Type III cements for moderate (8 % aluminate) and high sulfate resistance (5 %) are negligible. Finally, the compositional range for a Type IV low heat cement becomes fairly broad if the ± 9.5 % to 9.7 % uncertainties for both alite and belite are taken into account.

As another example, using the ASTM C150 calculations for the mean phase values, the new overall uncertainties for the four major phases in cements 163 (A) and 164 (B) are shown in a whisker plot (Figure 1). The relatively small displacements between the mean phase results of the individual analytical methods contrasted with the relatively large tails of the whisker plots, shows that that while there may be some modest differences between the methods, method uncertainties are so small compared to the uncertainties into the Bogue constants themselves that the results across methods appear to be quite consistent.

Cement specification limits for heat of hydration are based upon Bogue-calculated phase abundance of alite, aluminate and ferrite, for Type II and Type V cements. The Heat Index Equation[19] was derived based upon a cement heat of hydration of 335 kJ kg^{-1}, with a maximum Heat Index value of 100. The right-hand side of this equation, $C_3S+4.75 \cdot C_3A \leq 100$, based upon Bogue phase estimates, should

Table 6: Uncertainty in Bogue-calculated phase estimates by cement expressed as 1σ mass percent by method for cements A and B including multiplicative and additive covariance effects.

|	Alite	Belite	Aluminate	Ferrite	Alite	Belite	Aluminate	Ferrite
A		including covariances				no covariance correction		
Reference	9.55	9.49	2.27	1.07	9.64	9.63	2.40	1.44
WL-Glass	9.58	9.54	2.15	0.98	9.67	9.68	2.30	1.36
WL-Powder	9.72	9.74	2.11	0.98	9.81	9.88	2.25	1.36
B								
Reference	9.69	9.56	2.93	1.76	9.78	9.70	3.01	2.11
WL-Glass	9.71	9.59	2.90	1.74	9.80	9.73	2.98	2.10
WL-Powder	9.81	9.75	2.91	1.75	9.89	9.89	2.99	2.11
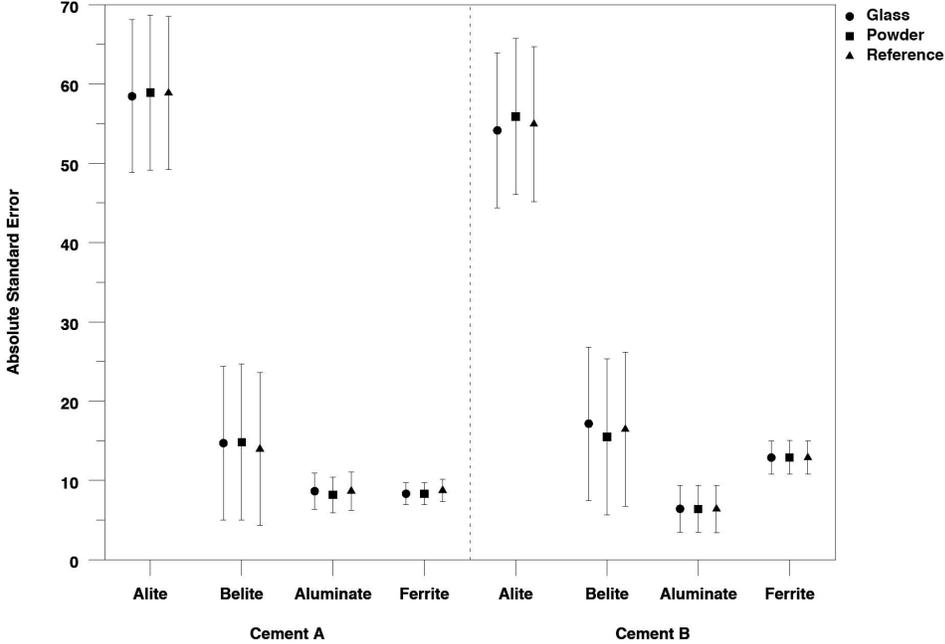
Figure 5.1: Whisker plot for cements A and B showing the Bogue calculated mass fractions and uncertainties as $\pm\,1\sigma$ mass percent for the four major cement phases indicates no significant difference by analytical method.

actually be expressed as 100 ± 15 (1σ) in order to account for the newer phase-related uncertainties. Plotting the CCRL and other cements in Figure 2, the uncertainty limits plotted in blue now incorporate those cements that actually exceeded the heat limit of 85, but not the heat index limit of 100. However, a large portion of the cements in the study exceed the limit when uncertainty is considered, suggesting strong limitations on the use of this indirect measure of heat of hydration. For Type V cements, limits on ferrite and aluminate expressed as $C_4AF + 2{\cdot}C_3A \leq 25$ would be more accurately expressed as 25 ± 5 (1σ).

An interesting comparison using the new uncertainty estimates may be seen in plots of Bogue values vs. quantitative X-ray powder diffraction (QXRD) results in Figures 3 and 4[21]. For the data plotted, the spread of the data points correspond roughly to the 1σ uncertainty value calculated in this study. While the QXRD procedure has its own associated uncertainties that contribute to the scatter, they are lower than those of the Bogue calculations[20].
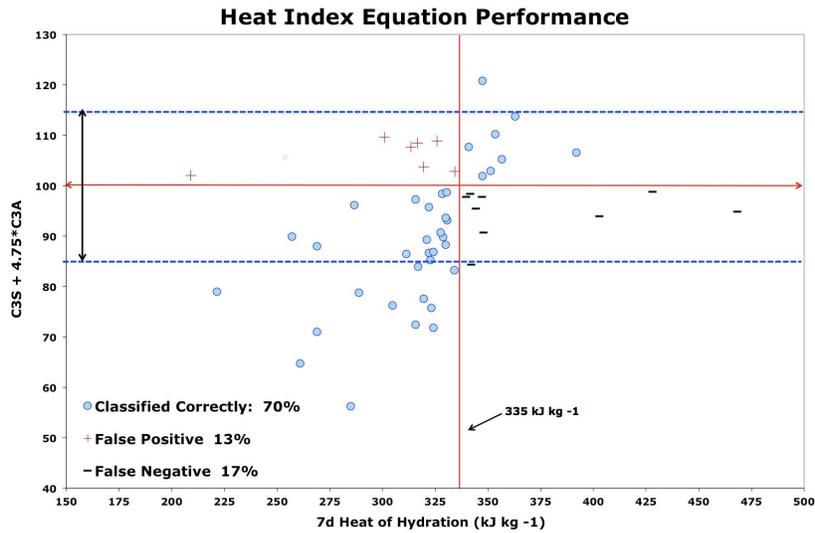
Figure 5.2: Heat Index Equation vs. 7d heat of hydration data with uncertainty bounds. The lower limit being 85 would include cements with 7 d heat of hydration values down to 260 kJ kg-1 and include those initially falsely ranked as within the 335 kJ kg-1 limit [21].
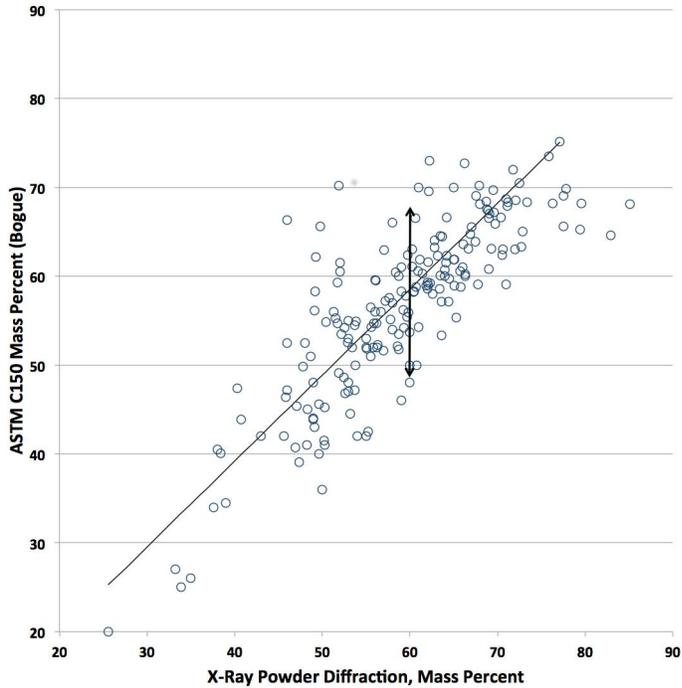
Figure 5.3: Calibration plot of X-ray powder diffraction vs. Bogue values for data from 11 data sets reflects a point spread along the Y direction approximately the width of the 9.7 % 1σ uncertainty calculated for alite [21].

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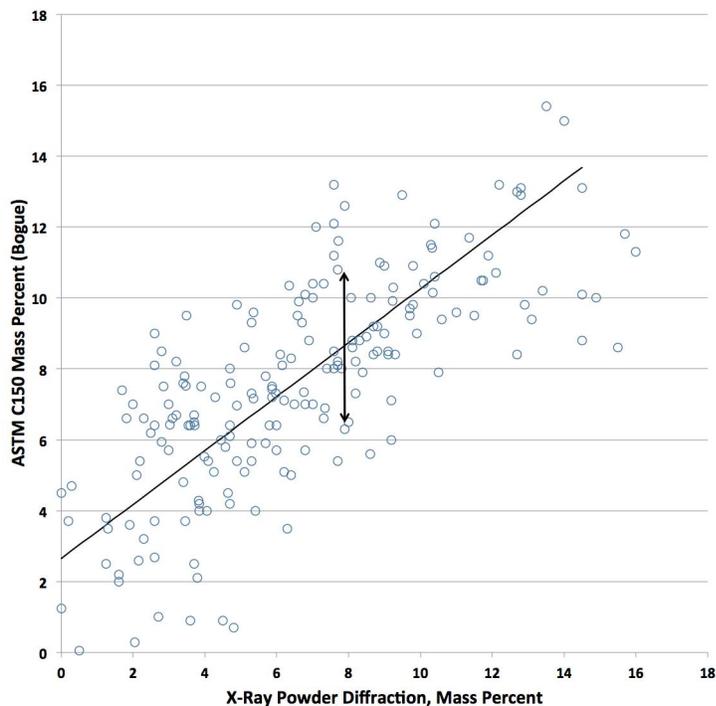
Figure 5.4: 1σ Bogue uncertainty of ± 2.2 % spans the point spread of the Bogue-estimated aluminate values along the y axis at the 8 % Bogue limit for Type III cements on this calibration plot of X-ray powder diffraction vs. Bogue values from 11 data sets [21].

6.0 Conclusions

The inclusion of uncertainties of the Bogue constants into overall uncertainty estimates for the calculated phases significantly inflates those overall estimates of uncertainty. These actual larger uncertainties, not always appreciated, have long posed implicit, unrecognized difficulties in efforts to relate phase compositions, estimated by Bogue calculations, to performance attributes. Such larger, more realistic uncertainty estimates complicate phase-specific limits in ASTM cement specifications, in some instances consideration of the true uncertainties rendering supposedly distinct classes of cements practically indistinguishable.

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Table 7: Phase Oxides, Bogue Constants and Condition Numbers

Source	Oxide	Mass Percent				Phase	Bogue Constants					K
		alite	belite	aluminate	ferrite		CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	
Ideal	CaO	73.68	65.12	62.26	46.10	alite	4.070	-7.6000	-6.7180	-1.4305	-2.8506	12
	SiO_2	26.32	34.88	0.00	0.00	belite	-3.0750	8.6080	5.0730	1.0710	2.1540	
	Al_2O_3	0.00	0.00	37.74	21.00	aluminate	0.0000	0.0000	2.6497	-1.6917	0.0000	
	Fe_2O_3	0.00	0.00	0.00	32.90	ferrite	0.0000	0.0000	0.0000	3.0432	0.0000	
	SO_3	0.00	0.00	0.00	0.00	anhydrite	0.0000	0.0000	0.0000	0.0000	1.7004	
Taylor 97	CaO	71.60	63.50	56.60	47.50	alite	4.5686	-8.6799	-6.9859	-1.5313	-3.1998	14
	SiO_2	25.20	31.50	3.70	3.60	belite	-3.6659	10.1679	5.2565	1.0471	2.5676	
	Al_2O_3	1.00	2.10	31.30	21.90	aluminate	0.1160	-0.3652	3.6726	-3.9545	-0.0813	
	Fe_2O_3	0.70	0.90	5.10	21.40	ferrite	-0.0229	-0.0567	-0.8680	5.6213	0.0161	
	SO_3	0.10	0.20	0.00	0.00	anhydrite	0.0047	-0.0198	-0.0060	-0.0010	1.6971	
Yamaguchi	CaO	72.76	62.53	53.00	45.50	alite	3.7455	-6.8197	-6.7259	1.3862	-2.6233	18
N1	SiO_2	24.15	31.85	4.60	4.30	belite	-2.8548	8.3829	4.5954	-1.0750	1.9995	
	Al_2O_3	1.30	2.68	27.20	25.10	aluminate	0.1090	-0.4730	7.6061	-9.6920	-0.0764	
	Fe_2O_3	0.66	1.25	11.40	20.00	ferrite	-0.0073	-0.0293	-4.4008	10.5459	0.0051	
	SO_3	0.00	0.27	0.00	0.00	anhydrite	0.0131	-0.0385	-0.0211	0.0049	1.6912	
Yamaguchi	CaO	71.46	62.38	53.40	44.90	alite	4.1096	-7.4135	-5.8969	-0.7756	-2.8784	20
N2	SiO_2	25.13	33.17	7.10	3.00	belite	-3.1108	8.6518	3.5467	1.1924	2.1788	
	Al_2O_3	1.17	1.61	27.50	24.60	aluminate	-0.0308	-0.0096	4.8596	-5.3214	0.0216	
	Fe_2O_3	0.61	1.05	6.00	22.20	ferrite	0.0425	-0.2029	-1.3191	5.9076	-0.0298	
	SO_3	0.00	0.05	0.00	0.00	anhydrite	0.0026	-0.0074	-0.0030	-0.0010	1.6985	
Yamaguchi	CaO	72.74	63.86	54.80	44.50	alite	4.0558	-7.7815	-6.2025	0.1674	-2.8406	13
N3	SiO_2	24.10	31.62	5.80	4.30	belite	-3.0999	9.1493	4.0730	-0.0169	2.1711	
	Al_2O_3	1.20	1.99	28.70	24.30	aluminate	0.0596	-0.2729	4.3140	-4.8104	-0.0418	
	Fe_2O_3	0.61	0.78	5.30	22.10	ferrite	-0.0168	-0.0427	-1.0071	5.6745	0.0118	
	SO_3	0.05	0.26	0.00	0.00	anhydrite	0.0103	-0.0338	-0.0127	-0.0001	1.6932	
Kristmann	CaO	71.00	64.40	55.30	49.00	alite	5.1386	-10.0815	-7.5498	-1.6437	-3.5990	16
2	SiO_2	25.00	30.50	3.70	3.10	belite	-4.2283	11.6114	5.8263	1.3135	2.9614	
	Al_2O_3	150	2.80	31.00	24.40	aluminate	0.1207	-0.4225	4.3110	-4.9679	-0.0845	
	Fe_2O_3	0.90	1.40	7.80	22.10	ferrite	0.0160	-0.1759	-1.5831	6.2620	-0.0112	
	SO_3	0.00	0.00	0.00	0.00	anhydrite	0.0000	0.0000	0.0000	0.0000	1.7004	
Kristmann	CaO	72.00	64.90	58.30	49.90	alite	4.7786	-9.1770	-7.5214	-2.2532	-3.3469	15
11	SiO_2	25.30	31.50	3.10	2.60	belite	-3.8475	10.5898	5.7557	1.7359	2.6948	
	Al_2O_3	1.40	2.70	31.70	22.30	aluminate	0.0719	-0.3130	3.7310	-4.1334	-0.0503	
	Fe_2O_3	0.60	1.50	5.20	20.80	ferrite	0.0292	-0.1662	-0.9925	5.8226	-0.0204	
	SO_3	0.00	0.00	0.00	0.00	anhydrite	0.0000	0.0000	0.0000	0.0000	1.7004	
Kristmann	CaO	72.40	63.70	53.30	50.00	alite	5.2449	-10.2876	-5.6885	-8.6383	-3.6735	16
25	SiO_2	25.10	31.70	4.30	1.80	belite	-4.2490	11.5937	4.2043	6.8132	2.9760	
	Al_2O_3	1.00	1.50	31.80	23.00	aluminate	0.1727	-0.6068	3.0452	-0.5448	-0.1209	
	Fe_2O_3	1.00	1.10	6.30	26.70	ferrite	-0.1360	-01469	-0.5925	4.0411	0.0952	
	SO_3	0.00	0.00	0.00	0.00	anhydrite	0.0000	0.0000	0.0000	0.0000	1.7004	
Kristmann	CaO	70.20	63.70	51.50	47.40	alite	5.0179	-9.6587	-6.6356	-3.1865	-3.5145	14
27	SiO_2	25.10	31.70	4.30	2.50	belite	-3.9784	10.8332	4.7600	2.6137	2.7865	
	Al_2O_3	1.00	1.50	28.70	20.20	aluminate	0.0668	-0.2167	4.4724	-3.7186	-0.0468	
	Fe_2O_3	1.00	1.10	8.30	25.00	ferrite	-0.0478	-0.0184	-1.4289	5.2470	0.0335	
	SO_3	0.00	0.00	0.00	0.00	anhydrite	0.0000	0.0000	0.0000	0.0000	1.7004	

Table 8: Phase Oxides, Bogue Constants and Condition Numbers

Source	Oxide	Mass Percent				Phase	Bogue Constants					K
		alite	belite	aluminate	ferrite		CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$	
Harrison	CaO	72.60	63.20	56.00	47.40	alite	4.4891	-8.4221	-6.5891	-1.7779	-3.1441	14
A	SiO$_2$	25.80	31.80	4.20	3.80	belite	-3.6529	10.0284	4.9654	1.2781	2.5585	
	Al$_2$O$_3$	1.00	2.10	31.30	22.10	aluminate	0.0404	-0.2273	3.9439	-4.5005	-0.0283	
	Fe$_2$O$_3$	0.40	0.80	5.00	19.60	ferrite	0.0462	-0.1737	-1.1749	6.3490	-0.0323	
	SO$_3$	0.00	0.20	0.00	0.10	anhydrite	0.0123	-0.0338	-0.0149	-0.0151	1.6917	
Harrison	CaO	70.60	62.90	54.80	47.90	alite	4.6050	-8.7587	-7.0249	-2.0288	-3.2253	14
B	SiO$_2$	24.60	31.00	5.00	4.00	belite	-3.6647	10.2349	5.0241	1.5413	2.5668	
	Al$_2$O$_3$	1.20	2.00	28.10	20.40	aluminate	0.0562	-0.2662	4.3615	-4.4191	-0.0393	
	Fe$_2$O$_3$	0.60	0.90	5.50	20.50	ferrite	0.0110	0.1216	-1.1851	6.0554	-0.0077	
	SO$_3$	0.00	0.70	0.00	0.20	anhydrite	0.0436	-0.1214	-0.0558	-0.0389	1.6699	
SRM2686	CaO	72.60	64.60	57.70	49.20	alite	4.4933	-8.8279	-6.6219	-2.2906	-3.1471	13
	SiO$_2$	25.10	31.80	4.30	4.10	belite	-3.5560	10.1506	4.8361	1.5940	2.4906	
	Al$_2$O$_3$	0.70	1.00	31.70	20.40	aluminate	-0.1042	0.1984	3.6879	-3.2837	0.0730	
	Fe$_2$O$_3$	0.00	1.00	3.60	21.60	ferrite	0.1820	-0.5030	-0.8385	5.1031	-0.1275	
	SO$_3$	0.00	0.20	0.00	0.10	anhydrite	0.0118	-0.0337	-0.0150	-0.0141	1.6921	
SRM 2687	CaO	73.40	65.40	57.30	50.10	alite	4.2881	-8.4168	-6.9919	-1.0484	-3.0033	15
	SiO$_2$	24.60	32.50	4.50	5.00	belite	-3.2390	9.4450	4.9046	0.3760	2.2686	
	Al$_2$O$_3$	1.10	0.90	28.60	22.10	aluminate	-0.0953	0.0401	5.4624	-6.7924	0.0667	
	Fe$_2$O$_3$	0.00	0.00	7.50	17.10	ferrite	0.0418	-0.0176	-2.3958	8.8271	-0.0293	
	SO$_3$	0.00	0.20	0.00	0.10	anhydrite	0.0109	-0.0321	-0.0126	-0.0163	1.6927	
SRM 2688	CaO	73.00	64.70	56.80	48.90	alite	4.3040	-8.1805	-6.0917	-2.1091	-3.0145	12
	SiO$_2$	25.70	33.00	2.40	3.10	belite	-3.3545	9.4119	4.5772	1.4143	2.3495	
	Al$_2$O$_3$	0.50	1.10	34.90	21.80	aluminate	0.0516	-0.2101	3.2888	-2.9664	-0.0361	
	Fe$_2$O$_3$	0.00	0.00	5.80	24.80	ferrite	-0.0121	0.0491	-0.7692	4.7260	0.0085	
	SO$_3$	0.30	0.60	0.00	0.00	anhydrite	0.0123	-0.0543	-0.0156	-0.0037	1.6918	
Mean	CaO	72.13	64.09	55.68	47.65	alite	4.4935	-8.5789	-6.6600	-1.9400	-3.1472	
	SiO$_2$	25.06	31.91	4.13	3.29	belite	-3.5408	9.9178	4.8136	1.4933	2.4800	
	Al$_2$O$_3$	1.04	1.83	30.11	22.42	aluminate	0.0453	-0.2246	4.2433	-4.3426	-0.0317	
	Fe$_2$O$_3$	0.57	0.86	6.59	22.58	ferrite	0.0090	-0.0937	-1.3254	5.9447	-0.0063	
	SO$_3$	0.04	0.21	0.00	0.03	anhydrite	0.0087	-0.0268	-0.0112	-0.0061	1.6943	
Standard	CaO	1.01	1.12	2.65	1.86	alite	0.43950	1.00251	0.55165	2.23391	0.30782	
Deviation	SiO$_2$	0.59	1.12	1.58	1.24	belite	0.43862	1.03645	0.61266	1.76067	0.30721	
	Al$_2$O$_3$	0.39	0.80	3.72	1.60	aluminate	0.07965	0.21919	1.21285	2.17089	0.05578	
	Fe$_2$O$_3$	0.46	0.49	3.58	3.69	ferrite	0.06833	0.15324	1.03718	1.85373	0.04786	
	SO$_3$	0.09	0.23	0.00	0.06	anhydrite	0.01147	0.03286	0.01483	0.01154	0.00803	
Standard	CaO	0.0028	0.0031	0.0074	0.0052	alite	0.11746	0.26793	0.14743	0.59704	0.08227	
Deviation of	SiO$_2$	0.0016	0.0031	0.0044	0.0034	belite	0.11723	0.27700	0.16374	0.47056	0.08210	
The Mean	Al$_2$O$_3$	0.0011	0.0022	0.0103	0.0044	aluminate	0.02129	0.05858	0.32415	0.58020	0.01491	
	Fe$_2$O$_3$	0.0013	0.0014	0.0099	0.0102	ferrite	0.01826	0.04096	0.27720	0.49543	0.01279	
	SO$_3$	0.0002	0.0006	0.0000	0.0002	anhydrite	0.00307	0.00878	0.00396	0.00308	0.00215	
Observations		14	14	14	14		14	14	14	14	14	